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

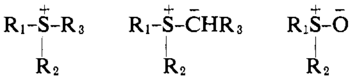
[I]	Solvent	Temp, °C	10^5k_α, sec^{-1}
0.0235	CH_2Cl_2	25.0	3.52 ± 0.05
0.021	C_6H_6	25.0	1.67 ± 0.01
0.044	CCl_4	25.0	1.34 ± 0.03
0.025	CCl_4	50.0	30.7 ± 0.4
0.030[a]	CH_3OH	50.0	75.0 ± 1.7
0.030[b]	CH_3OH	50.0	71.6 ± 1.8

[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 antici-



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

pated 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.

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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(1) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965; A. Streitwieser, Jr., and J. H. Hammons, *Progr. Phys. Org. Chem.*, **3**, 41 (1965); A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 156 (1963).

(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).

(3) L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.*, **90**, 807 (1968); R. A. Olofson and J. M. Landesberg, *ibid.*, **88**, 4263 (1966); R. A. Olofson, J. M. Landesberg, K. N. Houk, and J. S. Michelman, *ibid.*, **88**, 4265 (1966).

(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).

(6) P. Haake and J. Mantecon, *J. Am. Chem. Soc.*, **86**, 5230 (1964).

(7) J. Hine, K. G. Hampton, and B. C. Menon, *ibid.*, **89**, 2664 (1967).

(8) R. J. Chuck and E. W. Randall, *J. Chem. Soc.*, *B*, 261 (1967).

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

buffer solutions at 165° is approximated by the p*D* difference in these same solutions at 30°.[10] The rates of deprotonation are first order in deuterioxide ion and rates relative to the 4 position are given in Table I.

Table I. Relative Positional Rates of Hydrogen Exchange for N-Methylpyridinium Chloride (I) and Pyridine-d_5 N-Oxide (II) and of Decarboxylation of N-Methylpyridinium Carboxylates (III)

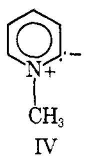
Ratio	I[a]	II[b]	III[c]
k^4/k^4	1.0	1.0	1.0
k^3/k^4	3.0	10	2.8
k^2/k^4	3400	1500	1600

[a] In $D_2PO_4^-$–DPO_4^{2-} buffers at 165°. Position 2 has $k\psi$ = 7.83×10^{-4} sec^{-1} (165°) at pD 6.46 (30°). [b] In CH_3OH–CH_3ONa at 138°. Position 2 has $k = 0.199$ M^{-1} sec^{-1}. [c] In ethylene glycol at 196.1°; data are taken from ref 6.

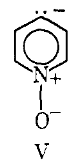
Hydrogen exchange was used to prepare II; each position was at least 80% deuterated. Rates of deuteration of II were obtained in CH_3OH–CH_3ONa. In basic solutions nmr signals for positions 3 and 5 overlapped with those for 4 but acidification of aliquots resulted in clean separation. Rates were first order in methoxide ion. Data for the 2,6 positions were extrapolated to 138° from results at 75 and 100°. Relative rates of exchange at 138° are given in Table I.

The kinetic data given in Table I indicate that the reactivity pattern for the deprotonation of I and II not only is qualitatively the same as that for the decarboxylation of III but also that the relative reactivities of corresponding positions within the three molecules are quantitatively similar. Reactivity is greatest adjacent to the activating heteroatom and rapidly decreases with increasing distance from this center.

The following conclusions are suggested by the results in the table. (i) Compounds I, II, and III react to form similar intermediates. Since carbanions such as IV[6] form during the decarboxylation of III, carbanionic intermediates such as IV and V are generated during hydrogen exchange. (ii) Resonance effects involving the distribution of positive charge onto carbon from nitrogen have little influence on deprotonation reactivity. Position 4 which may acquire such charge is less reactive than 3 which is not favored by such resonance. (iii) Resonance effects involving the oxygen atom of II do not seriously affect relative positional rates since the relative rate patterns for I, II, and III are similar.



