THE CHEMICAL GENERATION OF CARBENE ANION RADICALS

by

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TAIPEI INSTITUTE OF TECHNOLOGY, 1971

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A MASTER'S THESIS

submitted in partial fulfillment of the

requirement for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
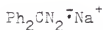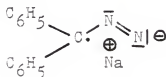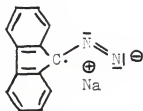Manhattan, Kansas

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The reactions of diphenyldiazomethane ($Ph_2CN_2$) and 9-di-azofluorene ($FlN_2$) with powdered sodium in ether under $N_2$ atmosphere were reported by Kauffman and Hage.[1] Hydrolysis of the deep-blue solution derived from $FlN_2$ gave 9,9'-bifluorenyl (FlH-FlH) (32%) and in the presence of oxygen 9,9'-bifluoreny-lidene (Fl=Fl) (28%) and fluorenone azine (Fl=N$\frac{}{}_2$) (34%) were produced. The deep-blue reduction solution obtained from $Ph_2CN_2$ and sodium in ether behaved similarly upon hydrolysis. The proposed reaction intermediates were diazo anion radical-sodium complexes, $FlN_2^{-}Na^{+}$ and $Ph_2CN_2^{-}Na^{+}$, respectively.



$FlN_2^{-}Na^{+}$                    $Ph_2CN_2^{-}Na^{+}$

Webster[2] reported that sodium iodide or bromide reacted with diazotetracyanocyclopentadiene (DTCC) to give halotetra-cyanocyclopentadiene, while sodium chloride required copper as a catalyst. If methanol or ethanol was present, the only product isolated, even with sodium iodide, was tetracyanocyclo-pentadienide. The mechanisms of these substitution-reductions appeared to be free radical.

DTCC



    In the above reactions the tetracyanocyclopentadienylide
anion radical (TCC$\overline{\cdot}$) was proposed as the intermediate and
could be generated polarographically at 0.23 V vs. SCE in ace-
tonitrile or by mild reducing agents, such as copper powder,
cuprous ion, or zinc powder. The structure of TCC$\overline{\cdot}$ was consi-
dered to be a $\underline{\pi}$-anion $\underline{\delta}$-radical ($\pi^2 \delta^1$).



TCC$\overline{\cdot}$

    The reduction of 1 M 2,2-dichloro-3,3-dimethylbutane with
1 M sodium naphthalene (Na$^+$C$_{10}$H$_8\overline{\cdot}$) in 1,2-dimethoxyethane
(DME) at 25$^o$C was reported by Sargent, et al.,[3] to yield 1,1,2-
trimethylcyclopropane (19%), 3,3-dimethyl-1-butene (38%) and
3,3-dimethylbutane (11.5%). It was proposed that tert-butyl-
methylcarbene was generated and was further reduced to the
carbene anion radical at a rate competitive with that of intra-
molecular C-H insertion.

$$Na^+C_{10}H_8^{\cdot -} + CH_3C(CH_3)_2CCl_2CH_3 \xrightarrow[25^\circ C]{DME}$$

$$\underset{CH_3}{\overset{CH_3}{\triangle}}\!\!\!\!CH_3 + (CH_3)_3CCH=CH_2 + (CH_3)_3CCH_2CH_3$$

Additional evidence for the formation of carbene anion radicals came in the reductions of methylene dihalides. Sargent, et al.,[4] reported that the reduction of $CH_2Cl_2$ in 60:40 (v/v) cyclohexene-DME with excess sodium naphthalene $(Na^+C_{10}H_8^{\cdot -})$ yielded low molecular weight hydrocarbons, such as, $CH_4$, $CH_2=CH_2$, $CH_3CH_3$, and $CH_3CH_2CH_3$, as the principal products of the reaction (>70%) and norcarane in yields of less than 1%. Akylated naphthalenes and dihydronaphthalenes were also found in less than 30% yield.

$$CH_2X_2 + Na^+C_{10}H_8^{\cdot -} \xrightarrow[DME]{cyclohexene} \begin{array}{cc} CH_4, \ CH_2=CH_2 \\ CH_3CH_3, \ CH_3CH_2CH_3 \end{array} + \bighexagon$$
$$> 70\% \qquad\qquad < 1\%$$

The low yield of norcarane from the above reaction led to the conclusion that the rate of formation of methylene anion radical $(CH_2^{\cdot -})$ must be greater than that of the formation of norcarane and that $CH_2^{\cdot -}$ must not itself readily add to cyclohexene. This was in keeping with Sargent's previous suggestion that tert-butylmethylcarbene could be reduced to the corresponding carbene anion radical at a rate competitive with that of intramolecular C-H insertion by the carbene.[3] The constant, relative yield of ethylene generated by the reaction of the three methylene halides ($CH_2X_2$, X = Cl, Br, or I) with sodium naphthalene indicated that $CH_2^{\cdot -}$ could dimerize to form ethylene

dianion, followed by electron transfer with naphthalene, or that an $CH_2^{\cdot-}-CH_2X_2$ encounter could lead to formation of ethylene.

Lineberger, et al.,[5] reported that $CH_2^{\cdot-}$ was generated by electron attachment to $CH_2N_2$ in the gas phase. The experiment of interest consisted of crossing a mass-analyzed $CH_2^{\cdot-}$ beam with an argon ion laser operating at 488 nm (2.540 eV) and measuring the kinetic energy of the electron photoejected. Coupled with ab initio calculations and a Franck-Condon factor analysis, the electronic structure of $CH_2^{\cdot-}$ was in good agreement with the experimental results. The structure of $CH_2^{\cdot-}$ ($^2B_1$) was determined to be $r_e \approx 1.1$ $^\circ$A and $\theta_e \approx 100^\circ$, and the energy separation between $:CH_2$ ($^1A_1$) and $\overset{..}{C}H_2$ ($^3B_1$) was found to be 19.5±0.7 kcal/mol.

Recently, the electrochemical reduction of $Ph_2CN_2$ in 0.1 M $DMF-Et_4N^+ClO_4^-$ has been reported by McDonald, January, Borhani, and Hawley.[6] The products were diphenylmethane ($Ph_2CH_2$), benzophenone azine ($Ph_2C=N\overset{)}{}_2$ and benzophenone ($Ph_2C=O$); the ketone was mistakenly identified as diphenylmethylamine ($Ph_2CHNH_2$) in the paper.[6] Diphenylcarbene anion radical ($Ph_2C^{\cdot-}$) was generated at -1.68 V vs. SCE from the chemically irreversible reduction of $Ph_2CN_2$. The results were believed to be consistent with a radical chain process. $Ph_2C^{\cdot-}$ was considered to behave primarily as a radical species in its reaction producing $Ph_2CH_2$. Dimerization of $Ph_2C^{\cdot-}$ was ruled out as an important reaction channel since only trace amounts of tetraphenylethene ($Ph_2C=CPh_2$) and tetraphenylethane ($Ph_2CH-CHPh_2$) were detected by

chromatographic methods.

These results were quite different from those reported by Elofson, et al.,[7] for the electrochemical reduction of $Ph_2CN_2$ in sulfolane. In this case the products were $Ph_2CH_2$ (40%), $Ph_2CHNH_2$ (20%), and nitrogen. However, the decomposition of $Ph_2CN_2^{-\cdot}$ was suggested to occur by protonation to give $Ph_2CHN_2\cdot$, which then either loses nitrogen to give benzhydryl radical and ultimately $Ph_2CH_2$, or couples with benzhydryl radical to give azodiphenylmethane. Reduction of this azo compound was postulated to give $Ph_2CHNH_2$.

Electrochemical reduction of $FlN_2$ in $DMF-(\underline{n}-Bu)_4N^+ClO_4^-$ afforded the azine, $(Fl=N{\rightarrow}_2$, in high yield (91±7%).[8] Fluorenone (Fl=0) was observed as a minor product when electrolysis was effected in the presence of adventitious amounts of oxygen. Neither fluorene nor any dimeric product was detected by gas chromatography in other than trace amount (<0.5%). It was proposed that fluorenylidene anion radical ($Fl^{-\cdot}$) was generated by reduction of $FlN_2$ at -1.35 V $\underline{vs}$. SCE from fast, unimolecular, irreversible decomposition of $FlN_2^{-\cdot}$. The increased production of the corresponding azine and concomitant decrease in the amount of hydrocarbon product from $Fl^{-\cdot}$ compared to $Ph_2C^{-\cdot}$ under similar electrochemical conditions was believed due to the dual relative reactivities of the two carbene anion radicals. Significantly, a reversible redox couple attributed to $Fl^{-\cdot}/Fl$: was observed in this study.
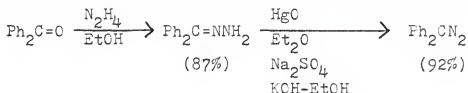
## OBJECTIVES OF THIS INVESTIGATION

The objectives of this investigation were:

1. To explore certain chemical reductions of diazo compounds ($R_2CN_2$) to yield the corresponding carbene anion radicals.

2. To study solvent effects on radical vs anion reactivities of these carbene anion radicals.

3. To investigate the possibility that 9-fluorenyl anion would react with $FlN_2$.

## EXPERIMENTAL RESULTS

Using the procedure of Miller[9], $Ph_2CN_2$ was synthesized as dark red crystals, mp 29-30°C, after recrystallization from petroleum ether (bp 35-60°C). Using double the volume of abso-

$$Ph_2C=O \xrightarrow[EtOH]{N_2H_4} Ph_2C=NNH_2 \xrightarrow[\substack{Na_2SO_4 \\ KOH-EtOH}]{HgO} Ph_2CN_2$$
$$(87\%) \qquad\qquad (92\%)$$

lute ethanol saturated with potassium hydroxide, the yield of $Ph_2CN_2$ could be increased to 92% compared to 89% in the old method. The ir and nmr spectra are consistent with the structure of $Ph_2CN_2$. To prevent decomposition, $Ph_2CN_2$ was stored in a freezer. Since $(Ph_2C=N)_2$ was a major product in the electrochemical reduction of $Ph_2CN_2$,[6] the azine was prepared by reaction of $Ph_2CN_2$ with $BF_3$-$Et_2O$ in ether at 0°C,[10] and was obtained as pale yellow rods, mp 162-163°C, in 70% yeild. The second expected product from reduction of $Ph_2CN_2$, $Ph_2CH_2$, was prepared by Wolff-Kishner reduction of benzophenone.[11] Other possible products, $Ph_2CH$-$CHPh_2$ (Columbia Organic), $Ph_2C=CPh_2$ (Aldrich), and $Ph_2CHNH_2$ (Aldrich), were purchased from commercial sources and their purities checked by mp, and ir and nmr spectroscopy.

