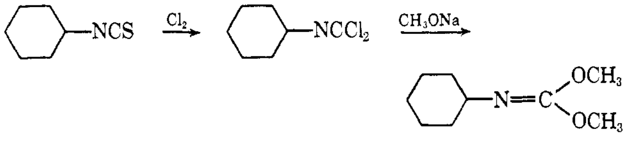
cm^{-1} (C=N). Compound IV was identical in every respect with an authentic specimen prepared by the published procedure.[5]

Compound V had bp 90° (5 mm); nmr spectrum, τ 8.0–9.0 (multiplet, 10 H), 6.8, 6.2 (two broad singlets, ratio 2:1, total 1 H), 6.83, 6.81 (two singlets, ratio 2:1, total 3 H), 5.47, 5.35 (two singlets, ratio 2:1, total 2 H), 2.0, 1.85 (two singlets, ratio 2:1, total 1 H); the nmr data suggest that compound V is a mixture (2:1) of two geometric isomers; ir spectrum, 1680 cm^{-1} (C=N); mass spectrum, *m/e* 171, 156, 140, 126, 110. *Anal.* Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 62.96; H, 10.26; N, 8.12. The electrolysis of IV under the same reaction condition gave V. Thus, the structure assigned to V is convincing.

Compound VI had bp 93–95° (22 mm); nmr spectrum, τ 8.1–8.95 (multiplet, 10 H), 6.75 (broad singlet, 1 H), 6.38 (singlet, 3 H), 6.39 (singlet, 3 H); ir spectrum, 1685 cm^{-1} (C=N); mol wt (mass spectrum), 171. *Anal.* Calcd for $C_9H_{16}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 63.07; H, 10.35; N, 7.95. The iminocarbonate VI was synthesized independently by the route[6] shown in Scheme II and the structure proposed for VI is convincingly established.

Scheme II



The structures of compounds VII and VIII were established by elemental analysis and comparisons of their spectroscopic data with those of authentic samples.

The total yield of the products was in the range of 20% and an example of product composition was as follows: II, 21.9%; III, 16.7%; IV, 9.5%; V, 4.9%; VI, 2.5%; VII, 4.3%; VIII, 22.6%. Although the detection of any radical intermediate by esr spectrometry could not be achieved, the formation of II–IV may be explained by a homolytic mechanism in which anodically generated methoxy radical plays an important role. A polarographic study of I indicated that I did not give any oxidation wave at below +2.5 V (*vs.* sce), while the discharge potential of methanol or methoxide anion may be around +2.5 V (*vs.* sce). Furthermore, the electrolysis of I in methanol using tetraethylammonium *p*-toluenesulfonate or ammonium nitrate as the supporting electrolyte did not give II–VI. Thus, it is conceivable that the primary attacking species is the methoxy radical. However, the possibility that the radicals generated from I yield cationic species by the anodic oxidation cannot be ignored. A detailed study of the mechanism of this novel electrolytic reaction is currently in progress. In addition, the fact that III and V could be obtained from II and IV, respectively, suggests a one-step electrolytic methoxylation reaction of aliphatic ethers. The mechanism and scope of this novel methoxylation reaction will be reported elsewhere.

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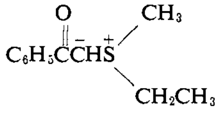
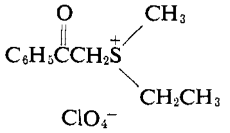
The Preparation and Racemization of an Optically Active Sulfonium Ylide. (−)-Ethylmethylsulfonium Phenacylide

Sir:

A number of reports[1–4] have indicated that sulfonium ylides have a pyramidal structure and should be capable of exhibiting optical activity. We wish to report on the preparation and isolation of the optically active ylide ethylmethylsulfonium phenacylide (I) and on its racemization.


