THE CHEMICAL GENERATION OF CARBENE ANION RADICALS FROM CERTAIN EPOXIDES

by

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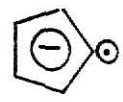
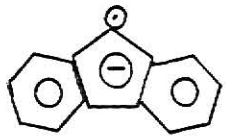
INTRODUCTION

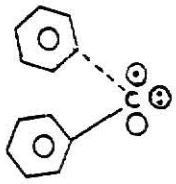
Carbene anion radicals ($R_2C^{-\cdot}$) are an interesting class of carbon-centered reactive intermediates since they have an electron pair and a spin unpaired electron formally localized on the central atom. Thus, the ground state doublet $R_2C^{-\cdot}$ species could undergo chemical reactions as bases, as nucleophiles, and/or as free radicals. The electronic structure of $H_2C^{-\cdot}$ has been examined by MINDO/3[1] and ab initio[3,4] calculations and is in excellent agreement with the estimated experimental structure derived from its photoelectron spectrum[3]. The electronic configuration of $H_2C^{-\cdot}$ is $\sigma^2\pi^1$ (σ-anion π-radical). It is assumed that the structure of $Ph_2C^{-\cdot}$ is similar with the phenyl rings twisted about their C_1-C_α bonds in order to relieve nonbonded repulsions. MINDO/3[1,5] calculations on the cyclopentadienylidene anion radical (c-$C_5H_4^{-\cdot}$) show that the ground state doublet has a $\sigma^1\pi^2$ (π-anion σ-radical) electronic configuration. The electronic configuration of the fluorenylidene anion radical ($Fl^{-\cdot}$) is assumed to be approximately the same as $C_5H_4^{-\cdot}$.



$C_5H_4^{-\cdot}$



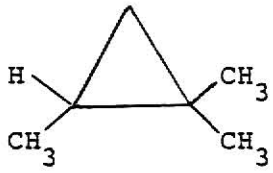
$Fl^{-\cdot}$



$Ph_2C^{-\cdot}$

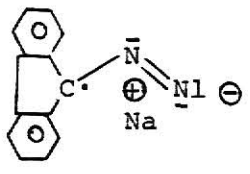
Carbene anion radicals have been proposed in the reductions of dihalo compounds (R_2CX_2) and diazo compounds (R_2CN_2). Sargent, et al.[6], reduced 2,2-dichloro 3,3-dimethylbutane with sodium naphthalene ($Na^+C_{10}H_8^{-\cdot}$) in 1,2-dimethoxyethane (DME) at 25°C to yield 1,1,2-trimethylcyclopropane (19%), 3,3-dimethyl-1-butene (38%) and 3,3-dimethylbutane (11.5%). The results were rationalized by formation of tert-butylmethylcarbene as an intermediate which was further reduced to the carbene anion radical at a rate competitive with that of intramolecular C-H insertion by the carbene.

$$CH_3C(CH_3)_2CCl_2CH_3 \xrightarrow[Na^+C_{10}H_8^{-\cdot}]{DME,\ 25^\circ} (CH_3)_2CH{=}CH_2 + (CH_3)_2CCH_2CH_3$$

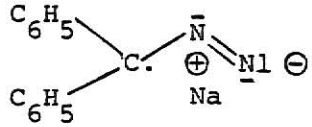


As further evidence for the formation of carbene anion radicals, Sargent, et al.[7], reduced CH_2Cl_2 in 60:40 (v/v) cyclohexene-DME with excess sodium naphthalene to yield CH_4, $CH_2{=}CH_2$, CH_3CH_3, and $CH_3CH_2CH_3$ as the principal products (>70%) of the reaction plus alkylated naphthalenes (<30%) and norcarane (<1%). The low yield of norcarane was explained by the conclusion that, if methylene was an intermediate in this reduction, it was reduced at a faster rate than it added to cyclohexene. To account for the constant, relative yield of ethylene generated by the reaction of the three methylene halides (X = Cl, Br, or I) with sodium naphthalene, it was suggested that $CH_2^{-\cdot}$ could dimerize to form ethylene dianion, followed by electron transfer with haphthalene, or that an $CH_2^{-\cdot} + CH_2X_2$ encounter could lead to formation of ethylene.

Kauffman and Hage[8] reported the reaction of diphenyldiazomethane (Ph_2CN_2) and 9-diazofluorene (FlN_2) with powdered sodium in ether under a N_2 atmosphere. The proposed reaction intermediates were diazo anion radical-sodium complexes, $FlN_2^{-\cdot}\ Na^+$ and $Ph_2CN_2^{-\cdot}\ Na^+$, respectively.

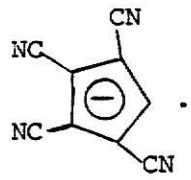


$FlN_2^{-\cdot}Na^+$



$Ph_2CN_2^{-\cdot}Na^+$

Webster[9] reported that tetracyanocyclopentadienylidene anion radical ($TCC^{-\bullet}$) was an intermediate in reactions of diazotetracyanocyclopentadiene (DTCC) with sodium halides to give halotetracyanocyclopentadiene. If ethanol or methanol was present, tetracyanocyclopentadiene was the only product isolated. The intermediate carbene anion radical could be generated polarographically in acetonitrile at 0.23 V vs. SCE, or by reaction with mild reducing agents, i.e. copper or zinc powder. The structure of $TCC^{-\bullet}$ was considered to be a π-anion σ-radical ($\pi^2\ \sigma^1$).



$TCC^{-\bullet}$

McDonald, et al.[10] reported on the electrochemical reduction of Ph_2CN_2 in 0.1 M DMF-$Et_4N^+ClO_4^-$. The principal product was benzophenone azine ($(Ph_2C{=}N{\rightarrow}_2$) along with lesser amounts of Ph_2CH_2 and several other compounds. Product formation was thought to occur by a chain process in which the carbene anion radical ($Ph_2C^{-\bullet}$) is produced from electrogenerated $Ph_2CN_2^{-\bullet}$ by rapid loss of nitrogen. Coupling of Ph_2CH^-, which is believed to come from $Ph_2C^{-\bullet}$ either by protonation followed by reduction or by H• abstraction, with Ph_2CN_2 ultimately produces the azine. In the presence of electro-inactive proton donors azine formation is interdicted and $Ph_2C{=}NNH_2$ from protonation of $Ph_2CN_2^{-\bullet}$ becomes a major product.

Elofson, et al.[11], reported quite different results for the polarographic reduction of Ph_2CN_2 in sulfolane. The products were Ph_2CH_2 (40%), Ph_2CHNH_2 (20%), and nitrogen. The decomposition of $Ph_2CN_2^{-\bullet}$ was suggested to occur by protonation to give $Ph_2CHN_2^{\bullet}$, which then either loses nitrogen

to give benzhydryl radical and ultimately Ph_2CH_2, or couples with benzhydryl radical to produce azodiphenylmethane. Reduction of this azo compound was postulated to give Ph_2CHNH_2.

McDonald, et al.[12], reported that the electrochemical reduction of FlN_2 in DMF-$(n\text{-}Bu)_4N^+ClO_4^-$ afforded the azine, $(Fl{=}N\rightarrow)_2$, in high yield (97%), and FlH_2 (1%). No dimeric product was detected by gas chromatography in other than trace amount. Electroreduction of FlN_2 in the presence of diethylmalonate (H^+ donor) produced a large increase in $Fl{=}NNH_2$ with no increase in FlH_2. Control experiments demonstrated that $Fl{=}NNH^-$ is only slowly protonated by DEM but reacts rapidly with FlN_2 to form the azine. Formation of Fl^- was not thought to be a major reaction channel.

Bethell, et al.[13], reacted FlN_2 in tert-butanol DMSO (9:1 v/v) containing potassium tert-butoxide to yield the azine, $(Fl\text{-}N\rightarrow)_2$, in almost 100% yield. From N^{15} labeling studies with mixed products, $Fl{=}N\text{-}N{=}CPh_2$, Bethell concluded that at least some of the azines were formed not via the carbene anion radical, $Fl^{-\cdot}$, but rather by reactions of $FlN_2^{-\cdot}$.

McDonald and Lin[14] reported that chemical reduction of Ph_2CN_2 and FlN_2 with $Na^+C_{10}H_8^{-\cdot}$ yield the carbene anion radicals, $Ph_2C^{-\cdot}$ and $Fl^{-\cdot}$, respectively. The products were Ph_2CH (15%) and benzhydrylamine (Ph_2CHNH_2, 84%) from Ph_2CN_2 and FlH_2 (40%) and 9-aminofluorene ($FlHNH_2$,53%) from FlN_2. These products were rationalized in terms of two reaction sequences. The arenes, Ph_2CH_2 and FlH_2, were formed from the reaction of the respective carbene anion radical by $H\cdot$ abstraction from the solvent followed by protonation upon quenching. The amines, Ph_2CHNH_2 and $FlHNH_2$, were thought to arise from the attack of that carbene anion radical on the parent diazo species, followed by reduction of the resulting azine anion radicals to the corresponding amines. The authors reported that dimerization of $Fl^{-\cdot}$ was possible if the reactions were carried out in a solvent

system (Na/NH_3) that did not allow for H· or H+ abstraction prior to the quench.