The dark-green $Na^+C_{10}H_8^{\bar{\cdot}}$ solution was prepared from a mixture of sodium and excess naphthalene in THF at -12°C under an argon atmosphere according to the procedure of Vora and Holy.[12] The mixture was stirred under an argon atmosphere for over 24 hr before two 5-ml aliquots were removed, quenched in 50-ml portions of water, and titrated for total base with standardized hydrochloric acid solution to a phenylphthalein

end-point.

The first experiment was to add crystals of $Ph_2CN_2$ to the $Na^+C_{10}H_8^{\bar{}}$ solution in THF cooled to $-12^{\circ}C$. After the solvent was removed, isolation of the products gave both $(Ph_2C=N)_2$ and $Ph_2CHNH_2$ along with unknown residues.

The reduction of $(Ph_2C=N)_2$ with excess $Na^+C_{10}H_8^{\bar{}}$ solution at $-12^{\circ}C$ under an argon atmosphere was carried out to yield $Ph_2CHNH_2$ in 98% yield after correcting for known loss of amine in the work-up procedure. The correction factor, 1.19 (100/-83.8), for recovered yield of amine was determined by following the same extraction procedure with a weighed amount of $Ph_2CHNH_2$.

A solution of $Ph_2CN_2$ in dry THF in a pressure-equalized addition funnel was added dropwise to an excess of $Na^+C_{10}H_8^{\bar{}}$ in THF, cooled to $-12^{\circ}C$, over a period of 0.5 hr (runs 1-3, Table I). After distilled water was added, the color of the mixture changed from dark to light brown. The THF was evaporated and ether was added. The two-phase mixture was separated and the ether layer extracted with 10% HCl solution. The aqueous acidic solution was basified to pH ~13 with 10% NaOH solution and extracted with ether. The ether extracts were washed with distilled water, saturated NaCl solution, and dried. After solvent removal, $Ph_2CHNH_2$ was obtained and identified by use of ir and nmr spectroscopy, and mp of an amine derivative in comparison to those of authentic $Ph_2CHNH_2$. Correcting the isolated yield of $Ph_2CHNH_2$ for known losses during work-up gave 83±2% yield of the amine.

Table I. Product Analysis for the Reaction of $Ph_2CN_2$ with Sodium Naphthalene Solution in THF at $-12°C$.

| Run no. | Method of Addition | $Ph_2CN_2$ mM | $Na^+C_{10}H_8^{-\cdot}$ mM | Product, % Yield[a] | |
|---------|--------------------|----------------|------------------------------|-----------------------|----------------------|
| | | | | $Ph_2CH_2$[b] | $Ph_2CHNH_2$[c] |
| 1 | Slow[d] | 15.7 | 62.8 | 13 | 84 |
| 2 | Slow[d] | 19.9 | 79.6 | 10 | 82 |
| 3 | Slow[e] | 15.8 | 159.0 | 17 | 85 |
| 4 | Fast[f] | 10.4 | 52.2 | 4 | 91 |
| 5 | Fast[f] | 10.3 | 51.6 | 5 | 93 |

[a]Tetraphenylethane and benzophenone azine were detected only in trace amounts by gas chromatography. [b]These were obtained from calculation of ratio of aromatic hydrogens on nmr. [c]These were corrected by multiplying the isolated yield by the recovery factor (1.19). [d]Dropwise addition of $Ph_2CN_2$ in 150 ml of THF to $Na^+C_{10}H_8^{-\cdot}$ in 400 ml of THF over a period of one hr. [e]Dropwise addition of $Ph_2CN_2$ in 100 ml of THF to $Na^+C_{10}H_8^{-\cdot}$ in 400 ml of THF over a period of 0.5 hr. [f]Syringe injection of $Ph_2CN_2$ in 10 ml of THF to $Na^+C_{10}H_8^{-\cdot}$ in 200 ml of THF over a period of 5 sec.

The neutral products of the reaction were obtained. These products were separated by sublimation at $35^{\circ}C$ and 0.2 torr. The nmr spectrum of the sublimate showed only the presence of naphthalene, 1,4-dihydronaphthalene, and $Ph_2CH_2$. Since the nmr absorption of these three components are cleanly separated from one another, the amount of $Ph_2CH_2$ was determined to be $11\pm2\%$ for runs 1 and 2, Table I. In run 3, Table I, the $[Na^+C_{10}H_8^{-}]/[Ph_2CN_2]$ mole ratio was increased from 4 to 10 with an increase in the amount of $Ph_2CH_2$ (17%) produced. The residue remaining in the sublimation tube was checked by mass spectrometry and appeared to be polymeric dihydronaphthalene. Only trace amounts of $Ph_2CH\text{-}CHPh_2$ and $(Ph_2C=N)_2$ were found in this residue by gas chromatography.

A solution of $Ph_2CN_2$ in dry THF was syringe injected into a solution of $Na^+C_{10}H_8^{-}$ in THF, cooled to $-12^{\circ}C$, over a period of 5 sec (runs 4 and 5, Table I). Isolation and identification of the products as described above in the slow additions resulted in $Ph_2CHNH_2$ ($92\pm1\%$) and $Ph_2CH_2$ ($5\pm1\%$).

The preparation of $FlN_2$ was similar to the method described above for the synthesis of $Ph_2CN_2$.[9] Recrystallization from petroleum ether (bp $35\text{-}60^{\circ}C$) gave orange-red needles, mp $94\text{-}95^{\circ}C$; the ir and nmr spectra agreed with this structure. To avoid decomposition, $FlN_2$ was stored in a freezer. Since

$$Fl=O \xrightarrow{\underset{EtOH}{N_2H_4}} Fl=NNH_2 \xrightarrow[\substack{Et_2O \\ Na_2SO_4 \\ KOH\text{-}EtOH}]{HgO} FlN_2$$
$$(52\%) \qquad\qquad (80\%)$$

the electrochemical reduction of $FlN_2$ yielded $(Fl=N\dot{+}_2$ in high yield,[8] it was prepared from a mixture of $Fl=0$, $N_2H_4$ (95%), and KOH-EtOH in ethanol.[13] Recrystallization from xylene gave violet needles of $(Fl=N\dot{+}_2$, mp 268-269°C, in 80% yield. Another possible product from reduction of $FlN_2$, 9,9'-bifluorenyl (FlH-FlH) was prepared in 15% yield by the reaction of $(Fl=N\dot{+}_2$ with $N_2H_4$ (95%) in the presence of KOH in diethylene glycol.[13] FlH-FlH was obtained as white needles, mp 244-245°C, after recrystallization from benzene-ethanol (1:2). A third possible product, 9,9'-bifluorenylidene (Fl=Fl), was prepared in 91% yield from coupling of $Fl=0$ with McMurray's reagent $(4TiCl_3-LiAlH_4)$.[14,15] After recrystallization from $CHCl_3$-EtOH (1:1), Fl=Fl was obtained as orange needles, mp 194-195°C. The other expected product, fluorene $(FlH_2)$ (Eastman), $Fl=0$ (Eastman), and 9-aminofluorene $(FlHNH_2)$ obtained from 9-aminofluorene hydrochloride (Aldrich), were purchased from commercial sources and their purities checked by mp, and ir and nmr spectroscopy. $FlHNH_2$ was obtained from neutralization of 9-aminofluorene hydrochloride with 10% NaOH solution. Recrystallization of the amine from n-hexane yielded white needles, mp 64-65°C.

The reduction of $(Fl=N\dot{+}_2$ with excess $Na^+C_{10}H_8^{\bar{\cdot}}$ solution was carried out to yield $FlHNH_2$ in 100% yield, after correcting for known losses of amine in the work-up procedure. The correction factor, 1.19 (100/83.8), was determined by following the same extraction procedure with a weighed amount of $FlHNH_2$.

The reductions of $FlN_2$ with excess $Na^+C_{10}H_8^{\bar{\cdot}}$ followed the

same procedures described above in the slow and fast additions of $Ph_2CN_2$ in dry THF to a THF solution of $Na^+C_{10}H_8^-$, and the results are listed in Table II. The same procedures for separation of the reaction products were applied to give $FlHNH_2$ which was identified by comparison to the mp, and ir and nmr spectra of an authentic sample. Naphthalene and 1,4-dihydronaphthalene were removed by sublimation and the yellow residue contained $FlH_2$ (identified by nmr spectroscopy and glpc). The yield of $FlH_2$ was determined by adding 1,3,5-trinitrobenzene as an internal standard and integrating the nmr spectrum of this mixture. Fl=Fl and FlH-FlH were detected in trace amounts by glpc of this same residue. From the slow addition of $FlN_2$, 40±2% of $FlH_2$ and 53±3% of $FlHNH_2$ (runs 1 and 2, Table II) were obtained. Fast addition of $FlN_2$ led to a reduced amount of $FlH_2$ (12%) with a concomitant increase in the quantity of $FlHNH_2$ (88%) (run 4, Table II). Run 3 is included in Table II to illustrate the dependence of the amount of the hydrocarbon $FlH_2$ produced on the amount of reducing agent present.

To investigate the effects of solvent on the nature of the reduction products, sodium in liquid ammonia ($Na/NH_3$) was examined as the reducing media with $FlN_2$. The reaction between ($Fl=N\overrightarrow{)_2}$ and excess Na in liquid $NH_3$ failed to give $FlHNH_2$, but did lead to extensive ring reductions (Birch reduction). Thus, it was decided to run the reaction with a 1:1 $FlN_2/Na$ mole ratio. The reaction of $FlN_2$ with $Na/NH_3$ solution under an argon atmosphere at $-34°C$ was carried out to yield Fl=Fl (3±1%), FlH-FlH (4±1%), ($Fl=N\overrightarrow{)_2}$ (79±0%), and Fl=0 (6±1%) as listed in

Table II.  Product Analysis for the Reaction of $FlN_2$ with

Sodium Naphthalene Solution in THF at $-12^{\circ}C$.

| Run no. | Method of Addition | $FlN_2$ mM | $Na^+C_{10}H_8^{\bar{\cdot}}$ mM | Product, % Yield[a] | | |
|---------|--------------------|-----------|-----------------------------------|---------------------|---------------|-----------------|
| | | | | $FlH_2$[b] | $FlHNH_2$[c] | $(Fl=N)_2$ |
| 1 | Slow[d] | 15.6 | 156.5 | 42 | 50 | - |
| 2 | Slow[d] | 15.1 | 151.0 | 39 | 55 | - |
| 3 | Fast[e] | 9.7 | 38.8 | 7 | 77 | 6 |
| 4 | Fast[e] | 11.3 | 112.3 | 12 | 88 | - |

[a]9,9'-Bifluorenylidene and 9,9'-bifluorenyl were found in trace amounts by gas chromatography.  [b]Employing 1,3,5-trinitrobenzene as an internal standard in the nmr determination.  [c]Corrected for recovery factor (1.19).  [d]Dropwise addition of $FlN_2$ in 100 ml of THF to $Na^+C_{10}H_8^{\bar{\cdot}}$ in 400 ml of THF over a period of 0.5 hr.  [e]Syringe injection of $FlN_2$ in 10 ml of THF to $Na^+C_{10}H_8^{\bar{\cdot}}$ in 200 ml of THF over a period of 5 sec.

