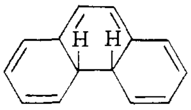

II

probably is the result of a ring closure corresponding to that which would give I as opposed to II. Finally, if the intermediate dihydrophenanthrene had the *cis* configuration II, it might be expected to give phenanthrene in the absence of an oxidant by ejection of molecular hydrogen since it is estimated that this process would be exothermic by about 49 kcal./mole. The lack of such a reaction in solution is in accord with the *trans* configuration I since concerted elimination of a hydrogen molecule from I would involve a drastic molecular distortion and a large activation energy; also, it is estimated that the stepwise loss of two hydrogen atoms from I would be endothermic by about 46 kcal./mole for the first hydrogen and endothermic by about 9 kcal./mole for the second hydrogen.

The recent observation that the photolysis of stilbene in the vapor phase gives phenanthrene and hydrogen[8] does not necessarily mean that the intermediate must be II rather than I. The dihydrophenanthrene is formed from excited *cis*-stilbene with an estimated 50–75 kcal./mole excess vibrational energy which would be transferred to solvent molecules very rapidly in solution but which would be retained by the dihydrophenanthrene for much longer periods in the vapor phase. Under the latter conditions this excess energy could conceivably allow either the concerted or the stepwise loss of two hydrogens from I as described above.

The fact that the reaction is not quenched by oxygen in solution suggests that the excited state undergoing ring closure is not a triplet. Convincing evidence that triplet states of stilbene are not involved in the ring closure reaction has been obtained recently from a study[9c] in which it was found that the initial rate of phenanthrene formation is finite starting from solutions of pure *cis*-stilbene but zero starting from solutions of pure *trans*-stilbene; phenanthrene is formed from irradiation of *trans*-stilbene only after some *cis*-stilbene has been produced by photoisomerization. Thus, the precursor to the dihydrophenanthrene is an excited state which can only be produced by absorption of a photon by *cis*-stilbene. It is generally accepted[9] that the triplet state which is reached by intersystem crossing from excited *trans*-stilbene singlet is either identical with or in rapid equilibrium at room temperature with the triplet state which is similarly reached from excited *cis*-stilbene singlet. On the other hand, it has been shown that the excited singlet states of *cis*-stilbene and *trans*-stilbene do not interconvert.[9a,10]

Further evidence for a singlet as opposed to a triplet mechanism is provided by the striking observation that the only substituted stilbenes which have been found not to undergo photochemical conversion to phenanthrenes are those with nitro or acetyl substituents; it is well known[11] that these substituents enhance intersystem crossing rates and thereby decrease excited singlet state lifetimes by several orders of magnitude.

We have developed this reaction into a valuable synthetic method for obtaining 1-, 3- or 9-substituted phenanthrenes in 60–90% yields starting from the readily accessible *o*-, *p*- or α-substituted stilbenes, respectively, with substituents such as CH_3, CH_3O, F, Cl, Br, CO_2H, CF_3 and C_6H_5. *m*-Substituted stilbenes give mixtures of 2- and 4-substituted phenanthrenes. These reactions are carried out by irradiation under an air atmosphere of solutions of 2–3 g. of the stilbene and 3–5 mole-% of iodine in 500 ml. of cyclohexane in a quartz vessel. For preparative work iodine is far superior to oxygen as the oxidant since it gives faster and cleaner reactions with higher yields.

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[8] Unpublished work of R. Srinivasan and J. C. Powers, IBM Research Center; the private communication of these results is gratefully acknowledged.

[9] (a) R. H. Dyck and D. S. McClure, *J. Chem. Phys.*, **36**, 2326 (1962); (b) S. Malkin and E. Fischer, Symposium on Reversible Photochemical Processes, preprints of papers, p. 281; (c) H. Stegemeyer, private communication.

[10] G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).

[11] (a) M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950); (b) W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

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ORGANOBORON COMPOUNDS. XIV. RAPID ALKOXY EXCHANGE BETWEEN DIALKYLALKOXYBORANES AND ALKYLDIALKOXYBORANES[1,2]

Sir:

Distillation studies in This Laboratory[3] have shown that facile exchange of alkoxy groups occurs among alkylalkoxyboranes and trialkoxyboranes on fractional distillation somewhat above room temperature. More recently Mikhailov and Vasil'ev[4] reported a similar result and, without citing any experimental evidence, added that the exchange is slow at room temperature and rapid at higher temperatures. We have investigated the speed of this exchange reaction at room temperature, using proton magnetic resonance spectra[5] for analysis of equilibrium mixtures, and have found the exchange to be extremely rapid.

The p.m.r. spectrum of diisobutylmethoxyborane in 33% by volume of benzene has a singlet at low field (3.69 p.p.m. above benzene) due to the methoxy hydrogens. The spectrum of isobutyldimethoxyborane in the same solvent has a similar singlet, due to the dimethoxy hydrogens, at somewhat higher field (3.77 p.p.m. above benzene).

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[1] Previous paper, P. A. McCusker, J. V. Marra and G. F. Hennion, *J. Am. Chem. Soc.*, **83**, 1924 (1961).

[2] Contribution from the Radiation Laboratory operated by the University of Notre Dame under contract with the Atomic Energy Commission.