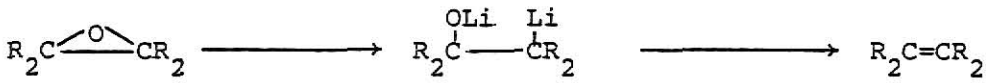
McDonald, et al.[15], has reported various gas-phase reactions of cyclopentadienylidene anion radical ($\underline{c}\text{-}C_5H_4^{\bullet-}$) in a flowing after glow apparatus. $\underline{c}\text{-}C_5H_4^{\bullet-}$ was generated by dissociative attachment of a thermal electron to diazocyclopentadiene ($\underline{c}\text{-}C_5H_4N_2$). Reaction of $\underline{c}\text{-}C_5H_4^{\bullet-}$ with diazocyclopentadiene gave cyclopentadienone azine anion radical ($C_{10}H_8N_2^{\bullet-}$, 64%), pentafulvalene anion radical ($C_{10}H_8^{\bullet-}$, 22%), and cyclopentadienyl anion ($C_5H_5^-$, 14%). These products were considered to arise from three separate reaction channels. The azine anion radical ($C_{10}H_8N_2^{\bullet-}$) was the result of $\underline{c}\text{-}C_5H_4^{\bullet-}$ adding to the terminal nitrogen of $\underline{c}\text{-}C_5H_4N_2$. In the second pathway, $C_{10}H_8^{\bullet-}$ was produced from attack of $\underline{c}\text{-}C_5H_4^{\bullet-}$ at C_1 of $\underline{c}\text{-}C_5H_4N_2$ and loss of nitrogen. $\underline{c}\text{-}C_5H_5^-$ would be formed by H· abstraction from $\underline{c}\text{-}C_5H_4N_2$. The cyclopentadienylidene anion radical ($\underline{c}\text{-}C_5H_4^{\bullet-}$) reacted with alcohols to H· abstract. Reaction of $\underline{c}\text{-}C_5H_4^{\bullet-}$ with alcohols showed both H· and H^+ abstraction. Reaction of $\underline{c}\text{-}C_5H_4^{\bullet-}$ with methyl halides gave nucleophilic displacement products.

The reductions of dihalo and diazo compounds suffer from several disadvantages. The use of diazo compounds in solution is plagued by attack of the carbene anion radical as it is formed on the parent compound thus removing it from further study. The dihalo compounds require very strong reducing agents, and require three sequential electron tranfer steps to yield $R_2C^{\bullet-}$.

Another possible class of compounds which when reduced could yield $R_2C^{\bullet-}$ species would be oxiranes ($R_2C\overset{O}{\diagup\!\!\diagdown}CR_2$). They are known to cleave during photolysis to generate the corresponding carbenes (R_2C) and the carbonyl compound[16-19]. Previous studies on reducing oxiranes have been concerned with the direction of opening of the epoxide ring to yield ultimately

the alcohol[20-22]. Boujlel and Simonet[23] have reported the direct and indirect electrochemical reductions of oxirane with at least one substituent group being an aromatic ring. Direct reduction of tetraphenyloxirane afforded benzhydrol (Ph_2CHOH, 37%), diphenylmethane (Ph_2CH_2, 58%), and tetraphenylethane ($Ph_2CHCHPh_2$, 5%). Indirect reduction of tetraphenyloxirane using naphthalene anion radical ($C_{10}H_8^{-\cdot}$) electrogenerated in situ gave Ph_2CH_2 (22%), Ph_2CHOH (23%), $Ph_2CHCHPh_2$ (5%), and 50% of the recovered oxirane.

Gurudutt and Ravindranath[24] have reported the deoxygenation of oxiranes when reacted with 2 equivalents of atomised lithium in THF. They also reported that reaction of the oxirane with sodium causes reduction to the alcohol stage. The deoxygenation was proposed to occur through the elimination of lithium oxide.



OBJECTIVE OF THIS INVESTIGATION

The objective of this investigation was to explore chemical reductions of certain aryl substituted oxiranes to see if cleavage would yield products potentially derived from further reactions of the corresponding carbene anion radicals.

RESULTS

Tetraphenyloxirane ($Ph_2C\overset{O}{\diagup\!\diagdown}CPh_2$) was synthesized from the epoxidation of tetraphenylethene ($Ph_2C{=}CPh_2$) by the procedure of Trumbull[25]; the ir and nmr spectra of the product were consistent with this structure. The potential products from reduction of tetraphenyloxirane were either synthesized by literature methods or were obtained from commercial sources: benzhydrol[26] (Ph_2CHOH), 1,1,2,2-tetraphenylethanol[27] ($Ph_2CH\text{-}COHPh_2$), benzopinacol[28] ($Ph_2COHCOHPh_2$), 1,1,2,2-tetraphenylethane ($Ph_2CHCHPh_2$, Columbia Organic), tetraphenylethene ($Ph_2C{=}CPh_2$, Aldrich), and diphenylmethane (Ph_2CH_2, Matheson).

The first reduction of $Ph_2C\overset{O}{\diagup\!\diagdown}CPh_2$ examined involved the slow, dropwise addition of a solution of the oxirane in dry THF over a period of an hour to a solution containing an excess of $Na^+C_{10}H_8^{\bullet-}$ in THF cooled to -12^oC under a N_2 atmosphere (runs 1-2, Table I). After distilled water was added, the original dark brownish green mixture turned yellow. The product mixture was analyzed using a Varian 5000 HPLC (10 ul loop injector) with a UV detector set at 254 nm with a solvent program that employed 40% CH_3CN/H_2O as eluent for 4 min., then increased the gradient to 100% CH_3CN after 15 min. retention time. The peak areas were measured and compared with standards of known concentration of each component to give the number of mmoles of compound when multiplied by the total volume of the solution. Product yields for the slow addition method were Ph_2CH_2 (55%±1), Ph_2CHOH (35%±2), $Ph_2CHCHPh_2$ (24%±1), $Ph_2CH\text{-}C(OH)Ph_2$ (11%±2), and $Ph_2C(OH)C(OH)Ph_2$ (7%±2), and $Ph_2C{=}CPh_2$ (2%±2).

Yields are reported on the basis of the mmoles of reactant used and mmoles of each product formed. Since cleavage of the epoxide can occur to yield two different fragmentation products, Ph_2CH_2 and Ph_2CHOH (from $Ph_2C{=}O$), the sum of the individual yields could be 200% if these were the only

Table I. Product Analysis for the Reaction of $Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$ with Sodium Naphthalene at -12°C[a]

Run No.	Method of Addition	$Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$ mM	$Na^+C_{10}H_8^{\bullet-}$ mM	Products, % Yield[d] Ph_2CH_2	Ph_2CHOH	$(Ph_2CH)_2$	$Ph_2CHC(OH)Ph_2$	$(Ph_2C(OH))_2$	$Ph_2C{=}CPh_2$
1	Slow[b]	1.3	13.1	56	34	24	13	5	1
2	Slow	1.9	17.4	54	37	24	10	8	3
3	Fast[c]	1.3	14.0	53	36	25	17	3	3
4	Fast	1.2	14.5	55	43	24	16	6	3

[a]All yields are based on comparison of the peak areas of the unknown sample with those of authentic standards. [b]Dropwise addition of $Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$ in 50 mL of THF to $Na^+C_{10}H_8^{\bullet-}$ in approximately 200 mL of THF over a period of one hour. [c]Syringe injection of $Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$ in 50 mL of THF to $Na^+C_{10}H_8^{\bullet-}$ in approximately 200 mL of THF over a period of 30 sec. [d]All yields are calculated on the % of reactant used. See test for explanation.

Table II. Product Analysis for Subsidiary Reactions with Sodium Naphthalene at -12°C[a]

Reactant[b]	mM	$Na^+C_{10}H_8^{\bullet-}$, mM	Products, % Yield
$Ph_2CHC(OH)Ph_2$	1.4	11.3	Ph_2CH_2 (96%), Ph_2CHOH (98%)
$Ph_2C{=}CPh_2$	1.7	16.8	$Ph_2CHCHPh_2$ (93%)
$Ph_2C{=}O$	2.1	20.9	Ph_2CHOH (93%), $(Ph_2C(OH))_2$ (<1%)

[a]All yields are based on comparison of peak areas from HPLC analysis of the unknown sample with those of authentic standards. [b]All reactions were done by syringe injection of the reactant dissolved in 50 mL of THF to $Na^+C_{10}H_8^{\bullet-}$ in 200 mL of THF over a period of 30 Sec.

products. The extent of recovery of products derived from the starting epoxide is found by adding the % of Ph_2CH_2 with those of $Ph_2CH\text{-}CHPh_2$, $Ph_2CHC(OH)Ph_2$, and $Ph_2C{=}CPh_2$ (55 + 24 + 11 + 2 = 92). This calculation assumes that the pinacol is produced by bimolecular reduction of $Ph_2C{=}O$ under these conditions.

