oily layer separated at the bottom of the reaction flask which was taken up in ether. Drying and evaporation gave an oil (0.7 g). The aqueous acidic layer was diluted with water (75 ml), precipitating the product (1.5 g). The analytical sample was obtained from methanol, mp 166–168°, nmr ($CDCl_3$) δ 2.80 (s, 3), M^+ 212 and 210.

Anal. Calcd for $C_9H_7N_2O_2Cl$: C, 51.30; H, 3.32; N, 13.25. Found: C, 51.32; H, 3.35; N, 13.38.

Thin layer chromotographc analysis of the above oil on silica gel (benzene) showed it to be a mixture of two compounds. Column chromotography (silica gel, 20 g) was used for their separation. Elution with hexane (300 ml) furnished diphenyl disulfide, mp 59–60° (0.28 g). Further elution with a 1:1 mixture of benzene–hexane (700 ml) gave *S*-phenyl benzenethiosulfonate (0.38 g) as a low-melting solid, mp 41–42°.

2-Bromo-3-methylquinoxaline 1,4-Dioxide (5b).—This compound was obtained using 48% HBr solution following the same procedure described for the preparation of **5a**. Crystallization from methanol–chloroform furnished the analytical sample, mp 163–164°, nmr ($CDCl_3$) δ 2.87 (s, 3), M^+ 256 and 254.

Anal. Calcd for $C_9H_7N_2O_2Br$: C, 42.35; H, 2.74; N, 10.98. Found: C, 42.12; H, 2.83; N, 11.03.

1-Acetoxy-3-methylquinoxaline-2-one 4-Oxide (6a). A.—The sulfone **4a** (1.0 g, 4 mmol) was dissolved in acetic acid (25 ml) and was allowed to stand at room temperature for 18 hr. Dilution with water (250 ml) was followed by extraction with chloroform. The chloroform layer was backwashed with water, dried over magnesium sulfate, filtered, and evaporated to dryness to give a gum (0.37 g). The analytical sample was obtained by crystallization from ether–chloroform without the use of heat, mp 142–143°, nmr ($CDCl_3$) δ 2.5 (s, 3), 2.57 (s, 3).

Anal. Calcd for $C_{11}H_{10}O_4N_2$: C, 56.41; H, 4.27; N, 11.96. Found: C, 56.38; H, 4.49; N, 11.77.

B.—The sulfoxide **3a** (2.5 g, 10 mmol) was dissolved in acetic acid (25 ml) by heating for 0.5 hr. Dilution with water (250 ml) was followed by extraction with chloroform. A similar work-up to that above gave a gum (1.9 g). This was chromatographed on Florisil eluting first with chloroform (400 ml) to give **6a** (0.32 g), followed by a 1:1 mixture of methanol–chloroform (500 ml) to furnish the hydroxamic acid **7** (1.0 g), mp 224–225°, identical with an authentic sample.[4]

1-*m*-Chlorobenzoxy-3-methylquinoxalin-2-one 4-Oxide(6b).—The sulfide **2b** (2.0 g, 7 mmol) was dissolved in chloroform (100 ml). To this solution MCPBA (2.83 g, 14 mmol) in chloroform (50 ml) was added and the resulting mixture was refluxed for 1 hr. One more equivalent of MCPBA (1.4 g) was added and the reaction mixture was refluxed for an additional 1 hr. The chloroform solution was first washed with a saturated solution of sodium bicarbonate (3 × 50 ml), and then with water, dried, filtered, and evaporated to dryness to yield a solid. The solid residue (0.6 g) was crystallized from methylene chloride–ether, mp 161–162°, nmr ($CDCl_3$) δ 2.6 (s, 3), M^+ 332 and 330.

Anal. Calcd for $C_{16}H_{11}N_2O_4Cl$: C, 58.09; H, 3.32; N, 8.47. Found: C, 57.98; H, 3.23; N, 8.40.

Acknowledgment.—The author wishes to thank Mr. Leo B. Keith, Jr., for his technical assistance.

Registry No.—**2a**, 39576-50-6; **2b**, 39576-56-2; **3a**, 39576-76-6; **3b**, 40735-40-8; **4a**, 39576-77-7; **4b**, 40735-42-0; **5a**, 39576-78-8; **5b**, 39576-79-9; **6a**, 40735-45-3; **6b**, 40735-46-4.

O-Nitrene and *O*-Nitrenium Cation Intermediates in Reactions of O-Substituted Hydroxylamines[1]

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Two methods were investigated for the generation of *O*-nitrenes (**3**) and/or *O*-nitrenium cations (**4**): lead tetraacetate oxidation of *O*-alkylhydroxylamines (**5**) and thermal base-catalyzed decomposition of *N*-*p*-toluenesulfonyl-*O*-alkylhydroxylamines (**6**). Lead tetraacetate oxidation of *O*-diphenylmethylhydroxylamine (**5a**) was solvent dependent and afforded mixtures of products containing *O*-diphenylmethylbenzophenone oxime, benzophenone, benzhydrol, and products corresponding to net O to N migration of Ph_2CH–, *N*-diphenylmethoxy-*N'*-diphenylmethyldiazine *N'*-oxide (**9**), and benzophenone oxime. *p*-Nitrobenzyl alcohol was the only product formed on oxidation of *O*-*p*-nitrobenzylhydroxylamine (**5b**) with lead tetraacetate. The stereochemical course of formation of *N*-alkoxyaziridines from lead tetraacetate oxidation of *O*-*n*-butylhydroxylamine in the presence of *cis*- and *trans*-2-butene was examined and found to be nonstereospecific. *trans*-2-Butene afforded *N*-*n*-butoxy-*trans*-2,3-dimethylaziridine (**12**) and *N*-*n*-butoxy-*cis*-2,3-dimethylaziridine (**13**) in an 82:18 ratio while the **12**:**13** ratio from *cis*-2-butene was 38:62. The dominant thermal reaction from **6** and sodium hydride involved O–N bond cleavage. Thus **6a** and excess sodium hydride gave benzhydrol as the major product which was shown to arise *via* cleavage of the carbanion of **6a** to benzophenone and *p*-toluenesulfonamide anion followed by reduction of benzophenone to benzhydrol. O to N migration was observed when either *n*-butyllithium or only small excesses of sodium hydride were used to yield benzophenone oxime (quantitative from *n*-butyllithium). No O to N migration was observed using **6c** or **6d** and NaH with the products being *p*-bromobenzoic acid and *p*-methoxybenzoic acid, respectively, probably arising *via* oxidation of the corresponding aldehydes. The suggestion is made that there is, as yet, no conclusive evidence for the intermediacy of **3** in any reactions of O-substituted hydroxylamines or its derivatives. Mechanisms not involving *O*-nitrenes are suggested including the possibility of organolead intermediates being the species undergoing O to N migration and addition to olefins in the lead tetraacetate oxidations, and fragmentation–recombination pathways for the base-catalyzed reactions of **6a**.

Species possessing an electron-deficient nitrogen have been proposed and, in some instances, detected as reactive intermediates in a great many organic reactions.[2] Even-electron intermediates of this type may be either nitrenes ($R\ddot{N}$:) or nitrenium ions (R^+-$\ddot{N}R'$), and each of these may exist either in a singlet or triplet electronic state with the triplet usually being lower in energy.[2c,3] If substituents are chosen so as to be able to interact electronically with the unfilled 2p orbital on nitrogen, the energy levels of the singlet and triplet states will be perturbed so that the singlet could become the ground state, *e.g.*, when R or R' is nitrogen, oxygen, or fluorine. With

(1) Portions of the work described here have been reported previously: (a) F. A. Carey, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, paper 69; (b) F. A. Carey and L. J. Hayes, *J. Amer. Chem. Soc.*, **92**, 7613 (1970).

