AN EXPERIMENTAL APPROACH TO THE

GENERATION OF PHENYLCARBYNE ANION

by

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B.A., Benedictine College, 1979

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


1983

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INTRODUCTION

Reactive carbon-centered intermediates have long been of
interest to chemists. There are nine carbon-centered inter-
mediates (either neutral or possessing unit charge) that can
be envisioned as arising from R_4C, by stepwise loss of R^-, $R\cdot$,
or R^+ as shown in Scheme I.[1] The structure and chemistry of
four of these nine molecular fragments R_3C^-, R_3C^+, R_2C, and
$R_3C\cdot$ have been widely investigated. Of the remaining five

SCHEME I
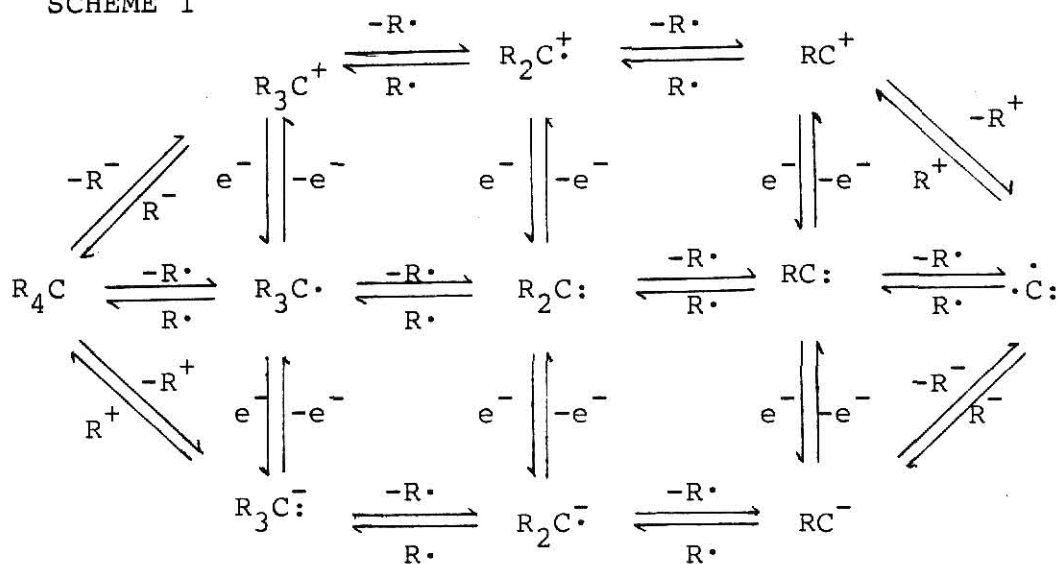
molecular fragments, only a few studies of examples of carbene
anion radicals $(R_2C\overline{\cdot})$ and carbynes (RC) have been reported.

Carbene anion radicals $(R_2C\overline{\cdot})$ are an interesting and
unusual class of carbon centered reactive intermedates. Since
$R_2C\overline{\cdot}$ possess both a pair of electrons and a spin unpaired
electron on the central carbon, the ground state doublet has
the potential to react as a base, a nulceophile, and/or a free
radical. The electronic structure of $H_2C\overline{\cdot}$ has been examined

by MINDO/3[1] and <u>ab initio</u>[2] calculations and is in good agreement with it's photoelectron spectrum.[2] The proposed electronic structure of $H_2C\overset{-}{\cdot}$ is $\sigma^2 \pi^1$ (σ-anion, π-radical). The thermochemical properties, ion-molecule chemistry, and MINDO/3[3] calculations of the cyclopentadienlydene anion radical ($\underline{c}$-$C_5H_4\overline{\cdot}$) establish the ground state doublet to be $\pi^2 \sigma^1$ (π-anion, σ-radical).

Diphenylcarbene anion radical ($Ph_2C\overline{\cdot}$) has been proposed as an intermediate in the electrochemical reduction of Ph_2CN_2. McDonald, <u>et al</u>.,[4] reported that the electrochemical reduction of Ph_2CN_2 in DMF-0.1$\underline{F}$ ($\underline{n}$-Bu)$_4$NClO$_4$ at a platinum electrode produced benzophenone azine (($Ph_2C=N)_2$), as the prinipal product, along with lesser amounts of Ph_2CH_2 and several other compounds. Product formation was shown to occur by a chain process in which $Ph_2C\overline{\cdot}$ is produced from electrogenerated $Ph_2CH_2\overset{-}{\cdot}$ by rapid loss of nitrogen. Ph_2CH^- was the first observed intermediate in Ph_2CN_2 electroreduction, and was obtained by protonation of $Ph_2C\overline{\cdot}$ followed by reduction or by H-atom abstraction by $Ph_2C\overline{\cdot}$ from the solvent. Attack at N_β of Ph_2CN_2 by Ph_2CH^- produced $Ph_2CH\overline{N}N=CPh_2$ which can transfer a proton to a base (e.g. $Ph_2C\overline{\cdot}$) producing ($Ph_2C=N)_2$. $Ph_2CN_2\overline{\cdot}$ is regenerated by electron transfer from ($Ph_2C=N)_2^{2-}$ or ($PH_2C=N)_2\overline{\cdot}$. The chain reaction was terminated upon protonation of Ph_2CH^-.

McDonald and Lin[5] reported that the chemical reduction of Ph_2CN_2, and 9-diazofluorene (FIN_2) also generate carbene anion radicals. Addition of either diazo compound to a THF solution of sodium napthalide, ($Na^+C_{10}H_8\overline{\cdot}$), by either dropwise
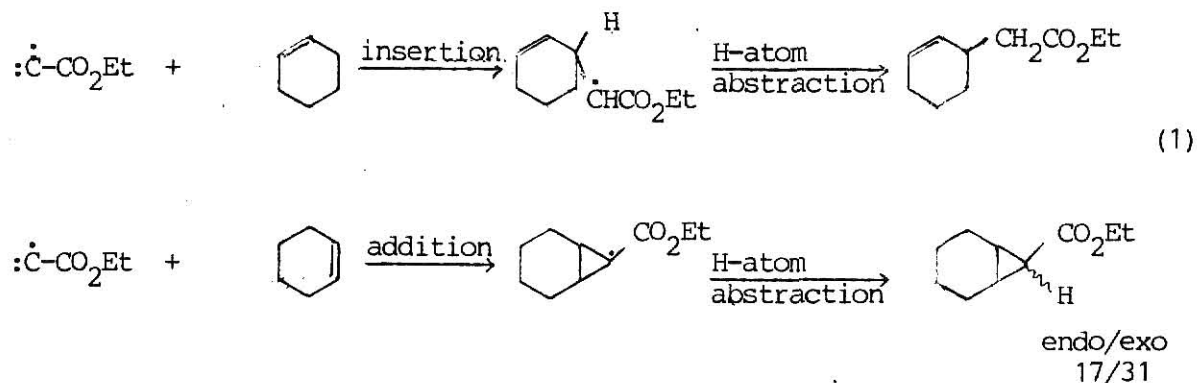
or by fast syringe injection addition, produced the hydrocarbons Ph_2CH_2 and FlH_2 and the amines Ph_2CHNH_2 and $FlHNH_2$. These products were rationalized in terms of two reaction sequences. The hydrocarbons, Ph_2CH_2, and FlH_2, were formed from H-atom abstraction by the respective carbene anion radicals, $Ph_2CH\overline{\cdot}$ and $Fl\overline{\cdot}$, from the solvent followed by protonation of the carbanions in the work-up. The amines Ph_2CHNH_2 and $FLHNH_2$ were considered to arise by reduction of the azine anion radicals or azine dianions.

McDonald, et al.,[3] reported generation and various reactions of cyclopentadienylidene anion radical ($\underline{c}$-$C_5H_4\overline{\cdot}$) in the gas phase using a flowing afterglow apparatus. $\underline{c}$-$C_5H_4\overline{\cdot}$ was generated by dissociative attachment of a thermal electron to diazocyclopentadiene ($\underline{c}$-$C_5H_4N_2$). The proton affinity and ΔH_f^O of $\underline{c}$-$C_5H_4\overline{\cdot}$ were determined, and $\underline{c}$-$C_5H_4\overline{\cdot}$ was shown to react as a base, a nucleophile, and a free radical in specific reactions with neutral molecules.

Another possible source of carbene anion radicals investigated by McDonald and McDowell involved chemical reduction of certain epoxides.[6] Reduction of tetraphenyloxirane ($Ph_2\overset{O}{\overset{\triangle}{C}}\text{-}CPh_2$) and 6,6-dimethyldibenzofulvene oxide ($Fl\overset{O}{\overset{\triangle}{-}C}(CH_3)_2$) with sodium napthalide ($Na^+C_{10}H_8\overline{\cdot}$) yielded products thought to arise from the intermediacy of the two carbene anion radicals $Ph_2C\overline{\cdot}$ and $Fl\overline{\cdot}$, respectively.

The class of reactive carbon-centered intermediates termed carbynes (RC) have been investigated to a limited extent.