A solution of $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ in dry THF was syringe injected over a period of 30 seconds (fast addition method) into a solution of $Na^+C_{10}H_8^{\cdot-}$ dissolved in THF cooled to -12°C (runs 3-4, Table 1). HPLC analysis of the product mixture showed the presence of Ph_2CH_2 (54%±2), Ph_2CHOH (40%±3), $(Ph_2CH)_2$ (25%±1), $Ph_2CHC(OH)Ph_2$ (17%±1), $Ph_2C(OH)O(OH)Ph_2$ (5%±2), and $Ph_2C{=}CPh_2$ (3%±1).

The stabilities of several of these products to the reducing, reaction conditions were determined. These reductions were carried out with the reactant dissolved in dry THF by the fast, syringe injection method and the results are given in Table II. 1,1,2,2-Tetraphenylethanol ($Ph_2CHC(OH)Ph_2$) produced Ph_2CH_2 (96%) and Ph_2CHOH (98%), while tetraphenylethene ($Ph_2C{=}CPh_2$) formed $Ph_2CH\text{-}CHPh_2$ (93%); and benzophenone gave Ph_2CHOH (93%) plus a trace of $Ph_2C(OH)C(OH)Ph_2$ (<1%).

The second epoxide, 6,6-dimethyldibenzofulvene oxide ($Fl\overset{O}{\diagup\!\!\diagdown}C(Me)_2$) was prepared from the epoxidation of 6,6-dimethyldibenzofulvene with m-chloroperbenzoic acid; ir, ^1H nmr and ^{13}C nmr of the product were consistent with this structure. The potential products from reduction of $Fl\overset{O}{\diagup\!\!\diagdown}C(Me)_2$ were either synthesized by literature methods or were obtained from commercial sources: 9-fluorenylisopropanol[29] ($Fl\text{-}C(OH)Me_2$, 6,6-dimethyldibenzofulvene[30] ($Fl{=}CMe_2$), 9-(2-propyl)fluorene[31] ($FlHCHMe_2$), 9,9-bifluorenylidene[32] (Fl=Fl), 9,9'-bifluorenyl[33] (FlH-FlH), and fluorene (FlH_2, Eastman Organic Chemicals).

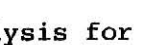
Both slow, dropwise addition and fast, syringe injection methods were

Table III. Product Analysis for Reaction of $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ and $Fl\overset{O}{\diagup\!\!\diagdown}CMe_2$ with Na/NH_3 at -34^oC[a]

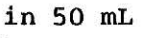
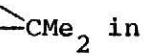
Na/NH_3, 4.3 mmol				$Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$, 1 mmol		
$Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$[b]	Ph_2CH_2	Ph_2CHOH	$Ph_2C\text{-}CPh_2$	$Ph_2CHCHPh_2$	$Ph_2CHC(OH)Ph_2$	$Ph_2C(OH)C(OH)Ph_2$
14%	66%	57%	<1%	1%	<1%	8%

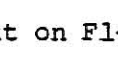
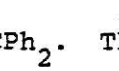
Na/NH_3, 4.3 mmol			Fl O CMe_2, 1.1 mmol	
FlH_2[b]	Me_2CHOH	$Me_2C{=}O$	$FlHC(OH)Me_2$	Fl-Fl
87%	60%	37%	7%	1%

[a]All yields are based on comparison of peak areas from HPLC analysis of the unknown sample with authentic standards.
[b]All yields are calculated on % of reactant used.

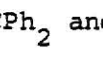
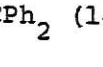
Table IV. Product Analysis for the Reaction of Fl  CMe_2 with Sodium Naphthalene at -12°C[a]

Run No.	Method of Addition	Fl  CMe_2 mM	$Na^+C_{10}H_8^{\cdot-}$ mM	Products, % Yield[d]		
				FlH_2	$FlHCHMe_2$	Me_2CHOH
1	Slow[b]	1.8	17.9	86	5	82
2	Slow	1.5	16.5	75	6	100
3	Fast[c]	1.7	21.0	89	4	92
4	Fast	1.6	21.0	95	4	92

[a]All yields are based on comparison of peak areas from HPLC analysis of unknown sample with authentic standards. [b]Dropwise addition of Fl  CMe_2 in 50 mL of THF to $Na^+C_{10}H_8^{\cdot-}$ in approximately 200 mL of THF over a period of one hour. [c]Syringe injection of Fl  CMe_2 in 50 mL of THF to $Na^+C_{10}H_8^{\cdot-}$ in approximately 200 mL of THF over a period of 30 sec. [d]All yields are calculated on mmoles of reactant used.

carried out on Fl  $C(Me)_2$ as previously described for the reductions of Ph_2C  CPh_2. The slow, dropwise addition method gave FlH_2 (81%±5), $FlHCHMe_2$ (5%±1), 2-propanol (Me_2CHOH, 91%±9), and traces of tetramethylethene glycol ($Me_2C(OH)C(OH)Me_2$) (runs 1-2, Table IV). For the analysis of these products a slightly different method was used. The compounds containing the fluorene system were determined by HPLC and comparison with authentic standards. Acetone, an expected cleavage product from the epoxide, could be determined at 270 nm on the HPLC with higher sensitivity. The amount of 2-propanol was determined by oxidizing a sample of the reduction solution with chromic acid. Authentic 2-propanol was oxidized at the same time and was found to yield acetone in 52-60% yield. This factor was then used to calculate the amount of 2-propanol in the sample. Fast, syringe injection reduction of Fl  CMe_2 gave FlH_2 (92%±3), $FlHCHMe_2$ (4%±1), and Me_2CHOH (92%±1) using the same HPLC analytical method (runs 3-4, Table IV).

The stabilities of several of these products to the reducing reaction conditions were determined. Using the syringe injection method, reduction of acetone gave Me_2CHOH (98%) and a trace of tetramethylethylene glycol, $Fl{=}C(Me)_2$ was reduced to $FlHCH(Me)_2$ (94%), and reduction of $FlHC(OH)Me_2$ gave FlH_2 (91%) and Me_2CHOH (85%) (Table V).

To investigate the effects of solvent on the reduction products, sodium in liquid ammonia (Na/NH_3) was examined as the reducing medium with both Ph_2C  CPh_2 and Fl$C(Me)_2$. The reaction of $Ph_2C$$CPh_2$ with Na/NH_3 solution under a N_2 atmosphere at $-34^{\circ}C$ was carried out to yield Ph_2C  CPh_2 (14%), Ph_2CH_2 (66%), Ph_2CHOH (57%), $(Ph_2C(OH)-)_2$ (8%), and $Ph_2CHCHPh_2$ (1%). The similar reduction of Fl  CMe_2 with Na/NH_3 solution produced FlH_2 (87%), $FlHC(OH)Me_2$ (7%), Fl-Fl (1%), $Me_2C{=}O$ (37%), and Me_2CHOH (60%) (Table III).

The two alcohols, $Ph_2CHC(OH)Ph_2$ and $FlHC(OH)Me_2$, were separatly allowed to react with sodium (freshly cut) in THF under a nitrogen atmosphere at $-12^{\circ}C$. The reaction with $Ph_2CHC(OH)Ph_2$ showed no cleavage had taken place with a high (95%) recovery of the alcohol. Reaction of $FlHC(OH)Me_2$ with sodium did show a small amount of cleavage taking place with the products being FlH_2 (1%) and $FlHC(OH)Me_2$ (92%).

Table V. Product Analysis for Subsidiary Reactions with Sodium Naphthalene at -12°C

Reactant[a]	nM	$Na^+C_{10}H_8^{-\cdot}$, mM	Products, %
$Me_2C=O$	2.1	20.9	Me_2CHOH (93%)[b]
$Fl=CMe_2$	1.7	15.6	$FlHCHMe_2$ (94%)
$FlHC(OH)Me_2$	1.8	20.0	FlH_2 (91%), Me_2CHOH (85%)

[a]All reactions were done by the syringe injection method. [b]Isopropanol was determined by oxidizing a sample with chromic acid and determining acetone on the HPLC at 270 nm. A standard was run at the same time to determine a correction factor based on % yield.

Table VI. Product Analysis for the Reaction of $Ph_2CHC(OH)Ph_2$ and $FlHC(OH)Me_2$ with Sodium[a]

Reactant	mM	Sodium, mM	Products, % yield[b]
$Ph_2CH(OH)Ph_2$	2.9	3.0	$Ph_2CH(OH)Ph_2$ (94%)[c]
$FlHC(OH)Me_2$	3.9	3.9	FlH_2 (1%), $FlHC(OH)Me_2$ (95%)

[a]The reactions were done by the syringe injection method using the same procedure as in the $Na^+C_{10}H_8^{-\cdot}$ reactions. [b]All % are based in comparison of peak areas from HPLC analysis of the unknown sample with authentic standards. [c]No trace of Ph_2CH_2 was detected.

DISCUSSION OF EXPERIMENTAL RESULTS

The reductions of $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ by $Na^+C_{10}H_8^{\bullet-}$ in THF were carried out by adding a solution of the oxirane to the reducing agent. As shown in Table I, the different methods of addition (slow, dropwise or fast, syringe injection) did not show a significant change in the product yields. Therefore, product formation from the reduction of the epoxide does not appear to show more than a first order dependency on the concentration of the epoxide. This conclusion is also reached for the similar reductions of $Fl\overset{O}{\diagup\!\!\diagdown}CMe_2$ (Table IV).