(2) (a) P. A. S. Smith in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963; (b) J. H. Boyer in "Mechanisms of Molecular Migrations," Vol. 2, B. S. Thyagarajan, Ec., Interscience, New York, N. Y., 1969; (c) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970); (d) P. A. S. Smith, "Open-Chain Nitrogen Compounds," W. A. Benjamin, New York, N. Y., 1965.

(3) R. S. Berry in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 2.

respect to this point *ab initio* SCF–CI calculations on NH_2^+ indicate the triplet to be *ca.* 45 kcal/mol lower in energy than the singlet,[4] while it has been suggested that NF_2^+ has a singlet ground state.[5] For nitrenes CNDO–INDO calculations indicate singlet ground states for both HON and H_2NN.[6]

N-Nitrenes (**1**, diazenes, azanitrenes) and *N*-nitrenium ions (**2**, diazenium, azanitrenium) are sufficiently

$R_2N\ddot{N}$ (**1**) $\qquad R_2N\overset{+}{\ddot{N}}H$ (**2**)

stabilized to be accessible by chemical means, have been the object of a number of investigations, and are known to be important in reactions of hydrazine and its derivatives.[7]

The analogous oxygen-stabilized species, *O*-nitrenes (**3**, oxyazenes, oxynitrenes) and *O*-nitrenium ions (**4**,

$RO\ddot{N}$ (**3**) $\qquad RO\overset{+}{\ddot{N}}H$ (**4**)

oxyazenium, oxynitrenium), have proved to be more elusive. This paper reports the results of numerous attempts o generate **3** and **4** by applying the techniques which had been shown to be useful for generation of **1** and **2**.

When these studies were begun there were no published reports of systematic attempts at generating **3** and **4**, although the possibility of an *O*-nitrene intermediate intervening in the oxidation of *O*-alkylhydroxylamines to yield hyponitrite esters had been noted.[2d]

During the course of this work several reports appeared which described attempts to generate **3** or postulated it as an intermediate.[8] *A priori*, **3** and **4** should be higher energy intermediate than **1** and **2** and presumably more difficult to generate, since oxygen is less effective at stabilizing an adjacent electron-deficient center than is nitrogen.

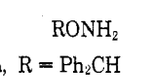
Results

Of the techniques which can be considered conventional for generation of nitrenes and related electron-deficient intermediates, two were chosen for detailed examination with respect to the question of *O*-nitrenes: (a) oxidation of *O*-alkylhydroxylamines (**5**) (eq 1) and (b) base-promoted α-elimination of *N*-sulfonyl-*O*-alkylhydroxylamines (**6** or **7**) (eq 2).

The required substrates for each process, *O*-alkylhydroxylamines (**5a–e**) and their corresponding sulfonamide derivatives (**6**, **7**), were conveniently available using standard synthetic routes.

$RONH_2$ (**5**)

5a, R = Ph_2CH
b, R = p-$O_2NC_6H_4CH_2$
c, R = CH_3
d, R = $CH_3CH_2CH_2CH_2$
e, R = $PhCH_2$
f, R = p-$ClC_6H_4CH_2$

$RONHSO_2$–  –CH_3 (**6**)

6a, R = Ph_2CH
b, R = $PhCH_2$
c, R = p-$BrC_6H_4CH_2$
d, R = p-$CH_3OC_6H_4CH_2$

$RONHSO_2CH_3$ (**7**)

7a, R = Ph_2CH

$$RONH_2 \xrightarrow{[O]} RO\ddot{N}: \quad (1)$$

5

$$RONHSO_2R' \xrightarrow{\text{base}} RO\bar{N}SO_2R' \xrightarrow{\Delta} RO\ddot{N} + RSO_2^- \quad (2)$$

6

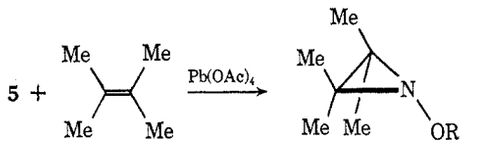
Oxidation of *O*-Substituted Hydroxylamines.—A number of oxidizing agents were briefly surveyed using *O*-diphenylmethylhydroxylamine (**5a**) as the substrate. Nickel peroxide,[9] a source of hydroxyl radicals reported to oxidize amines to nitrenes, reacted rapidly with **5a** to cleave the O–N bond, yielding benzhydrol in 83% yield. *N*-Bromosuccinimide in carbon tetrachloride converted **5a** to benzophenone (29%) and *O*-diphenylmethylbenzophenone oxime ($Ph_2CHON{=}CPh_2$, **8**, 51%), presumably formed by condensation of **5a** with benzophenone. Mercuric oxide, a commonly used oxidant of *N*,*N*-dialkylhydrazines,[10] failed to react with **5a**.

Lead tetraacetate reacted readily with **5a**, as well as other *O*-alkylhydroxylamines, to afford product mixtures the composition of which was solvent dependent. In dichloromethane at 25°, **5a** yielded a white, crystalline solid formulated on the basis of nmr[11] and ir[12] data as *N*-diphenylmethoxy-*N'*-diphenylmethyldiazine *N'*-oxide [$Ph_2CHON{=}N(O^-)CHPh_2^+$, **9**] in 32% yield. This product was also isolated from lead tetraacetate oxidation of **5a** in trichloroethylene as solvent. Complex reaction mixtures containing benzophenone, benzhydrol, and either benzhydryl acetate or benzhydryl methyl ether were obtained in acetic acid and methanol, respectively. When **5a** was oxidized with lead tetraacetate in pyridine or dimethylformamide there was formed, in addition to benzophenone and **8**, small amounts of benzophenone oxime. The lead tetraacetate oxidation of *O*-*p*-nitrobenzylhydroxylamine was relatively clean and gave *p*-nitrobenzyl alcohol as the only product in high yield.

Since Brois[8c] had reported that oxidation of *O*-methylhydroxylamine (**5c**) in the presence of tetramethylethylene resulted in the formation of the *N*-methoxyaziridine **10**, a number of oxidations were carried out in the presence of olefins as trapping reagents.

For reasons of convenience we chose to use *O*-*n*-butylhydroxylamine (**5d**) and found that this compound afforded the *N*-*n*-butoxyaziridine (**11**) in 40% yield on oxidation with lead tetraacetate in tetramethylethylene.