Table III.   Product Analysis for the Reaction of $FlN_2$ with
            $Na/NH_3$ Solution at $-34°C$ by Fast Syringe Injection
            Method.

| Run no. | $Na/NH_3$[a] mM | $FlN_2$[b] mM | Product, % Yield[c] | | | |
|---------|-----------------|--------------|---------|---------|----------|------------|
|         |                 |              | Fl=O    | Fl=Fl   | FlH-FlH  | $(Fl=N)_2$ |
| 1       | 10.2            | 10.2         | 6       | 4       | 4        | 79         |
| 2       | 10.2            | 10.4         | 7       | 3       | 5        | 79         |

[a]Assumed the reaction of Na with 100 ml of $NH_3$ was 100%. [b]In 10 ml of THF. [c]Separation of these components was achieved by silica gel column chromatography.

Table IV.  Product Analysis for the Reaction of $FlN_2$ with 9-
           Fluorenyl Anion in 100 ml of THF at $-12°C$.

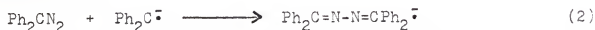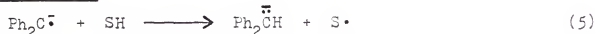| Run no. | $FlN_2$ mM | $FlH_2$ mM | PhLi mM | Product, mM[a] | | |
|---------|------------|------------|---------|------------------|---------|------------|
|         |            |            |         | $FlH_2$          | FlH-FlH | $(Fl=N)_2$ |
| 1       | 11.0       | 15.1 (10.8)[b] | 10.8 | 11.7 (7.4)[b] | -       | 6.5        |
| 2       | 10.9       | 12.5 (10.9)[b] | 10.9 | 7.2 (5.6)[b]  | 0.3     | 6.6        |

[a]The two major components were separated by column chromatography; a trace amount of Fl=Fl was found by glpc of the original mixture. [b]These values represent those corrected for the excess $FlH_2$ originally employed.

Table III. The products were separated by silica gel column chromatography.

To determine if 9-fluorenyl anion (FlH$^-$) would react with FlN$_2$, FlH$^-$ was prepared (FlH$_2$ + PhLi in THF) and allowed to react with FlN$_2$ in THF under an argon atmosphere at -12$^\circ$C. The products were FlH$_2$, (Fl=N$\}_2$, and FlH-FlH as listed in Table IV. The products were separated by silica gel column chromatography.
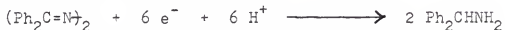
DISCUSSION OF EXPERIMENTAL RESULTS

The results of the electrochemical reduction of $Ph_2CN_2$ were consistent with the radical chain process shown in Scheme I[6]. Propagation of the chain involved coupling of $Ph_2C^{\cdot-}$ with

Scheme I

Initiation

$$Ph_2CN_2 \; + \; e^- \; \longrightarrow \; Ph_2CN_2^{\cdot-} \; \xrightarrow{\text{fast}} \; Ph_2C^{\cdot-} + N_2 \quad (1)$$

Propagation

$$Ph_2CN_2 \; + \; Ph_2C^{\cdot-} \; \longrightarrow \; Ph_2C=N-N=CPh_2^{\cdot-} \quad (2)$$

$$Ph_2C=N-N=CPh_2^{\cdot-} \; + \; Ph_2CN_2 \; \longrightarrow \; (Ph_2C=N)_2 + Ph_2CN_2^{\cdot-} \quad (3)$$

$$Ph_2CN_2^{\cdot-} \; \xrightarrow{\text{fast}} \; Ph_2C^{\cdot-} + N_2 \quad (4)$$

Termination

$$Ph_2C^{\cdot-} \; + \; SH \; \longrightarrow \; Ph_2\overset{\cdot\cdot}{C}H \; + \; S\cdot \quad (5)$$

$$Ph_2\overset{\cdot\cdot}{C}H \; + \; SH \; \longrightarrow \; Ph_2CH_2 \; + \; \overset{\cdot\cdot}{S}{:}^- \quad (6)$$

$Ph_2CN_2$ to give $(Ph_2C=N)_2^{\cdot-}$ (reaction (2)), followed by electron transfer between $Ph_2CN_2$ and $(Ph_2C=N)_2^{\cdot-}$ to produce azine and $Ph_2CN_2^{\cdot-}$ (reaction (3)). Loss of nitrogen from the latter species regenerated $Ph_2C^{\cdot-}$, the chain carrying species. Termination of the chain occurred by reactions (5) and (6) in that sequence.

In addition, the present study involves the further reduction of $(Ph_2C=N)_2$ to $Ph_2CHNH_2$. This reduction is believed to be similar to that reported by lund for the reduction of the closely related benzalazine.[16] The reduction of $(Ph_2C=N)_2$ by excess sodium or potassium produced an adduct containing 2-g atoms of alkali metal per mole of azine. After hydrolysis,

this gave N-benzhydryl benzophenone hydrazone in 54% yield.[17a]
However, lithium was shown to be capable of reducing $(Ph_2C=N)_2$
to $Ph_2CHNH_2$ (76%) and $Ph_2C=O$ (20%) after work-up.[17b] The ketone
was believed to result from hydrolysis of $Ph_2C=N-Li$ and the
amine from a "polylithio species", e.g. $Ph_2CLi-NLi_2$. This
suggests that the overall stoichiometry in the azine to amine
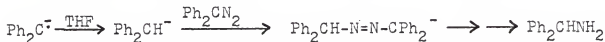reduction is given by the equation,

$$(Ph_2C=N)_2 \; + \; 6\;e^- \; + \; 6\;H^+ \; \longrightarrow \; 2\;Ph_2CHNH_2$$

The reductions of $Ph_2CN_2$ by $Na^+C_{10}H_3^-$ in THF were carried
out by adding a solution of diazo compound to the reducing
agent. As shown in Table I, the variation of the mole ratio of
reducing agent to $Ph_2CN_2$ from 4 to 10 in the slow, dropwise
addition method did not have a major effect in the yields of
the products, although a small increase in the yield of $Ph_2CN_2$
was observed. However, the different methods of addition did
show a significant change in the product yields. As we can see,
the yield of $Ph_2CHNH_2$ increases from 83±2% to 92±1% and that
of $Ph_2CH_2$ decreases from 13±4% to 5±1% on changing from slow
to fast addition. These results could be explained as due to
the increased concentration of $Ph_2CN_2$ in which $Ph_2C^{\bar{\cdot}}$ finds it-
self in the fast, syringe injection method. Thus, coupling to
give azine anion radical becomes even more important. Since
$Ph_2CH^-$ may also react with $Ph_2CN_2$ to yield azine (as will be
discussed with the reaction of $FlH^-$ with $FlN_2$), the yield of
$Ph_2CH_2$ may be a minimum value.

Although $Ph_2CH^-$ has been produced in THF as a reactive
intermediate to give excellent yields of products from its bi-

molecular reaction with other substrates,[18] the lifetime of this basic species ($pK_a$ ($Ph_2CH_2$) = 33)[19] in THF under the present conditions has not been established. In the case of the slow addition method, the required lifetime may be several seconds to minutes as subsequent drops of $Ph_2CN_2$ in THF are added, and $Na^+C_{10}H_8^{-\bullet}$ and $Ph_2CH^-Na^+$ would then compete for the diazo compound.

The results appear to be consistent with those obtained by electrochemical reduction of $Ph_2CN_2$.[6] However, certain differences in the way the chemical and electrochemical experiments were carried out deserve comment at this point. The radical chain process depicted in Scheme I for the electrochemical reduction of $Ph_2CN_2$ may, in fact, not apply to the chemical reductions of this substrate especially in the slow, dropwise addition method. In this case, very small amounts of $Ph_2CN_2$ ($E_{p,c}$ = -1.68 V, DMF-($\underline{n}$-Bu)$_4$N$^+$ClO$_4^-$ $\underline{vs}$. SCE)[6] are added to a large excess of the powerful reducing agent $Na^+C_{10}H_8^{-\bullet}$ ($E_{p,c}$ = -2.46 V, DMF-Et$_4$N$^+$Br$^-$ $\underline{vs}$. SCE).[20] Further, $(Ph_2C=N\dot{-})_2^{-\bullet}$ and $(Ph_2C=N\dot{-})_2^{2-}$ which serve as electron transfer-reducing agents in the electrochemical reduction (Scheme I) of $Ph_2CN_2$ are removed at unknown rates of reduction processes to finally yield $Ph_2CHNH_2$.[17] It is not known if the intermediates in this azine $\longrightarrow$ amine reduction can serve in electron transfer steps to $Ph_2CN_2$. Also, the solvent in these chemical reductions, THF, is known to be a better hydrogen atom donor than DMF used in the electrochemical reductions.[21] For these reasons, the chain length of the free radical chain reaction in
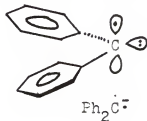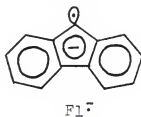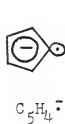
the chemical reductions must be considerably attenuated compared to that in the electrochemical reductions or the chain process may be nonexistent. This could mean that a principle source of azine (then to amine), especially in the slow drop-wise addition method, might be the following sequence.

$$Ph_2C^{\cdot -} \xrightarrow{THF} Ph_2CH^- \xrightarrow{Ph_2CN_2} Ph_2CH-N=N-CPh_2^- \longrightarrow \longrightarrow Ph_2CHNH_2$$

This suggested pathway will be considered in the following discussion on the related reductions of $FlN_2$.