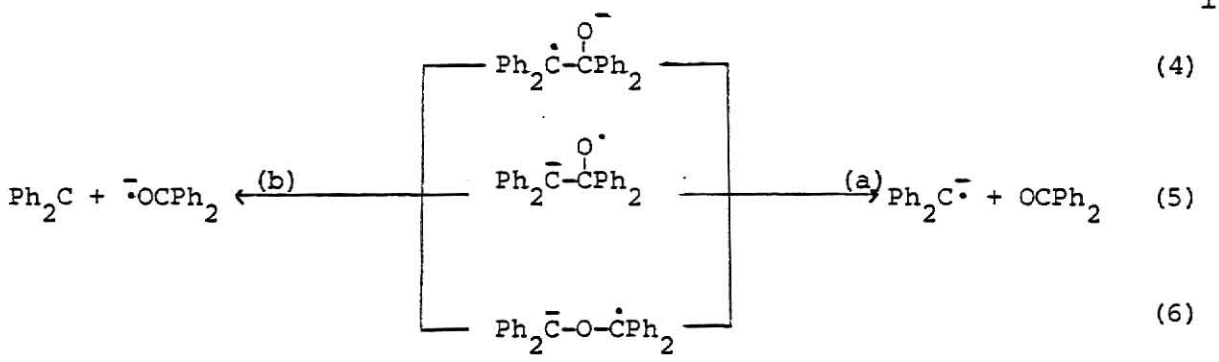
The results appear to be consistent with two competing processes, (a) electron transfer from the reducing reagent to the oxirane with the resulting opening of the epoxide ring, and (b) deoxygenation of the oxirane to the corresponding olefin. Using the symmetrical $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ structure there are three possible ring opening modes for process (a) which are shown in eqns. (1) - (3). Of the two intermediates

$$Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2 + e^- \longrightarrow Ph_2\dot{C}-\overset{O^-}{\underset{|}{C}}Ph_2 \qquad (1)$$

$$\longrightarrow Ph_2\bar{C}-\overset{O\cdot}{\underset{|}{C}}Ph_2 \qquad (2)$$

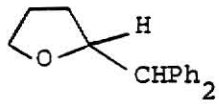
$$\longrightarrow Ph_2\bar{C}-O-\dot{C}Ph_2 \qquad (3)$$

shown in eqns. (1) and (2), that from eqn. (1) seems most reasonable in this system based on electronegativity considerations. Ring opening by carbon-carbon bond cleavage from the oxirane anion radical (eqn. 3) seems less plausible than the processes shown in eqns. (1) or (2), but cannot be ruled out of consideration. Each of these three ring-opened structures (eqns. (1) - (3)) could undergo fragmentation reactions shown in eqns. (4) - (6). The oxidation state of



the divalent carbon species and of the ketone products of these fragmentations depend on whether bond heterolysis or homolysis is involved.

The isolated products of fragmentation are Ph_2CH_2 and Ph_2CHOH. Both of these products could conceivably be formed from the intermediates from either fragmentation mode (a) ($Ph_2C^{\bullet} + O{=}CPh_2$) or (b) ($Ph_2C + {}^{\bullet} O{=}CPh_2$) in eqns. (4) - (6). However, mode (b) yielding Ph_2C as the singlet and/or triplet electronic state would be expected to yield considerable of the solvent (THF) insertion product 1 rather than only Ph_2CH_2.[19] The absence of compound 1 could be accommodated



1

with fragmentation mode (b) if the reduction of Ph_2C to $Ph_2C^{\bullet}$ by $Na^{+}C_{10}H_8^{\bullet}$ occurred more rapidly than did the potential insertion reaction of Ph_2C with the solvent.

When $Ph_2CHC(OH)Ph_2$ was allowed to react with sodium in THF and the reaction mixture quenched with water, only the starting alcohol was recovered (Table VI). This result established that the retro-condensation to Ph_2CH^{-} and Ph_2CO was not occurring to a measurable extent. However, the reaction of $Ph_2CHC(OH)Ph_2$ with excess $Na^{+}C_{10}H_8^{\bullet}$ in THF

$$Ph_2CH\text{—}\overset{OH}{\overset{|}{C}}Ph_2 \xrightarrow{Na} Ph_2CH\overset{O^-}{\overset{|}{C}}Ph_2 \xrightarrow{H_2O} Ph_2CH\text{—}\overset{OH}{\overset{|}{C}}Ph_2 \qquad (7)$$

produced complete fragmentation with Ph_2CH_2 and Ph_2CHOH as the isolated products (Table II). These two results establish that the intermediate that leads to fragmentation is a further reaction product from $Ph_2CHC(O^-)Ph_2$ and $Na^+C_{10}H_8^{-\cdot}$. One such structure is shown in eqn. (8) formed by first H^+ transfer from $Ph_2CHC(OH)Ph_2$ to $C_{10}H_8^{-\cdot}$ followed by H· abstraction from the alkoxide by further $C_{10}H_8^{-\cdot}$ producing the anion-radical, which is proposed as one of the intermediates from reduction of the epoxide in eqn. (1).

$$Ph_2CH\text{—}\overset{OH}{\overset{|}{C}}Ph_2 \xrightarrow{C_{10}H_8^{-\cdot}} Ph_2CH\text{—}\overset{O^-}{\overset{|}{C}}Ph_2 \xrightarrow{C_{10}H_8^{-\cdot}} Ph_2\dot{C}\text{—}\overset{O^-}{\overset{|}{C}}Ph_2 \qquad (8)$$

From the reduction of $Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$ with $Na^+C_{10}H_8^{-\cdot}$ in THF, $Ph_2CHC(OH)Ph_2$ was isolated in 10-17% yield (Table I). If reductive ring opening occured according to eqn. (1), an explanation for isolation of $Ph_2CHC(OH)Ph_2$ after workup of the reaction would be that the excess $C_{10}H_8^{-\cdot}$ was consumed before all of the anion-radical species could undergo unimolecular decomposition. This might be the case if H· abstraction from the solvent (THF) by the anion-radical were competitive with unimolecular decomposition, i.e. $k_2(THF) > k_3$ in eqn. (9). However, this suggestion

$$Ph_2CH\text{—}\overset{O^-}{\overset{|}{C}}Ph_2 \underset{k_2,THF}{\overset{k_1,\ C_{10}H_8^{-\cdot}}{\rightleftharpoons}} Ph_2\dot{C}\text{—}\overset{O^-}{\overset{|}{C}}Ph_2 \xrightarrow{k_3} \begin{matrix} Ph_2C^{-\cdot} + OCPh_2 \\ \text{or} \\ Ph_2C + {}^{=}{}^{\cdot}OCPh_2 \end{matrix} \qquad (9)$$

would lead to the prediction that a similar recovery of $Ph_2CHC(OH)Ph_2$ would be observed from the reaction of this alcohol with $Na^+C_{10}H_8^{-\cdot}$ since the conditions were similar to those used with $Ph_2C\overset{O}{\diagdown\!\diagup}CPh_2$. This was

not observed.

Formation of the remaining major product, $Ph_2CHCHPh_2$, from the reaction of $Ph_2C\overset{O}{\diagup\diagdown}CPh_2$ with $Na^+C_{10}H_8^{\cdot-}$ is believed to be the further reduction of $Ph_2C{=}CPh_2$, the olefin being the primary reaction product. If we use the mechanism proposed for deoxygenation of several oxiranes (e.g. stilbene oxides $\longrightarrow$ stilbene)[24] by two equivalents of lithium, we arrive at eqn. (10) for the present case. In eqn. (11)

$$Ph_2C\overset{O}{\diagup\diagdown}CPh_2 \xrightarrow{2Na^+C_{10}H_8^{\cdot-}} Ph_2\overset{Na}{C}-\overset{ONa}{C}Ph_2 \xrightarrow{-Na_2O} Ph_2C{=}CPh_2 \qquad (10)$$

$$\begin{array}{ccccc} Ph_2C{=}CPh_2 & \xrightarrow{Na^+C_{10}H_8^{\cdot-}} & Ph_2\dot{C}-\bar{C}Ph_2 & \xrightarrow{THF} & Ph_2CH\bar{C}Ph_2 \\ & & \downarrow Na^+C_{10}H_8^{\cdot-} & & \downarrow H_2O \\ Ph_2CHCHPh_2 & \xleftarrow{H_2O} & Ph_2\bar{C}-\bar{C}Ph_2 & & Ph_2CHCHPh_2 \end{array} \qquad (11)$$

two possible mechanisms are shown for the reduction of $Ph_2C{=}CPh_2$ to $Ph_2CHCHPh_2$.