(4) S. T. Lee and K. Morokuma, *J. Amer. Chem. Soc.*, **93**, 6863 (1971).
(5) A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *J. Chem. Phys.*, **54**, 1872 (1971).
(6) (a) L. J. Hayes, F. P. Billingsley, II, and C. Trindle, *J. Org. Chem.*, **37**, 3924 (1972); (b) J. Peslak, Jr., D. S. Klett, and C. W. David, *J. Amer. Chem. Soc.*, **93**, 5001 (1971).
(7) D. M. Lemal in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 10; D. M. Lemal, F. Menger, and E. Coats, *J. Amer. Chem. Soc.*, **86**, 2395 (1964).
(8) (a) J. H. Boyer and J. D. Woodyard, *J. Org. Chem.*, **33**, 3329 (1968); (b) A. Hassner, R. Wiederkehr, and A. J. Kascheres, *ibid.*, **35**, 1962 (1970); (c) S. L. Brois, *J. Amer. Chem. Soc.*, **92**, 1079 (1970); (d) R. Partch, B. Stokes, D. Bergman, and M. Budnik, *Chem. Commun.*, 1504 (1971); (e) R. O. C. Norman, R. Purchase, and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1701 (1972); (f) B. V. Ioffe and E. V. Koroleva, *Zh. Org. Khim.*, **8**, 1548 (1972); *Tetrahedron Lett.*, 619 (1973).
(9) (a) K. Nakagawa, R. Konaka and T. Nakata, *J. Org. Chem.*, **27**, 1597 (1962); (b) K. Nakagawa and H. Onoue, *Tetrahedron Lett.*, 1433 (1965).
(10) See, for example, C. G. Overberger and S. Altscher, *J. Org. Chem.*, **31**, 1728 (1966); P. S. Forgione, G. S. Sprague, and H. J. Troffkin, *J. Amer. Chem. Soc.*, **88**, 1079 (1966).
(11) J. P. Freeman, *J. Org. Chem.*, **28**, 2508 (1963).
(12) M. V. George, R. W. Kierstead, and G. F. Wright, *Can. J. Chem.*, **37**, 679 (1959).



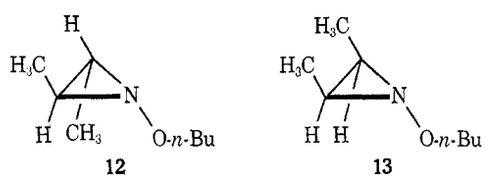
10, R = CH_3
11, R = $CH_3CH_2CH_2CH_2$

The nmr spectrum of **11** exhibited two singlets at δ 1.15 and 1.19 of equal intensity for the aziridine ring methyl groups which are nonequivalent by virtue of the slow rate of pyramidal inversion at nitrogen.[3c]

Since an important piece of evidence in deducing the nature of the intermediate formed by lead tetraacetate oxidation of O-substituted hydroxylamines is whether the intermediate reacts with olefin to afford aziridines in a concerted or nonconcerted fashion, it was considered important to try to trap the intermediate with *cis*- and *trans*-2-butene. Generally speaking, stereospecific addition to *cis*- and *trans*-2-butene is taken as supporting concerted addition, although a nonconcerted addition can be stereospecific. Nonstereospecific addition, however, requires that the process not be concerted.

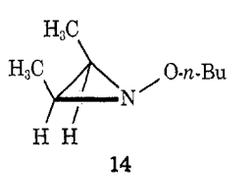
When the necessary reactions were performed two observations were made. First, both *cis*-2-butene and *trans*-2-butene were much less effective at trapping the reactive intermediate than tetramethylethylene, giving yields of less than 20% of *N*-*n*-butoxyaziridines. Secondly, the *reactions were not stereospecific*. Thus, addition of a solution of **2b** in dichloromethane to a well-stirred slurry of lead tetraacetate in *trans*-2-butene at −78° afforded *N*-*n*-butoxy-*trans*-2,3-dimethylaziridine (**12**) and *N*-*n*-butoxy-*cis*-2,3-dimethylaziridine (**13**) in a ratio of 82:18. Using *cis*-2-butene as the trap under identical conditions gave **12** and **13** in a ratio of 38:62. Control experiments demonstrated that neither the *cis*- and *trans*-2-butene nor the products isomerized under the reaction conditions.

Assignment of structure to the adducts was made by considering their nmr spectra. The isomer with the shorter retention time on glpc (1.7 min) was identified as **12** by the presence of two nonequivalent methyl doublets at δ 1.13 (J = 5 Hz) and 1.33 (J = 5 Hz). The isomer with the longer retention time (2.2 min) exhibited a single methyl peak at δ 1.11 (doublet, J = 6 Hz) consistent with **13**. The other cis isomer **14**



12

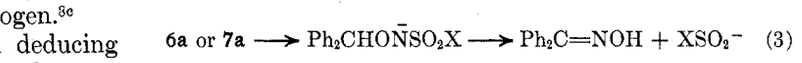
13



14

did not appear to be present. Both **12** and **13** gave similar mass spectra with m/e 70 as the most intense peak in each, corresponding to loss of BuO· from the molecular ion to leave $(C_4H_8N)^+$. The next most intense peak in each was m/e 41, while m/e 143 (parent) was observed to be of quite low intensity (1.1 and 2.8%).

Base-Promoted Decomposition of *N*-Sulfonyl-*O*-alkylhydroxylamines.—Conversion of **6a** or **7a** to the corresponding sodium or lithium salt with sodium hydride or *n*-butyllithium, respectively, followed by pyrolysis in triglyme at 160-200° resulted in the loss of sulfinate and net O to N migration of the diphenylmethyl substituent to afford benzophenone oxime. These results are summarized in Table I and eq 3.



(3)

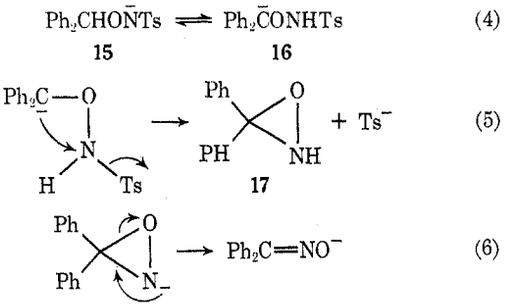
TABLE I
THERMAL DECOMPOSITION OF ANIONS DERIVED FROM **6a** AND **7a**

Substrate	Base	Leaving group	Yield of $Ph_2C{=}NOH$, %
6a	NaH (2 equiv)	Ts^-	58
7a	NaH (2 equiv)	$CH_3SO_2^-$	48
6a	BuLi (1.1 equiv)	Ts^-	100

When large excesses of NaH were employed the reaction took a different course and produced benzhydrol exclusively.

Although the reaction was chosen as one likely to produce an *O*-nitrene and the formation of benzophenone oxime is consistent with the anticipated behavior of such an intermediate, there do exist a number of alternative mechanisms which could afford benzophenone oxime without an *O*-nitrene being involved. Efforts were made to test the more reasonable possibilities by experiment.

One such possibility for the case of **6a** is shown in eq 4–6. This scheme assumes that the expected



(4)

15 16

(5)

17

(6)

anion **15** is in equilibrium with the carbanion **16**, which undergoes an intramolecular displacement of *p*-toluenesulfinate to afford the oxazirane **17**, which in turn rearranges to benzophenone oxime.

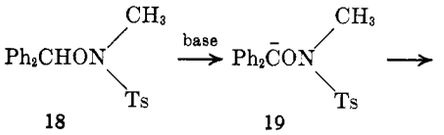
This sequence of events is analogous to one tentatively suggested by Paquette to explain the O to N migration observed in the base-catalyzed decomposition of *N*-chloro-O-substituted hydroxylamines.[13]

This possibility could not be tested directly using **6a** but rather required the *N*-methyl compound **18**. If the carbanion → oxazirane transformation is important, then **18** should undergo this as readily as **6a** and lead to products derived from *N*-methyldiphenyloxazirane.[14] Treatment of **18** with 2 equiv of sodium hydride in triglyme at 200° for 19 hr and separation of

(13) L. A. Paquette, *Tetrahedron Lett.*, 485 (1962).
(14) For a review of oxazirane chemistry see W. D. Emmons in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part One, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, Chapter IV.

the products by preparative tlc led to the isolation of benzophenone (13%), benzhydrol (72%), and *N*-methyl-*p*-toluenesulfonamide (46%). These products are most reasonably explained as arising from cleavage of the carbanion derived from **18** to benzophenone and *N*-methyl-*p*-toluenesulfonamide followed by reduction of the benzophenone to benzhydrol by sodium hydride.[15]

Evidence to support the notion that the benzhydrol is formed by reduction of the benzophenone resulting from cleavage of the carbanion was obtained by repeating the experiment using **18** substituted with deuterium at the carbon atom which bears the two phenyl groups. The benzhydrol formed in this reaction was isolated in 65% yield and determined to have lost completely its deuterium label in accordance with the prediction based on eq 7.