IV



V

A strong likeness exists between the positional reactivity pattern found in these heteroaromatic systems and in monosubstituted carbocyclic aromatic molecules. In the latter base-catalyzed deprotonation also takes place most rapidly at an annular position adjacent to the activating substituent and decreases in the order *ortho*, *meta*, and *para*. Thus, heterocycles I and II and these carbocyclic molecules respond in fundamentally the same way in deprotonation reactions.[12]

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[10] This is a good approximation so long as the same buffer is used but, in general, is a poor one if different buffers are compared.[11]

[11] R. G. Bates, "Determination of pH. Theory and Practice," John Wiley and Sons, Inc., New York, N. Y., 1964, p 76 and Chapter 5.

[12] Pyridine constitutes a significant exception to this pattern; its positional reactivity order is reversed relative to that for I and II.[2a]

[13] Member of the National Science Foundation Summer Research Participation Program for College Teachers, 1967.

[14] National Science Foundation Fellow, 1967–1968.

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Acid–Base Reactions and Hydrogen Exchange in Fused Acetate Eutectics. The Decomposition of Trimethylolethane

Sir:

Since many covalent organic compounds capable of hydrogen bonding with the solvent are soluble in fused salts,[1] the study of homogeneous solutions and reactions is possible as an important addition to the many known heterogeneous reactions.[2] We wish to report several interesting phenomena observed in the ternary eutectic, lithium–potassium–sodium acetate (32–30–38 mol %, mp 162°).[3]

This fused-salt solvent is quite basic. Phenolic indicators such as alizarin, alizarin yellow, *p*-nitrophenol, and *m*-nitrophenol ionize to give the colors of their conjugate bases, as alizarin does in fused K^+,Na^+–SCN^- with sodium hydroxide.[1b,4] The less acidic aromatic amine indicators differ in degree of dissociation, depending on the substituent: 2,4-dinitroaniline (pK_a = 15.00 in methanol at 20°)[5] is dissociated in 0.1% solutions in K^+,Li^+,Na^+–OAc^- at 200° while *o*-nitroaniline (pK_a = 17.88) and *p*-nitroaniline (pK_a = 18.37) are chiefly undissociated. It is more quantitatively significant to specify the extent of indicator dissociation at a known acid concentration: in 0.074 *M* acetic acid in the fused salt, the concentrations of dissociated and undissociated 2,4-dinitroaniline appear approximately equal. The equilibrium constant for the reaction, $ArNH_2 + OAc^- \rightarrow ArNH^- + HOAc$ is, therefore, about 4.5×10^{-3}, the density of the fused salt being 1.39 g/ml at 200°.

Exchange of the hydrogen atoms in the methyl groups takes place in K^+,Na^+–OAc^- eutectic (54–46 mol %, mp 233°)[6] to the extent of 40% in 10 hr at 250°. The nmr singlet of CH_3COO^- changes, in the presence of CD_3COO^-, to the triplet of CH_2DCOO^- and the quintet of CHD_2COO^- due to the geminal H–D coupling constant of 2.10 ± 0.05 cps, comparable to 2.32 ± 0.07 for CH_2DCOOH.[7] Each deuterium substitution causes an upfield chemical shift of 1.3 cps at 100 Mc.

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[1] (a) O. K. Khaishbashev, *Bull. Acad. Sci. URSS, Classe Sci. Chim.*, 587 (1945); *Chem. Abstr.*, **40**, 5981[1] (1946); (b) T. I. Crowell and P. Hillery, *J. Org. Chem.*, **30**, 1339 (1965); (c) J. E. Gordon, unpublished review.

[2] W. Sundermeyer, *Angew. Chem. Int. Ed. Engl.*, **4**, 222 (1965).

[3] E. I. Pochtakova, *Zh. Neorg. Khim.*, **10**, 2333 (1965); *Russ. J. Inorg. Chem.*, **10**, 1268 (1965). We used the slightly different proportions, 32–27–41 mol %, published earlier: G. C. Diogenov, *Zh. Neorg. Khim.*, **1**, 2551 (1956); *Chem. Abstr.*, **51**, 7825*d* (1957).

[4] B. J. Brough, D. H. Kerridge, and M. Mosley, *J. Chem. Soc.*, *A*, 1556 (1966).

[5] R. A. M. O'Ferrall and J. H. Ridd, *ibid.*, 5030 (1963).

[6] F. J. Hazlewood, E. Rhodes, and A. K. Ubbelohde, *Trans. Faraday Soc.*, **62**, 3101 (1966).

[7] H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962).