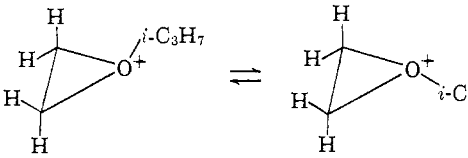
unsuitable, Meerwein's trialkyloxonium salts, isoelectronic to amines,[5] offer an acceptable possibility. The stereochemistry of Meerwein's salts and of protonated alcohols and ethers[6] is presumed but not proved to be tetrahedral, by analogy with the hydronium ion.[7] The configurational stability of trivalent oxygen may be tested by examination of the nmr spectrum of a methylene group adjacent to trivalent oxygen and contained in a rigid cyclic system of appropriate symmetry. Configurational stability would be indicated by an AB spectrum (complicated by coupling to adjacent protons); rapid inversion or fortuitous degeneracy would give an $A_2$ spectrum.

We have examined the methyl, ethyl, and isopropyloxonium salts of oxirane, oxetane, tetrahydrofuran, and tetrahydropyran[8] in liquid $SO_2$. At 40° the spectrum of the isopropyloxonium salt of ethylene oxide (oxirane) contains a very sharp singlet 149 Hz below internal cyclopentane due to the ring protons, a doublet centered at 13 Hz below cyclopentane due to the methyl protons,[9] and a septet at 182 Hz below cyclopentane due to the methinyl proton. As the temperature is lowered, the ring proton resonance broadens to coalescence at $-50°$ ($T_c$) and sharpens to a closely coupled ($\nu_{AB} \sim 3$ Hz) AA'BB' spectrum at $-70°$. The half-height method,[10] the coalescence temperature, and a complete line-shape analysis above $T_c$ all indicate an activation energy ($E_a$) of $10 \pm 2$ kcal/mole. Analogously reversible effects were observed for the methyl and the ethyl salts. The physical basis for these changes must be a slowing of the rate of oxygen inversion that results in magnetically nonequivalent ring protons at the lowest temperatures. The stereochemistry of these trialkyloxonium salts must therefore be tetrahedral, rather than planar.



The spectra of the oxonium salts of the six-membered tetrahydropyran are temperature independent.[11,12] The rates of oxygen inversion in these salts must therefore be too rapid to cause spectral alterations even at $-70°$. The situation is similar to that of nitrogen, the inversion of which was first examined in aziridines.[13]

The spectral data described thus far could also be explained in terms of a bimolecular mechanism in which inversion is effected by rapid intermolecular exchange of the alkyl groups between two oxonium ions or between one oxonium ion and a free ether molecule. This mechanism has been excluded by two lines of reasoning. The rate of a bimolecular reaction should be concentration dependent. We have examined the methyloxonium salt of ethylene oxide over the concentration range 0.2–2.0 mmole/ml and found the observed rate process to be independent of concentration. Various competition experiments were also carried out to test the exchange properties of the alkyl substituents. (1) Two equivalents of tetrahydropyran was allowed to react with 1 equiv each of $CH_3I$ and $AgBF_4$. The nmr spectrum showed equal amounts of complexed ($\alpha$ protons at 198 Hz below cyclopentane) and uncomplexed ($\alpha$ protons at 130 Hz) tetrahydropyran. Rapid exchange would have required only one averaged resonance for the $\alpha$ protons. (2) The O-methyl, O-ethyl, and O-isopropyl derivatives of ethylene oxide were prepared in the usual manner;[8] after several days, 1 equiv of tetrahydropyran was added to each. The nmr spectra of the three-membered-ring oxonium complexes remained unchanged, and the only resonances from the six-membered ring were of uncomplexed tetrahydropyran. Thus, none of the O-alkyl substituent was transferred from the three-membered ring to the six-membered ring. (3) To show that tetrahydropyran is not at a thermodynamic disadvantage in obtaining an O-alkyl substituent in the presence of ethylene oxide, 1 equiv of each was allowed to compete for 1 equiv of alkylating agent. Under these conditions both complexes formed. It is thus clear from both the concentration and the competition experiments that the alkyl groups do not undergo an intermolecular interchange on the nmr time scale of observation. The physical process causing the spectral changes must therefore be the unimolecular thermal inversion of oxygen.

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[5] H. Meerwein in Houben-Weyl's "Methoden der Organischen Chemie," Vol. 6, Part 3, Georg Thieme Verlag, Stuttgart, 1965, p 325.

[6] G. A. Olah and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 1725 (1967).

[7] L. W. Schroeder and J. A. Ibers, *ibid.*, **88**, 2601 (1966), and references therein. These studies may, however, be exceptional because the experiments were on the solid state and the materials were extensively hydrogen bonded.