18 **19**

$$Ph_2CO + CH_3\bar{N}Ts \quad (7)$$

It thus appears that carbanions in these systems, when generated, undergo efficient fragmentation to carbonyl compounds rather than intramolecular O to N rearrangement. This also served to explain the results of reactions in which the *p*-toluenesulfonamide derivatives **6b–d** of *O*-benzyl-, *O*-*p*-bromobenzyl-, and O-*p*-methoxybenzylhydroxylamine were treated with sodium hydride in triglyme at elevated temperature. The products were those formed by cleavage of the oxygen–nitrogen bond, affording initially substituted benzaldehydes and *p*-toluenesulfonamide. The isolated products from **6b**, **6c**, and **6d**, exclusive of *p*-toluenesulfonamide, were benzoic acid (30%), *p*-bromobenzoic acid (41%), and *p*-methoxybenzoic acid (39%), respectively. In one experiment benzonitrile was isolated from **6b** in 35% yield along with a small amount (8%) of *N*-*p*-toluenesulfonylbenzylamine. Both the conversion of benzaldehyde to benzoic acid and the formation of $PhCH_2NHTs$ were established as occurring under the reaction conditions by a control experiment in which the anion of *p*-toluenesulfonamide was generated using sodium hydride and heated in triglyme with benzaldehyde to yield benzoic acid (48%), benzyl alcohol (15%), and *N*-*p*-toluenesulfonylbenzylamine (11%).

The dominant reaction path of **6b**, **6c**, and **6d** therefore appears to be base-catalyzed cleavage to aldehyde and *p*-toluenesulfonamide anion. The formation of *N*-*p*-toluenesulfonylbenzylamine probably results from condensation of these two fragments followed by dehydration and reduction of the tosylimine with sodium hydride as formulated in Scheme I.

It is reasonable that PhCH=NTs is also the precursor to benzonitrile *via* base-catalyzed β-elimination, although benzonitrile was not observed in the control experiment. It is not known exactly how oxidation of the aldehyde to the carboxylic acid occurs, and speculation on that point will not be offered, since it is not essential to the central question, *i.e.*, whether *O*-nitrenes are formed in these reactions.

(15) F. W. Swamer and C. R. Hauser, *J. Amer. Chem. Soc.*, **68**, 2647 (1946).

SCHEME I

$$PhCH_2O\bar{N}Ts \rightleftharpoons PhCHONHTs \longrightarrow PhCHO + Ts\bar{N}H$$

$$PhCHO + Ts\bar{N}H \longrightarrow PhCH(NHTs)O^-$$

$$PhCH(NHTs)O^- \rightleftharpoons PhCH(\bar{N}Ts)OH \longrightarrow PhCH{=}NTs$$

$$PhCH{=}NTs \xrightarrow{\text{reduction}} PhCH_2NHTs$$

Discussion

It is apparent that many of the experimental methods which are suitable for the generation of *N*-nitrenes (**1**) from hydrazine derivatives are not directly applicable to the generation of *O*-nitrenes (**3**) from hydroxylamine derivatives. The most common observation in reactions of *O*-alkylhydroxylamines and their derivatives is cleavage of the O–N bond. This has been observed previously, for example, in the attempted deoxygenation of benzyl nitrite and *tert*-butyl nitrite by trivalent phosphorus compounds as a route to **3**.[8a] Oxidation of **5e** with chromic acid[16] or bromine afforded mixtures of benzaldehyde and benzyl alcohol with the bromine oxidation having been shown[17] to proceed by initial formation of a hyponitrite ester,[18] which undergoes fragmentation to nitrogen and alkoxy radicals which in turn disproportionate to an aldehyde and an alcohol.[19] The formation of the hyponitrite ester need not involve the intermediacy of **3**, since a reasonable alternative path exists. The overall process can be represented by Scheme II for the case of **5e**.

SCHEME II

$$\mathbf{5e} + Br_2 + OH^- \longrightarrow PhCH_2ONHBr + H_2O + Br^-$$

$$PhCH_2ONHBr + \mathbf{5e} + OH^- \longrightarrow PhCH_2ONHNHOCH_2Ph + Br^- + H_2O$$

$$PhCH_2ONHNHOCH_2Ph + Br_2 + 2OH^- \longrightarrow PhCH_2ON{=}NOCH_2Ph + 2H_2O + 2Br^-$$

$$PhCH_2ON{=}NOCH_2Ph \longrightarrow N_2 + 2PhCH_2O\cdot$$

$$2PhCH_2O\cdot \longrightarrow PhCHO + PhCH_2OH$$

Cleavage of the O–N bond was the dominant reaction course in most of the reactions carried out in this study as well. It was not considered significant for our purposes to determine whether hyponitrite esters were involved in these processes, because, as in the example cited above, hyponitrite ester formation does not require an *O*-nitrene to be present as its precursor.[20] The more important concerns were those reactions which afforded products having the O–N bond intact. In the case of lead tetraacetate oxidation of **5** these were the formation of nitroso compounds (as dimers) from **5e** and **5f**,[8d,e] the formation of **9** from **5a**, and the formation of *N*-alkoxyaziridines when the oxidation of **5c**[8c] and **5d** was performed in the presence of olefins.

While O to N migration of an aralkyl group to afford a nitroso compound is consistent with the anticipated

(16) R. Kothe, *Justus Liebigs Ann. Chem.*, **266**, 310 (1891).

(17) L. Seed, British Patent 795,824; *Chem. Abstr.*, **53**, 219 (1959).

(18) For a review on hyponitrite esters see M. N. Hughes, *Quart. Rev., Chem. Soc.*, **22**, 1 (1968).

(19) S. K. Ho and J. B. DeSousa, *J. Chem. Soc.*, 1788 (1961); H. Kiefer and T. G. Traylor, *Tetrahedron Lett.*, 6163 (1966); C. Walling and J. A. McGuiness, *J. Amer. Chem. Soc.*, **91**, 2053 (1969).

(20) See ref 8e for a plausible mechanistic scheme to rationalize formation of dibenzyl hyponitrite in the lead tetraacetate oxidation of **5e**.

behavior of an *O*-nitrene, the observation of products resulting from O to N migration does not demand the intermediacy of **3**. The most probable initial reaction of **5** with lead tetraacetate is formation of the organolead intermediate **20**.