Methyne (HC) has been detected in highly energetic reactions involving bombardment of organic compounds with x-ray or vacuum ultraviolet radiation.[7] Strausz, et al.,[8] have generated carbethoxymethyne ($CCO_2C_2H_5$) and investigated it's reactions with olefins. Photolysis of diethyl mercurybis(diazoacetate),[9] $Hg(N_2CCO_2C_2H_5)_2$, in cyclohexene was thought to produce the carbyne which inserted into the allylic C-H bond or added across the double bond followed by H-atom abstraction to produce the three products shown in eq (1).

$$:\overset{.}{C}-CO_2Et \;+\; \text{cyclohexene} \xrightarrow{\text{insertion}} \text{(intermediate, } CHCO_2Et) \xrightarrow[\text{abstraction}]{\text{H-atom}} \text{product, } CH_2CO_2Et$$

$$:\overset{.}{C}-CO_2Et \;+\; \text{cyclohexene} \xrightarrow{\text{addition}} \text{(} CO_2Et \text{)} \xrightarrow[\text{abstraction}]{\text{H-atom}} \text{product, } CO_2Et, H$$

$$\tag{1}$$

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Patrick and Wu[10] photodecomposed $Hg(N_2CCO_2C_2H_5)_2$ in the presence of tetrahydrofuran, tetrahydrothiophene, and pyrrolidene. The investigators postulated that only 10-20% of the mercury diazo compound produced the carbyne, the remainder yielding the diazomercury carbene, $C_2H_5O_2C\overset{..}{C}\,HgC(N_2)CO_2C_2H_5$. The prinicpal products obtained from the carbyne intermediate were those produced by insertion of the carbyne into the αC-H bond of the heterocyclic rings.

The reduced form of a carbyne, carbyne anions (RC^-) are of interest since the singlet/triplet multiplicity problem found in carbenes/methylenes emerges. To date, only studies
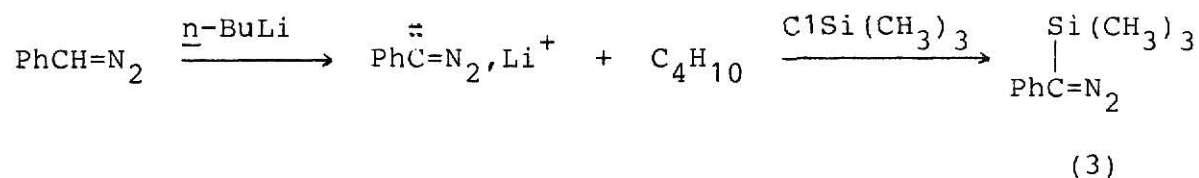
of the parent carbyne anion, HC^- have been reported. Lineberger, et al.,[11] produced HC^- from a methane discharge. The photoelectron spectrum showed that the ground state of HC^- was a triplet.

One possible route to produce RC^- is shown in eq (2) which involves H^+-transfer from a monosubstituted diazo compound with a base followed by photolysis. Photochemical decomposition

$$RCH{=}N_2 \xrightarrow[(-BH)]{B:^-} R\ddot{\overline{C}}{=}N_2 \xrightarrow{h\nu} RC^- + N_2 \qquad (2)$$

of $R\overline{C}{=}N_2$ should yield the singlet RC^- species. If successful, this sequence might have considerable generality.

The conjugate bases of diazo compounds ($R\overline{C}{=}N_2$) have been prepared by several investigators. Bryce-Smith, et al.,[12] prepared disilverdiazomethane ($Ag_2C{=}N_2$) by reaction of silver-acetate in pyridine with diazomethane. In earlier investigations, the sodium and lithium salts of diazomethane were prepared by reaction of $(Ph)_3CNa$ and CH_3Li, respectively, with diazomethane.[13,14] Shechter prepared ɑ-trimethylsilyl-phenyldiazomethane ($PhC(Si(CH_3)_3)N_2$) by reacting $PhCH{=}N_2$ with n-butyllithium via the intermediate anion $Ph\overline{C}{=}N_2$ followed by addition of trimethylsilylchloride (eq 3).[15]

$$PhCH{=}N_2 \xrightarrow{n\text{-BuLi}} Ph\ddot{\overline{C}}{=}N_2,Li^+ + C_4H_{10} \xrightarrow{ClSi(CH_3)_3} \begin{array}{c} Si(CH_3)_3 \\ | \\ Ph\overline{C}{=}N_2 \end{array}$$

$$(3)$$

As shown in eq (3), $Ph\bar{C}=N_2$ should be a convient molecule for potential generation of a carbyne anion. The expected products from reaction of PhC^- should be UV-active and product analysis would be possible using a high performance liquid chromatography (HPLC) with a UV-detector.

OBJECTIVE OF THIS INVESTIGATION

The objective of this investigation was to prepare the conjugate base from phenyldiazomethane via proton abstraction with an alkyllithium base and photolyze the anion in an appropriate solvent. Following characterization of the products obtained before and after photolysis, the possible intermediacy of PhC⁻ would be evaluated from mechanisms used to describe formation of the photolysis products.

EXPERIMENTAL RESULTS

Valuable structural and chemical information about reactive intermediates can often be obtained or deduced from molecular orbital (MO) calculations. However, the SCF methods normally used in such MO calculations frequently have difficulty with molecular systems involving radicals and especially anions. MINDO/3[16,17] MO calculations were carried out on the three phenylcarbyne species, PhC, PhC^+, and PhC^-. The initial structural data included ring C-C bond lengths of 1.39Å, C-H bond lengths of 1.10Å, the carbynic-C-to-ring-C bond length of 1.34Å, and symmetric C-C-C and C-C-H angles of $120°$. The structures and other pertinent data of the energy minimization routine for these three species are shown in Figure 1.

The neutral phenylcarbyne (PhC) can exist as a doublet electronic configuration where two of the three nonbonded electrons would be spin paired (Aufbau principle) and probably occupy a hybrid orbital on C_1 leaving the unpaired electron in an atomic P-orbital. However, PhC could also exist as a quartet where the three nonbonded electrons would singly occupy separate orbitals on C_1 (Hund's rule). For the present calculations, the multiplicity of the ground state was not specified. The calculation started and minimized with the doublet as the ground state of PhC. The calculated structure and other pertinent data are given in Figure 1. The HOMO of ^{2}(PhC) was singly occupied and was π-delocalized over the seven-carbon skeleton. The electron pair presumably occupies a hybrid inplane orbital on C_1 and the residual p-orbital of C_1 is empty.

C₇H₅⁻ C₇H₅ C₇H₅⁺
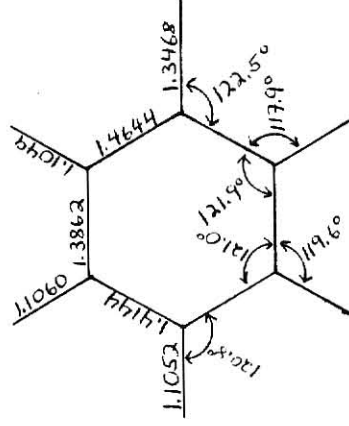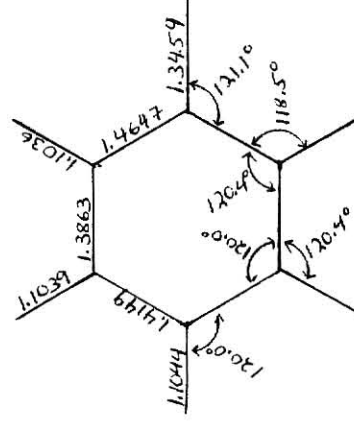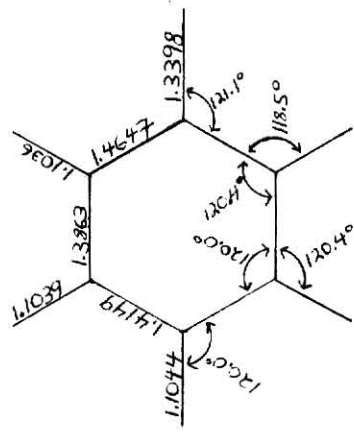
Heat of Formation	131.3 kcal mole^{-1}	149.0 kcal mole^{-1}	300.3 kcal mole^{-1}
Charge	-1	0	+1
Ionization Potential	1.09 eV	3.65 eV	14.67 eV
Dipole Moment	8.79 Debye	1.50 Debye	11.29 Debye

The phenylcarbyne anion (PhC$^-$) can exist as a singlet ^{1}(PhC$^-$) or a triplet ^{3}(PhC$^-$) species. ^{1}(PhC$^-$) is simply viewed as adding an electron to the delocalized out-of-plane orbital in ^{2}(PhC). Indeed, the MINDO/3 HOMO has this MO doubly occupied in ^{1}(PhC$^-$). The calculated structure and other data for ^{1}(PhC$^-$) are given in Figure 1. An attempt to carry out a MINDO/3 calculation of ^{3}(PhC$^-$) failed due to nonconvergence of the SCF calcualation. Thus, the ground state of PhC$^-$ was not determined by these calculations.

The phenylcarbyne cation (PhC$^+$) can exist in two electronic configurations, the triplet state with both nonbonded electrons spin unpaired, ^{3}(PhC$^+$), and the singlet state ^{1}(PhC$^+$). Only the singlet species was calculated for comparison with the ^{1}(PhC$^-$) species, both of which are formally derived from ^{2}(PhC). The calculated structure and other data for ^{1}(PhC$^+$) are given in Figure 1. The MINDO/3 HOMO for PhC$^+$ is doubly occupied and the electron pair is π-delocalized over the seven-carbon skeleton.