[8] All oxonium salts were prepared *in situ* by reaction of an alkyl halide with silver tetrafluoroborate and an ether. About 1 mmole

$$RX + AgBF_4 + R_2'O \longrightarrow R_2'RO^+BF_4^- + AgX\downarrow$$

each of $AgBF_4$ and the ether were placed in an nmr tube under anhydrous conditions. The tube was cooled to $-78°$ and the volume was brought to 1 ml with $SO_2$. One equivalent of the halide was added, together with the standard (cyclopentane), and the tube was sealed and shaken for a short time. After about 1 day the silver halide was centrifuged to one end of the tube. All spectra were recorded on a Varian A-60.

[9] The position of the methyl doublet serves as a convenient indicator for the charge on the methinyl carbon. The methyls of 2-bromopropane in $SO_2$ center at 11 Hz below cyclopentane. When $AgBF_4$ is added to form the dimethylcarbonium ion (no ether present), the methyls respond to the adjacent positive charge by shifting downfield to 48 Hz below cyclopentane. When the ether is then added to form the oxonium salt, the methyls move back upfield to 13 Hz below cyclopentane, indicating that the charge has passed from the adjacent carbon to the more distant oxygen.

[10] J. B. Lambert, *Tetrahedron Letters*, 1901 (1963).

[11] The spectra of the four- and five-membered rings were too complicated for a straightforward analysis. The isopropyl derivative of tetrahydropyran did not form,[9] presumably for the same steric reason that Meerwein failed to isolate triisopropyloxonium tetrafluoroborate; *cf.* H. Meerwein, E. Battenberg, H. Gold, E. Pfeil, and G. Willfang, *J. Prakt. Chem.*, **154**, 96 (1939).

[12] The nmr spectrum of such an ion was reported by F. Klages, J. E. Gordon, and H. A. Jung, *Ber.*, **98**, 3748 (1965).

[13] A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5126 (1956).

[14] This work was supported by the National Science Foundation (Grant GP-6611).

[15] National Institutes of Health Predoctoral Fellow, 1967–1968.

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## The Stereomutation of Arsenic

*Sir:*

Because of its configurational stability, trivalent arsenic is capable of supporting optical activity.[1,2]

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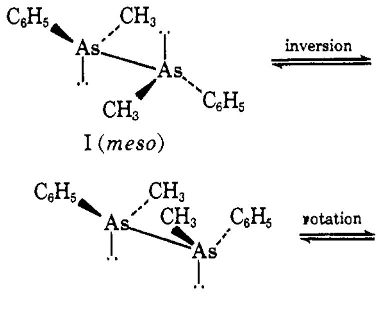
[1] V. I. Sokolov and O. A. Reutov, *Russ. Chem. Rev.*, **34**, 1 (1965).

[2] K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966, pp 87–88.

Horner, Campbell, and others[3] took advantage of this property in their successful resolutions of tertiary arsines. Moreover, all efforts by Horner to racemize the arsines by purely thermal means have failed.[4] Such an observation contrasts sharply with the properties of the analogous phosphines, which have a reported half-life for racemization of 3–5 hr at 130°.[5] In fact, racemization of (+)-methyl-*n*-propylphenylarsine could only be achieved in a first-order process by photolytic means.[6] In the Costain–Sutherland scheme used by Miller and coworkers,[7] the calculated inversion barrier for trimethylarsine is about 8–9 kcal/mole higher than that for trimethylphosphine.

In the present paper, we describe the first kinetic observation of the uncatalyzed, thermal stereomutation of arsenic. In order to circumvent the problems of configurational stability encountered by Horner in his work,[4] we have selected an appropriate diarsine for nmr studies. The diarsine system should invert much more rapidly than do simple arsines, because of more favorable $p_\pi$–$d_\pi$ overlap in the transition state to inversion, in which half or all the molecule is planar, than in the ground state.[8] 1,2-Dimethyl-1,2-diphenyldiarsine[9] exists in *meso* (I) and *dl* (II) modifications, the stable *trans* forms of which are interconvertible by inversion of arsenic followed by bond rotation.[10] The nmr spectrum of this diarsine at 100° contains a multiplet from the phenyl protons at 6.5–7.2 ppm and two sharp peaks from the methyl protons in a ratio of 0.47:0.53 at 0.77 and 0.70 ppm below external TMS, the smaller peak being at lower field. Although $^{75}$As (100% abundant) has a spin of $^{3}/_{2}$, coupling with adjacent protons is removed by the large quadrupolar interaction.[11] The two methyl peaks must therefore be due to the *meso* and the *dl* forms, respectively. Since the distance between the two peaks increases from 4.1 Hz at 60 MHz to 7.0 Hz at 100 MHz, the separation must be a chemical-shift difference rather than a coupling constant.