$C_6H_5C(=O)\overset{-}{C}H\overset{+}{S}(CH_3)CH_2CH_3$

I


$C_6H_5C(=O)CH_2\overset{+}{S}(CH_3)CH_2CH_3\ ClO_4^-$

II

The ylide I is readily formed in solvent methanol from ethylmethylphenacylsulfonium perchlorate (II) by treatment with sodium methoxide. The formation of the ylide is indicated by the ultraviolet spectrum of the solution. Compound II has $\lambda_{\max}^{\mathrm{MeOH}}$ 250 $m\mu$ (log ϵ 4.14) in neutral or acidic methanol and exhibits $\lambda_{\max}$ 297 $m\mu$ (log ϵ 4.0) in methanol containing 3–7 equiv of sodium methoxide. Using optically active II[5] the same changes in the ultraviolet spectrum are observed. Compound II racemizes very slowly in neutral or acidic methanol at room temperature. In basic methanol II is converted to I and racemization is relatively fast.

The optically active ylide I can be isolated as a solid using the method described by Ratts and Yao for the preparation of stable sulfonium ylides.[6] The preparation involves treatment of optically active II with 5% aqueous sodium hydroxide and extraction of the solution with chloroform. The chloroform extracts were washed with water and dried over magnesium sulfate and the chloroform was removed using a rotary evaporator. The residual yellow oil crystallized on drying *in vacuo*. The active ylide, after recrystallization from benzene–Skellysolve B, had mp 83–85° and $[\alpha]^{25}\mathrm{D}$ −137° (*c* 0.487, benzene). *Anal.* Calcd for $C_{11}H_{14}OS$: C, 68.0; H, 7.26; S, 16.50. Found: C, 68.06; H, 7.33; S, 16.47.

The first-order rate constants for racemization of I in a variety of solvents are summarized in Table I. The ylide does not decompose under the conditions required for racemization. For example, after 4 half-lives (160 min) for racemization of I in solvent carbon tetrachloride at 50.0° less than 5% of the ylide has decomposed as gauged by ultraviolet spectroscopy.

As regards the mechanism of the racemization only two nondestructive processes need be considered. The

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Table I. The Racemization of (−)-Ethylmethylsulfonium Phenacylide (I)

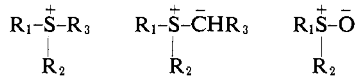
[I]	Solvent	Temp, °C	10^5k_α, sec^{-1}
0.0235	CH_2Cl_2	25.0	3.52 ± 0.05
0.021	C_6H_6	25.0	1.67 ± 0.01
0.044	CCl_4	25.0	1.34 ± 0.03
0.025	CCl_4	50.0	30.7 ± 0.4
0.030[a]	CH_3OH	50.0	75.0 ± 1.7
0.030[b]	CH_3OH	50.0	71.6 ± 1.8

[a] 0.030 *M* II and 0.090 *M* $NaOCH_3$. [b] 0.030 *M* II and 0.21 *M* $NaOCH_3$.

first would involve carbon–sulfur bond fission to yield a carbene and ethyl methyl sulfide, which could recombine to give racemic ylide. This process had been considered and ruled out previously by Nozaki and coworkers for a variety of ylides[3] and therefore can be ruled out in this case. Moreover, the principal product of decomposition of I in carbon tetrachloride is methyl phenacyl sulfide (67% yield) which is not the product of a carbene reaction. This leaves only pyramidal inversion as an appropriate mechanism for racemization of I.

The ylide I racemizes *ca.* 200 times faster than the sulfonium salt II in solvent methanol at 50°. The difference in inversion rate could be accounted for by assuming that the much greater electronegativity of the phenacyl group relative to the phenacylide slows down the inversion process or that p–dπ bonding facilitates racemization of I relative to II.

While the behavior of the ylide can be rationalized relative to the sulfonium salt, the facile racemization of I is somewhat surprising when contrasted with the behavior of the sulfoxides. It might have been anticipated that the ylide would serve as a bridge between the sulfonium salts which undergo relatively facile inversion[5] and the sulfoxides which are configurationally quite stable. The activation enthalpies for racemization are 25–29 kcal for several sulfonium salts,[7a] 35–43 kcal for sulfoxides,[7b] and 23.3 kcal for I in solvent carbon tetrachloride. At 25° in solvent benzene the racemization of I is *ca.* 10^{13} times faster than the racemization of methyl *p*-tolyl sulfoxide, extrapolated from data at other temperatures.[7b] While it would be premature to draw firm conclusions on the relative behavior of these three classes of compounds until the structures of some sulfonium salts are known,[8] some factors which can conceivably account for the difference in behavior of the sulfoxides and ylides should be considered.