Alternative possibilities for producing $Ph_2C{=}CPh_2$ or reduced forms of the olefin from eqn. (10) are shown in eqns. (12) - (15). The problem with the reactions shown in eqns. (12) - (15) is that they require two reactive

$$2\ Ph_2C \longrightarrow Ph_2C{=}CPh_2 \qquad (12)$$

$$Ph_2C^{\cdot-} + Ph_2C \longrightarrow Ph_2\bar{C}-\dot{C}Ph_2 \qquad (13)$$

$$2\ Ph_2C^{\cdot-} \longrightarrow Ph_2\bar{C}-\bar{C}Ph_2 \qquad (14)$$

$$Ph_2CH^- + Ph_2C \longrightarrow Ph_2CH-\bar{C}Ph_2 \qquad (15)$$

intermediates to find one another in a fairly reactive medium, THF, toward H· abstraction, C-H insertion, and, possibly, as a H^+ donor toward strong bases. The expected longer lifetime of Ph_2CH^- in THF would seem to allow the reaction shown in eqn. (15) to have the greatest probability of success of these four reactions. The fact that the yields of $Ph_2CHCHPh_2$ and

$Ph_2C{=}CPh_2$ are independent of the mode of addition, slow or fast (Table I), would appear to rule out all four of these pathways since the concentrations of these reactive intermediates at any given time should depend on the mode of addition of the two solutions.

The results from the reaction of $Fl\overset{O}{\frown}CMe_2$ with excess $Na^+C_{10}H_8^{\cdot-}$ in THF (Table IV) can be rationalized in terms of many of the same reactions discussed above for $Ph_2C\overset{O}{\frown}CPh_2$. Reduction of $Fl\overset{O}{\frown}CMe_2$ would be expected to proceed by one of the pathways shown in eqns. (16) - (18), analogous to eqns. (1) - (3) for the reduction of $Ph_2C\overset{O}{\frown}CPh_2$. In this case, however, C_9–O fission could more readily proceed by eqn. (17)

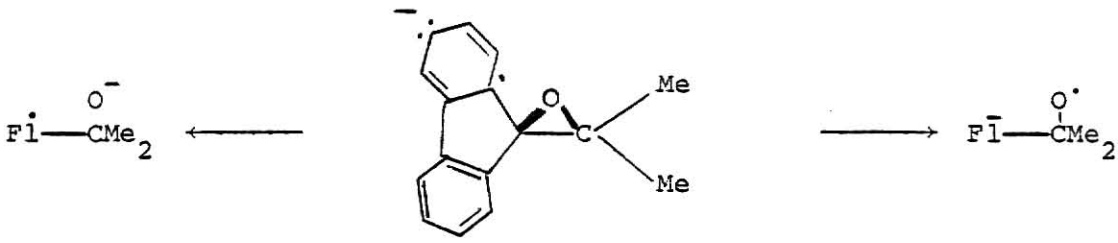
$$Fl\overset{O}{\frown}CMe_2 + e^- \longrightarrow Fl\text{—}\overset{\cdot}{C}(O^-)Me_2 \quad (16)$$

$$\longrightarrow Fl^-\text{—}C(O^{\cdot})Me_2 \quad (17)$$

$$\longrightarrow Fl^-\text{—}O\text{—}\overset{\cdot}{C}Me_2 \quad (18)$$

because of the increased stabilization of the carbanion by the 9-fluorenyl ring compared to that of the diphenylmethyl unit in eqn. (2). We assume that the opposite mode of ring opening to those of eqns. (16) and (17) do not occur because (a) of the expected stabilities of these products compared to those involving C_{10}–O rupture, and (b) no oxygen containing derivative (e.g. FlHOH) was observed in the products.

Formation of the structure of the intermediate in eqn. (17) can be rationalized if the electron is transferred from $C_{10}H_8^{\cdot-}$ into LUMO orbital of the fluorenyl ring of $Fl\overset{O}{\frown}CMe_2$. One of the contributing resonance structures of this reduction product is shown as structure 2. Homolytic β-cleavage of the C_9–O bond of 2 would give $Fl^-\text{—}C(O^-)Me_2$ while heterolytic β-cleavage of this bond would yield $Fl^{\cdot}\text{—}C(O^-)Me_2$. This approach to the reductive ring opening of $Fl\overset{O}{\frown}CMe_2$ strongly suggests that cleavage

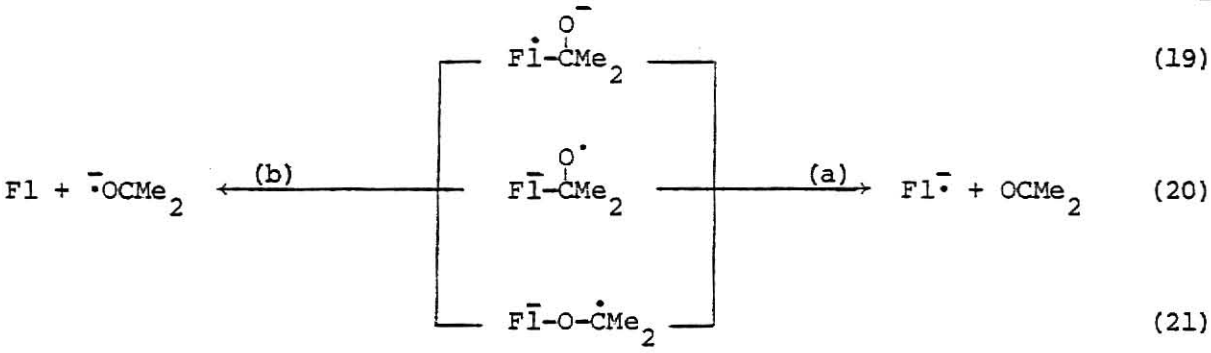


2

of the C_9-C_{10} shown in eqn. (18) would not occur from the oxirane anion radical since the C_9-C_{10} bond in 2 is almost orthogonal to the π-system.

The essential absence of retro-condensation when $FlHC(OH)Me_2$ was allowed to react with Na in THF (1% FlH_2 was observed: Table VI) shows that the simple alkoxide structure does not yield the fragmentation products, FlH_2 and Me_2CHOH (Table IV), when the oxirane is reduced. The fact that the reaction of $FlHC(OH)Me_2$ with excess $Na^+C_{10}H_8^{\bullet-}$ produces FlH_2 and Me_2CHOH in excellent yields (Table V) suggests that a further reaction product of $Na^+C_{10}H_8^{\bullet-}$ with the alkoxide is the precursor to the fragmentation products. The obvious structure for this precursor is $Fl^{\bullet}—C(O^-)Me_2$ or $Fl^-—C(O^{\bullet})Me_2$, the same structures shown in eqns. (16) and (17). These results and arguments are analogous to those found in the discussion for the reactions of $Ph_2CHC(OH)Ph_2$ (eqns. (7) and (8)).

Fragmentation of the anion radical intermediates in eqns. (16) - (18) could yield the sets of divalent carbon and ketonic species shown in eqns. (19) - (21). Here, fragmentation process (a) would be considered to be more favorable due to the expected greater stability of $Fl^{\bullet-}$ due to



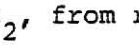
(19)

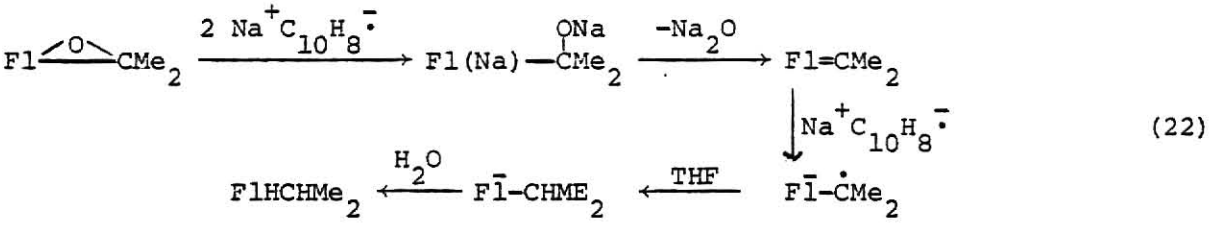
(20)

(21)

delocalization compared to $Ph_2C^{\bullet-}$, and lower stability of $Me_2CO^{\bullet-}$ compared to $Ph_2CO^{\bullet-}$ (-2.80 vs -1.84 V vs SCE)[35]. However, this can only be considered to be a best guess at this point.

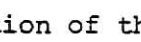
Formation of $Fl^{\bullet-}$ would most likely involve H• abstraction from THF to yield FlH^- which would be protonated in the work-up procedure. Since the ground state of fluorenylidene is the triplet[34], H• abstraction from THF followed reduction of FlH• by $Na^+C_{10}H_8^{\bullet-}$ would yield FlH^- which on protonation in the work-up procedure produces FlH_2. It was shown that Me_2CO was converted to the other major product Me_2CHOH under these reaction conditions and work-up procedure.

The minor reaction product, $FlHCHMe_2$, from reaction of Fl  with excess $Na^+C_{10}H_8^{\bullet-}$ (Table IV) is believed formed by a series of reduction steps shown in eqn. (22)



(22)

by analogy with those processes given in eqn. (11). In this case, no bifluorenyl (FlH-FlH) or bifluorenylidene (Fl=Fl) was observed, and the analogous reactions shown in eqns. (12) - (15) involving Fl, $Fl^{\bullet-}$, or FlH^- were not considered.