[3] Abstracts of Papers, 140th Meeting of the American Chemical Society, 22-N, Chicago, September, 1961.

[4] B. M. Mikhailov and L. S. Vasil'ev, *Bull. Acad. Sci. U.S.S.R.* (Div. of Chem. Sci.) Eng. Trans., **11**, 1962 (1961).

[5] Proton magnetic resonance spectra were obtained using a Varian Associates Model H-60, high resolution, 60 mc., NMR spectrometer. Chemical shifts were obtained using the side-band technique with benzene as internal standard.

The relative positions of these absorptions is almost certainly due to the effects of p-π bonding between oxygen and boron. A similar result was observed for the alpha hydrogens of the alkoxy groups in the corresponding ethoxy compounds. The diethoxy quartet is centered at 3.41 p.p.m. above benzene and the monoethoxy quartet at 3.35 p.p.m. above benzene.

In 33% benzene solution the ethoxy quartets do not overlap the methoxy singlets and these singlets may thus be used for quantitative analyses of equilibrium mixtures. The analytical procedure was checked with samples of known composition.

Equilibrium mixtures resulting from the reaction of diisobutylmethoxyborane (A) with isobutyldiethoxyborane (B) to produce diisobutylethoxyborane (C), isobutylmethoxyethoxyborane (D), and isobutyldimethoxyborane (E) were obtained by mixing the reactants in molar ratios ranging from 2A:1B to 2B:1A. Four different ratios of A and B for the forward reaction and a 2C:3E ratio for the reverse reaction were analyzed by p.m.r. As soon after mixing as possible, the solutions were analyzed[6] and found to have reached a statistical distribution of alkoxy groups between monoalkyl- and dialkylalkoxyboranes.

The most dilute solution which was analyzed satisfactorily had initial concentrations, $a = b = 0.1\ M$. Within an analytical uncertainty of 5%, this solution was found to reach equilibrium in 30 seconds or less.

On the basis of the reactions

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} C + D$$

$$A + D \underset{k_4}{\overset{k_3}{\rightleftarrows}} C + E$$

$$E + B \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2D$$

and taking $k_1 = 2k_2 = 2k_3 = k_4 = {}^1/_2k_5 = 2k_6$ from statistical considerations, the rate equation, $\frac{-dA}{dt} = k_1[(A)(2b + a) - a^2]/2$, was obtained for the approach of the system to equilibrium. On the assumption that the reaction products reached at least 95% of their equilibrium values in 30 seconds or less, a minimum reaction rate constant, k_1, of 0.66 M^{-1} sec.$^{-1}$ was calculated.

In an equilibrated mixture formed by adding 2 moles of A to 1 mole of B, the populations of methoxy groups on A is equal to the sum of the populations of methoxy groups on D and E. Using the minimum rate constant, the maximum mean lifetime of methoxy groups on the two sites was calculated to be 1.8 seconds. This 2:1 mixture was examined in the absence of benzene and found to give separate, essentially non-broadened, singlets for the monomethoxy and dimethoxy hydrogens with a separation of 10 c.p.s., compared to a separation of 5 c.p.s. in 33% benzene. Since, in the 2:1 mixture of A and B, the populations on the two alternate sites are equal, and in view of the noncoalescence of the two methoxy peaks, the equation[7] $\tau\pi(V'_A - V'_B) = 10$ was used to calculate a minimum mean lifetime of 0.32 second for the methoxy groups on the two sites. From this minimum mean lifetime and the rate equation, a maximum reaction rate constant of 3.8 M^{-1} sec.$^{-1}$ was calculated. Thus from the 95% approach to equilibrium in less than 30 seconds, and from the noncoalescence of absorption peaks, the reaction rate constant, k_1, is given an upper limit of 3.8 and a lower limit of 0.66.

Measurements at higher temperatures are planned to determine whether the exchange can be accelerated sufficiently to produce coalescence of the absorption peaks.

Similar results were obtained when mixtures of diisobutylethoxyborane and trimethoxyborane were examined. Further details on this and related work will be reported at a later date.

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[6] In the analysis isobutylmethoxyethoxyborane could not be distinguished from a mixture of isobutyldimethoxyborane and isobutylethoxyborane because the chemical shift of the alpha hydrogen is determined by the number of oxygens attached to boron and not on the nature of the alkoxy group. This analytical difficulty does not, however, interfere with calculations of the rate constants.

[7] Pople, Schneider and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 223.

BOOK REVIEWS

Basic Principles of the Tracer Method. Introduction to Mathematical Tracer Kinetics. By C. W. Sheppard, Professor of Physiology, University of Tennessee Medical Units, Memphis, Tennessee. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. xviii + 282 pp. 15.5 × 23.5 cm. Price, $8.00.

Tracer techniques are being used in many areas of chemistry and biology, particularly in applications of radioisotopes to problems in biological research. In the latter area, multi-compartmented, polyphasic systems of cells, organs and intact animals are the rule. The intrinsic complexity of such systems has discouraged rigorous mathematical analysis of the dynamics of exchange between the various compartments. The great majority of published tracer studies in biology involve a variety of assumptions which in retrospect are gratuitous, if not indefensible.

Although from time to time writers have dealt with the simplest possible problems of precursor–product relationships in intermediary metabolism, and with problems in the dynamics of distribution and exchange in living organisms,