Phenyldiazomethane was synthesized by a literature procedure.[18] Benzaldehyde p-tosylhydrazone was prepared from the reaction of benzaldehyde with p-tosylhydrazine. Reaction of the hydrazone with sodium methoxide produced the sodium salt which when heated to 100-160°C under vacuum (0.05 torr)yielded PhCH=N$_2$ (eq 4). It was necessary to redistill the PhCH=N$_2$ at 25°C under vacuum to obtain reasonably pure ($\sim$ 98%) PhCH=N$_2$. Despite repeated distillations, it was not

$$PhCHO + \underline{p}\text{-}H_3CC_6H_4SO_2NHNH_2 \xrightarrow{\quad CH_3OH \quad} \underline{p}\text{-}H_3CC_6H_4SO_2NHN=CHC_6H_5$$

$$\Big\downarrow CH_3ONa \qquad (4)$$

$$PhCH=N_2 \xleftarrow[\Delta]{\quad 0.05 \text{ torr} \quad} \underline{p}\text{-}H_3CC_6H_4SO_2\bar{N}N=CHC_6H_5, Na^+$$
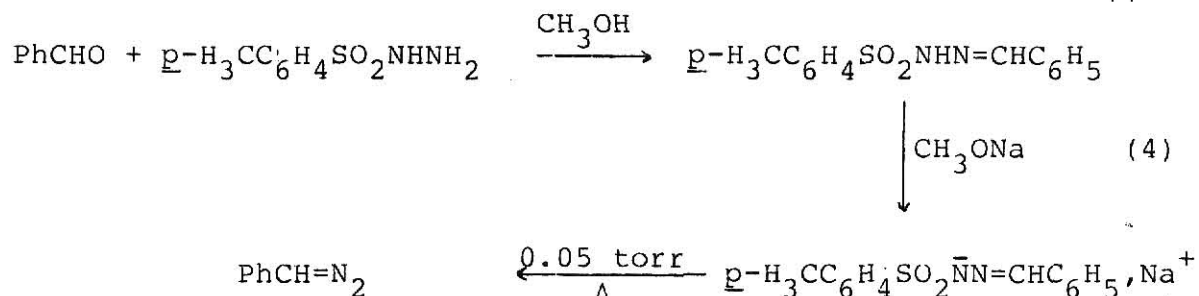
possible to remove small amounts of the decomposition products of $PhCH=N_2$, $(PhCH=N)_2$ and $\underline{trans}$-PhCH=CHPh and the starting material PhCHO; each impurity was observed to be present in about 0.2% by weight. Due to the instability of $PhCH=N_2$ it was necessary to use it immediately after preparation; it was noted that $PhCH=N_2$ was light and heat labile.

Of the three common alkyl lithium bases ($\underline{tert}$-butyllithium, $\underline{n}$-butyllithium, and methyllithium), that could be used to irreversibly remove the proton from $PhCH=N_2$, methyllithium was chosen since it would be possible to quantitate the amount of proton removal by collecting the total gas volume liberated followed by GLPC quantitation of the CH_4. The reaction of $PhCH=N_2$ with CH_3Li was carried out and the total evolved gases were swept from the reaction vessel and were collected. Generally, 12-13 moles of $PhCH=N_2$ in 50 mL of anhydrous THF was added dropwise to a solution containing 13 mmoles of CH_3Li and 16 mmoles of N,N,N',N'-tetramethylethylenediamine (TMEDA) in 75 mL of anhydrous THF at $-78^{\circ}C$. The sealed system was connected to several 1- or 2-liter flasks filled with water and inverted in a tub of water.

The methane produced from the reaction of $PhCH=N_2$ and CH_3Li displaced the H_2O in the flasks. After complete addition of the $PhCH=N_2$ solution, the whole mixture was stirred at $-78^{\circ}C$ for 0.5 hr to insure complete reaction. The closed system was then swept with N_2 while still connected to the flasks to displace the H_2O with the CH_4 formed. The gas filled flasks were capped while under H_2O with rubber septa, and the contents were then injected into a gas chromatograph using a 6' x ¼" Poropak Q column connected to a FID. The GLPC peak from the reaction was identified as CH_4 by comparison of the retention time with that of authentic CH_4. Quantitation was obtained by measuring the peak areas of the evolved gases from the reaction mixture compared with those of standard CH_4 concentrations and multiplying by the total volume of the displaced H_2O, the latter obtained by refilling the flasks with measured volumes of H_2O. Methane yields were generally > 90%.

After determining that there was adequate generation of $Ph\bar{C}=N_2$, the reaction was run several times followed by quenching the reaction mixture with $\sim$ 1 mL of water while still at $-78^{\circ}C$. The solution was allowed to warm to room temperature after which it was diluted to a total volume of 250 mL with THF. The mixture was analyzed by HPLC (10 μl loop injector, universal MCH-10 reverse phase column) with a UV-detector set at 260 nm. Several solvent mixtures and programs were tried before separation of all components was obtained. It was observed that the best solvent mixture and program was a

Figure 2. HPLC chromatogram of reaction of $PhCH=N_2$ with CH_3Li in THF followed by addition of water.
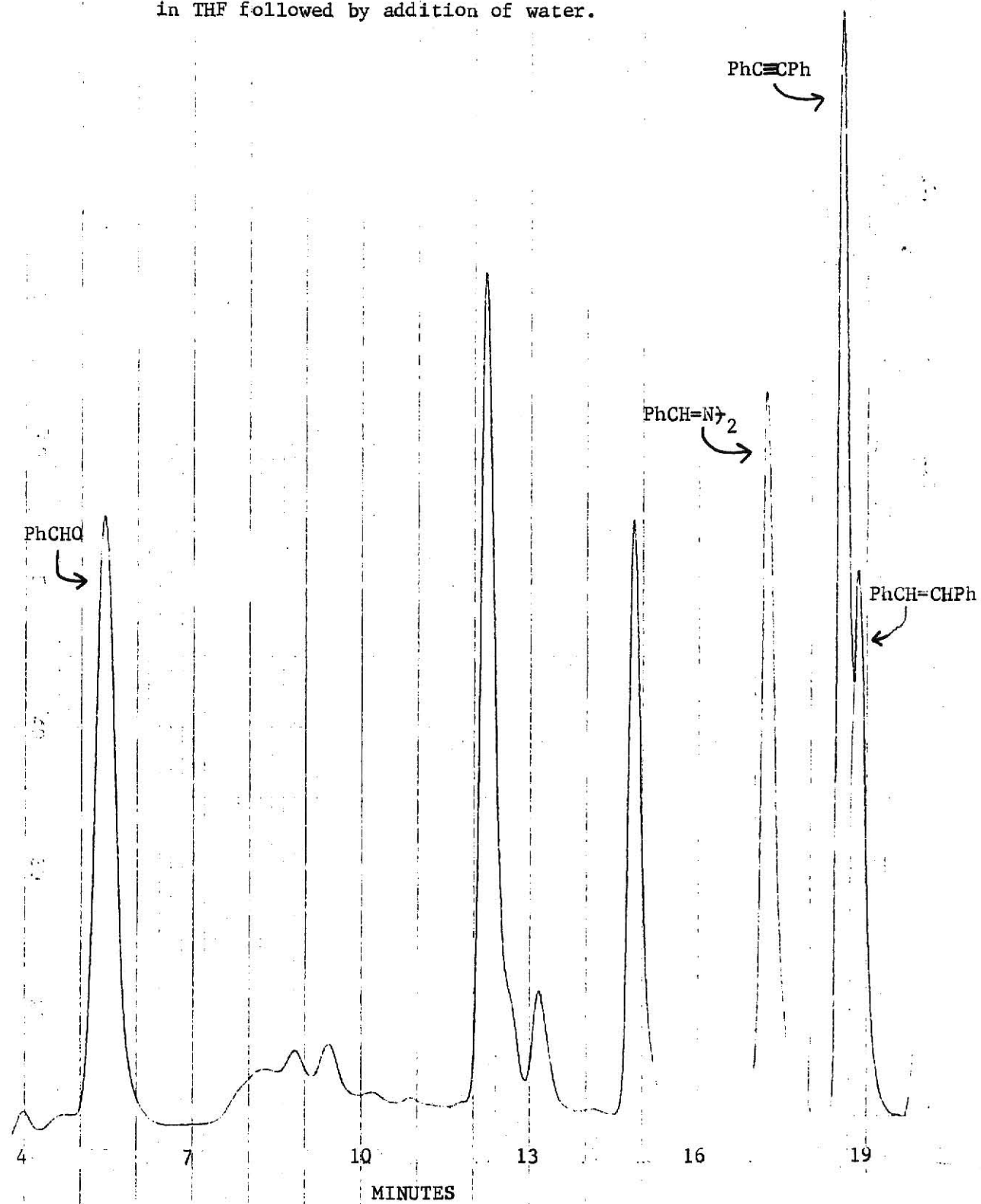
50:50 mixture of CH_3OH and H_2O initially and increasing this to 100% CH_3OH at an elapsed time of 18 min in a gradient. The chromatogram peaks in the quenched mixture were identified where possible by comparison of their retention times with those of authentic materials and by the "spiking" method (addition of a known compound to increase the magnitude of a peak). The peak areas were measured and compared with those of authentic compounds of known concentration for each component to give the number of mmoles of the compound present when multiplied by the total volume of the solution. The products considered possible from the quenching and photolysis of $Ph\bar{C}=N_2$ were $PhCH_3$, trans-$PhCH=CHPh$, $PhC\equiv CPh$, $PhCHO$, $PhCH_2-CH_2Ph$, phenanthrene, $PhCH=N-N=CHPh$, $Ph(CH_2)_5OH$, $PhCH=CH(CH_2)_3OH$, and $PhCH_2OH$. The observed products and their yields from the H^+-abstraction/quenching experiment were $PhCHO$ (3.0 ± 0.6%), $PhCH=N-N=CHPh$ (5.9 ± 0.7%), $PhC\equiv CPh$ (5.1 ± 0.4%) $PhCH=CHPh$ (11.1 ± 0.6%), and $PhCH_3$ ("trace"). The products identified accounted for 25.1 ± 2.3% of the $PhCH=N_2$ used in the reaction. As can be seen in Figure 2, there are a number of peaks that were not identified including a major peak with a retention time of ∿12.2 min. It was not possible to determine how much, if any, of $PhCH=N_2$ was unreacted or was regenerated with the water quench, primarily because $PhCH=N_2$ was not completely stable to the HPLC conditions. Freshly distilled $PhCH=N_2$ showed a peak at ∿9.2 min which was though to be $PhCH=N_2$ along with the other minor peaks from the decomposition products mentioned previously.