In this initial study of the reduction of the epoxides Ph_2C 

$Fl\angle^{O}\!\!\rangle CMe_2$ with excess $Na^{+}C_{10}H_8^{-\cdot}$ in THF, the major products were Ph_2CH_2, Ph_2CHOH, and $Ph_2CH\text{-}CHPh_2$, and FlH_2, Me_2CHOH, and $FlHCHMe_2$, respectively. The products were rationalized in terms of two competing pathways, fragmentation of the epoxide leading to Ph_2CH_2 and Ph_2CHOH or FlH_2 and Me_2CHOH, and deoxygenation of the epoxide followed by reduction of the olefins to give $Ph_2CH\text{-}CHPh_2$ or $FlHCHMe_2$. In the fragmentation reactions, the carbenes, Ph_2C or Fl, or carbene anion radicals, $Ph_2C^{-\cdot}$ or $Fl^{-\cdot}$, are thought to be involved. If carbenes are the fragmentation products, it may be possible to trap them with olefins. However, such olefin trapping reagents must be unreactive toward $Na^{+}C_{10}H_8^{-\cdot}$ in THF. The alcohols, $Ph_2CH(OH)Ph_2$ and $FlHC(OH)Me_2$, surprisingly were found to be stable when allowed to react with Na to form the corresponding alkoxide, and yet when allowed to react with excess $Na^{+}C_{10}H_8^{-\cdot}$ gave the fragmentation products, Ph_2CH_2 and Ph_2CHOH, and FlH_2 and Me_2CHOH, respectively.

SUMMARY

Investigations of the generation of diphenylcarbene anion radical ($Ph_2C^{-\bullet}$) from tetraphenyloxirane ($Ph_2C\langle O \rangle CPh_2$) were carried out by reducing the oxirane with excess $Na^+C_{10}H_8^{-\bullet}$ in THF under a nitrogen atmosphere at -12^oC. There was no significant difference between slow, dropwise addition and fast, syringe injection. Both methods gave the cleavage products Ph_2CH_2 (54±1%) and Ph_2CHOH (37±3%). Tetraphenylethane ($Ph_2CHCHPh_2$) was shown to arise by the reduction of tetraphenylethene ($Ph_2C{=}CPh_2$) which was the result of deoxygenation of the oxirane. Tetraphenylethanol ($Ph_2CH{-}C(OH)Ph_2$, 11±2%) was the simple reduction product of the epoxide. Benzopinacol ($(Ph_2C(OH)-)_2$, 7±2%) was thought to arise from dimerization of the benzophenone ketyl radical.

Reduction of $Ph_2C\langle O \rangle CPh_2$ in Na/NH_3 (4:1) gave the cleavage products Ph_2CH_2 (66%) and Ph_2CHOH (57%), a small amount of deoxygenation product, $Ph_2CHCHPh_2$ (1%), and some unreacted epoxide, $Ph_2C\langle O \rangle CPh_2$ (14%). Along with this was benzopinacol (8%), which was assumed came from the dimerization of the benzophenone ketyl.

Analogous reductions of $Fl\langle O \rangle CMe_2$ by $Na^+C_{10}H_8^{-\bullet}$ in THF were also examined. Both methods of slow addition and fast injection again showed no significant difference. The major products were FlH_2 (86±5%) and Me_2CHOH (92±1%). Only small amounts of the deoxygenation product, 9-(2-propyl)fluorene, were found. The deoxygenation product, $Fl{=}CMe_2$, was shown to be further reduced to the alkane, $FlHCHMe_2$. Reduction of $Fl\langle O \rangle CMe_2$ in Na/NH_3 gave FlH_2 (87%), $FlHC(OH)Me_2$ (7%), and FlHFlH (1%).

These results are rationalized in terms of two competing processes, (a) electron transfer from the reducing reagent to the oxirane with the resulting opening of the epoxides ring, and (b) deoxygenation of the oxirane to the corresponding olefin. In the fragmentation of the epoxide

rings either the carbenes (Ph_2C, Fl) or carbene anion radicals ($Ph_2C^{\bullet -}$, $Fl^{\bullet -}$) are possible intermediates. Further tests are planned to trap the carbenes to test this hypothesis.

EXPERIMENTAL SECTION[36]

Tetraphenylethene. This compound was obtained from Aldrich Chemical Company, mp 222-224°C (lit.[37] mp 220°C); ir (KBr): 1575 cm^{-1} (C=C); nmr: δ^{CDCl}_{TMS} 3 7.1 (s, aromatic H's).

1,1,2,2-Tetraphenylethane. The compound was obtained from Columbia Organic Company and recrystallized from $CHCl_3$-EtOH(1:1) with mp 210-211°C (lit.[38] mp 209-211°C): ir (KBr): 3000 cm^{-1} and 2900 cm^{-1} (C-H); nmr: $\delta^{CDCl_3}_{TMS}$ 6.9-7.3 (m, aromatic H's, 20), 4.8 (s, CH, 2).

Diphenylmethane. This compound was obtained from Matheson Chemical Company and distilled under vacuum, bp 73.5°C/0.6 mm. (lit.[39] 154-155°C/33 mm).

Benzhydrol. The procedure of Wiselogle[26] with alcoholic KOH and zinc dust was used to reduce benzophenone in 90% yield. The product was recrystallized from 95% ethanol, mp 66-67°C; (lit.[40] mp 68-69°C); ir (KBr): 3200-3500 cm^{-1} (O-H); nmr: $\delta^{CDCl_3}_{TMS}$ 7.2(s, aromatic H's, 10), 5.6 (s, CH,1), 2.3 (s, OH, 1).

Tetraphenyloxirane. This compound was obtained from epoxidation of tetraphenylethene[25] in $CHCl_3$ by m-chloroperbenzoic acid in 95% yield, mp 208-209°C, (lit.[41] mp 208°C); ir (KBr): 1220 cm^{-1} and 905 cm^{-1} (C-O-C); nmr: $\delta^{CDCl_3}_{TMS}$ 7.1-7.3 (s, aromatic H's, 20).

1,1,2,2-Tetraphenylethanol. This compound was obtained by the Grignard reaction of phenylmagnesium bromide with diphenylacetophenone in 70% yield[27], mp 227-228°C (lit.[42] 227-229°C); ir (KBr): 3200-3500 cm^{-1} (OH); nmr: δ^{CDCL}_{TMS} 3 7.0-7.6 (m, aromatic H's, 20), 5.2 (s, CH, 1), 2.8 (s,OH,1).

Benzopinacol. This compound was obtained from the photolysis of benzophenone in isopropanol in 45% yield[28], mp 185-186°C; (lit.[43] mp 186°C); ir (KBr): 3200-3600 cm^{-1} (OH), nmr: $\delta^{CDCl_3}_{TMS}$ 7.0-7.5 (m, aromatic H's, 20),

3.0 (s, OH, 2).

9.9'-Bifluorenylidene. This compound was prepared from the coupling of fluorenone with McMurray's reagent[44] (4 $TiCl_3$-$LiAlH_4$ from Alfa). To 100 mL of freshly distilled THF was added slowly 3.3 g of McMurray's reagent under an nitrogen atmosphere. The solution was stirred for 15 min. when 3.6 g (20 mmol) of fluorenone in 50 mL of THF was added dropwise. The mixture was heated under reflux under a nitrogen atmosphere for 6 hr. The cooled mixture was poured into 1.5 L of distilled water and extracted with CCl_4. After the solvent was removed, the residue was eluted through a column of silica gel (100 g) with hexanes to give 1.7 g of crude product. Recrystallization from $CHCl_3$-EtOH (1:1) gave 1.5 g (42%) of 9.9-bifluorenylidene, mp 193-194°C, (lit.[45] mp 194°C); ir (KBr): 1600 cm^{-1} (C=C); nmr: $\delta^{CDCl_3}_{TMS}$ 7.0-7.7 (m, aromatic H's, 12), 8.2-8.4 (m, aromatic H's, 4).

9.9'-Bifluorenyl. This compound was prepared by decomposing fluorenyltosylhydrazone in ethylene glycol.[33] To 6.2 g (34 mmol) Fl=O was added 6 g (34 mmol) tosylhydrazine in 50 mL EtOH. This mixture was refluxed for 10 min. and filtered. The solid material in 50 mL of ethylene glycol was added to a solution of 0.3 g Na in 100 mL ethylene glycol which had been heated under nitrogen. The mixture was heated at 120°C for 4 hr. and cooled. Eight-hundred mL of H_2O was added and the product was extracted with 200 mL of ether and dried ($MgSO_4$). Evaporation of the solvent gave 3 g of pale white solid, mp 244-245°C (lit.[46] 245-246°C); ir (KBr): 3000 cm^{-1} (CH); nmr: $\delta^{CDCl_3}_{TMS}$ 7.0-7.7 (m, aromatic H's, 16), 4.8 (s, Ch, 2).

Fluorene. This compound was purchased from Eastman Organic Chemicals, mp 115-117°C; ir (KBr): 2950 cm^{-1}; nmr: $\delta^{CDCl_3}_{TMS}$ 7.2-7.9 (m, aromatic H's, 8), 3.8 (s, CH_2, 2).