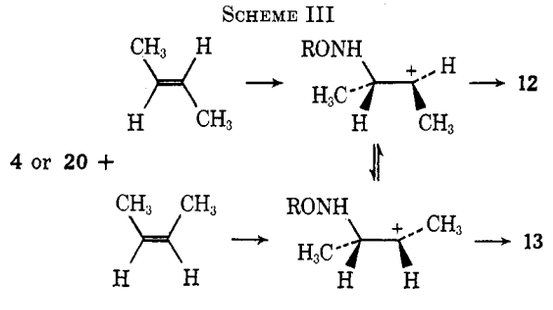
$$5 + Pb(OAc)_4 \longrightarrow \underset{\mathbf{20}}{RONHPb(OAc)_3} + HOAc \qquad (8a)$$

By analogy[21] with other reactions of organolead intermediates, **20** could be expected to serve as a source of the *O*-nitrenium ion **4**, with **3** resulting from deprotonation of **4**.

$$\mathbf{20} \longrightarrow \underset{\mathbf{4}}{RO\overset{+}{N}H} + Pb(OAc)_2 + OAc^- \qquad (8b)$$

The *O*-nitrenium cation **4** seemingly has the capacity to do all of the things anticipated for **3**: O to N migration of R and addition to alkenes are very likely reactions of **4**. Additionally, these reactions could occur in a manner concerted with cleavage of the nitrogen–lead bond of **20**. The available data do not allow a choice to be made regarding the point at which reactions occur during the process **20** → **4** → **3**, and the conclusion that **3** and/or **4** are intermediates in the lead tetraacetate oxidation of O-substituted hydroxylamines is not warranted. This conclusion receives support from the lack of stereospecificity observed in *N*-alkoxyaziridine formation from *cis*- and *trans*-2-butene and **5d**. Formation of *N*-alkoxyaziridine is not nearly so efficient as from tetramethylethylene and the total amount formed is not large, being estimated at 10–20%. Nevertheless, both **12** and **13** are formed (in different amounts) from each olefin, providing evidence that at least a portion of the adduct arises by a nonstereospecific process. Triplet *O*-nitrene is not a reasonable intermediate, because calculations[6a] indicate the singlet *O*-nitrene to be more stable than the triplet and the reaction conditions are those which because of spin conservation would not be expected to yield the triplet state directly. Nonstereospecific addition requires at least a two-step mechanism and either **20** or **4** could add in a two-step process as shown in Scheme III.

SCHEME III



Complete equilibration of the initial carbonium ion intermediates would not occur if the rate of closure were competitive with the rate of rotation around the carbon–carbon bond. The reaction mixtures were complex, and if pinacol-type rearrangement products were formed they were not detected.

(21) For references and mechanistic discussion of lead tetraacetate oxidations see (a) W. H. Starnes, Jr., *J. Amer. Chem. Soc.*, **90**, 1807 (1968); (b) J. K. Kochi, *Rec. Chem. Progr.*, **27**, 207 (1966); (c) R. Criegee in "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press, New York, N. Y., 1965, Chapter V.

The results of the base-catalyzed thermal decomposition reactions of *N*-*p*-toluenesulfonyl-*O*-alkylhydroxylamines are similarly inconclusive with regard to the intermediacy of **3**. In most cases the reactions appeared to be those of carbanions formed in equilibrium with the desired amide ions leading to cleavage to an aldehyde or ketone plus *p*-toluenesulfonamide anion. In this respect the reactions of **6** and **7** parallel closely the well-known Wittig rearrangement of *O*-benzyl esters for which a fragmentation–recombination mechanism has been shown to be operative.[22] (Compare Schemes I and IV.)

SCHEME IV

$$ROCH_2Ph \xrightarrow{base} ROCHPh$$
$$ROCHPh \longrightarrow R^- + PhCHO$$
$$R^- + PhCHO \longrightarrow RCHPh \quad (O^-)$$

The condensation of *p*-toluenesulfonamide anion with aldehydes and ketones is not very efficient and alternative reactions, such as reduction by sodium hydride or oxidation (mechanism not known), compete effectively.

The fragmentation–recombination pathway could conceivably lead to benzophenone oxime from **6a** *via* oxazirane **17** formed by condensation of benzophenone and *p*-toluenesulfonamide ion (eq 9).

$$Ph_2C{=}O + TsNH^- \longrightarrow \underset{\mathbf{19}}{Ph_2C(O^-)NHTs} \longrightarrow \underset{\mathbf{17}}{\text{Ph, Ph, O, NH}} \qquad (9)$$

This possibility was tested by attempting to condense *p*-toluenesulfonamide with benzophenone in the presence of sodium hydride under the conditions of reaction. No benzophenone oxime was obtained. The isolated products were benzhydrol (32%) and recovered benzophenone (36%). Although the results of this control experiment were not supportive of eq 9, we are reluctant to discard this possibility totally, since it is not always possible to ensure that the conditions of a control experiment are identical with those which exist during a reaction. This mechanism fits best into the total picture which emerges for base-catalyzed thermal decomposition of **6** and **7**.

The conclusions to be reached from this study are that the methods used to generate *N*-nitrenes from hydrazine derivatives when applied to the generation of *O*-nitrenes from hydroxylamine derivatives afford results which do not uniquely require the involvement of *O*-nitrenes.

Experimental Section[23]

Reactions of *O*-Diphenylmethylhydroxylamine with Oxidizing Agents. A. Nickel Peroxide.—To a solution of 383 mg (1.92 mmol) of **5a** in 5 ml of dry benzene was added 1.6 g of nickel peroxide.[9a] A rapid reaction occurred with **5a** being entirely consumed within 5 min (tlc examination). The solution was

(22) D. L. Dalrymple, T. L. Kruger, and W. N. White in "The Chemistry of the Ether Linkage," S. Patai, Ed., Interscience, New York, N. Y., 1967, Chapter 14.

(23) See paragraph at end of paper regarding supplementary material.

filtered and evaporated to yield 291 mg (83%) of benzhydrol, identified by comparison of its ir spectrum with that of authentic material. After recrystallization from hexane the melting point was 64–65.5° (reported mp 68–69°).[24]

B. *N*-Bromosuccinimide.—A solution containing 386 mg (1.93 mmol) of **5a** and 352 mg (1.93 mmol) of *N*-bromosuccinimide in 5 ml of carbon tetrachloride was refluxed under nitrogen for 20 hr. The solution was filtered and evaporated and the residue was chromatographed on 30 g of Woelm silica gel. Elution with chloroform (100 ml) afforded 178.5 mg (51%) of *O*-diphenylmethyl benzophenone oxime (**8**) as a clear syrup which soon crystallized (identified by comparison of its ir spectrum with that of authentic material). The product on recrystallization from ethanol had mp 96–98.5° (reported mp 101.5–102°).[25]

The second fraction, eluted with 100 ml of 10:1 chloroform–ether, was a syrup (102 mg, 29%) identified as benzophenone by its ir spectrum.

C. Lead Tetraacetate in Methylene Chloride.—To 746 mg (3.75 mmol) of **5a** in 20 ml of methylene chloride was added 1.68 g (3.75 mmol) of lead tetraacetate while stirring at 0°. A vigorous reaction occurred. After 10 min the reaction mixture was worked up and evaporated to leave a syrup which was taken up in ethanol, cooled, and filtered to afford 223 mg of **9** as a tan solid, mp 114–127° (crude yield 32%). Recrystallization from ethanol gave the analytical sample: mp 146.7–147.7°; ir ($CHCl_3$) 3100–3000, 1500, 1460, 1004, 994, 940, 910, 700 cm^{-1}; nmr ($CDCl_3$) δ 7.4 (s, 20, aromatic), 6.45 (s, 1, HCO), 6.35 (s, 1, HCN).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.17; H, 5.62; N, 7.10; mol wt, 394.5. Found: C, 79.03; H, 5.62; N, 7.30; mol wt, 375 (Rast).

The same product was formed in 19% yield when the oxidation was carried out in trichloroethylene. In this case the major product was benzhydrol (36%).