Attempted generation of PhC$^-$ involved the above reaction of PhCH=N$_2$ with CH$_3$Li in THF followed by photolysis of that reaction mixture at -78°C. The photolyzed solution was quenched with H$_2$0. PhCH=N$_2$ was added to the THF solution of CH$_3$Li and TMEDA at -78°C, the dark brown solution was stirred for 0.5 hr and was photolyzed for 2.5-3 hrs at -78°C using a 100 watt mercury lamp placed in a quartz immersion well. During the initial 15 minutes of irradiation, a gas, presumably N$_2$, was produced as evidenced by bubbling from within the system and the pressure released through a mercury bubbler. After photo-lysis, the solution was quenched while still at -78°C with $\sim$ 1 mL of water, allowed to warm to room temperature, and diluted to a total volume of 250 mL with THF. This THF solu-tion was analyzed using HPLC with the above solvent program, and the products were identified by comparison with authentic standards as above; PhCHO (5.4 $\pm$ 0.6%), PhC≡CPh (6.1 $\pm$ 0.7%), PhCH$_3$ ("trace"), PhCH=N-N=CHPh (6.4 $\pm$ 0.6%), and PhCH=CHPH (19.6 $\pm$ 0.8%). These products accounted for 37.5 $\pm$ 2.7% of the PhCH=N$_2$ used in the reaction. As in the quenched reaction there was a considerable amount of the PhCH=N$_2$ unaccounted for and as can be seen in Figure 3 there are several peaks uniden-tified, the major peak coming between 12-13 min retention time. Although the peak assignments in Figure 2 and 3 do not share the exact same retention times, this is attributed to tempera-ture differences of the column on different days that the HPLC chromatograms were obtained. The above yields of products from both reactions are summarized in Table I.

Figure 3. HPLC chromatogram of reaction of $PhCH=N_2$ with CH_3Li in THF followed by photolysis then addition of water.
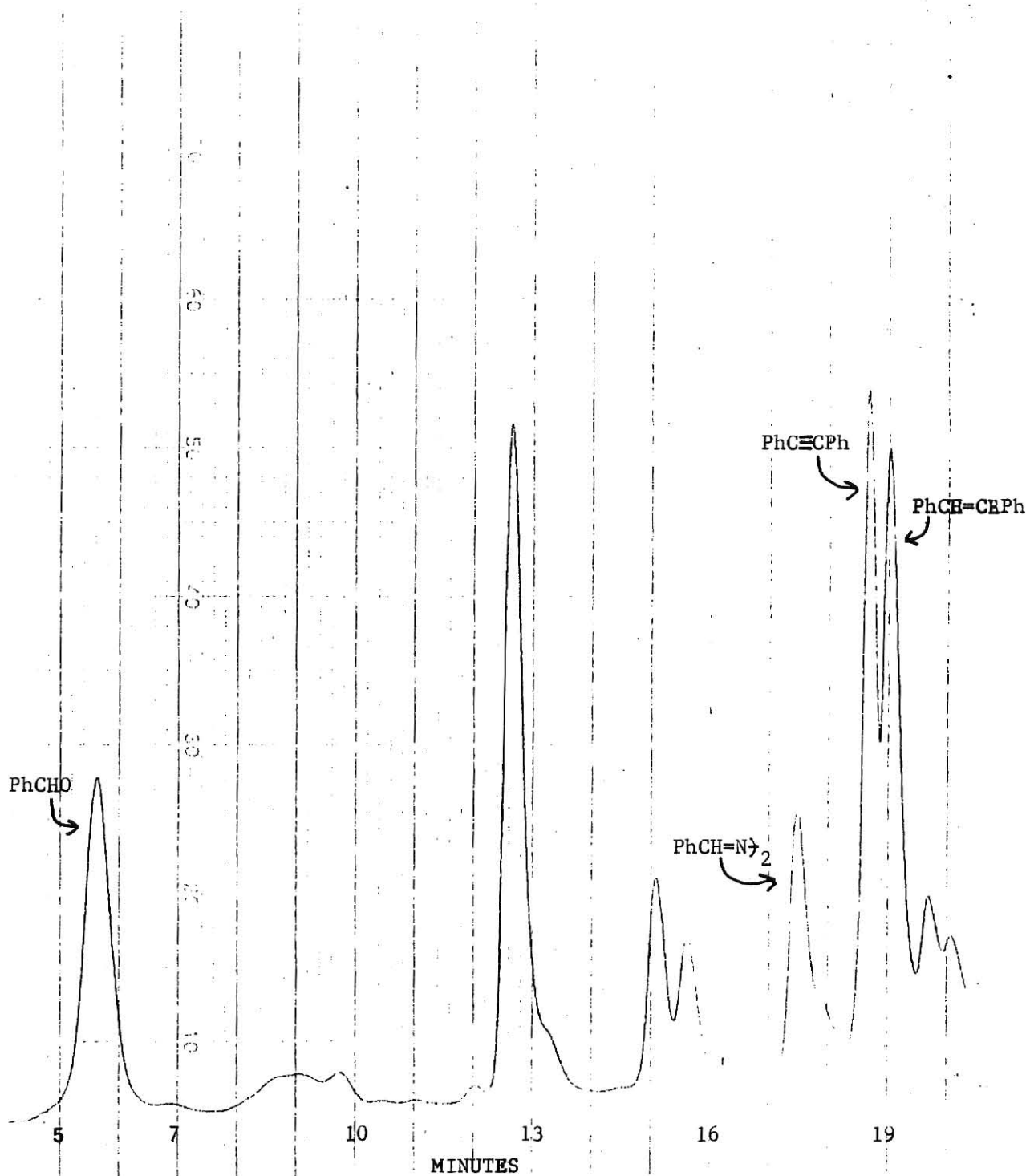
TABLE I. Product Analysis for the Reactions

a. $PhCH=N_2$ + CH_3Li followed by H_2O-quench[a]

Products, % Yield

Run No.	PhCHO	$PhCH_3$	$PhCH{\ddagger}_2$	$PhCH=N{\ddagger}_2$	$PhC{\ddagger}_2$
1	2.4	trace[b]	11.6	5.2	4.7
2	3.6	trace	10.5	6.5	5.5
avg.	3.0±0.6	trace	11.1±0.6	5.9±0.7	5.1±0.4

b. $PhCH=N_2$ + CH_3Li followed by Photolysis Then H_2O-quench[a,c]

Products, % Yield

Run No.	PhCHO	$PhCH_3$	$PhCH{\ddagger}_2$	$PhCH=N{\ddagger}_2$	$PhC{\ddagger}_2$
1	4.8	trace[b]	18.8	5.8	5.4
2	5.9	trace	10.3	7.0	6.7
avg.	5.4±0.6	trace	19.6±0.8	6.4±0.6	6.1±0.7

[a]All yields are based on comparison of the peak areas of the unknown sample with those of authentic standards.

[b]A small peak was seen at the retention time for toluence,[23] however, unambigous identification was not possible due to the small size of the peak.

[c]Photolysis was carried out in an immersion type photoreactor with a General Electric H100-A4 100 watt mercury lamp.

DISCUSSION OF EXPERIMENTAL RESULTS

The attempted generation of PhC^- according to the sequence in eqs (5) and (6) assumed that the conjugate base of phenyldiazomethane, $Ph\bar{C}=N_2$ was reasonably stable under the reaction conditions. Evidence indicating that conjugate

$$PhCH=N_2 \ + \ CH_3Li \ \longrightarrow \ Ph\bar{C}=N_2,Li^+ \ + \ CH_4 \qquad (5)$$

$$Ph\bar{C}=N_2 \ \xrightarrow{h\nu} \ Ph\bar{C} \ + \ N_2 \qquad (6)$$
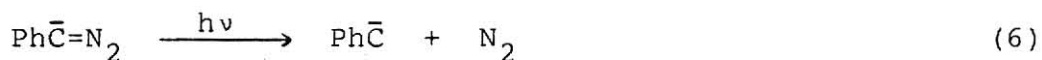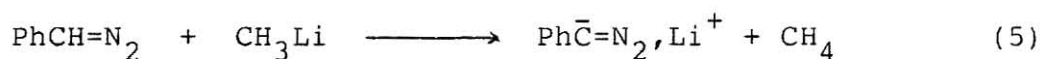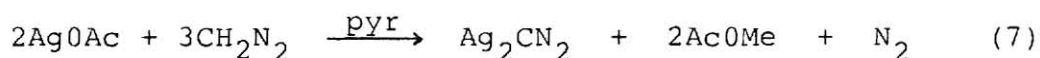
bases of various diazoalkanes are stable comes from both solution and gas phase results. Bryce-Smith, et al.[12] prepared the stable (in the dark, under argon) salt disilverdiazomethane from the reaction of AgOAc in pyridine with excess CH_2N_2 (eq 7). Prior to this report, investigators prepared the

$$2AgOAc + 3CH_2N_2 \ \xrightarrow{pyr} \ Ag_2CN_2 \ + \ 2AcOMe \ + \ N_2 \qquad (7)$$

sodium and lithium salts of diazomethane by reaction of diazomethane with $(Ph)_3CNa$ and CH_3Li, respectively.[13,14]

DePuy, et al.[19] generated α-diazoalkyl anions in the gas phase from reactions of several allylic anions with N_2O (eq 8). McDonald and Chowdhury[20] observed formation of $Ph\bar{C}=N_2$ from the reaction of $PhCH=N_2$ with H_2N^- in a flowing afterglow apparatus (eq 9). McDonald and McGhee[21] observed formation

$$RCH=CH-\bar{C}H_2 \quad + \quad N_2O \quad \longrightarrow \quad RCH=CH\bar{C}=N=N \quad + \quad H_2O \qquad (8)$$

$$PhCH=N_2 \quad + \quad H_2N^- \quad \longrightarrow \quad Ph\bar{C}=N_2 \quad + \quad NH_3 \qquad (9)$$
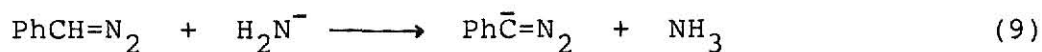
of $CF_3\bar{C}=N_2$ in the flowing afterglow by H^+-transfer between 2,2,2-trifluorodiazoethane and perfluoropropylidene anion radical (eq 10).