1-(9-fluorenyl)isopropanol. This compound was obtained from reaction of fluorenyllithium with acetone,[29] mp 101-102°C (lit.[47] mp 99-101°C); ir (Nujol mull): 3500-3900 cm^{-1} (OH); nmr: $\delta_{TMS}^{CDCl_3}$ 7.0-7.8 (m, aromatic H's, 8), 1.0 (s, CH_3, 6), 1.9 (2, OH, 1), 4.0 (s, CH,1).

Dimethyldibenzofulvene. The technique of Garbisch[30] was used to dehydrate the alcohol above, mp 114-116°C (lit.[48] 113-117°C); ir (KBr): 1600 cm^{-1} (C=C); nmr: $\delta_{TMS}^{CDCl_3}$ 7.1-7.8 (m, aromatic H's, 8), 2.5 (s,CH_3, 6).

6.6-Dimethyldibenzofulvene oxide. This compound was obtained from epoxidation of dimethyldibenzofulvene by m-chloroperbenzoic acid in 96% yield[25], mp 89-90°C; ir (KBr): 1200, 755 cm^{-1} (COC); nmr: $\delta_{TMS}^{CDCl_3}$ 7.1-7.8 (m, aromatic H's, 8), 1.7 (s, CH_3, 6).

9-(2-propyl)fluorene. 9-Fluorenyllithium was reacted with isopropyl-bromide according to the procedure of Miller[31] in 65% yield, mp 54-55°C (lit.[48] 53-55°C); ir (KBr): 1460 cm^{-1} (CH_3): nmr: $\delta_{TMS}^{CDCl_3}$ 7.2-7.8 (m, aromatic H's, 8), 9.0 (d, CH_3, 6), 2.5 (m, CH, 1), 3.9 (d, CH, 1).

Preparation of Sodium Naphthalene Solution. Into a 1 L, four-necked, round bottom flask, 200 mL of THF (distilled from sodium with benzophenone ketyl as indicator) was distilled under nitrogen. Naphthalene (3.0 g, 0.023 mol) was added and the solution was degassed by bubbling nitrogen through it for 6 hrs. The solution was then cooled to -12°C and 400 mg (17 mmol) sodium was added (freshly cut and rinsed with petroleum ether before use). The solution was cooled and stirred for 24 hrs. Two 2-ml aliquots were removed and each was quenched with 50 mL of water, and titrated for total base with standardized hydrochloric acid to a phenolphthalein endpoint to obtain a solution approximately 17.4 mmol in $Na^+C_{10}H_8^{-\cdot}$.

Reaction of Tetraphenyloxirane with Sodium Naphthalene. (a). Slow, Dropwise Addition. To a 17.4 mmol $Na^+C_{10}H_8^{-\cdot}$ solution, a solution of 660 mg (1.9 mmol) of $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ in 50 mL of THF, which had been degassed

by the freeze-thaw method, was added dropwise over a period of one hour. After 10 min., 5 mL of water was added and the mixture turned light yellow. The solution was allowed to warm to room temperature and the volume was measured. A sample of this solution was then injected into the HPLC[36b]. The products and their retention times (min) were Ph_2CHOH (6.3), Ph_2CH_2 (12.3), $Ph_2CHC(OH)Ph_2$ (13), $(Ph_2C(OH)\rightarrow_2$ (12.5), $(Ph_2CH\rightarrow_2$ (13.4), and $Ph_2C{=}CPh_2$ (15.5). Authentic standards of known concentration (approximately 0.5 mg/mL) were run on the HPLC under the same conditions at the same time. Areas were measured and yields of products were calculated as illustrated below.

$$\frac{\text{Area of Product}}{\text{Area of standard}} \times \text{std(mg/mL)} \times \frac{\text{Volume of solution (mL)}}{1000\ (\text{MW of product})} = \text{moles}$$

$$\frac{\text{moles of product}}{\text{moles of reactant}} \times 100 = \%\ \text{yield}$$

HPLC analysis for the mixture gave Ph_2CHOH (151/234,0.468, 265mL; 34%), Ph_2CH_2 (269/252, 0.431; 56%), $(Ph_2C(OH)\rightarrow_2$ (50/372, 0.604; 5%), $Ph_2CHC(OH)Ph_2$ (170/204, 0.273; 13%), $(Ph_2CH\rightarrow_2$ (319/348, 0.41; 24%), and $Ph_2C{=}CPh_2$ (140/477, 0.052; 1%).

The experiment was repeated following the same procedure with 1.9 mmol reactant. HPLC analysis [36b] gave Ph_2CH_2 (428/260, 0.431, 235 mL,; 54%), Ph_2CHOH (280/245, 0.468; 37%), $Ph_2CHC(OH)Ph_2$ (219/225, 0.273; 10%), $(Ph_2CH\rightarrow_2$ (560/345, 0.41; 24%), $(Ph_2C(OH)\rightarrow_2$ (155/400, 0.604; 8%), and $Ph_2C{=}CPh_2$ (825/510, 0.052; 3%).

(b). Fast, Syringe Injection. To $Na^+C_{10}H_8^{\cdot-}$ (14 mmol) in 200 mL of THF a solution of 660 mg (1.3 mmol) of $Ph_2C\overset{O}{\frown}CPh_2$ in 50 mL of THF was injected via a syringe over a period of 30 sec. HPLC analysis[36b] gave

Ph_2CHOH (196/234,0.468, 216 mL; 36%), Ph_2CH_2 (252/312, 0.431; 53%), $(Ph_2C(OH))_2$ (36/372, 0.604; 3%), $Ph_2CHC(OH)Ph_2$ (270/204, 0.273; 17%), $(Ph_2CH)_2$ (414/348, 0.41; 25%), and $Ph_2C{=}CPh_2$ (525/477, 0.052; 3%).

The experiment was repeated following the same procedures to give Ph_2CHOH (224/234, 0.468, 205 mL; 43%), Ph_2CH_2 (361/300, 0.431; 55%), $(Ph_2CH)_2$ (414/378, 0.41; 24%), $(Ph_2C(OH))_2$ (72/372, 0.604; 6%), $Ph_2CHC(OH)Ph_2$ (240/204, 0.273; 16%), and $Ph_2C{=}CPh_2$ (828/696, 0.052; 3%).

Reaction of 1,1,2,2-Tetraphenylethanol with Sodium Naphthalene. Tetraphenylethanol (490 mg, 1.4 mmol) in 50 mL of THF was treated in the same manner as the fast, syringe injection method with $Na^+C_{10}H_8^{-\cdot}$ (11.3 mmol). HPLC analysis[36b] gave Ph_2CHOH (574/244, 0.468, 226 mL; 98%) and Ph_2CH_2 (650/285, 0.431; 96%).

Reaction of Tetraphenylethene with Sodium Naphthalene. Tetraphenylethene (570 mg, 1.7 mmol) in 50 mL of THF was treated in the same manner as the fast, syringe injection method with $Na^+C_{10}H_8^{-\cdot}$ (16.8mmol). HPLC analysis[36b] gave $Ph_2CHCHPh_2$ (2300/385, 0.41, 210 mL; 93%).

Reaction of Benzophenone with Sodium Naphthalene. Benzophenone (380 mg, 2.1 mmol) in 50 mL of THF was treated in the same manner as the fast, syringe injection method with $Na^+C_{10}H_8^{-\cdot}$ (20.9 mmol). HPLC analysis[36b] gave Ph_2CHOH (788/250, 0.468, 248 mL; 93%) and a trace of benzopinacol.

Reaction of Tetraphenyloxirane with Sodium in Liquid Ammonia. Into a 500 mL, three-necked, round bottomed flask, 100 mL of anhydrous NH_3 (distilled from Na) was condensed under a nitrogen atmosphere and 100 mg (4 mmol) of freshly cut Na was added. The Na/NH_3 solution was allowed to stir magnetically for 30 min, then 350 mg (1 mmol) of $Ph_2C\overset{O}{—}CPh_2$ was added to the reducing solution. The whole solution turned red-blue. The mixture was allowed to stir for 5 min. and then was quenched with solid NH_4Cl. After evaporating the NH_3, 200 mL of THF was added to the flask. HPLC

analysis[36b] of the mixture gave Ph_2CHOH (252/224, 0.468; 57%), Ph_2CH_2 (497/384, 0.431; 66%), $(Ph_2C(OH)\frac{}{})_2$ (83/345, 0.604; 8%), $Ph_2C\overset{O}{\diagup\!\!\diagdown}CPh_2$ (262/570, 0.53; 14%), $(Ph_2CH\frac{}{})_2$ (27/474, 0.41; 1%), and a trace of $Ph_2C{=}CPh_2$ and $Ph_2CHC(OH)Ph_2$.

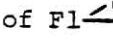
Reaction of 1,1,2,2-Tetraphenylethanol with Sodium. Tetraphenylethanol (1.0 g, 2.9 mmol) in 50 mL of THF was treated in the same manner as the fast, syringe injection method with freshly cut sodium (70 mg, 2.9 mmol). HPLC analysis[36b] gave $Ph_2CHC(OH)Ph_2$ (4700/212, 0.273, 155 mL; 94%) and no trace of Ph_2CH_2.

