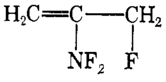
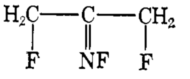
Interestingly, only one addition product was isolated from the allene reaction although a search was made for the isomer of I with F on the terminal carbon atom (V).[11] On the basis of previous observations V


V


VI

would be expected to rearrange to VI which should be stable and isolatable under the experimental conditions.[4a] However, no evidence for V or VI was obtained. Substituted allenes are currently under investigation.

(11) CF_3 radicals attack the terminal carbon of allene: H. G. Meunier and P. I. Abell, *J. Phys Chem.*, 71, 1430 (1967). For addition of Br to allene see E. I. Heiba and W. O. Haag, *J. Org. Chem.*, 31, 3814 (1966).

Carl L. Bumgardner, Kenneth G. McDaniel
Department of Chemistry, North Carolina State University
Raleigh, North Carolina 27607

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Stereospecific Hydroxyalkylation of Chloromethyl Phenyl Sulfoxide

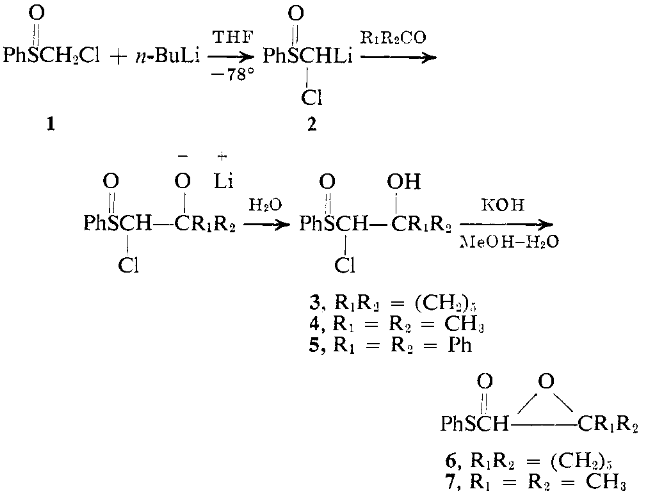
Sir:

The generation and synthetic applications of α-sulfinyl carbanions have been actively investigated since the initial reports of Corey and Chaykovsky regarding the preparation and synthetic utility of methylsulfinyl carbanion.[1] The stereochemical preference of such carbanions has been studied to a considerable extent and a number of interesting results have been reported in this area. For instance, the unequal rate of exchange of the methylene hydrogens of a number of benzyl alkyl and benzyl aryl sulfoxides[2–6] in D_2O–NaOD was suggested by Wolfe and Rauk[3] to be due to preferred abstraction of the hydrogen bisecting the internal oxygen–sulfur–lone pair angle. Molecular orbital calculations by Wolfe and coworkers[7] on the hypothetical carbanion $^-CH_2S(O)H$ and on methylsulfinyl carbanion also indicated a marked stability of the carbanion in such a conformation.

We have been investigating the metalation of sulfoxides and sulfones bearing heteroatoms in the α position, *i.e.*, $RSOCH_2X$ and RSO_2CH_2X, and report preliminary results derived from such a study of chloromethyl phenyl sulfoxide (**1**) that are of synthetic utility and of unusual stereochemical specificity.

Addition of *n*-butyllithium to a 0.3 *M* solution of chloromethyl phenyl sulfoxide[8] in tetrahydrofuran at −78° produced an immediate bright yellow solution containing the lithio derivative **2** which was stable for at least 2 hr at −78°. Decomposition occurred rapidly above −20° with the solution becoming turbid and the color changing to dark brown.[9]

Reaction of a solution of **2** with cyclohexanone, acetone, or benzophenone for 10 min at −78° followed by 30 min at −20° yielded after hydrolysis the adducts **3**, **4**, and **5** in 79, 75, and 68% yields, respectively.[10]



3, $R_1R_2 = (CH_2)_5$
4, $R_1 = R_2 = CH_3$
5, $R_1 = R_2 = Ph$

6, $R_1R_2 = (CH_2)_5$
7, $R_1 = R_2 = CH_3$

Each of these compounds appeared to be a *single* isomer as judged by sharp melting points and tlc behavior in various solvents. In addition, the nmr spectrum of each adduct taken in $CDCl_3$ and in either acetone-d_6 or acetonitrile-d_3 showed only one methine proton as a sharp singlet; the positions in $CDCl_3$ were 4.31, 4.32, and 5.36 ppm downfield from TMS for the adducts **3**, **4**, and **5** respectively.