The electronic structure of $H_2C^{\cdot -}$ has been examined by ab initio[5,22] and MINDO/3 [23a,24] calculations and is in excellent agreement with the estimated experimental structure derived from its photoelectron spectrum.[5] The electronic configuration of $H_2C^{\cdot -}$ is $\delta^2\pi^1$ (a $\underline{\delta}$-anion $\underline{\pi}$-radical) with the H-C-H angle of about $100°$ which is structurally similar to the singlet of $:CH_2$. At this point, it is assumed that this is also approximately the structure of $Ph_2C^{\cdot -}$ with both phenyl rings twisted about their $C_1$-$C^{\cdot -}$ bonds to relieve nonbonded repulsions.

MINDO/3 calculations on cyclopentadienylidene anion radical ($C_5H_4^{\cdot -}$) show the ground state doublet to have a $\delta^1\pi^2$ electronic configuration.[23a,25] It was assumed that this electronic configuration would also be that expected for the fluorenylidene anion radical ($Fl^{\cdot -}$), where fusion of the benzene rings onto $C_5H_4^{\cdot -}$ would be expected to further separate the energies



$C_5H_4^{\cdot -}$        $Fl^{\cdot -}$        $Ph_2\dot{C}^{\cdot -}$

of the $\delta$- and $\pi$-orbitals of $C_5H_4^-$. Thus, the chemical reduc-
tion of $FlN_2$ was investigated to determine if the change in
electronic configuration between $Ph_2C^-$ and $Fl^-$ would result in
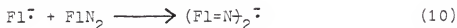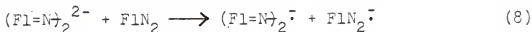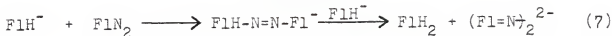observable chemical differences.

The reductions of $FlN_2$ by $Na^+C_{10}H_8^-$ in THF were carried
out using the slow, dropwise and fast, syringe injection
methods previously described for the reductions of $Ph_2CN_2$.
However, in the experiments to be considered here (runs 1, 2,
and 4 in Table II), the $[Na^+C_{10}H_8^-]/[FlN_2]$ ratio of 10 was
employed. With the slow addition method, $FlH_2$ $(41\pm2\%)$ and
$FlHNH_2$ $(53\pm3\%)$ were obtained. Use of the fast, syringe injec-
tion method led to a reduced amount of $FlH_2$ (12%) and an in-
crease in the yield of $FlHNH_2$ (88%). Run 3 illustrates the
effect on the product distribution in the fast injection me-
thod when the ratio $[Na^+C_{10}H_8^-]/[FlN_2]$ was reduced to 4. The
result was a decrease in the yield of $FlH_2$ (7%) and isolation
of a small amount of azine (6%).

To demonstrate that the reaction

$$R_2C^- + R_2CN_2 \longrightarrow R_2C=N-N=CR_2^-$$

is not the only potential source of azine (and, therefore, of
amine), 9-fluorenyl anion ($FlH^-$) was prepared in THF and al-
lowed to react with one molar equivalent of $FlN_2$ (Table IV).
The results are interpreted mechanistically in Scheme II. The
initial concentration of $FlH^-$ was consumed in its reaction
with $FlN_2$ to form the conjugate acid of azine dianion followed
by deprotonation (reaction (7)). The remaining $FlN_2$ (0.5 of
original $[FlN_2]$) was then reduced by $(Fl=N-)_2^{2-}$ (reaction (8)),

## Scheme II

$$FlH^- + FlN_2 \longrightarrow FlH\text{-}N\text{=}N\text{-}Fl^- \xrightarrow{FlH^-} FlH_2 + (Fl\text{=}N\text{-}\!\!\text{-}\!\!)_2^{2-} \quad (7)$$

$$(Fl\text{=}N\text{-}\!\!\text{-}\!\!)_2^{2-} + FlN_2 \longrightarrow (Fl\text{=}N\text{-}\!\!\text{-}\!\!)_2^{-} + FlN_2^{-} \quad (8)$$

$$FlN_2^{-} \longrightarrow N_2 + Fl^{-} \quad (9)$$

$$Fl^{-} + FlN_2 \longrightarrow (Fl\text{=}N\text{-}\!\!\text{-}\!\!)_2^{-} \quad (10)$$

$$Fl^{-} \xrightarrow{THF} FlH^- \quad (11)$$

and $Fl^{-}$ then went on to yield the "extra" amounts of azine and $FlH_2$ (reactions (10) and (11)). The azine anion radical is oxidized to azine in the work-up.

In an attempt to determine the extent to which each reaction potentially produced azine, the reduction of $FlN_2$ was carried out and quenched with $D_2O$ followed by acidification with 6 M hydrochloric acid. The isolated fluorene was found to contain an excess of deuterium compared to that expected for simple neutralization of $FlH^-$ (Table V). Since it was possible that H-D exchange might have occurred during the $D_2O$ quench and $H^+$ acidification of the reduction mixture, the reduction was rerun and quenched by syringe injection of excess $CF_3COOD\text{-}D_2O$. The $^1H$ and $^{13}C$ nmr analysis of the resultant fluorene showed an increase in the amount of excess deuterium ($FlD_2$) compared to that observed in the $D_2O$-quenched reaction (Table V).

To determine the efficiency of the $CF_3COOD\text{-}D_2O$ quench method, $FlH_2$ was allowed to react with 6 equivalents of $Na^+C_{10}H_8^{-}$ in THF under similar concentration conditions used in the $Na^+C_{10}H_8^{-}$ reduction of $FlN_2$. This reaction mixture, which should produce $FlH^-$, was quenched with excess $CF_3COOD\text{-}$

Table V. Calculation of Percentage Compositions of Deuterated Fluorene by $^1$H and $^{13}$C NMR Spectroscopy.

| Sample Origin | NMR | Total Aryl[g] | Integral | | | $^{13}$C Conversion Factor[d] | PMR Calculated No. of H's at $C_9$[e] | % Composition[c] | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $^{13}$C Ref. | | $C_9$-D(H)[c] | | | F1H2 | F1HD | F1D2 |
| | | | $C_9$ | Aryl | | | | | | |
| F1H2 | $^1$H | 52.5 | 12.0[g] | | | | (2.0) | 100 | | |
| | $^{13}$C | | 4171 | 7098 | | 0.588 | | 100 | | |
| | | | | 6820 | | 0.612 | | 100 | | |
| F1M2 + PhLi; D2O-CF3COOD | $^1$H | 46.6 | 6.5[g] | | | | 1.24 | 24 | 76 | |
| | $^{13}$C | | 1743 | 13177[a] | 1605 | 0.158 | | 23 | 77 | |
| | | | | 13361[b] | | 0.152 | | 21 | 79 | |
| F1M2 + 10 R[h]; D2O;H2O-HCl | $^1$H | 55.0 | 2.8[g] | | | | 0.45 | 5[i] | 35[i] | 60[i] |
| | $^{13}$C | | 148 | 5022[a] | 306 | | | 5 | 39 | 56 |
| | | | | 5407[b] | | | | 5 | 37 | 58 |
| F1M2 + 10 R[h]; D2O-CF3COOD | $^1$H | 50.0 | 2.0[g] | | | | 0.35 | 5[i] | 25[i] | 70[i] |
| | $^{13}$C | | 1105 | 39065[a] | 2033 | | | 5 | 33 | 62 |
| | | | | 39505[b] | | | | 5 | 34 | 61 |
| F1H2 + 6 R[h]; D2O-CF3COOD | $^1$H | 60.0 | 6.0[g] | | | | 0.88 | 8[i] | 72[i] | 20[i] |
| | $^{13}$C | | 1268 | 25745[a] | 2853 | | | 8 | 70 | 22 |
| | | | | 25540[b] | | | | 8 | 73 | 19 |

[a]Fluorene signal at 124.5 ppm. [b]Fluorene signal at 119.5 ppm. [c]Integral of upfield peak of the $C_9$-D(H) triplet in proton-decoupled $^{13}$C nmr spectrum. [d]Ratio of $[C_9$-D(H)/($^{13}$C ref. aryl)] corrected from 77% and 79% to 100% F1HD. [e]Calculated by $[(C_9)/(\text{total aryl})] \times 3.75$. [f]Calculated from the $^{13}$C nmr data using $[(C_9)/(\text{ref. } ^{13}\text{C aryl})]/(\text{conversion factor for F1M}_2)$ = % F1H$_2$, and $[(C_9$-D(H)$^c$/(ref. $^{13}$C aryl)]/(conversion factor for F1HD) = % F1HD. The % F1D$_2$ is calculated by difference. [g]Unit = mm. [h]R = Na$^+$C$_{10}$H$_8$$^-$. [i]Percent compositions from $^1$H nmr use the value of F1H$_2$ determined for this species by $^{13}$C nmr using relative integrals of two different aryl C's and C$_9$-H$_2$ of authentic F1M$_2$. In the $^{13}$C nmr analysis known relative integrals of these aryl C's to the triplet of authentic F1HD were used to determine the % of this species. The amount of F1D$_2$ was by difference.
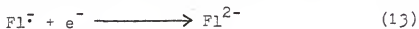
$-D_2O$. The isolated fluorene was found to contain considerably less $FlD_2$ (40-50%) than was observed in the similar reduction of $FlN_2$.

While the amount of $FlH_2$ in these samples of fluorene could be readily determined from the integral ratios of the $C_9(H_2)$ vs. certain aryl carbons in their proton decoupled $^{13}C$ nmr spectra, an authentic sample of FlHD was required. This compound was obtained from the reaction of $FlH_2$ and 10% mole excess of commercial PhLi (dissolved in 70:30 benzene-ether) in THF. The reaction mixture was quenched by syringe injection of excess $CF_3COOD-D_2O$. Surprisingly, the isolated fluorene was found to be a mixture of 24% $FlH_2$ and 76% FlHD by $^1H$ nmr (Table V). The $^{13}C$ nmr spectrum of this sample agreed quite well with this composition. That a significant amount of $FlH_2$ was observed in this product may indicate either a measuring error, or that the commercial PhLi contains bases other than PhLi. These bases would be titrated in the total base standardization of the solution, but they may not deprotonate $FlH_2$ in THF.

However, this sample was still useful in determining the amount of FlHD in the fluorene products from the above reactions by correcting the integral of the upfield line of the $C_9$-D triplet to 100% FlHD. This is corporated into $^{13}C$ conversion factor for this compound in Table V.