$$(F_3C)_2C^{\cdot -} \quad + \quad CF_3CH=N_2 \quad \longrightarrow \quad CF_3\bar{C}=N_2 + (F_3C)_2CH\cdot \quad (10)$$

From the above solution and gas phase results, it may be assumed that the formation of $Ph\bar{C}=N_2$ would occur in the reaction of $PhCH=N_2$ with a sufficiently strong base, i.e. CH_3Li (eq 5). It was not possible to determine the amount of $PhCH=N_2$ regenerated in the water quench of the reaction product because $PhCH=N_2$ hydrolyzes to $PhCH_2OH$, and $PhCH=N_2$ is weakly absorbing at 260 nm in the HPLC analysis. It was determined that $\sim$ 25% of the $PhCH=N_2$ used in the reaction produced identifiable products while a portion of the remaining 75% formed unknown products. The reaction products formed can be rationalized to arise from reaction of $Ph\bar{C}=N_2$ with $PhCH=N_2$.
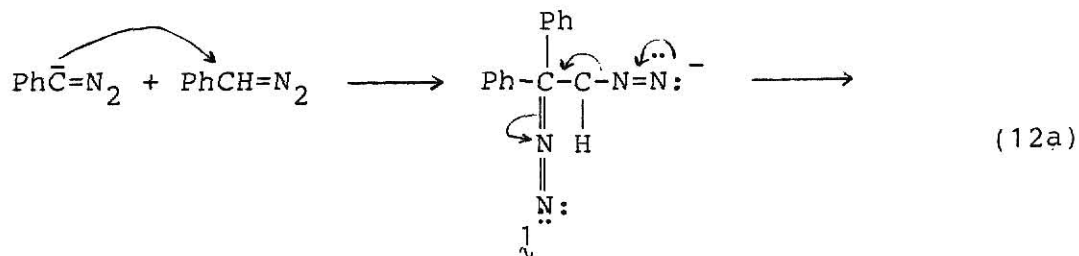
The results of the H^+-abstraction/water quench process (without photolysis) will be considered first. From the CH_4 evolved in the reaction of $PhCH=N_2$ with CH_3Li, it appeared that > 90% of the $PhCH=N_2$ had been converted to the conjugate base $Ph\bar{C}=N_2$ (eq 5). It is possible to propose pathways to the *various* reaction products through reaction of $Ph\bar{C}=N_2$ with

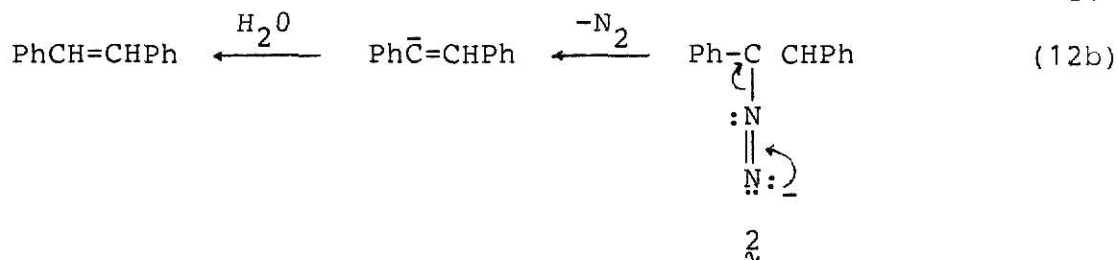$PhCH=N_2$. However, with < 10% of $PhCH=N_2$ remaining after the H^+-transfer reaction with CH_3Li, some mechanism for partial regeneration of $PhCH=N_2$ appears to be required to account for the 25% net conversion of $PhCH=N_2$ into identifiable products. This regenerative step for $PhCH=N_2$ may involve the slow attack of $Ph\bar{C}=N_2$ on the solvent, THF (eq 11), or may involve the H_2O added as the quenching reagent. If the H^+-source is the added water, a series of fast reactions

$$Ph\bar{C}=N_2, Li^+ + \quad\longrightarrow\quad PhCH=N_2 + Li^+ \ ^-O(CH_2)_2CH=CH_2 \quad (11)$$
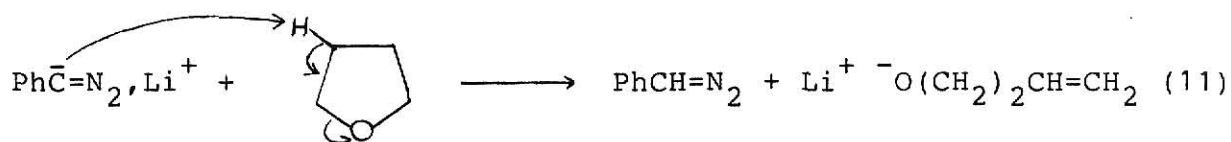
must then occur to yield one or more of the identified products. The nature and distribution of the products formed may be different depending on which reagent (THF or H_2O) serves as the H^+-donor. However, no information is available on this point.

Formation of trans-stilbene is considered to arise by nucleophilic attack of $Ph\bar{C}=N_2$ on the C_1 of $PhCH=N_2$ to yield intermediate 1. Loss of N_2 from 1 would produce 2 which extrudes a second N_2 molecule giving the conjugate base of stilbene, $Ph\bar{C}=CHPh$. This vinyl anion is probably sufficiently stable with the anion delocalized by the phenyl ring at C_1 and would exist until protonated by added H_2O in the quench (eqs.12a, 12b).

$$Ph\bar{C}=N_2 + PhCH=N_2 \quad\longrightarrow\quad$$

$$\begin{array}{c} Ph \\ | \\ Ph-C-C-N=N: \ ^- \\ \| \ | \\ N \ H \\ \| \\ N: \end{array} \quad\longrightarrow\quad$$

$$(12a)$$

1

$$PhCH=CHPh \xleftarrow{H_2O} Ph\bar{C}=CHPh \xleftarrow{-N_2} Ph-\underset{\substack{\|\\ :N\\ \|\\ \ddot{N}:\\ \underset{2}{}}}{C}\;CHPh \qquad (12b)$$

This mechanism for producing $Ph\bar{C}=CHPh$ has an analogy in recent gas phase results.[21] In the reaction of $(CF_3)_2\bar{C}\cdot$ with $CF_3CH=N_2$, a minor channel involves H^+-transfer yielding $\underline{m/z}$ 109 $(CF_3\bar{C}=N_2)$ which reacts further with $CF_3CH=N_2$ to produce $\underline{m/z}$ 163, considered to be the vinyl anion $CF_3\bar{C}=CHCF_3$. The mechanism thought to be involved in the formation of $\underline{m/z}$ 163 is shown in eq (13). The loss of N_2 from intermediate $\underset{\sim}{2}$ in eq (12b) is related to the formation of vinyl anions in the condensed phase from the reaction of ketone p-tosylhydrazones with excess CH_3Li.[22]

If the nucleophilic addition of $Ph\bar{C}=N_2$ to $PhCH=N_2$ occured at N_β rather than C_1, a reasonable pathway leading to formation of the conjugate base of the azine $Ph\bar{C}=N-N=CHPh$ is generated (eq 14). The loss of N_2 from intermediate $\underset{\sim}{3}$

$$CF_3\bar{C}=N_2 + CF_3CH=N_2 \longrightarrow$$

(m/z 109)

$$\bigg\downarrow -N_2$$

$$CF_3\bar{C}=CHCF_3 \xleftarrow{-N_2}$$

(m/z 163)

(13)

yielding $Ph\bar{C}=N-N=CHPh$ is analogous to the decomposition of 2 forming $Ph\bar{C}=CHPh$ and N_2 in eq (12). Protonation of $Ph\bar{C}=N-N=CHPh$ by the solvent (related to eq 8) or by H_2O in the quench would

$$Ph\bar{C}=N_2 + \overset{+}{N}\equiv\overset{-}{N}-CHPH \longrightarrow \left[\begin{array}{c} Ph-\overset{..}{C}-\overset{+}{N}\overset{-}{=}N-CHPh \\ \parallel \\ N+ \\ \parallel \\ \overset{..}{N}:- \end{array} \longrightarrow \begin{array}{c} Ph-\overset{..}{C}-\overset{..}{N}=\overset{..}{N}=CHPH \\ | \\ :N \\ \parallel \\ \overset{..}{N}:- \quad 3 \end{array} \right] \downarrow -N_2 \quad (14)$$

$$PhCH=N-N=CHPh \xleftarrow{\quad SH \text{ or } H_2O \quad} Ph\bar{C}=N-N=CHPh$$
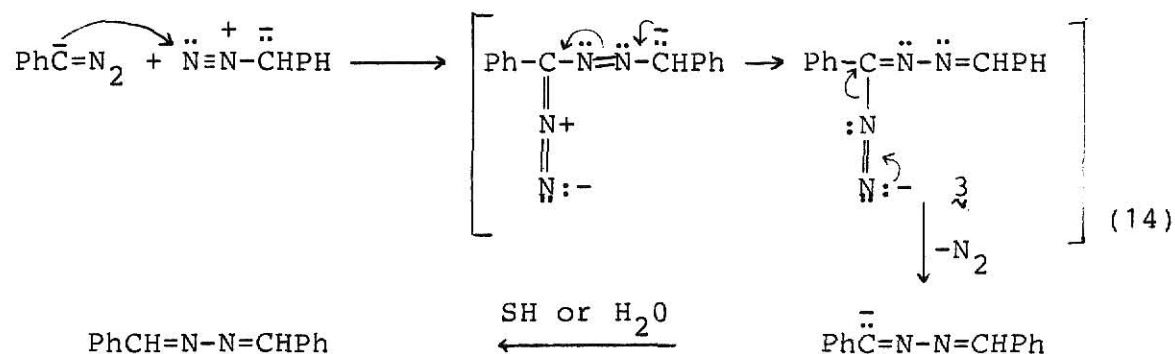
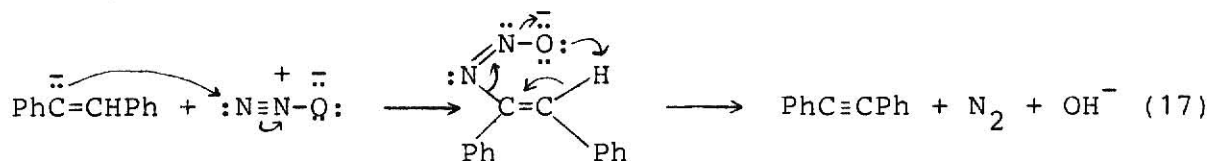yield the azine.