The nmr spectrum of the acetone adduct **4** in $CDCl_3$ showed, in addition to the singlet at δ 4.32, another singlet at δ 1.58 which was attributed to the two methyl groups. In acetone-d_6 the singlet for the methine proton shifted to δ 4.52, but the methyl groups gave rise to two singlets at δ 1.44 and 1.48. Examination by nmr of the total crude product from each reaction failed to reveal the presence of any trace of isomeric products.[11]

Treatment of the adducts **3** and **4** with dilute methanolic KOH at room temperature for 10 min gave the epoxy sulfoxides **6** and **7** in greater than 90% yield. α-Epoxy sulfoxides have to our knowledge not been reported, and an investigation of their properties is under way. The ease of intramolecular displacement of chloride ion from the adducts contrasts with the great difficulty in displacing chloride ion from chloromethyl phenyl sulfoxide by external nucleophiles.[8]

Oxidation of the sulfoxide adducts **3**–**5** with *m*-chloroperbenzoic acid gave the corresponding sulfones (yield >85%) which were identical with the adducts obtained by reaction of the lithium derivative of chloro-

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(1) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1345 (1965).

(2) A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *ibid.*, **87**, 5498 (1965).

(3) S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966).

(4) E. Bullock, J. M. W. Scott, and P. D. Golding, *ibid.*, 168 (1967).

(5) M. Nishio, *ibid.*, 562 (1968).

(6) R. R. Fraser and F. Schuber, private communication.

(7) S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

(8) M. Hojo and Z. Yoshida, *ibid.*, **90**, 4496 (1968). Contrary to the report of these authors we have found that chloromethyl phenyl sulfoxide is obtained in greater than 70% yield by oxidation of chloromethyl phenyl sulfide with *m*-chloroperbenzoic acid. Chloromethyl phenyl sulfoxide was obtained as colorless needles, mp 35–36°; lit. mp 28–29° (F. G. Bordwell and W. T. Branner Jr., *ibid.*, **86**, 4645 (1964).

(9) The possible decomposition of **2** by α elimination to form either phenylsulfinylcarbene or chlorocarbene is being investigated.

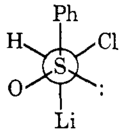
(10) All new compounds reported herein gave correct elemental analysis.

(11) It is estimated that 2% of an isomeric adduct would have been readily detected.

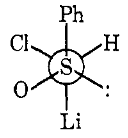
methyl phenyl sulfone[12] with the corresponding ketone.

The benzophenone adduct **5**, mp 128°, when heated to 130° for 1 min underwent a clean thermal decomposition to afford 2-chloro-1,1-diphenylethylene in 92% yield. A similar decomposition has been observed for the β-hydroxy sulfoxide obtained from the addition of methylsulfinyl carbanion to benzophenone.[13] In contrast to the thermal instability of **5**, the adducts **3** and **4** were stable at temperatures up to 180°.

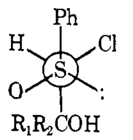
The unusually high stereoselectivity in the formation of the adducts from **1** and ketones is probably due to a free energy difference of at least 2 kcal/mol at $-60°$ between the diastereomeric lithio derivatives **8** and **9**; the activation energy differences for the reaction of **8** and **9** with a ketone should be quite small. These lithio derivatives, which can be obtained by abstraction of the hydrogen bisecting the oxygen–sulfur–lone pair angle in two of the rotomers of chloromethyl phenyl sulfoxide, should, according to theory, be readily equilibrated by the carbanion inversion mechanism.[14] On the basis of steric and dipole–dipole interactions, one could suggest that **8** should be more stable than **9** and thus the adducts would possess the stereochemistry shown in **10**.



8



9



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Preliminary experiments[15] on the metalation of sulfoxides of the general formula RSOCH$_2$R′ (R or R′ = alkyl or aryl) followed by reaction with symmetrical ketones indicate that these reactions also display significant stereoselectivity. Refinement of the results and the stereochemistry of the adducts will be reported shortly.

Acknowledgment. Support of this research by the Department of University Affairs of the Province of Ontario is gratefully acknowledged.