As mentioned above, the 40-50% excess $FlD_2$ found in the reductions of $FlN_2$ must now be considered. Since a dibasic intermediate containing the fluorene skeleton is required, it is proposed that this intermiate is the fluorenylidene dianion

$(Fl^{2-})$, a carbene dianion. Generation of $Fl^{2-}$ can be rationalized by the reduction of the carbene anion radical, $Fl\overline{\cdot}$, according to

$$FlN_2 + e^- \longrightarrow \left[ FlN_2\overline{\cdot} \right] \longrightarrow Fl\overline{\cdot} + N_2 \qquad (12)$$

$$Fl\overline{\cdot} + e^- \longrightarrow Fl^{2-} \qquad (13)$$

$$Fl^{2-} + 2D_2O \longrightarrow FlD_2 + 2OD^- \qquad (14)$$

The possible involvement of $Fl^{2-}$ in this scheme of the reduction of $FlN_2$ by excess $Na^+C_{10}H_8\overline{\cdot}$ in THF deserves some further comments. The apparent absence of $Fl^{2-}$ in reactions of $FlH_2$ with strong bases is of no consequence in the present instance. We would be entering the energy surface containing $Fl^{2-}$ from a completely different direction by a one-electron reduction of $Fl\overline{\cdot}$. If the ground state electronic configuration of $Fl\overline{\cdot}$ is that as suggested from MINDO/3 calculations for cyclopentadienylidene anion radical, $\delta^1\pi^2$, reduction would add an electron to the singly occupied $\delta$-orbital of $Fl\overline{\cdot}$ to yield $Fl^{2-}$. This reductive reaction is electron transfer from $Na^+$-$C_{10}H_8\overline{\cdot}$ and thus involves no covalent bond either made or broken. It requires that $Fl\overline{\cdot}$ be reduced up to a potential not much more negative than that of naphthalene in THF ($E_{p,c}$ = -2.46 V, DMF-$Et_4N^+Br^-$ vs. SCE).[20] Otherwise the equilibrium,

$$Fl\overline{\cdot}Na^+ + Na^+C_{10}H_8\overline{\cdot} \longrightarrow Fl^{2-}2Na^+ + C_{10}H_8$$

would not be favorable to give the observed results.

Further, the reduction of $Fl\overline{\cdot}$ must be competitive with hydrogen atom abstraction by $Fl\overline{\cdot}$ from THF. This, of course, requires a reasonable lifetime for $Fl\overline{\cdot}$ in this medium. This
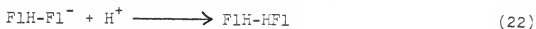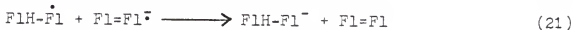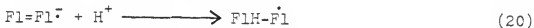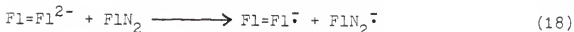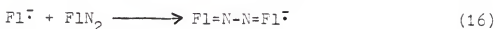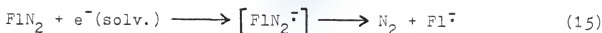
conclusion is in agreement with that from the electrochemical generation of $Fl^{\bar{\cdot}}$ where it was proposed that the reversible red-ox couple $Fl^{\bar{\cdot}}/Fl^{\colon}$ was observed in DMF-$(\underline{n}\text{-Bu})_4N^+ClO_4^{\bar{}}$.[8]

In the electrochemical reduction of $Ph_2CN_2$,[6] it was suggested that the sequence from $Ph_2C^{\bar{\cdot}}$ to $Ph_2CH_2$ involved first hydrogen atom abstraction followed by protonation. This proposal was based on a low value of $\underline{n}$, and the absence of the resulting radical dimer, $Ph_2CH\text{-}CHPh_2$, if the reverse sequence had occurred. To test this proposed mechanistic sequence, the reduction of $FlN_2$ was examined in sodium in liquid ammonia. Ammonia was chosen as solvent because of its large N-H bond dissociation energy ($D_H^{\circ}$ = 110 or 103 kcal/mole),[26,27] and thus should be a poor hydrogen atom donor. The $pK_a$ of ammonia $(33)$[28] should also make it a rather poor proton donor.

The first experiment was to examine the reduction of $(Fl\text{=}N\!\!+\!\!)_2$ with an excess of solvated electrons in liquid ammonia. While no amine was produced, extensive Birch-type reduction of the fluorene ring system was evident from the nmr spectrum of the complex reaction mixture.
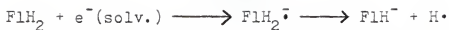
The reduction of $FlN_2$ was accomplished using one mole equivalent of sodium in liquid ammonia. The $FlN_2$ dissolved in a small amount (10 ml) of THF was rapidly syringe injected into the reducing medium (100 ml of liquid $NH_3$) to minimize Birch-type reduction. The products of this reduction (Table III) were $(Fl\text{=}N\!\!+\!\!)_2$ (79%), $Fl\text{=}O$ (7±1%), $Fl\text{=}Fl$ (4±1%), and $FlH$-$HFl$ (5±1%). The pathways by which these products are believed to be produced are given in Scheme III.

## Scheme III

$$FlN_2 + e^-(solv.) \longrightarrow \left[ FlN_2 \cdot^- \right] \longrightarrow N_2 + Fl \cdot^- \tag{15}$$

$$Fl \cdot^- + FlN_2 \longrightarrow Fl=N-N=Fl \cdot^- \tag{16}$$

$$2 \; Fl \cdot^- \longrightarrow Fl=Fl^{2-} \tag{17}$$

$$Fl=Fl^{2-} + FlN_2 \longrightarrow Fl=Fl \cdot^- + FlN_2 \cdot^- \tag{18}$$

$$FlH^- + O_2 \longrightarrow Fl=O \tag{19}$$

$$Fl=Fl \cdot^- + H^+ \longrightarrow FlH-\overset{\cdot}{Fl} \tag{20}$$

$$FlH-\overset{\cdot}{Fl} + Fl=Fl \cdot^- \longrightarrow FlH-Fl^- + Fl=Fl \tag{21}$$

$$FlH-Fl^- + H^+ \longrightarrow FlH-HFl \tag{22}$$

Several of these results are interesting in the general understanding of the chemistry of the carbene anion radical $Fl \cdot^-$. The first is that $FlH_2$ is not produced under these reaction conditions. However, we cannot exclude the possibility that some hydrogen atom abstraction by $Fl \cdot^-$ did occur from the THF used to dissolve and introduce the $FlN_2$ to the $Na/NH_3$ reducing medium. Since most common solvents which are stable to $Na/NH_3$ behave similarly as hydrogen atom donors to phenyl radical,[21] the only such semi-quantitative study reported, experiments involving a change from THF to another solvent were not considered at this point. Further, the 10 ml of THF was essentially the minimum quantity needed to dissolve the $FlN_2$.

Although we might expect $FlH_2$ to be produced if $FlH^-$ was so generated and react with $FlN_2$ by the reactions (7) and (11) in Scheme II, it is possible that the hydrocarbon is further reduced by $e^-(solv.)$ to $FlH^-$ by the reaction

$$FlH_2 + e^-(solv.) \longrightarrow FlH_2^{-\bullet} \longrightarrow FlH^- + H\bullet$$

This reaction sequence is known electrochemically.[29] Alternately, any strong bases, e.g. $NaNH_2$ or $Fl=Fl^{2-}$, present in the reduction process could abstract a proton from $FlH_2$. If $FlH^-$ was present in this reduction mixture it could also account for the formation of ketone[30] if oxygen was introduced during addition of the solid ammonium chloride as quench (reaction (19)). The ketone may also have been formed by $O_2$ oxidation of $(Fl=N)_2^{-\bullet}$ when the solid $NH_4Cl$ was introduced into the reduction mixture.[23b]

The major feature of the results in liquid ammonia is the isolation of significant quantities of the olefin, 9,9'-bifluorenylidene (Fl=Fl), and its reduction product, 9,9'-bifluorenyl (FlH-HFl). While one or sometimes both of these compound have been observed previously in the reductions of $FlN_2$, they have only been seen in trace quantities by glpc of reaction mixtures. Here, there appears to be no reasonable alternative but to propose dimerization of the carbene anion radical $Fl^{-\bullet}$ (reaction (17)). Since the first and second reduction potentials of Fl=Fl are essentially the same as those of the $(Fl=N)_2$, reaction (18) is included in Scheme III. The equal amounts of Fl=Fl and FlH-HFl could be produced by reaction (20)-(22) shown in Scheme III. Although we cannot extrapolate the present results with $Fl^{-\bullet}$ to those of the proposed intermediacy of $H_2C^{-\bullet}$, the observation of dimers adds credence to Sargent's proposal that $H_2C^{-\bullet}$ could dimerize in THF to produce ethylene and ethane.[4]
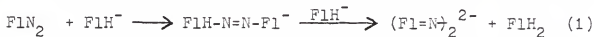
SUMMARY

Investigations of the chemical generation of diphenyl-
carbene anion radical ($Ph_2C^{-}$) were carried out by reducing
diphenyldiazomethane ($Ph_2CN_2$) with excess $Na^+C_{10}H_8^{-}$ in THF
under an argon atmosphere at $-12°C$. From the slow, dropwise
addition of a THF solution of $Ph_2CN_2$ to a solution of $Na^+C_{10}H_8^{-}$
in THF (1:5 mole ratio), product analysis showed the presence
of diphenylmethane ($11\pm2\%$; $Ph_2CH_2$) and benzhydrylamine ($83\pm1\%$;
$Ph_2CHNH_2$) along with trace amounts of tetraphenylethane ($Ph_2CH$-
$CHPh_2$) and benzophenone azine ($(Ph_2C=N\rightarrow_2$) detected by glpc.
Using a 10:1 ratio of $Ph_2CN_2$ and $Na^+C_{10}H_8^{-}$ gave $Ph_2CH_2$ (17%)
and $Ph_2CHNH_2$ (85%). Fast, syringe injection of the THF solu-
tion of $Ph_2CN_2$ into the $Na^+C_{10}H_8^{-}$ solution (mole ratio 1:5)
led to a decrease in the amount of $Ph_2CH_2$ ($5\pm1\%$) while the
yield of $Ph_2CHNH_2$ ($92\pm1\%$) increased. The amine $Ph_2CHNH_2$ was
shown to arise by $Na^+C_{10}H_8^{-}$ reduction of $(Ph_2C=N\rightarrow_2$. These re-
sults are compared and contrasted with those reported from the
electrochemical reduction of $Ph_2CN_2$ in $DMF-(\underline{n}-Bu)_4N^+ClO_4^-$
where a chain reaction was shown to be involved.