Formation of PhCHO as a reaction product is somewhat more difficult to rationalize from $Ph\bar{C}=N_2$ as the principal reactive intermediate. PhCHO was a starting material in the preparation of $PhCH=N_2$ and there was on the average 0.2% present in the $PhCH=N_2$ used. However, this PhCHO impurity should have been removed by reaction with CH_3Li. PhCHO had been shown to be a reaction product of $Ph\overset{..}{C}H$ with O_2 by Bethell and Whittaker who thermolyzed $PhCH=N_2$ in CH_3CN in the presence of air.[23] However, since a carbene intermediate is not probable in the present reactions, there must be another source of PhCHO. In the H^+-abstraction/water quench reactions, a N_2 atmosphere was used, however, this does not entirely preclude traces of O_2 from being present. If trace amounts of O_2 were present, it would be possible for electron transfer to occur between $Ph\bar{C}=N_2$ and O_2 yielding a radical pair which would be expected to collapse with little or no activation

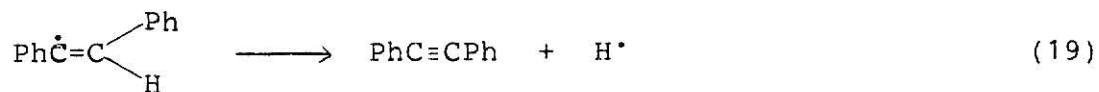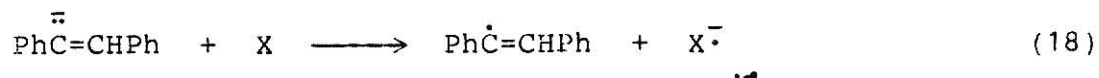energy to produce anion $\underset{\sim}{4}$. Cyclization of $\underset{\sim}{4}$ could yield the anionic azadioxetane species $\underset{\sim}{5}$ which would be expected to decompose to N_2O and the benzoyl anion (eq 15a) or abstract H^+ from the solvent or $PhCH=N_2$ and decompose according to eq (15b). Since the acyl anion $PhCO^-$ should be a strong base,[24] it would be expected to deprotonate THF or any unreacted $PhCH=N_2$.

$$Ph\overset{\cdot\cdot}{\underset{-}{C}}=N_2 + O_2 \longrightarrow PhC=N_2 + O_2^{-\cdot} \longrightarrow PhC\overset{+}{=}N=\overset{\cdot\cdot}{N}:^-$$

$$PhCHO + S^- \xrightarrow{\quad SH \quad} PhCO^- + N_2O \qquad (15)$$

$$PhCHO + N_2O \longrightarrow PhC\overset{+}{H}-N=\overset{\cdot\cdot}{N}: + S^-$$

$\underset{\sim}{4}$

$\underset{\sim}{5}$

PhC≡CPh is an extremely interesting and unexpected reaction product. There are three potential pathways that may lead to formation of PhC≡CPh. The first, and simplest, pathway would involve loss of H^- from $Ph\bar{C}=CHPh$ (eq 12) according to eq (16). However, $\Delta H_{rxn}(16) = +29.3$ kcal mole^{-1}. Although several assumptions were required for this calcula- tion,[25] the significant endothermicity was in keeping with

expectations for loss of H⁻ from a hydrocarbon anion. Thus, this pathway is not considered reasonable for formation of PhC≡CPh.

$$PhC=C\begin{matrix} Ph \\ H \end{matrix} \longrightarrow PhC\equiv CPh + H^- \qquad (16)$$
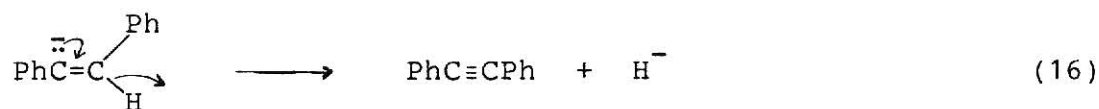
The second possibility involves the reaction of PhC̄=CHPh with N_2O (N_2O being generated in the proposed pathway to PhCHO) by a mechanism related to that described for the gas phase reaction of allyl anion with N_2O to produce $CH_2=CHC̄=N_2$.[19] This process is shown in eq (17).

$$PhC=CHPh + :N\equiv N-\underset{..}{O}: \longrightarrow \overset{N-O:}{\underset{Ph}{C}}=C\overset{H}{\underset{Ph}{}} \longrightarrow PhC\equiv CPh + N_2 + OH^- \quad (17)$$

The third possibility considered would involve electron transfer between the vinyl anion PhC̄=CHPh and some species present in the reaction mixture to form the vinyl radical PhĊ=CHPh according to eq (18). This would be followed by a radical β-fragmentation reaction yielding PhC≡CPh and a H-atom (eq 19).

$$PhC̄=CHPh + X \longrightarrow PhĊ=CHPh + X\cdot^- \qquad (18)$$

$$PhĊ=C\begin{matrix} Ph \\ H \end{matrix} \longrightarrow PhC\equiv CPh + H\cdot \qquad (19)$$

The electron affinity (EA) of PhĊ=CHPh is estimated to be considerably less than 1 eV (EA($\cdot CH_3$) ≤ 0.5 eV, EA($H_2C=C$)

≤ 0.43 eV, EA(PhCH$_2$·) <0.88 eV).[29] The EA(X) must be $\geq$ EA

(PhĊ=CHPh) for effective electron transfer to occur. Possible

X species in the reaction mixture include O_2 (EA ≈ 0.5 eV),[29]

PhCH=N$_2$ (EA unknown), and N$_2$O (EA ≤ 1.465 eV),[29] EA (PhCH=N$_2$)

> 0 since the diazo compound attaches thermalized electrons

in the gas phase to yield PhCH=N$_2$⁻:[20] Further characterization

of this pathway as the source of PhC≡CPh formed in these

reactions is not possible at this time. However, this and

the second pathway are favored over the first considered as

that involved in production of PhC≡CPh in this reaction.

The major difference between the product composition of

the photolyzed versus the non-photolyzed reactions is the

approximately two-fold increase in the amount of _trans_-stilbene

formed in the photolysis reaction. If, as proposed, PhC̄=N$_2$

is slowly protonated by the solvent THF (eq 11), photolysis

of the solution containing PhCH=N$_2$ would produce phenylcarbene

(PhCH) which would react at C$_1$ of PhC̄=N$_2$ to yield PhC̄=CHPh as

shown in eq (20). Generally, the intermediacy of PhCH in the

$$\text{PhCH} + \text{PhC=N}_2 \longrightarrow \text{PhCH=C-N=N:}$$
$$\text{Ph}$$
$$(20)$$
$$\text{PhCH=CHPh} + \text{OH}^- \xleftarrow{\text{H}_2\text{O}} \text{PhCH=C̄Ph} + \text{N}_2$$
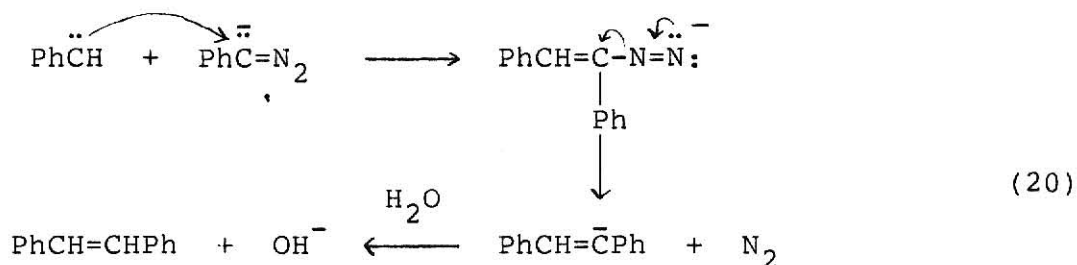
absence of any trapping agents is evidenced by both azine and

stilbene production.[23,30] However, formation of additional

benzalazine through a _carbene_ intermediate may be precluded

in the photolysis conditions used. Complete information is

unavailable on this point, as PhCH was not specifically generated under identical reaction conditions, and previous work involving PhCH employed different conditions.

Since there is no identifiable product in the photo-lysis reaction that is different from the quench reaction, the intermediacy of PhC^- is not required. Potentially, this could be due to experimental conditions; e.g., too low of temperature, or too weak of light source. Alternatively, PhC^- may be simply too high an energy fragment to form by the proposed scheme. Most probably, it will be possible to unequivocally generate a carbyne anion either by modification of these solution experiments, or by using similar reaction schemes in gas phase reactions.