D. Lead Tetraacetate in Pyridine.—Lead tetraacetate (1.73 g, 3.9 mmol) was added to 487 mg (2.4 mmol) of **5d** in 5 ml of pyridine. An exothermic reaction occurred. The solution was refluxed for 17 hr (N_2 atmosphere) and worked up. The extracts were evaporated and the pyridine was removed by coevaporation with 50 ml of toluene on the rotary evaporator. The residue was chromatographed on 40 g of Woelm silica gel and eluted first with chloroform, collecting 50-ml fractions. The first three fractions contained 61 mg (14%) of **8**, mp 96–99°, identified by its ir spectrum (lit. mp 101.5–102°).[25] Fractions 4–8 contained 216 mg (48%) of benzophenone identified by its ir spectrum and R_f on tlc. Fractions 9 and 10 contained 81 mg (17%) of benzophenone oxime identified by ir and R_f on tlc.

The same compounds were obtained when the oxidation was carried out in dimethylformamide at 25° for 2 hr. The yield of **8** was 42%, benzophenone was 12%, and the oxime was *ca.* 30% (chromatographic fraction contaminated with benzhydrol).

Reaction of *O*-*p*-Nitrobenzylhydroxylamine with Lead Tetraacetate.—To a solution of 400 mg (2.4 mmol) of **5b** in 5 ml of methanol was added 1.2 g (2.7 mmol) of lead tetraacetate. The reaction mixture was worked up after 20 hr and evaporated to leave 231 mg (69%) of crude *p*-nitrobenzyl alcohol, mp 65–76°, the ir spectrum of which was identical with that of authentic material. Recrystallization from water afforded material of mp 90–92° (lit. mp 93°).[24]

A similar experiment in methylene chloride at 25° for 10 min afforded *p*-nitrobenzyl alcohol in 68% yield.

Reaction of *O*-*n*-Butylhydroxylamine (5d) with Lead Tetraacetate in the Presence of Olefins.—A mixture of lead tetraacetate (6.2 g, 13.9 mmol) and excess olefin was cooled in an isopropyl alcohol–Dry Ice bath while a solution of 1.0 g (11.2 mmol) of **5d** in 20 ml of dichloromethane was added slowly over the course of 1 hr. The reaction mixture was allowed to warm to room temperature and then stirred for an additional 1 hr, during which time a precipitate formed. The reaction mixture was filtered and the precipitate was washed thoroughly with a small amount of dichloromethane. The dichloromethane solution was washed with 5% sodium carbonate and water and dried ($MgSO_4$), and the solvent was distilled at atmospheric pressure to leave the crude product.

A. Tetramethylethylene.—The crude product obtained when **5d** 7 ml (68.5 mmol) of tetramethylethylene was used as the trapping reagent was chromatographed on 50 g of silica gel. Elution with *n*-hexane (200 ml) followed by a 90% *n*-hexane–ether solution (200 ml) yielded 715 mg (37%) of 1-*n*-butoxy-2,2,3,3-tetramethylaziridine (**11**): ir ($CHCl_3$) 2975, 1460, 1380, 1170, 1120, 1070, and 1043 cm^{-1}; nmr ($CDCl_3$) δ 3.65 (t, 2 H, J = 6 Hz), 1.19 (s), 1.15 (s), and 0.7–1.8 (m), the area between 0.7 and 1.8 integrated for 19 H.

The analytical sample was prepared by preparative glpc.

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.03; H, 12.29; N, 8.14.

The reaction was repeated with 2 ml of acetic acid added to the initial lead tetraacetate–olefin mixture. A 40% yield of the aziridine was obtained.

B. *trans*-2-Butene.—Analysis of the crude product by glpc at a column temperature of 80° and a flow rate of 85 ml/min revealed only two products with retention times greater than 1 min. The major one (retention time 1.7 min) was isolated by preparative glpc and determined to be 1-*n*-butoxy-*trans*-2,3-dimethylaziridine (**12**): ir ($CHCl_3$) 2975, 1740, 1450, 1380, 1250, 1075, 1035, and 970 cm^{-1}; nmr ($CDCl_3$) δ 3.7 (t, 2 H, J = 6.5 Hz) and 0.7–2.0 (m, 15 H); mass spectrum m/e 70 (base peak), M^+ 143, 56, 41.

Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.08; H, 11.82; N, 9.98.

The minor component had the same retention time (2.2 min) as 1-*n*-butoxy-*cis*-2,3-dimethylaziridine (**13**). Sufficient material was trapped from the glpc to measure the ir spectrum of this product. It was identical with that of **13**.

The ratio of trans (**12**) to cis (**13**) was 4:1. Control experiments (glpc analysis) established that *trans*-2-butene did not isomerize to *cis*-2-butene under the reaction conditions.

C. *cis*-2-Butene.—Analysis of the crude product by glpc indicated that the same products were formed as in the previous experiment but that in this case the ratio of the *trans*-aziridine to the *cis*-aziridine was 1:1.6. The major isomer was isolated by preparative glpc and determined to be 1-*n*-butoxy-*cis*-2,3-dimethylaziridine (**13**): ir ($CHCl_3$) 2975, 1740, 1460, 1380, 1210, 1070, and 970 cm^{-1}; nmr ($CDCl_3$) δ 3.7 (t, 2 H, J = 6 Hz) and 0.7–2.3 (m, 15 H); mass spectrum m/e 70 (base peak), 57, 56, 55, 42, 41.

Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.19; H, 12.08; N, 9.68.

The minor component was isolated by preparative glpc and determined to be **12** by comparison of its ir spectrum with that of material from the previous experiment.

Pyrolysis of Lithio Derivative of *N*-*p*-Toluenesulfonyl-*O*-diphenylmethylhydroxylamine (6a).—*n*-Butyllithium in hexane (2.6 ml, 6.1 mmol) was added to a solution of 2.00 g (5.67 mmol) of **6a** in 25 ml of triglyme and the solution was heated at 165° for 18 hr. The reaction mixture was poured into 200 ml of water and extracted with four 50-ml portions of ether and the ether extracts were washed with three 20-ml portions of water and dried ($MgSO_4$). Evaporation of the ether left the crude product, which was chromatographed on 30 g of silica gel. The column was eluted with 100 ml of hexane, 200 ml of 1:1 hexane–ether, and 100 ml of ether. All of the product was eluted in the hexane–ether mixture fraction and was identified as benzophenone oxime (1.13 g, 100%), mp 134–139° (reported mp 143–144°).[24] The ir spectrum of the product was identical with that of authentic material. Recrystallization from ethanol–water raised the melting point to 136–138°.

The aqueous layers from the extractions were combined and acidified with 12 *N* hydrochloric acid and extracted with three 50-ml portions of ether. The ether extracts were washed with 20-ml portions of water, dried over magnesium sulfate, and evaporated to leave 1.07 g of crude product which was washed well with *n*-hexane to afford 500 mg (57%) of *p*-toluenesulfinic acid, mp 83–87° (reported mp 85–90°),[24] which was identical with authentic material in its ir spectrum.

Pyrolysis of Sodio Derivative of 6a. Two Equivalents of NaH.—A solution containing 2.00 g (5.67 mmol) of **6a** and 0.546 g (11.3 mmol) of sodium hydride as a 50% dispersion in mineral oil in 25 ml of triglyme was heated at 200° for 14 hr. The reaction mixture was poured into 400 ml of water and extracted with four 50-ml portions of ether and the combined ether extracts were washed with four 25-ml portions of water. After drying ($MgSO_4$) and evaporation of the solvent, the crude product was chromatographed on 30 g of silica gel and eluted successively with 150 ml of *n*-hexane, 100 ml of 1:1 hexane–ether, and 200 ml of ether. The first fraction contained 0.13 g of mineral oil.