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(12) T. Durst, unpublished observations.

(13) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966).

(14) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(15) T. Durst and M. M. McClory, unpublished observation.

T. Durst
Department of Chemistry, University of Ottawa
Ottawa 2, Canada

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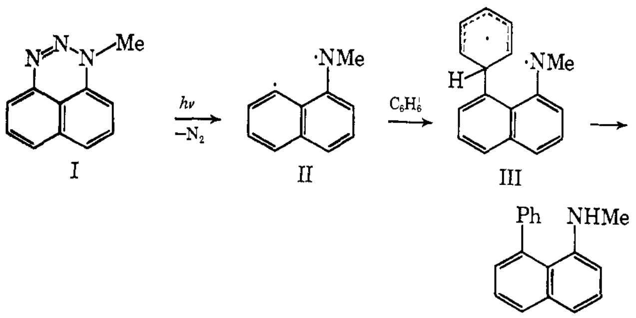
A Novel Heterocyclic Transformation

Sir:

We wish to report a one-step photochemical transformation of a 1,2,3-triazine ring to a pyridine ring and its application to the synthesis of a novel heteroaromatic system.

In the course of investigations of the chemistry of *peri*-fused naphtho heterocycles,[1-3] we have turned our attention to photolysis of 1-methylnaphtho[1,8-*de*]-triazine (I)[1] and related compounds. The products from photolysis[4] of I in cyclohexane included 1-methylaminonaphthalene and bicyclohexyl, as expected for a homolytic reaction following extrusion of nitrogen. The photolysis of I in benzene gave 1-methylamino-8-phenylnaphthalene[5] as the sole detectable product, suggesting that an initial diradical (II)[6] adds to benzene *via* its reactive aryl radical center, and that this is followed by intramolecular hydrogen transfer in the diradical adduct III.



It seemed possible that in a diradical adduct to an olefin, cyclization would compete effectively with hydrogen migration; in particular, the adduct IV with vinyl bromide[8] might cyclize with subsequent elimination of hydrogen bromide assisted by the residual nitrogen atom. Such a reaction, the net result of which is replacement of nitrogen (N$_2$) by the elements of acetylene, has now been effected, both with triazine I (to give N-methyl-1-azaphenalene, V[5]) and with the acenaphthylene analog VI.[2]

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(1) M. J. Perkins, *J. Chem. Soc.*, 3005 (1964).

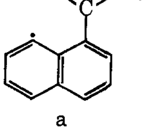
(2) A. R. J. Arthur, P. Flowerday, and M. J. Perkins, *Chem. Commun.*, 410 (1967).

(3) P. Flowerday and M. J. Perkins, *Tetrahedron Letters*, 1261 (1968).

(4) Irradiations employed a Phillips MLU 300-W lamp with a Pyrex filter. Reactions were carried out in an atmosphere of nitrogen; the experiments with vinyl bromide were conducted at 0° and employed a 20% solution of olefin in benzene containing *ca.* 2.5% triethylamine to remove hydrogen bromide.

(5) Satisfactory elemental analyses and spectroscopic data (ir, nmr, mass) were obtained for all new compounds, with the exception of the azaphenalene V. This compound was isolated as a crystalline solid after chromatography of reaction mixtures on basic alumina in yields of 30–40%, but samples deteriorated rapidly during attempts at further purification, and satisfactory analytical figures were not obtained. However spectroscopic data including a molecular weight of 181 (mass spectrometry) together with the close similarity of the uv and visible absorbtions with those of 1-azaphenalene itself (D. C. C. Smith and S. O'Brien *J. Chem. Soc.*, 2907 (1963)) left no doubt as to the identity of the product.

(6) We could find no evidence for intramolecular hydrogen transfer in II to give an azomethine, nor was such a reaction evidenced in photolysis of the N-isopropyl analog[5] of I. Possibly there exists an appreciable barrier to rotation about the naphthyl-nitrogen bond in II, as hydrogen migration appears to be the preferred reaction path open to diradical a.[7]



a

(7) E. M. Burgess, R. Carrithers, and L. McCullagh, *J. Am. Chem. Soc.*, **90**, 1923 (1968).

(8) Addition to vinyl bromide would be expected at the unsubstituted carbon atom, as shown.