I (*meso*)

II (*dl*)

The two methyl peaks collapse to a clean singlet over the range 150–210° ($T_c$ ~180° at 100 MHz). These spectral changes indicate the rapid interconversion of *meso*- and *dl*-1,2-dimethyl-1,2-diphenyldiarsine (I $\rightleftharpoons$ II) by stereomutation of arsenic. The kinetics of the process were determined by a complete line-shape analysis.[12] The preliminary Arrhenius activation energy is 27 ± 3 kcal/mole.

Two alternative mechanisms may be excluded. A bimolecular inversion, in which two diarsine molecules exchange halves, requires that the rates be concentration dependent. The kinetics were found to be identical for 7 to 86% solutions by weight in biphenyl and only slightly different for a neat sample. Such an observation substantiates the unimolecularity of the reaction. It could also be argued that the two methyl peaks arise from different rotamers and that the observed rate process is therefore a rotation about the As–As bond. Tetramethyldiarsine (cacodyl) is capable of existing in several rotational conformations, but not in diastereomeric modifications. The observation by Harris and Hayter[11] that the nmr spectrum of cacodyl contains only one peak in the methyl region indicates that the rotamers indeed are conformationally averaged.

With the completion of the present work, unimolecular stereomutation by pyramidal inversion has now been observed for nitrogen,[13] oxygen,[14] phosphorus,[5a,b] sulfur,[15] and arsenic.

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(3) L. Horner and H. Fuchs, *Tetrahedron Letters*, 203 (1962); I. G. M. Campbell and R. C. Poller, *J. Chem. Soc.*, 1195 (1956); M. S. Lesslie and E. E. Turner, *ibid.*, 1172 (1934).

(4) L. Horner and W. Hofer, *Tetrahedron Letters*, 3281 (1965).

(5) (a) L. Horner and H. Winkler, *ibid.*, 461 (1964); (b) for a comparison with diphosphines, see J. B. Lambert and D. C. Mueller, *J. Am. Chem. Soc.*, **88**, 3669 (1966).

(6) L. Horner and W. Hofer, *Tetrahedron Letters*, 3323 (1966).

(7) G. W. Koeppl, D. S. Sagatys, G. S. Krishnamurthy, and S. I. Miller, *J. Am. Chem. Soc.*, **89**, 3396 (1967).

(8) Many of the properties of diarsines are analogous to those of diphosphines, which have been reviewed recently by A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965).

(9) J. W. B. Reesor and G. F. Wright, *J. Org. Chem.*, **22**, 382 (1957). The conjugating effects of the phenyl group may also serve to lower the barrier in this case.

(10) Spectral data point toward a preference for the *trans* rotamer; see ref 8 and (a) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961); (b) S. G. Frankies, *Spectrochim. Acta*, **23A**, 554 (1967); (c) E. G. Finer and R. K. Harris, *Mol. Phys.*, **12**, 457 (1967); (d) E. G. Finer and R. K. Harris, *ibid.*, **13**, 65 (1967).

(11) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

(12) J. B. Lambert, W. L. Oliver, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 5085 (1965).

(13) For a review, see G. Binsch, "Topics in Stereochemistry," Vol. III, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, Inc., New York, N. Y., in press.

(14) J. B. Lambert and D. H. Johnson, *J. Am. Chem. Soc.*, **90**, 1349 (1968).

(15) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *ibid.*, **88**, 3138 (1966); D. Darwish and G. Tourigny, *ibid.*, **88**, 4303 (1966).

(16) This work was supported by the National Science Foundation (Grant GP-6611).

(17) National Institutes of Health Predoctoral Fellow, 1966–1968.

(18) The authors are indebted to Dr. M. I. Levenberg and Mr. R. S. Egan of Abbott Laboratories, North Chicago, Ill., for the 100-MHz spectra.

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## Temperature Dependence of Product Composition in Reactions of Carbethoxynitrene with Anthracene and with Butene-2

*Sir:*

Reaction of carbethoxynitrene with polycyclic aromatic hydrocarbons yields a spectrum of products indicative of a dichotomy of mechanism.[1] Our suggestion that two different mechanistic pathways are initiated by attack on the substrate of the singlet and triplet forms of the nitrene[1] had sound analogy in reactions of 4-methylpentene-2[2] and was supported by a study of the concentration dependence of the isomer distribution of prod-

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(1) A. L. J. Beckwith and J. W. Redmond, *Australian J. Chem.*, **19**, 1859 (1966).

(2) W. Lwowski and J. S. McConaghy, *J. Am. Chem. Soc.*, **87**, 5490 (1965).