(24) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.

(25) A. C. Cope and A. C. Haven, Jr., *J. Amer. Chem. Soc.*, **72**, 4896 (1950).

The second fraction contained 650 mg (58%) of benzophenone oxime identified by its ir spectrum, which was identical with that of authentic material. Recrystallization from ethanol–water gave material of mp 141–142°.

Four Equivalents of NaH.—To a solution of 353 mg (1.0 mmol) of **6a** in 10 ml of diglyme was added 172 mg (4 mmol) of a 56% sodium hydride dispersion in mineral oil and the reaction mixture was refluxed for 1 hr, during which time a large amount of solid formed. The reaction mixture was poured into 75 ml of water and extracted with three 20-ml portions of ether and the combined ether extracts were washed with three 10-ml portions of water. After drying ($MgSO_4$) and evaporation of the ether the product was heated at 100° (1 mm) to remove residual diglyme and the residue was taken up in hexane. Cooling of the hexane solution resulted in the deposit of 98.3 mg (56%) of benzhydrol, mp 62–65° (reported mp 68–69°),[24] identified by its ir spectrum, which was identical with that of authentic material.

Similar results were obtained when **6a** was heated at 200° for 22 hr with 10 equiv of sodium hydride in triglyme.

Ten Equivalents of NaD.—Sodium deuteride was added as a 50% suspension in mineral oil (1.0 g, 20 mmol) to a solution of 748 mg (2.1 mmol) of **6a** in 25 ml of triglyme and the solution was refluxed for 15 hr. Work-up afforded 245 mg (64%) of benzhydrol, mp 63–64°. The ir and nmr were identical with those of an authentic sample and showed no evidence for deuterium incorporation.

Pyrolysis of Sodio Derivative of *N*-*p*-Toluenesulfonyl-*O*-diphenylmethylhydroxylamine (7a).—A solution of **7a** (530 mg, 1.92 mmol) in 25 ml of triglyme was heated with 184 mg (3.84 mmol) of a 50% dispersion of sodium hydride in mineral oil at 200° for 14 hr. The reaction mixture was worked up as described above for **6a** and the crude product was washed with pentane to afford 180 mg (48%) of benzophenone oxime, mp 136–140°.

Reaction of *N*-Methyl-*N*-*p*-toluenesulfonyl-*O*-diphenylmethylhydroxylamine (18) with NaH.—To 1.0 g (2.7 mmol) of **18** in 50 ml of triglyme was added 5.4 mmol of sodium hydride and the solution was heated at 210° for 19 hr. The reaction mixture was quenched with 400 ml of water and worked up as in previous experiments. The crude product was purified by preparative tlc using a *n*-hexane–ether (2:1) solution to yield 66 mg (13%) of benzophenone, 281 mg (57%) of benzhydrol, mp 61–62°, and 122 mg (24%) of *N*-methyl-*p*-toluenesulfonamide, mp 65–72° (lit.[24] mp 78–79°). The ir and nmr were shown to be identical with those of authentic samples of benzophenone, benzhydrol, and *N*-methyl-*p*-toluenesulfonamide, respectively.

The base-soluble fraction was purified by preparative tlc using a *n*-hexane–ether (2:1) solution to yield 73 mg (14.7%) of benzhydrol, mp 58–63°, 10 mg (3%) of benzoic acid, and 111 mg (22%) of *N*-methyl-*p*-toluenesulfonamide. The ir and nmr were shown to be identical with those of authentic samples of benzhydrol, benzoic acid, and *N*-methyl-*p*-toluenesulfonamide, respectively.

Reaction of *N*-Methyl-*N*-*p*-toluenesulfonyl-*O*-diphenylmethylhydroxylamine-α-d_1 with NaH.—Repetition of the preceding experiment using 441 mg (1.2 mmol) of the title compound afforded a crude product which was purified by preparative tlc (2:1 hexane–ether) to yield 168 mg (65%) of unlabeled benzhydrol, mp 63–65°. The ir, nmr and mass spectra were identical with those of an authentic sample.

A control experiment in which Ph_2CDOH was heated at 135° for 18 hr in triglyme resulted in a 71% recovery of benzhydrol which retained 90% of the original deuterium (nmr analysis).

Attempted Reaction of Benzophenone with *p*-Toluenesulfonamide.—*p*-Toluenesulfonamide (970 mg, 5.67 mmol) was dissolved in dry triglyme (25 ml). A 50% oil dispersion of sodium hydride (545 mg, 10.4 mmol) was added slowly and the reaction was stirred for 15 min. Benzophenone (1.0 g, 5.67 mmol) was added and the reaction was heated at 185° for 19 hr. Work-up was carried out as described in previous experiments. The crude product weighed 1.13 g. A portion of this product (405 mg) was separated by preparative tlc using 2:1 hexane–ether as the developing solvent to yield 125 mg of benzophenone and 114 mg of benzhydrol, mp 64–65°. These amounts correspond to yields of 36 and 32%, respectively. The identity of the products was established by comparison of their ir spectra with those of authentic material.

Reactions of *N*-*p*-Toluenesulfonyl-*O*-benzylhydroxylamine with Sodium Hydride. A.—To 2.0 g (7.2 mmol) of **6b** in 200 ml of purified tetrahydrofuran was added 1 equiv of sodium hydride. The reaction mixture was stirred for 30 min and the solvent was evaporated under reduced pressure. The salt was then heated at 192° in 100 ml of triglyme for 18 hr under nitrogen. The reaction mixture was poured into 400 ml of water and extracted with five 50-ml portions of ether. The ether extracts were then washed with three 50-ml portions of water and dried over magnesium sulfate. The residue after evaporation of the ether was chromatographed on 50 g of silica gel and eluted successively with 100 ml of hexane, 200 ml of 3:1 hexane–ether, and 200 ml of 1:1 hexane–ether. The middle fractions on evaporation afforded 263 mg (35%) of benzonitrile, which was identified by comparison of its ir spectrum and glpc retention time with those of authentic material. Further elution with ether removed 162 mg (8%) of *N*-*p*-toluenesulfonylbenzylamine, mp 108–112° (reported[26] mp 116°), which was identical with an authentic sample prepared from benzylamine and *p*-toluenesulfonyl chloride (mp 110–112°).

B.—In another experiment 1.27 g (4.6 mmol) of **6b** was treated with 2 equiv of sodium hydride in 75 ml of triglyme at 100° for 18 hr. After work-up as described above, no product was found in the ether extracts, so the aqueous phase was acidified with 2 *N* HCl and extracted with ether (4 × 50 ml). These ether extracts were washed with two 20-ml portions of water, dried ($MgSO_4$), and evaporated and the residue was chromatographed on 30 g of silica gel. Elution with 100 ml of 1:1 ether–hexane afforded 170 mg (30%) of impure benzoic acid (mp 92–105°) the ir of which was identical with that of an authentic sample. Further elution with ether yielded 710 mg (91%) of *p*-toluenesulfonamide.

Reaction of *N*-*p*-Toluenesulfonyl-*O*-*p*-bromobenzylhydroxylamine with Sodium Hydride.—Two equivalents of sodium hydride was added to a solution of 2.0 g (5.6 mmol) of **6c** in 50 ml of triglyme and heated at 200° for 21 hr. The reaction mixture was worked up as described for the reactions of **6b**. No identifiable products could be obtained from the neutral fraction.