SUMMARY

In this attempted generation of a carbyne anion (RC$^-$),
PhCH=N$_2$ was allowed to react with CH$_3$Li in THF containing
N,N,N',N'-tetramethylethylenediamine at -78°C to produce
Ph$\bar{\text{C}}$=N$_2$ as evidenced by the CH$_4$ collected and quantitated from
the reaction. The resulting solution was then photolyzed in
an attempt to extrude N$_2$ and produce the carbyne anion Ph$\bar{\text{C}}$.
Reaction products for the reactions with and without photo-
lysis were determined. From the reaction of PhCH=N$_2$ with CH$_3$Li
followed by addition of H$_2$0 to quench the reaction, the follow-
ing products and yields were obtained; PhCHO (3.0 ± 0.6%),
PhCH$_3$ ("trace"), _trans_-PhCH=CHPh (11.1 ± 0.6%), PhCH=N-N=CHPh
(5.9 ± 0.7%), and PhC≡CPh (5.1 ± 0.4%). From the reaction
mixture where the solution of Ph$\bar{\text{C}}$=N$_2$ was photolyzed prior to
addition of H$_2$O, the following products and yields were
obtained; PhCHO (5.4 ± 0.6%), PhCH$_3$ ("trace"), _trans_-PhCH=CHPh
(19.6 ± 0.8%), PhCH=N-N=CHPh (6.4 ± 0.6%), and PhC≡CPh (6.1 ±
0.7%).

Formation of three of the five products are rationalized
by reaction of the intermediate Ph$\bar{\text{C}}$=N$_2$ with PhCH=N$_2$. PhCH=N$_2$
is thought to be present in sufficient amounts either from H$^+$-
abstraction from the solvent by Ph$\bar{\text{C}}$=N$_2$ or when H$_2$0 is added
as the quench. _trans_-PhCH=CHPh and (PhCH=N$\frac{}{}$)$_2$ are considered
to arise from nucleophilic attack of Ph$\bar{\text{C}}$=N$_2$ on PhCH=N$_2$ at C$_1$
and N$_\beta$, respectively. PhCHO is thought to result from electron
transfer from Ph$\bar{\text{C}}$=N$_2$ to trace amounts of O$_2$ in solution followed

by cyclization of the resulting radical-radical anion pair to an azadioxetane species which decomposes to PhCHO and N_2O. PhC≡CPh is proposed to arise from either electron transfer from the conjugate base of stilbene (PhC̄=CHPh) to some species in solution followed by radical β-fragmentation, or reaction between the conjugate base of stilbene and N_2O to produce an intermediate which eliminates N_2 and OH^- to produce PhC≡CPh. The intermediacy of PhC^- is not required to explain the results obtained.

EXPERIMENTAL[31,32]

Toluene. This compound was obtained from Fisher Chemical Company; bp 111°C; nmr $\delta_{TMS}^{CDCl_3}$ 7.2 (s, aromatic H's), 2.3 (s, CH_3, 3); HPLC retention time 12.2 min,[32a] 8.4 min.[32c]

trans-Stilbene. This compound was obtained from Eastman Chemical Company; mp 121-122°C; nmr $\delta_{TMS}^{CDCl_3}$ 7.4 (m, aromatic H's,10), 7.1 (s, vinyl H's, 2); HPLC retention time, 19 min.[32a]

Benzaldehyde. This compound was obtained from Mallink-rodt Chemical Company; bp 65-67°C/10 torr; nmr $\delta_{TMS}^{CDCl_3}$ 10.0 (s, CHO, 1), 7.7 (m, aromatic H's, 5); HPLC retention time, 5.5 min[32a]

Diphenylacetylene. The compound was present in our laboratory; mp 58-60°C; nmr $\delta_{TMS}^{CDCl_3}$ 7.3 (m, aromatic H's); HPLC retention time, 18.7 min.[32a]

1,2-Diphenylethane. This compound was obtained from Aldrich Chemical Company; mp 50-52°C; nmr $\delta_{TMS}^{CDCl_3}$ 7.2 (s, aromatic H's, 10), 2.8 (s, CH_2, 4); HPLC retention time, 18.6 min.[32a,33]

Anthracene. This compound was present in our labora-tory; mp 212-214°C; nmr $\delta_{TMS}^{CDCl_3}$ 8.5 (m, aromatic H's); HPLC retention time, 19.1 min.[32a,34]

Benzalazine. This compound was present in our labora-tory; mp 91-92°C; nmr $\delta_{TMS}^{CDCl_3}$ 8.5 (s, CH, 2), 7.8 (m, aromatic H's, 10); HPLC retention time, 17.4 min.[32a]

<u>5-Phenyl-1-pentanol</u>. This compound was obtained from Aldrich Chemical Company; bp 155°C/20 torr; nmr $\delta_{TMS}^{CDCl_3}$ 7.2 (s, aromatic H's, 5), 3.6 (t, CH_2-O, 2), 2.6 (t, Ph-CH_2, 2), 1.6 (m, CH_2's, 6), 1.1 (s, OH, 1); HPLC retention time, 12.0 minutes.[32a]

<u>5-Phenyl-4-pentene-1-ol</u>. 1,4-Butanediol (DuPont) was converted to the monobenzoate[35] when a solution of 51.2 g (0.57 moles) of 1,4-butanediol in 60 mL of CCl_4 was added dropwise to 20 g (0.14 moles) of freshly distilled benzoyl chloride (Fisher). After addition, the solution was stirred for 0.5 hr, water was added, the mixture was extracted with ether, the ether extracts were washed with water, aqueous $NaHCO_3$, and brine, separated and dried over $MgSO_4$. The ether was removed under reduced pressure (rotovap) and the monobenzoate of 1,4-butanediol was isolated by fractional distillation, bp 105°C/0.05 torr, yield 19.3 g (71.1%); nmr $\delta_{TMS}^{CDCl_3}$ 8.0 (m, aromatic ortho H's, 2), 7.4 (m, aromatic m' and p-H's, 3), 4.4 (t, O-CH_2-, 2), 3.7 (t, CH_2-OH, 2), 3.0 (s, OH, 1), 1.8 (m, CH_2's, 4).

The above monobenzoate of 1,4-butanediol (10.5 g, 0.054 moles) was oxidized to 4-benzoyloxybutanal according to Corey's procedure using pyridinium chlorochromate as the oxidizing agent;[36] yield 6.0 g (58%); nmr $\delta_{TMS}^{CDCl_3}$ 9.8 (s, CHO, 1), 7.8 (m, aromatic ortho H's, 2), 7.4 (m, aromatic m- and p-H's, 3), 4.4 (t, O-CH_2-, 2), 2.7 (t, $C\underline{H}_2$CHO, 2), 2.2 (m, CH_2, 2).

4-Benzoyloxybutanal was coupled with triphenylphos-
phonium benzyl bromide in a classical Wittig reaction.[37]
Benzyltriphenylphosphonium bromide (6.77 g, 0.0156 moles)
was suspended in 100 mL of dry ether under a N_2 atmosphere.
Phenyllithium (9.48 mL of 1.65 $\underline{M}$ in ether) was added dropwise
imparting an orange-red color to the solution which was then
stirred for 1 hr before 3.0 g (0.0156 moles) of 4-benzoyl-
osybutanal dissolved in 10 mL of ether was added rapidly.
The resulting mixture was stirred overnight, and the LiBr
and $(Ph)_3PO$ were removed by filtration. The ether was removed
under reduced pressure (rotovap) and 1-phenyl-5-benzoyloxy-1-
pentene was isolated by distillation; bp $129^{\circ}C/0.05$ torr;
yield 1.82 g (44%); nmr $\delta_{TMS}^{CDCl_3}$ 8.0 (m, aromatic ortho H's
of benzoate, 2), 7.3 (m, aromatic H's, 8), 6.3 (m, vinyl H's,
2), 4.4 (t, $COO-CH_2-$, 2), 2.2 (m, CH_2's, 4).

1-Phenyl-5-benzoyloxy-1-pentene was saponified.[38] One
gram of 1-phenyl-5-benzoyloxy-1-pentene in 5% KOH in ethanol
was refluxed 3 hrs. Water was added, the solution was extracted
with ether, the ether extracts were washed with water, brine,
separated, and then dried over $MgSO_4$. The ether was removed
to yield a colorless oil; yield 0.52 g (86%); nmr $\delta_{TMS}^{CDCl_3}$ 7.2
(s, aromatic H's, 5), 6.3 (m, vinyl H's, 2), 3.6 (m, C$\underline{H}_2$-OH,
2), 2.2 (m, allylic H's, 2), 2.1 (s, OH, 1), 1.8 (m, CH_2 2);
HPLC retention time, 12.5 min.[32a]

Benzyl Alcohol. This compound was obtained from Fisher
Chemical Company; nmr $\delta_{TMS}^{CDCl_3}$ 7.3 (s, aromatic H's, 5), 4.6

(s, CH_2-O, 2), 2.4 (s, OH, 1); HPLC retention time, 4.2 min.[32a]

Methyllithium. This reagent was prepared according to the procedure of Patsch, et al.[39] It was standardized by addition to distilled H_2O and titration with standard hydrochloric acid to a phenolphtalein end point.

Reaction of PhCH=N_2 with CH_3Li: Methane Quantitation.
PhCH=N_2 (1.5 g, 12.7 mmoles) in 50 mL of dry THF was added dropwise to a solution of 1.96 g (16.9 mmoles) of TMEDA, 4.8 mL (2.6 $\underline{M}$) of CH_3Li in 75 mL of dry THF under N_2 at -78°C. The reaction flask was vented to several round bottom flasks (1- or 2-L) which were filled with H_2O and inverted in a tub of H_2O. During addition of the PhCH=N_2 solution, the CH_4 evolved displaced the H_2O from the inverted flasks. After addition and stirring for 0.5 hr, the system was flushed with N_2 to displace all of the CH_4 into the inverted flasks. The flasks were capped under H_2O with rubber septa and their contents were analyzed by GLPC (Hewlett-Packard 5750) using a 6' x ¼" poropak Q column and a flame ionization detector. Only one peak was observed in the chromatogram of the injected gas from the flasks. This was identified as CH_4 by comparison of it's retention time with authentic CH_4.[40] Known concentrations of CH_4 were injected and the yields of CH_4 from the PhCH=N_2 + CH_3Li reaction were obtained by measuring the peaks and comparing them to the standards followed by multiplying by the total volume of the evolved gases (found by refilling the flasks with measured volumes of H_2O). Yields for the CH_4 production were generally ≥90%.