$$R_1\text{–}\overset{+}{S}(R_2)\text{–}R_3 \qquad R_1\text{–}\overset{+}{S}(R_2)\text{–}\overset{-}{C}HR_3 \qquad R_1\overset{+}{S}(R_2)\text{–}\overset{-}{O}$$

At the transition state for inversion electronic repulsion between unshared electron pairs on the sulfur and oxygen of the sulfoxide will be greater than in the ground state. In the ylide such repulsion can be reduced by rotation about the sulfur–carbon bond. The transition state for inversion of the sulfoxide will be destabilized relative to that for the ylide by electronic repulsion.

Secondly the pyramidal ground state of the sulfoxide, in which two p–dπ orbitals can be formed by utilizing the two unshared electron pairs in p orbitals on oxygen and the appropriate orbitals on sulfur, may be more stabilized than the planar transition state by p–dπ bonding. Thus both stabilization of the ground state and destabilization of the transition state of the sulfoxide could contribute to the enormous difference in activation enthalpies for the inversion of sulfoxides and ylides.

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(7) (a) Unpublished results of G. Tourigny, S. H. Hui, and R. L. Tomilson; (b) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Am. Chem. Soc.*, 88, 3138 (1966).

(8) X-Ray analyses of the structures of several sulfonium salts have been undertaken in this department under the direction of Professor David Hall.

(9) National Research Council of Canada Scholarship holder, 1966–1968.

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Mechanism of Base-Catalyzed Hydrogen Exchange for N-Methylpyridinium Ion and Pyridine N-Oxide. Relative Positional Rates

Sir:

Base-catalyzed hydrogen exchange at the annular positions of carbocyclic aromatic systems has been investigated extensively;[1] similar explorations of heteroaromatic substrates largely has been lacking.[2,3]

We wish to report that the relative positional rates of base-catalyzed hydrogen exchange at the annular positions of N-methylpyridinium chloride[4] (I) and pyridine-d_5 N-oxide[5] (II) are very similar to the known relative rates of decarboxylation of the isomeric N-methylpyridinium carboxylates[6] (III). These similar rate relationships provide considerable insight into the mechanism of the deprotonation reactions and the mode of activation by the heteroatom groupings.

Rates of deprotonation were obtained using established techniques;[2,7] the nmr spectra of I[8] and II[9] (not deuterated) have been reported. Substrate I was satisfactorily stable in proteophosphate buffers at 165° and was recovered from these solutions as its mercuric chloride salt in 75% yield. Hydrogen–deuterium exchange rates for the annular positions of I were obtained in $D_2PO_4^-$–DPO_4^{2-} buffers at 165°. It is not practical to obtain the p*D* of buffers at this temperature. However, ratios of the second-order constants, *k*, for positions 2 and 4, for example, were obtained from ratios of pseudo-first-order constants $k\psi$, by the use of the equation $\log (k^4\psi/k^2\psi) = \log (k^4/k^2) + pD_4 - pD_2$. The assumption here is that the p*D* difference in the

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(2) (a) J. A. Zoltewicz and C. L. Smith, *J. Am. Chem. Soc.*, 89, 3358 (1967); (b) J. A. Zoltewicz and G. M. Kauffman, *Tetrahedron Letters*, 337 (1967).

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(4) A referee indicated that a report of hydrogen exchange involving N-methylpyridinium ion appears in a Ph.D. thesis submitted by Dr. Elijah H. Gold to Yale University in 1963. Professor Martin Saunders has kindly informed us that the deuterioxide ion catalyzed rates for N-methylpyridinium perchlorate reported therein are in agreement with our own.

(5) Deprotonation of I and pyridine N-oxide in NaOD–D_2O was reported. Neither the relative reactivities of positions 3, 5, and 4 nor rate data were indicated, however. See Y. Kawazoe, M. Ohnishi, and Y. Yoshioka, *Chem. Pharm. Bull.* (Tokyo), 12, 1384 (1964).

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(9) R. A. Abramovitch and J. B. Davis, *ibid.*, *B*, 1137 (1966).