The base-soluble fraction was chromatographed on silica gel and eluted with chloroform (3 × 50 ml), a *n*-hexane–ether (1:1) solution (4 × 50 ml), and finally ether (100 ml). Fractions 1, 3, 4, and 6 yielded 71 mg of unidentifiable products. Fractions 2 and 5 yielded 480 mg (41%) of *p*-bromobenzoic acid, mp 235–240° (lit. mp 254.4°).[24] Fractions 7 and 8 yielded 350 mg (36%) of *p*-toluenesulfonamide, mp 134–136° (lit. mp 137.5°).[24] The products were shown to be identical with authentic samples of *p*-bromobenzoic acid and *p*-toluenesulfonamide, respectively, by ir and mixture melting point.

Reaction of *N*-*p*-Toluenesulfonyl-*O*-*p*-methoxybenzylhydroxylamine with Sodium Hydride.—The title compound **6d** (1.0 g, 3.26 mmol) was dissolved in 100 ml of tetrahydrofuran and treated with 3 equiv of sodium hydride, and the reaction mixture was stirred for 30 min. The solvent was evaporated under reduced pressure. The salt was heated in 50 ml of triglyme at 150–160° for 18 hr under a nitrogen atmosphere. The reaction was worked up according to the procedure described previously. No product was obtained from the base-insoluble fraction.

The base-soluble fraction was eluted with chloroform (100 ml) and a *n*-hexane–ether (1:1) solution (100 ml) to yield 94 mg of unidentifiable products. Elution with more *n*-hexane–ether (1:1) solution (100 ml) yielded 195 mg (39%) of *p*-methoxybenzoic acid, mp 176–181° (lit. mp 185°).[24] Elution with ether (100 ml) yielded 150 mg (27%) of *p*-toluenesulfonamide, mp 121–123° (lit. mp 137.5°).[24] The ir and nmr were shown to be identical with those of authentic samples of *p*-methoxybenzoic acid and *p*-toluenesulfonamide, respectively.

Reaction of Benzaldehyde with *p*-Toluenesulfonamide in the Presence of NaH.—*p*-Toluenesulfonamide (1.0 g, 5.85 mmol) was dissolved in dry triglyme (25 ml) and treated with 2 equiv of a 50% oil dispersion of sodium hydride, and the reaction mixture was stirred for 15 min. Benzaldehyde (620 mg, 5.85 mmol) was added and the reaction was heated at 205° for 18 hr under a nitrogen atmosphere. Work-up was accomplished as described in the preceding experiments and the crude mixture of products was separated by preparative tlc using chloroform to yield 172 mg (11%) of *N*-*p*-toluenesulfonylbenzylamine, mp 107–109°, and 93 mg (15%) of benzyl alcohol shown by ir and nmr to be identical with authentic samples.

The base-soluble fraction was purified by preparative tlc using a *n*-hexane–ether (2:1) solution to yield 340 mg (48%) of benzoic

(26) "Handbook of Tables for Organic Compound Identification," 3rd ed, Z. Rappaport, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1967.

acid and 550 mg (55%) of *p*-toluenesulfonamide. The ir were shown to be identical with that of authentic samples.

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Registry No.—**5a,** 1782-38-3; **5b,** 1944-96-3; **5d,** 5622-7-5; **6a** lithio derivative, 40780-47-0; **6a** sodio derivative, 40780-48-1; **6b,** 1576-39-2; **6c,** 40780-50-5; **6d,** 40780-51-6; **7a** sodio derivative, 40780-52-7; **9,** 30542-59-7; **11,** 40780-54-9; **12,** 40780-55-0; **13,** 40780-56-1; **18,** 30646-06-1; **18** α-d_1 derivative, 40780-58-3; nickel peroxide, 1313-99-1; *N*-bromosuccinimide, 128-08-5; lead tetraacetate, 546-67-8; tetramethylethylene, 563-79-1; *trans*-2-butene, 624-64-6; *cis*-2-butene, 590-18-1; sodium hydride, 7646-69-7; benzophenone, 119-61-9; *p*-toluenesulfonamide, 70-55-3; benzaldehyde, 100-52-7; *O*-*p*-bromobenzylhydroxylamine hydrochloride, 40780-59-4; *O*-*p*-methoxybenzylhydroxylamine hydrochloride, 876-33-5; benzhydrol-d_1, 17498-07-6; bromodiphenylmethane-d_1, 40780-62-9.

Supplementary Material Available.—A description of the instruments used and details of the syntheses, spectral and physical properties, and microanalytical combustion data of the starting materials will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3107.

The Effect of Added Electron Acceptor on the Methylene–Azomethine Rearrangement, a Trapped Transamination

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It has been shown that the carbanion intermediate in the hydrogen–deuterium exchange of *N*-neopentylidenebenzylamine, IV, can be intercepted by nitrobenzene and in the presence of oxygen converted to benzoic acid, pivalic acid, benzamide, and pivalamide. A detailed kinetic analysis of exchange, isomerization, and trapping processes has been carried out. Evidence that this reaction occurs for other azaallylic anions is also presented.

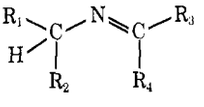
For many years, the methylene–azomethine rearrangement was thought to occur *via* a one-step mechanism involving a single transition state.[1] More recently it has been shown that the reaction actually involves a carbanion intermediate.[2] Although the evidence presented for this mechanistic revision has met with some skepticism,[3] the number of examples of imine systems for which one of the tautomers undergoes base-catalyzed hydrogen–deuterium exchange faster than isomerization has grown to the point where there can be little doubt as to the generality of the carbanion mechanism.[4]

Our recent success in the application of electron-transfer trapping to the elucidation of the mechanistic details of carbanion reactions[5] prompted us to apply the technique to the base-catalyzed methylene–azomethine rearrangement. We did this not so much to demonstrate the intermediacy of carbanions, a point which we feel has been adequately documented, but rather to extend the technique to a new kind of carbanion intermediate, to examine the kinetic problems of dealing with isomerizing systems by this method, and hopefully to find ways in which the technique can be applied to cases for which electron-transfer trapping can be coupled with the subtleties of stereochemistry in such reactions. We hope in this way to learn more about both the methylene–azomethine rearrangement and the process of electron transfer. We report here our preliminary efforts.

Results

The major remaining problem to application of the electron transfer trapping technique to the entire spectrum of carbanion reactions is the requirement that the acceptor be stable to the reaction conditions. In reactions where carbanions are generated by proton removal this means that the acceptor must not react with the base. Nitroaromatics work well but have limitations. As regards alkoxide bases, primary and secondary alkoxides will reduce aromatic nitro compounds to azoxy compounds in the vicinity of 70°.[6] Potassium *tert*-butoxide, a stronger base, will not react appreciably at 50°.

In the general formulation shown the R groups must then be selected such that the ionization can be carried



out either below 70° in methoxide–methanol or ethoxide–ethanol or between 20° and 50° in potassium *tert*-butoxide–*tert*-butyl alcohol. When $R_1 = R_3$ = aryl and $R_2 = R_4 = H$, isomerization can be effected at 80° in ethanol–ethoxide.[7]

When *N*-benzylidenebenzylamine (I) was allowed to react with nitrobenzene and 0.6 *N* potassium *tert*-butoxide in *tert*-butyl alcohol at 30°, the imine was destroyed within 20 min and a precipitate of potassium

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