<u>Reaction of PhCH=N$_2$ with CH$_3$Li Followed by Addition of</u>

<u>H$_2$0: Analysis of Products</u>. PhCH=N$_2$ (1.6 g, 13.6 mmoles) in

50 mL of dry THF was added dropwise to a solution of 2.1 g

(17.9 mmoles) TMEDA, 5.5 mL (2.4 $\underline{M}$) CH$_3$Li in 75 mL of dry

THF at -78°C under N$_2$. After complete addition of the PhCH=N$_2$

solution, the dark brown solution was stirred an additional

0.5 hr then 1 mL of H$_2$0 was added to quench the system while

still at -78°C. The solution was allowed to warm to room

temperature where it was diluted to a total volume of 250 mL

with THF. A sample of this solution was then injected into

the HPLC (Varian Model 5000)[32a] The identified products and

their retention times (Min) were; PhCHO (5.8), PhCH=N-N=CHPh

(17.4), PhC≡CPh (18.8), PhCH=CHPh (19.0), and a peak tenta-

tively identified as PhCH$_3$ (8.4).[32c] Authentic samples of

known concentration were injected at the same time.

Peak areas were measured and the yields of the products

were calculated according to eq (21).

$$\frac{\text{Area of Product}}{\text{Area of Standard}} \text{ X std (mg/mL) X } \frac{\text{Vol. of Solution}}{\text{M. W. of Product}} = \text{mmoles}$$

(21)

$$\frac{\text{mmoles of product}}{\text{mmoles of PhCH=N}_2} \text{ X (D) X 100 = \% Yield}$$

D = 2 for PHC≡CPh, PhCH=CHPh, and PhCH=N-N=CHPh

D = 1 for PhCHO

An example for PhCH=N-N=CHPh is illustrated below.

(1202/555) x (0.136) x (250/208.27) = 0.354 mmoles

(0.354/13.6) X (2) x (100) = 5.2%

Yields for the identified products are listed below
(ratio of areas, standard concentration, mmoles of PhCH=N_2,
% Yield); PhCHO (410/659, 0.222, 13.6, 2.4%), PhCH=CHPh
(532/269, 0.288, 13.6, 11.6%), PhCH=N-N=CHPh (1202/555, 0.136,
5.2%), PhC≡Ph (797/489, 0.140, 13.6, 4.7%), and PhCH$_3$ ("trace").
In a successive reaction, the data were as follows; PhCHO (620/
662, 0.222, 13.6, 3.6%), PhCH=CHPh (456.255, 0.288, 13.6,
10.5%), PhCH=N-N=CHPh (1345/497, 0.136, 13.6, 6.5%), PhC≡CPh
(930/456, 0.140, 13.6, 5.5%), and PhCH$_3$ ("trace"). The yield
data are summarized in Table Ia.

Reaction of PhCH=N_2 with CH$_3$Li Followed by Photolysis and Quenched with H$_2$O: Analysis of Products.

PhCH=N_2 (1.45
g, 12.3 mmoles) in 50 mL of dry THF was added dropwise to a
solution of 1.89 g (16.4 mmoles) of TMEDA, 6.1 mL (2.0$\underline{M}$)
CH$_3$Li in 75 mL of dry THF under a N_2 atmosphere in a photo-
lysis cell at -78°C. After the addition was complete, the
solution was allowed to stir at -78°C for 0.5 hr before
initiation of photolysis. The light source was a General
Electric H100-A4 100 watt mercury lamp. The dark brown
solution was photolyzed 2.5-3 hr, after which 1 mL of H$_2$O
was added to the solution while still at -78°C. The solution
was allowed to warm to room temperature where it was diluted
to a total volume of 250 mL with THF. A sample of this
solution was then injected into the HPLC (Fig. 3).[32a] The
identified products and their retention times (min) were;
PhCHO (5.8), PhCH=N-N=CHPh (17.4), PhC≡CPh (18.8), PhCH=CHPh

(19.0), and a peak tentatively identified as $PhCH_3$ (8.4).[32c]
Authentic samples of known concentration were injected at the
same time. Areas were measured and the yields were calculated
as above (eq 21). Yield data for the identified products
were PhCHO (736/654, 0.222, 12.3, 4.8%), PhCH=N-N=CHPh (1220/
559, 0.136, 12.3, 5.8%), PhC≡CPh (830/392, 0.140, 12.4, 5.4%),
PhCH=CHPh (750/259, 0.288, 12.3, 18.8%), and $PhCH_3$ ("trace").
In a successive reaction the yield data were; PhCHO (990/670,
0.222, 13.1, 6.7%), PhCH=N-N=CHPh (1600/570, 0.136, 13.1,
7.0%), PhC≡CPh (1112/498, 0.140, 13.1, 6.7%), PhCH=CHPh (816/
245, 0.288, 13.1, 20.3%), and $PhCH_3$ ("trace"). The yield
data are summarized in Table Ib.

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17. I wish to thank Professor S. D. Worley, Auburn University for making this program written for an IBM-370 computer available, and Professor Keith Purcell for his effort to get it running on our machine.

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24. Professor C. H. DePuy has *found* that the *benzoyl* anion, $PhCO^-$, is produced in the reaction of H_2N^- with PhCHO in a flowing afterglow experiment; personal communication with Professor R. N. McDonald.

25. The ΔH^O_{rxn} was calculated using $\Delta H^O_f(PhC\equiv CPh)$ = 71.91 kcal mole^{-1} calculated,[26] $\Delta H^O_f(H^-)$ = 34.2 kcal mole^{-1},[27] and $\Delta H^O_{acid}(Ph\bar{C}=CHPh)$ = 395 kcal mole^{-1}, estimated to be between C_6H_6 (ΔH^O_{acid} = 398±7 kcal mole^{-1})[28] and $CH_3CH=CH_2$ (ΔH^O_{acid} = 390.8 kcal mole^{-1}).[28]

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31. Melting points were determined on a Kofler Hot Stage and are uncorrected; boiling points are uncorrected. ^{1}H nmr spectra were obtained on a Varian T-60 spectrometer.

32. HPLC analyses were recorded using a Varian Model 5000 Liquid Chromatograph with a Varian MCH-10, universal, reverse-phase column. Three solvent programs were used in the analyses. a) 50:50, $CH_3OH:H_2O$ to start increasing to 100% CH_3OH at 18 min in a gradient. b) A constant

composition of 55:45 $CH_3CN:H_2O$ c) 45:55, $CH_3CN:H_2O$ to start, this was held constant til four minutes elapsed, then increased to 100% CH_3CN at 18 minutes in a gradient.

33. This compound had approximately the same retention time as diphenylacetylene however, it was ruled out as a reaction product due to it's small extinction coefficient.

34. Anthracene has a retention time similar to stilbene in the CH_3OH/H_2O (ref, 32a) program, however, it was ruled out as a reaction product by using the CH_3CN/H_2O isocratic program (ref 32c). With this program anthracene eluted 0.5 min before stilbene in a standard mixture, and in the quench and photolyses there was no peak corresponding to anthracene's retention time.

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40. Dr. A. K. Chowdhury prepared the standard methane samples.

ACKOWLEDGMENTS

AN EXPERIMENTAL APPROACH TO THE

GENERATION OF PHENYLCARBYNE ANION

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B.A., Benedictine College, 1979

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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

1983

ABSTRACT

The attempted generation of phenylcarbyne anion (PhC^-)
was investigated by proton abstraction from phenyldiazomethane
($PhCH=N_2$) to produce the conjugate base ($Ph\bar{C}=N_2$) which was
photolyzed. Addition of a solution of $PhCH=N_2$ in THF to a
methyllithium/N,N,N',N'-tetramethylethylenediamine (TMEDA)
solution in THF at -78^OC, followed by addition of 1 mL of H_2O
as a quench produced the following products; benzaldehyde (PhCHO,
3.0 ± 0.6%), toluene ($PhCH_3$, "trace"), trans-stilbene (PhCH=CHPh,
11.1 ± 0.6%), benzalazine (PhCH=N-N=CHPh, 5.9 ± 0.7%), and
diphenylacetylene ($PhC\equiv CPh$, 5.1 ± 0.4%). Preparation of the
above THF solution followed by photolysis for 2.5-3 hr at -78^OC
with a 100 watt mercury lamp, and then quenched with 1 mL of
H_2O produced the following products; PhCHO (5.4 ± 0.6%), $PhCH_3$
("trace"), trans-PhCH=CHPh (19.6 ± 0.8%), PhCH=N-N=CHPh (6.4 ±
0.6%), and $PhC\equiv CPh$ (6.1 ± 0.7%).

$(PhCH=N)_2$ and PhCH=CHPh are thought to arise from attack
of $Ph\bar{C}=N_2$ at C_1 or N_β, respectively of $PhCH=N_2$. Ample amounts
of $PhCH=N_2$ are proposed to be present for these reactions from
H^+-transfer to $Ph\bar{C}=N_2$ from the solvent or from H_2O in the
quench. If the H_2O is the H^+-donor, the reaction products
could be formed by a series of fast reactions before the H_2O
is completely dispersed. PhCHO is considered to result from
reaction of $Ph\bar{C}=N_2$ with trace amounts of O_2 in solution, with
N_2O formed as a byproduct. Formation of $PhC\equiv CPh$, a most
unusual product is rationalized by two possible processes,

(a) a condensation/decomposition reaction of PhC̄=CHPh with N_2O yielding PhC≡CPh, N_2, and OH⁻, or (b) electron transfer from PhC̄=CHPh to some species in solution followed by radical β fragmentation of PhĊ=CHPh giving PhC≡CPh and a H-atom. The intermediacy of the phenylcarbyne anion is not required to explain the results.