Reaction of 6,6-Dimethyldibenzofulvene oxide with Sodium Naphthalene. (a). Slow, Dropwise Addition. To $Na^+C_{10}H_8^{\bullet-}$ (17.9 mmol) in 200 mL of THF, a solution of 390 mg (1.8 mmol) of $Fl\overset{O}{\diagup\!\!\diagdown}CMe_2$ in 50 mL of THF, which had been degassed by the freeze-thaw method, was added dropwise over a period of one hour. After 10 min, 5 mL of water was added and the solution turned yellow. The HPLC retention times were $FlHC(OH)Me_2$ (10.1), FlH_2 (11.9), $FlHCHMe_2$ (14), $Fl{=}CMe_2$ (14.6), FlH-FlH (13.0), and Fl=Fl (17.0). HPLC analysis[36b] of the reaction mixture gave FlH_2 (2840/371, 0.15, 218 mL; 86%) and $FlHCHMe_2$ (116/845, 0.599; 5%).

The non-aromatic product Me_2CHOH from the reduction was determined by oxidation to $Me_2C{=}O$ which could be determined at 270nm on the HPLC at high sensitivity. A sample of the reduction solution was oxidized with a chromic acid solution along with that of a known sample. The amount was then determined on the HPLC with the % yield from the known sample used as a correction factor. The amount of Me_2CHOH obtained by this method was (300/150, 0.1, correction factor 1.9) 82%.

The experiment was repeated using a 16.5 mmol $Na^+C_{10}H_8^{\bullet-}$ solution in 200 mL of THF and 340 mg (1.5 mmol) of $Fl\overset{O}{\diagup\!\!\diagdown}CMe_2$ in 50 mL of THF. HPLC analysis[36b] gave FlH_2 (2160/371, 0.15, 215 mL; 75%), $FlHCHMe_2$ (130/845,

0.599; 6%), and Me_2CHOH (370/165, 0.1, correction factor 1.8; 100%).

(b). Fast, Syringe Injection. To $Na^+C_{10}H_8^{\cdot-}$ (21 mmol) in 200 mL of THF a solution of 380 mg (1.7mmol) of Fl  CMe_2 in 50 mL of THF was injected via a syringe over a period of 30 sec. HPLC analysis[36b] of the products gave FlH_2 (2700/371, 0.15, 238 mL; 89%), $FlHCHMe_2$ (94/845, 0.599; 6%), and Me_2CHOH (390/172, 0.1, correction factor 1.7; 92%).

The experiment was repeated to give FlH_2 (3250/371, 0.15, 190mL; 95%), $FlHCHMe_2$ (100/845, 0.599; 4%), and Me_2CHOH (388/140, 0.1, correction factor 1.6; 92%).

Reaction of Acetone with Sodium Naphthalene. To $Na^+C_{10}H_8^{\cdot-}$ (20.9 mmol) solution in 200 mL of THF was injected via a syringe 120 mg (2.1 mmol) of $Me_2C{=}O$ in 50 mL of THF. The Me_2CHOH was determined in the same manner as in part (a) to give Me_2CHOH (440/150, 0.1, 205 mL, correction factor 2; 98%).

Reaction of 6,6-dimethyldibenzofulvene with Sodium Naphthalene. Using the procedures for the fast injection method, a $Na^+C_{10}H_8^{\cdot-}$ (15.6 mmol) solution was injected with 350 mg (1.7mmol) of $Fl{=}CMe_2$ in 50 mL of THF. HPLC analysis[36b] gave $FlHCHMe_2$ (1900/816, 0.599, 238 mL; 94%).

Reaction of 2-(9-Fluorenyl)-2-propanol with Sodium Naphthalene. Using the procedures for the fast injection method, $Na^+C_{10}H_8^{\cdot-}$ (20.0 mmol) solution was injected with 400 mg (1.8 mmol) of $FlHC(OH)Me_2$ in 50 mL of THF. HPLC analysis[36b] gave FlH_2 (2800/346, 0.15, 220 mL; 91%) and Me_2CHOH (330/165, 0.1, correction factor 2; 85%).

Reaction of 6,6-Dimethyldibenzofulvene oxide with Sodium in Liquid Ammonia. Into a 500 mL, three-necked, round bottomed flask, 100 mL of anydrous NH_3 (distilled from Na) was condensed under a nitrogen atmosphere and 100 mg (4.3 mmol) of freshly cut Na was added. The Na/NH_3 solution was

allowed to stir for 30 min and then 250 mg (1.1 mmol) of Fl$\overset{\diagup O \diagdown}{\text{———}}CMe_2$ was added in solid form to the solution. The solution turned orange-vlue. The mixture was allowed to stir for 5 min and then quenched with NH_4Cl. The NH_3 was allowed to evaporate and then 200 mL of THF was added. HPLC analysis[36b] gave FlH_2 (1750/330, 0.15, 200 mL; 87%), FlH-FlH (18/384, 0.27; 1%), $FlHC(OH)Me_2$ (233/1620, 0.62; 7%), $Me_2C{=}O$ (34/144, 0.1; 37%), and Me_2CHOH (151/144, 0.1, correction factor 1.8, 60%).

Reaction of 2-(9-Fluorenyl)-2- propanol with Sodium in THF. 2-(9-Fluorenyl)-2-propanol (390 mg, 1.8 mmol) in 50 mL of THF was treated in the same manner as the fast, syringe injection method with freshly cut sodium (40 mg, 1.8 mmol) in THF. HPLC analysis[36b] gave $FlHC(OH)Me_2$ (1340/1550, 0.62, 155 mL; 95%) and FlH_2 (12/375, 0.15; 1%)

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36. (a) Melting points were determined on a Kofler hot stage and are uncorrected, as are boiling points. Spectra were obtained on commercial instruments (ir, P-E 137; nmr, Varian T-60). (b) HPLC analyses were recorded using a Varian model 5000 liquid chromatograph with a varian MCH-10, universal, reverse-phase column. The solvent used was 40% CH_3CN/H_2O for 4 min then increasing gradient to 100% CH_3CH at 15 min.

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THE CHEMICAL GENERATION OF CARBENE ANION RADICALS FROM CERTAIN EPOXIDES

by

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ABSTRACT

The generation of diphenylcarbene anion radical ($Ph_2C^{\cdot-}$) and fluorenylidene anion radical ($Fl^{\cdot-}$) by chemical reduction of selected epoxides was investigated. Slow, dropwise addition of a THF solution of tetraphenyloxirane ($Ph_2C\overset{O}{\frown}CPh_2$) to excess sodium naphthalene in THF at -12°C under a nitrogen atmosphere gave the cleavage products diphenylmethane (Ph_2CH_2, 55±1%) and benzhydrol (Ph_2CHOH, 35±2%) along with the ring-opened product 1,1,2,2-tetraphenylethanol ($Ph_2CHC(OH)Ph_2$, 11±2%) and the deoxygenation products tetraphenylethane ($Ph_2CHCHPh_2$, 24±1%) and tetraphenylethene ($Ph_2C{=}CPh_2$, 2±2%). The dimerization product of benzophenone ketyl, benzopinacol ($(Ph_2C(OH)\text{-})_2$, 7±2%), was also observed. Fast, syringe injection of the $Ph_2C\overset{O}{\frown}CPh_2$ into excess of the reducing agent produced Ph_2CH_2 (54±2%), Ph_2CHOH (40±3%), $(Ph_2CH\text{-})_2$ (25±1%), $Ph_2CHC(OH)Ph_2$ (17±1%), $(Ph_2C(OH)\text{-})_2$ (5±2%), and $Ph_2C{=}CPh_2$ (3±1%).

Slow, dropwise addition of 6,6-dimethyldibenzofulvene oxide ($Fl\overset{O}{\frown}CMe_2$) in THF to excess sodium naphthalene in THF gave the cleavage products fluorene (FlH_2, 81±5%) and isopropanol (Me_2CHOH, 91±9%) along with the deoxygenated product 9-isopropylfluorene ($FlHCHMe_2$, 5±1%). Fast, syringe injection of $Fl\overset{O}{\frown}CMe_2$ into excess of the reducing agent gave FlH_2 (92±3%), Me_2CHOH (92±1), and $FlHCHMe_2$ (4±1%).

Reductions of both epoxides were also carried out with sodium in liquid ammonia. The reduction of $Ph_2C\overset{O}{\frown}CPh_2$ (4:1) gave $Ph_2C\overset{O}{\frown}CPh_2$ (14%), Ph_2CH_2 (66%), Ph_2CHOH (57%), $(Ph_2C(OH)\text{-})_2$ (8%), and $Ph_2CHCHPh_2$ (1%). The reduction of $Fl\overset{O}{\frown}CMe_2$ (4:1) gave FlH_2 (87%), $FlHC(OH)Me_2$ (7%), FlHFlH (1%), $Me_2C{=}O$ (37%), and Me_2CHOH (60%).

These results are rationalized in terms of two competing processes; (a) electron transfer from the reducing reagent to the oxirane with the resulting opening of the epoxide ring, and (b) deoxygenation of the oxirane

to the corresponding olefin. In the fragmentation of the epoxide rings either the carbenes (Ph_2C, Fl) or carbene anion radicals ($Ph_2C^{-\bullet}$, $Fl^{-\bullet}$) are possible intermediates. Further tests are planned to trap the carbenes to test this hypothesis.