Analogous reductions of 9-diazofluorene ($FlN_2$) by $Na^+$-
$C_{10}H_8^{-}$ (1:10 mole ratio) in THF were also examined. The slow
addition method gave fluorene ($40\pm2\%$; $FlH_2$) and 9-aminofluorene
($53\pm3\%$; $FlHNH_2$), while the fast, syringe injection method pro-
duced the same two components in 12% and 88% yields, respec-
tively. As in the reductions of $Ph_2CN_2$, the yield of hydro-
carbon, $FlH_2$, decreased substantially when the mole ratio of

$FlN_2/Na^+C_{10}H_8^-$ was reduced. The amine $FlHNH_2$ was shown to be produced quantitatively in the reduction of azine $(Fl=N\frac{}{})_2$ by $Na^+C_{10}H_8^-$ in THF.

9-Fluorenyl anion $(FlH^-)$ was prepared and allowed to react with $FlN_2$ in THF. The products were $(Fl=N\frac{}{})_2$ and $FlH_2$, and were believed formed by nucleophilic addition of $FlH^-$ to the terminal nitrogen of $FlN_2$ in the primary reaction sequence,

$$FlN_2 + FlH^- \longrightarrow FlH\text{-}N\text{=}N\text{-}Fl^- \xrightarrow{\ FlH^-\ } (Fl=N\frac{}{})_2^{2-} + FlH_2 \quad (1)$$

The azine dianion would then be expected to reduce excess $FlN_2$ by electron transfer to yield $Fl^-$ and its further reaction products, $FlH_2$ and azine.

This result suggested two possible pathways for azine formation in the reduction of $FlN_2$, one by reaction (1) and the second by direct coupling of $Fl^-$ and $FlN_2$ to yield $(Fl=N\frac{}{})_2^-$. To test for the involvement of these two pathways, the slow addition method for reduction of $FlN_2$ with $Na^+C_{10}H_8^-$ in THF was run with $D_2O$ in one case and $CF_3CO_2D\text{-}D_2O$ in a second experiment added to quench the reaction. The results showed the presence of fluorene containing 60% and 70%, respectively, of excess deuterium as $FlD_2$. To see if some H-D exchanges at $C_9$ of fluorene might have occurred in the $CF_3COOD\text{-}D_2O$ quench, the reaction of $FlH_2$ with $Na^+C_{10}H_8^-$ (1:6 mole ratio ) in THF as in the slow addition method followed by the quench of $CF_3COOD\text{-}D_2O$ was carried out to give fluorene containing 20% of excess $FlD_2$. After correction for H-D exchanges, the large excess of 40% and 50%, respectively, of excess $FlD_2$ indicated the for-

mation of the carbene dianion, $Fl^{2-}$. Generation of $Fl^{2-}$ can
be rationalized by the further reduction of $Fl^{\bar{}}$.

Reduction of $FlN_2$ in $Na/NH_3$ gave $(Fl=N)_2$ (79%), fluorenone
(6±1%), 9,9'-bifluorenyl (4±1%; FlH-HFl) and 9,9'-bifluoreny-
lidene (3±1%; Fl=Fl). Since ammonia should not serve as a hy-
drogen atom donor, the dimeric products, FlH-HFl and Fl=Fl,
are believed to be produced by radical dimerization of $Fl^{\bar{}}$.

## EXPERIMENTAL SECTION[31]

Benzophenone Hydrazone. The procedure of Smith and Howard[32] was followed to afford 37.5 g (87%), mp 97-98°C (lit.[33] 97-98°C); ir (KBr): 3350 cm$^{-1}$ (doublet, NH$_2$); nmr: $\delta_{TMS}^{CCl_4}$ 7.0-7.5 (m, aromatic H's, 10), 5.0-5.5 (s, NH$_2$, 2).

Diphenyldiazomethane. This compound was prepared from a mixture of 13 g (66 mmol) of benzophenone hydrazone, 15 g of anhydrous sodium sulfate, 200 ml of anhydrous ether, 10 ml of absolute ethanol saturated with potassium hydroxide, and 35 g (0.160 mol) of yellow mercuric oxide (new Fisher brand) according to the procedure of Miller[9] except using double the volume of absolute ethanol saturated with potassium hydroxide. The mixture was shaken for 75 min. in a parr shaker. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure at about 30°C. The dark red oil obtained was dissolved in petroleum ether (bp 35-60°C) and again filtered. Removal of the solvent from the filtrate under reduced pressure at about 30°C gave an oil. Freezing this in a stopped flask with Dry Ice and then allowing the flask to warm spontaneously to room temperature gave dark red crystals in an average yield of 12.2 g (92%), mp 29-30°C (lit.[34] mp 29-30°C); ir (KBr): characteristic absorption at 2050 cm$^{-1}$ (-N$^+$=N$^-$); nmr: $\delta_{TMS}^{CDCl_3}$ 7.3 (s, aromatic H's).

Tetraphenylethylene. This compound was obtained from Aldrich Chemical Company, mp 222-224°C (lit.[35] mp 220°C); ir (KBr): 1575 cm$^{-1}$ (C=C); nmr: $\delta_{TMS}^{CDCl_3}$ 7.1 (s, aromatic H's).

Tetraphenylethane. The compound was obtained from Colum-
bia Chemical Company and recrystallized from $CHCl_3$-EtOH (1:1)
with mp 210.5-211.5°C (lit.[36] mp 209-211°C); ir (KBr): 3000
cm$^{-1}$ and 2900 cm$^{-1}$ (C-H); nmr: $\delta_{TMS}^{CDCl_3}$ 6.9-7.3 (m, aromatic H's,
20), 4.8 (s, CH, 2).

Benzophenone Azine. The preparation of this azine was
carried out according to the procedure of Whitlock.[10] The pale
yellow rods, mp 162-163°C (lit.[37] mp 164°C), were obtained in
a 90% yield after recrystallization from ethyl acetate; ir
(KBr): 1600 cm$^{-1}$ (C=N); nmr: $\delta_{TMS}^{CDCl_4}$ 7.2-7.4 (m, aromatic H's).

Benzhydrylamine. This compound was obtained from Aldrich
Chemical Company, mp 12°C, in 96% purity; ir (thin film): 3300
cm$^{-1}$ (doublet, $NH_2$); nmr: $\delta_{TMS}^{CDCl_3}$ 7.1-7.4 (m, aromatic H's, 10),
5.1 (s, CH, 1), 1.7 (s, $NH_2$, 2).

Diphenylmethane. This compound was prepared from a mix-
ture of 18.2 g of $Ph_2C=O$, 7 g of NaOH, 100 ml of triethylene
glycol and 10 ml of 85% hydrazine hydrate. Distillation over
sodium gave 14.0 g (83%) of pure hydrocarbon, bp 73.5°C/0.6mm.
(lit.[38] 154-155°C/33mm).

Fluorenone Hydrazone. The procedure of Smith and Howard[32]
was followed to afford 22.4 g (52%), mp 148-150°C (lit.[39] 149-
150°C); ir (KBr): 3350 cm$^{-1}$ (doublet, $NH_2$); nmr: $\delta_{TMS}^{CDCl_3}$ 7.2-
7.9 (m, aromatic H's, 8), 6.2-6.6 (s, $NH_2$, 2).

9-Diazofluorene. This procedure of Miller[9] was followed
to give orange-red needles, mp 94-95°C (lit.[39] mp 94-95°C) in
85% yield after recrystallization from petroleum ether (bp 35-
60°C).

**9,9'-Bifluorenylidene.** This compound was prepared from coupling of fluorenone with McMurray's reagent ($4TiCl_3$-$LiAlH_4$ from Alfa).[14],[15] To 100 ml of THF was slowly added 3.3 g of McMurray's reagent under an argon atmosphere. The solution was allowed to stir magnetically with formation of a dark black suspension. To this suspension 3.6 g (20 mmol) of fluorenone in 50 ml of THF was added in small portions. After the addition was complete, the mixture was heated under reflux and a positive pressure of argon for 6 hr. The cooled mixture was poured into 1.5 liters of distilled water and extracted with $CCl_4$. After the solvent was removed, the residue was eluted through a column of alumina (100 g) with n-hexane to give 4.0 g of crude product. Recrystallization from $CHCl_3$-EtOH (1:1) gave 3.0 g (91%) of 9,9'-bifluorenylidene, mp 194-195° (lit.[40] mp 194°C); ir (KBr): 1600 cm$^{-1}$ (C=C); nmr: $\delta_{TMS}^{CDCl_3}$ 7.0-7.7 (m, aromatic H's, 13.5), 8.2-8.4 (m, aromatic H's, 2.5).

**9,9'-Bifluorenyl.** To 2.14 g (6 mmol) of (Fl=N$\dot{-}_2$) in 8 ml of distilled diethylene glycol was added 0.1 g (3 mmol) of hydrazine (95%) and a solution of 1.2 g (3 pellets) of potassium hydroxide in 5 ml of diethylene glycol (prepared by brief warming in a test tube). The mixture was kept on the steambath for 10 min., then gently heated on a hot-plate for 3 hrs under a reflux condenser. The color changed from red-brown to dark-green. At the end of reduction period, the material in the condenser was rinsed into the flask with 5 ml of ethanol, and the mixture heated under reflux for 15 min., The mixture was allowed to cool and was acidified with 8 ml of 12 N HCl,

diluted with 50 ml of distilled water, and cooled in an ice
bath. The deep-brown crude product was filtered and recrystal-
lized three times from benzene-ethanol (1:2) to give 0.3 g
(15%) of white needles of 9,9'-bifluorenyl, mp 244-245°C (lit.[41]
mp 246°C); ir KBr): 3000 cm$^{-1}$ (C-H); nmr: $\delta_{TMS}^{CDCl_3}$ 6.8-7.4 (m,
aromatic H's, 13), 7.4-7.7 (m, aromatic H's, 4), 4.8 (s, CH,
2).

Fluorene. This compound was obtained from Eastman Organic
Chemicals, mp 115-117°C. Recrystallization from ethanol afford-
ed white needles, mp 115-117°C; ir (KBr): 2950 cm$^{-1}$; nmr:
$\delta_{TMS}^{CDCl_3}$ 7.2-7.9 (m, aromatic H's, 8.75), 3.9 (s, CH, 2).

9-Aminofluorene. 9-Aminofluorene hydrochloride (obtained
from Aldrich), 99%, in ether solution was basified to pH ~13,
and then extracted with ether. The ether solution was washed
with distilled water, saturated sodium chloride solution, and
dried (MgSO$_4$). Separation from solvent afforded white crude
product. Recrystallization from hexane yielded 9-aminofluorene,
mp 64-65°C (lit.[42] mp 64-65°C); ir (KBr): 3350 cm$^{-1}$; nmr:
$\delta_{TMS}^{CDCl_3}$ 7.1 7.7 (m, aromatic H's, 9), 4.8 (s, CH, 1), 1.7 (s,
NH$_2$, 2).

Fluorenone Azine.[13] A solution of 17.0 g of KOH in 60 ml
of ethanol was added to a magnetically stirred hot mixture of
16.3 g (45 mmol) of fluorenone, 21 ml of hydrazine (95%), and
225 ml of ethanol. The whole mixture immediately turned deep-
red. Formation of the azine was completely by heating under
reflux for 15 min.. Upon cooling, 15.5 g (96%) of violet needles
were removed by filtration. Recrystallization from xylenes

yielded 13.0 g (81%) of fluorenone azine, mp 268-269°C (lit.[43] mp 265°C); ir (KBr): 1600 cm$^{-1}$; nmr: $\delta_{TMS}^{CDCl_3}$ 7.1-7.7 (m, aromatic H's, 12), 7.8-8.2 (m, aromatic H's, 4).

Preparation of Sodium Naphthalene Solution.   Into a 1-l., four-necked, round-bottomed flask, 400 ml of THF (distilled from LiAlH$_4$ under an argon atmosphere) was distilled under argon. After addition of 12.8 g (0.10 mol) of naphthalene and 2.0 g (0.087 mol) of sodium (freshly-cut under a layer of xylene and rinsed with petroleum ether before use) the deep-green mixture was cooled to -12°C and magnetically stirred for over 24 hr under argon to insure complete reaction. Two 5-ml aliquots were removed, and each was quenched in 50 ml of water, and titrated for total base with standardized hydrochloric acid to a phenolphthalein end-point to obtain a solution approximately 62.8 mmol in Na$^+$C$_{10}$H$_8^{-}$.

Reaction of Diphenyldiazomethane with Sodium Naphthalene.[44]
(a). _Slow, Dropwise Addition_.   To a 62.8 mmol Na$^+$C$_{10}$H$_8^{-}$ solution, a solution of 3.06 g (15.7 mmol) of Ph$_2$CN$_2$ in 150 ml of THF was added dropwise over a period of one hr. After 10 min., 50 ml of water was added and the mixture turned light yellow. The solvent was removed (rotavaporator) and the residue dissolved in ether. The ether solution was separated from the aqueous layer, and the ether layer was extracted with three 100-ml portions of 10% HCl solution. The aqueous acidic solution was basified to pH~13 with 10% NaOH solution, and the alkaline solution extracted with three 100-ml portions of ether. The combined ether extracts were washed with 150 ml of dis-

tilled water followed by 150 ml of saturated NaCl solution and
dried ($MgSO_4$). After solvent removal, 2.00 g (70%) of benzhy-
drylamine was obtained and identified by comparison of its nmr
and ir spectra with those of an authentic sample. After cor-
rection for the preestablished recovery of this amine (83.8%),
an 84% yield of benzhydrylamine was obtained. The benzamide
derivative was prepared as white crystals, mp 170-171.5$^{\circ}$C
(lit.[45] 172$^{\circ}$C).

The original ether solution was washed with 150 ml of dis-
tilled water, 150 ml of saturated NaCl solution, and dried
($MgSO_4$). After removal of the solvent, the residue was separa-
ted by sublimation at 35$^{\circ}$C/0.2 mm. The nmr spectrum of this
sublimate showed only the presence of naphthalene, 1,4-dihydro-
naphthalene, and $Ph_2CH_2$. Since the nmr absorptions of these
three components are cleanly separated from one another, the
amount of $Ph_2CH_2$ could be determined from the relative peak
areas multiplied by the total weight of the sublimate. In order
to get satifactory results for $Ph_2CH_2$, the sublimate was dis-
solved in $CH_2Cl_2$ and about 10 ml of this homogeneous solution
removed for the nmr spectral determination. After solvent re-
moval, the white solid was dissolved in $CDCl_3$ and the nmr spec-
trum and integrals recorded yielding 0.33 g (13%) of $Ph_2CH_2$
(run 1, Table I).

The experiment was repeated following the same procedures
described above to give $Ph_2CH_2$ (10%) and $Ph_2CHNH_2$ (82%) (run 2,
Table I). Another experiment was carried out following the
same procedures as described above to give $Ph_2CH_2$ (17%) and

$Ph_2CHNH_2$ (85%) except that 3.08 g (15.8 mmol) of $Ph_2CN_2$ in 100 ml of THF was added dropwise to $Na^+C_{10}H_8^{\bar{.}}$ (159 mmol) in 400 ml of THF over a period of 0.5 hr. (run 3, Table I).

(b). <u>Fast, Syringe Injection</u>. To $Na^+C_{10}H_8^{\bar{.}}$ (52.2 mmol) in 200 ml of THF a solution of 2.01 g (10.4 mmol) of $Ph_2CN_2$ in 10 ml of THF was injection via a syringe over a period of 5 sec.. Isolation of the products as described in the slow addition method gave 0.07 g (4%) of $Ph_2CH_2$ and 1.74 g (91%) of $Ph_2CHNH_2$ (run 4, Table I).

This experiment was repeated following the same procedures to give $Ph_2CH_2$ (5%) and $Ph_2CHNH_2$ (93%) (run 5, Table I).

<u>Reaction of Benzophenone Azine with Sodium Naphthalene.</u>[44]
Benzophenone azine (1.04 g, 2.91 mmol) in 100 ml of THF was treated in the same manner as the slow, dropwise addition of $Ph_2CN_2$ with $Na^+C_{10}H_8^{\bar{.}}$ (34.9 mmol). Benzhydrylamine (0.87 g, 82%) was obtained. After correction with the recovery factor for this amine, a 98% yield for benzhydrylamine was obtained.

<u>Reaction of 9-Diazofluorene with Sodium Naphthalene.</u>[44]
(a). <u>Slow, Dropwise Addition</u>. To $Na^+C_{10}H_8^{\bar{.}}$ (156.5 mmol) in 400 ml of THF, a solution of 3.00g (15.6 mmol) of $FlN_2$ in 100 ml of THF was added dropwise over a period of 0.5 hr. After 10 min, 50 ml of water was added which decolorized the reaction mixture. The procedures of separation as those in the reduction of $Ph_2CN_2$ with $Na^+C_{10}H_8^{\bar{.}}$ were followed to give 1.18 g (42%) of $FlHNH_2$ (run 1, Table II). After correction for its recovery factor (83.8%), this gave a 50% yield of $FlHNH_2$. Naphthalene and 1,4-dihydronaphthalene were removed by sub-

limation and fluorene remained in the sublimation tube. Using
1,3,5-trinitrobenzene as an internal standard and integrating
the nmr spectrum, 1.08 g (42%) of fluorene in the mixture was
determined.

The experiment was repeated using a 151 mmol $Na^+C_{10}H_8^-$
solution in 400 ml of THF and 2.90 g (15.1 mmol) of $FlN_2$ in
100 ml of THF and gave $FlH_2$ (39%) and $FlHNH_2$ (55%) (run 2,
Table II).

(b). Fast, Syringe Injection.  To a solution of 38.8 mmol of
$Na^+C_{10}H_8^-$ in 200 ml of THF, a solution of 1.86 g (9.7 mmol) of
$FlN_2$ in 10 ml of THF was injected via a syringe over a period
of 5 sec. Isolation of the products as described above in (a)
gave 1.35 g (77%) of $FlHNH_2$ (run 3, Table II). Naphthalene and
1,4-dihydronaphthalene were removed by sublimation and the
residue was eluted through a silica gel column (100 g) with
n-hexane to give 0.31 g of a mixture of compounds. Using 1,3,5-
trinitrobenzene as an internal standard, the nmr spectrum of
this mixture showed it to contain 0.10 g (7%) of $FlH_2$. Benzene-
$CHCl_3$ (50:50, v/v) eluted 0.10 g (6%) of $(Fl=N)_2$ checked by
TLC and glpc.

Another experiment was carried out by syringe injection of
a solution of 2.16 g (11.3 mmol) of $FlN_2$ in 10 ml of THF into
a solution of 112.3 mmol of $Na^+C_{10}H_8^-$ in 200 ml of THF over a
period of 5 sec. Separation of the products as described above
in the slow additions of $FlN_2$ gave $FlH_2$ (12%) and $FlHNH_2$ (88%)
(run 4, Table II).

Reaction of Fluorenone Azine with Sodium Naphthalene.[44]

A solution of 1.00 g (2.80 mmol) of (Fl=N$\overleftarrow{)}_2$ in 100 ml of THF
was treated by the same procedure as those in the reaction of
FlN$_2$ with 33.70 mmol of Na$^+$C$_{10}$H$_8$$^{\overline{}}$ in 400 ml of THF, yielding
0.85 g (84%) of FlHNH$_2$. After correction for its recovery fac-
tor, this gave 100% yield for FlHNH$_2$.

   Reaction of 9-Diazofluorene with Sodium-Ammonia.   Into a
500-ml, three-necked, round-bottomed flask, 100 ml of anhy-
drous NH$_3$ (distilled from Na) was condensed under an argon
atmosphere and 0.24 g (10.4 mmol) of freshly-cut Na was added.
The Na-NH$_3$ solution was allowed to stir magnetically for 30
min. Then 1.96 g (10.2 mmol) of FlN$_2$ in 9.5 ml of THF was sy-
ringe injected into the reducing solution over a period of 5
sec. The whole solution turned red-blue with a precipitate of
black solids. The mixture was allowed to stir for additional
3 min and quenched with solid NH$_4$Cl. After evaporating the NH$_3$
with an argon gas, 200 ml of ether was added to the flask. The
mixture turned purple with a black-blue precipitate. The mix-
ture was extracted with 800 ml of hexane and then 50 ml of CCl$_4$-
CHCl$_3$ to give deep-red solids and a orange-red solution. The
deep-red solids gave 1.40 g of (Fl=N$\overleftarrow{)}_2$ identified by TLC and
glpc. Evaporation of solvent from the orange-red solution re-
sulted in 0.31 g of an orange solid. This orange solid was
eluted through a column of silica gel (50 g) with hexane to
give 0.06 g (6%) of Fl=Fl, with hexane-CCl$_4$ (1:1, v/v) to give
0.07 g (4%) of FlH-HFl, with benzene to give 0.04 g of (Fl=N$\overleftarrow{)}_2$,
and with benzene-CH$_2$Cl$_2$ (1:1, v/v) to give 0.11 g (6%) of Fl=O
checked by TLC and glpc. The combined yield of (Fl=N$\overleftarrow{)}_2$ was

1.44 g (79%) (run 1, Table III).

The experiment was repeated and resulted in the isolation of Fl=Fl (3%), FlH-HFl (5%), (Fl=N$)_2$ (79%), and Fl=O (7%). (run 2, Table III).

### Reaction of 9-Fluorenyl Anion with 9-Diazofluorene.

Into a 500-ml, three-necked, round-bottomed flask, 200 ml of THF (distilled from LiAlH$_4$) was distilled under an argon atmosphere. To this was added 2.08 g (12.5 mmol) of FlH$_2$ followed by 6 ml (10.8 mmol) of phenyllithium (1.79 M, in 70:30 benzene/ether) by syringe injection. The orange solution was allowed to stir magnetically for 15 min under an argon atmosphere at -12°C. Then, 2.10 g (10.9 mmol) of FlN$_2$ in 10 ml of THF was injected with syringe. The whole solution turned deep-red. After stirring for 30 min, the reaction was quenched with 20 ml of distilled water. Rotavaporation of solvent afforded deep-red solids as crude product. The mixture was eluted through a column of silica gel (150 g) with hexane to give 1.20 g (7.23 mmol) of FlH$_2$, with hexane-CCl$_4$ (1:1, v/v) to give 0.10 g (0.3 mmol) of FlH-HFl, and with benzene to give 2.35 g (6.60 mmol) of (Fl=N$)_2$ (checked by TLC and glpc). Only trace amount of Fl=Fl was detected by glpc (run 2, Table IV).

The experiment was repeated with 2.12 g (11.0 mmol) of FlN$_2$ in 10 ml of THF to give 1.94 g (11.7 mmol) of FlH$_2$ and 2.31 g (6.5 mmol) of (Fl=N$)_2$; FlH-HFl or Fl=Fl were not detected (run 1, Table IV).

### Reaction of 9-Fluorenyl Anion with CF$_3$COOD-D$_2$O.

To 100 ml of dry, deoxygenated THF in a 500-ml, three-necked, round-

bottomed flask under an argon atmosphere at -12°C was added
2.00 g (12.0 mmol) of $FlH_2$ followed by syringe injection of
7.4 ml (13.3 mmol) of phenyllithium solution (1.79 M, in 70:30
benzene/ether). The orange solution was allowed to stir magne-
tically for 15 min under an argon atmosphere at -12°C. To this
was injected a solution of $(CF_3CO)_2O$ (1.96 g, 9.33 mmol) and
$D_2O$ (1.99 g, 100 mmol). The orange solution immediately turned
light-yellow. After removal of the solvent, the residue was
dissolved in 100 ml of ether. The ether solution was washed
with two 150-ml portions of distilled water, 150 ml of satura-
ted NaCl solution, and dried ($MgSO_4$). Evaporation of the sol-
vent gave 2.10 g of white solids. Recrystallization from ethanol
gave 1.90 g of white needles in a 95% yield. This compound was
identified as a mixture of 22% $FlH_2$ and 78% FlHD by $^{13}C$ nmr
spectrum, and 24% $FlH_2$ and 76% FlHD by $^1H$ nmr spectrum (Table
V).

Reaction of Fluorene with Sodium Naphthalene.[44]  To a
44.0 mmol of $Na^+C_{10}H_8^{\bar{}}$ in 400 ml of THF was added, dropwise,
a solution of 1.20 g (7.2 mmol) of $FlH_2$ in 100 ml of THF over
a period of 15 min at -12°C under an argon atmosphere. After
30 min, a mixture of $(CF_3CO)_2O$ (10.6 g, 50.5 mmol) and $D_2O$
(7.0 g, 350 mmol) was syringe injected to the deep-green solu-
tion over a period of 10 sec. The solution turned white after
addition of the acidic quench. After 15 min, the solvent was
removed by rotovaporation, and the residue was dissolved in
100 ml of ether. The ether solution was washed with two 150-ml
portions of distilled water and dried ($MgSO_4$). Evaporation of

the solvent gave a white solid. Naphthalene and 1,4-dihydro-
and -deuterionaphthalene were removed by sublimation at 30°C/-
0.2 torr and light yellow solids remained in the sublimation
tube. The bath temperature was raised up to 60°C and fluorene
sublimed, which was recrystallized from ethanol (1.10 g) and
identified as a mixture of 8% $FlH_2$, 72% FlHD, and 20% $FlD_2$ by
$^{13}C$ nmr spectrum; 8% $FlH_2$, 72% FlHD, and 20% $FlD_2$ by $^1H$ nmr
spectrum (Table V).

Calculation of Percentage Compositions of Deuterated Fluo-
rene by $^1H$ and $^{13}C$ NMR Spectroscopy. From multiple integration
of the $^1H$ nmr spectrum of authentic $FlH_2$, the total aryl-H's/-
$C_9$-$H_2$ ratio was determined to be 8.75/2 (see Table V). The
number of protons at $C_9$ of a sample of $C_9$-deuterated fluorene
were determined from its integral ratio, ($C_9$/total aryl), mul-
tiplied by 8.75. Using the amount of $FlH_2$ found in the sample
by $^{13}C$ nmr, the %'s FlHD and $FlD_2$ were then calculated in the
sample.

In the proton decoupled $^{13}C$ nmr spectrum of authentic
$FlH_2$, integrals of the $C_9$ and two of the aryl carbon absorp-
tions, $C_a$ (124.5 ppm) and $C_b$ (119.5 ppm), were used to give
$C_9/C_a$ = 0.588 and $C_9/C_b$ = 0.612 ratios (conversion factors,
Table V). The ratios of these integrals for the deuterated
fluorene were then divided by these correction factors to
obtain the percent $FlH_2$ in this sample.

To determine the percent FlHD in the sample, the mixture
of 24% $FlH_2$ and 76% FlHD (by $^1H$ nmr) was used. The ratio of the
integrated upfield absorption line of the $C_9$-D(H) triplet to

$C_a$ or $C_b$, corrected to 100% FlHD, gave the conversion factors 0.158 and 0.152, respectively (Table V). The ratio of these integrated absorptions for the deuterated fluorene samples divided by these conversion factors gave the percent of FlHD in the sample. The percent $FlD_2$ was then taken as the difference, $100 - \%\ FlH_2 - \%\ FlHD$.

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## ACKNOWLEDGMENTS

# VITA

Kuo-Wei Lin was born in Lo-Tung, Taiwan, on March 8, 1951. He was reared in Lo-Tung, where he lived until graduation from Taipei Institute of Technology in 1971.

In the summer of 1971, he entered the navy and was discharged from military service in June, 1973. He then entered Nan Ya Plastics Corporation in Taipei. In December, 1974, he married the former Virginia Su-O of Taipei, Taiwan.

In January, 1975, he entered the Graduate School at Kansas State University. His research program in organic chemistry for the M.S. degree was directed by Dr. Richard N. McDonald.

Kuo-Wei and Virginia have one son, Christopher, born in June of 1977.

THE CHEMICAL GENERATION OF CARBENE ANION RADICALS

by

KUO-WEI LIN

TAIPEI INSTITUTE OF TECHNOLOGY, 1971

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AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE UNIVERSITY
Manhattan, Kansas
1978

# ABSTRACT

The chemical generation of diphenylcarbene anion radical ($Ph_2C^{\overline{\cdot}}$) and fluorenylidene anion radical ($Fl^{\overline{\cdot}}$) was investigated. Slow, dropwise addition of a THF solution of diphenyldiazomethane ($Ph_2CN_2$) to excess sodium naphthalene in THF at -12°C under an argon atmosphere gave diphenylmethane ($Ph_2CH_2$) (11±2%) and benzhydrylamine ($Ph_2CHNH_2$) (83±1%) along with trace amounts of tetraphenylethane and benzophenone azine. Fast, syringe injection of the $Ph_2CN_2$ solution into the reducing agent produced 5±1% $Ph_2CH_2$ and 92±1% $Ph_2CHNH_2$.

Analogous slow, dropwise addition of 9-diazofluorene ($FlN_2$) in THF to excess sodium naphthalene in THF gave fluorene ($FlH_2$) (40±2%) and 9-aminofluorene ($FlHNH_2$) (53±3%), while fast, syringe injection gave the same components in 12% and 88% yields, respectively. The amines, $Ph_2CHNH_2$ and $FlHNH_2$, were shown to be the further reduction products of the corresponding azines, ($Ph_2C=N\overline{\overset{\cdot}{)}}_2$ and ($Fl=N\overline{\overset{\cdot}{)}}_2$. Fast, syringe injection of $FlN_2$ dissolved in a small amount of THF into sodium in liquid ammonia gave 79±0% ($Fl=N\overline{\overset{\cdot}{)}}_2$, 6±1% fluorenone, 4±1% 9,9'-bifluorenyl, and 4±1% 9,9'-bifluorenylidene.

These results are rationalized in terms of the intermediacy of the two carbene anion radicals, $Ph_2C^{\overline{\cdot}}$ and $Fl^{\overline{\cdot}}$. The formation of the arenes, $Ph_2CH_2$ and $FlH_2$, is established as the sequence H· followed by $H^+$ abstraction. Isolation of the two dimers, Fl=Fl and FlH-HFl, from the $Na/NH_3$ reduction of $FlN_2$ demontrates that $Fl^{\overline{\cdot}}$ can dimerize if certain other reactions of the carbene anion radical are surpressed.

Addition of $D_2O$ or $CF_3COOD-D_2O$ to the reduction mixture from slow addition of $FlN_2$ to sodium naphthalene in THF gave fluorene containing 40% and 50%, respectively, of excess deuterium as $FlD_2$. This excess deuterium content has been corrected for some H-D exchanges of $C_9$ of fluorene occurring in the $CF_3COOD-D_2O$ quench of related reaction mixtures. To account for the excess deuterium, it was proposed that $Fl^{\cdot-}$ was reduced by sodium naphthalene to the carbene dianion, $Fl^{2-}$.

Reaction of 9-fluorenyl anion ($FlH^-$) with $FlN_2$ in THF gave $FlH_2$ and $(Fl=N\overset{\cdot}{)_2}$. The results suggested two possible pathways for azine formation, one by reaction of $FlH^-$ with $FlN_2$ and the second by direct coupling of $Fl^{\cdot-}$ and $FlN_2$.