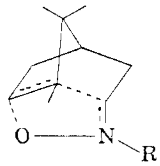
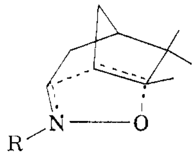
isolated, b.p. 99–102° (0.9 mm.), λ_{max}^{EtOH} 238 mμ (ϵ = 9760). Heating VII in refluxing xylene did not afford a cyclized product, but rather a rearrangement to the amide VIII occurred.[9]

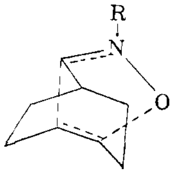
The unique cyclizations reported here are further examples of 1,3-dipolar additions of nitrones to olefins. In these situations, the ring closure reactions are thought to be initiated by electrophilic attack of the nitrone on the olefin, the nitrone carbon atom thus resembling a carbonium ion center. We picture the transition states for the formation of the products as IX, X and XI which collapse to give the isoxazolidines. No distinction is made between a one-step process or a two-stage mechanism involving a *rapid* second step. The transition states thus resemble the proposed bridged-ion intermediates of the solvolysis reactions; however, with the nitrone addition, the charge distribution in the activated complex involves five atoms and the nucleophile is built into the molecule. In addition to the obvious utility for the synthesis of *difunctional* derivatives of bicyclic hydrocarbons, we hope that this reaction can be extended to parallel other situations in which π-routes to non-classical cations have been demonstrated. On the other hand, anchimeric assistance by double bonds in solvolysis reactions may also be expected with substrates analogous to those which have been observed to undergo facile intramolecular nitrone–olefin addition.[2] Such investigations are in progress. One final point is worthy of note: namely, that the product(s) from solvolysis of esters of the alcohol derived from campholenic aldehyde should prove interesting in view of the formation of two products, II and III, from the nitrone reaction.



IX



X



XI

This work was supported by the National Science Foundation.

(9) *Cf.* W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

(10) Alfred P. Sloan Fellow, 1961-1963.

(11) National Institutes of Health Predoctoral Fellow, 1961-1962.

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RECEIVED SEPTEMBER 7, 1962

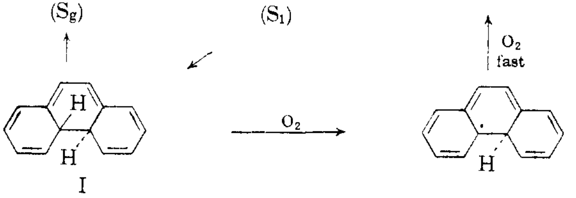
PHOTOCHEMISTRY OF STILBENES. I.[1,2]

Sir:

The photochemical conversion of stilbenes to phenanthrenes has been discovered independently by a number of workers and some limited studies have been reported.[3] This type of reaction has also been found in more complicated molecules such as the bianthrones[4] and mechanistically related ring closures have been observed in the simpler 1,3,5-hexatriene system.[5]

We have shown that the formation of phenanthrene by irradiation of stilbene in cyclohexane solution requires a suitable oxidant such as dissolved molecular oxygen; on irradiation under a nitrogen atmosphere with careful exclusion of oxygen the only net reaction is *cis–trans* isomerism[6] with no detectable conversion to phenanthrene. It seems probable, therefore, that oxidants such as oxygen or peroxides were inadvertently present in the two cases reported recently[3f,3h] of photochemical formation of phenanthrene systems under nitrogen atmospheres.

The reaction is formulated as proceeding by way of the unorthodox dihydrophenanthrene (I) shown below. The molecular oxygen or other oxidant is believed to function by abstracting the tertiary allylic hydrogens from this intermediate. Since I has not been isolated as a product of irradiation in the absence of an oxidant it must also undergo ring opening to give back *cis*-stilbene; this process is estimated from appropriate bond and resonance energy values to be exothermic by about 35 kcal./mole and is therefore expected to occur thermally at a reasonably rapid rate at room temperature. With the light source used in this work[7] it is probable that the steady-state concentration of I is too low for the photochemical ring opening of this intermediate to be of much importance relative to the thermal process.



The *trans* stereochemistry of the tertiary hydrogens in I is tentatively suggested by three lines of argument. First, from consideration of models it appears that the approach of an *ortho* and an *ortho′* carbon of *cis*-stilbene to within bond-forming distance of one another would involve much more severe hydrogen–hydrogen interaction in the transition state leading to the *cis*-dihydrophenanthrene (II) than in the transition state leading to the *trans*-dihydrophenanthrene (I). Second, the analogous photochemical ring closure of 2,4,6-octatriene has been shown[5c] to give *trans*-1,2-dimethyl-3,5-cyclohexadiene; this *trans* stereochemistry

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(1) Presented at the Ninth Conference on Reaction Mechanisms, Brookhaven National Laboratory, Sept. 7, 1962.

(2) Supported by grants from the Research Corporation.

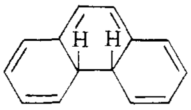
(3) (a) C. O. Parker and P. E. Spoerri, *Nature*, **166**, 603 (1950); (b) R. E. Buckles, *J. Am. Chem. Soc.*, **77**, 1040 (1955); (c) D. G. Coe, E. W. Garnish, M. M. Gale and C. J. Timmons, *Chemistry and Industry*, 665 (1957); (d) F. B. Mallory, Ph.D. Thesis, California Institute of Technology, 1958; (e) E. A. Rick, Ph.D. Thesis, Yale University, 1959; (f) P. Hugelshofer, J. Kalvoda and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960); (g) H. Stegemeyer, *Z. Naturforsch.*, **17b**, 153 (1962); (h) G. J. Fonken, *Chemistry and Industry*, 1327 (1962); (i) E. J. Moriconi, private communication; (j) G. W. Griffin, private communication; (k) D. H. R. Barton, private communication.

(4) H. Brockmann and R. Mühlmann, *Ber.*, **82**, 348 (1949). See also A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, pp. 47–70.

(5) (a) E. Havinga and J. L. M. A. Schlatmann, *Tetrahedron*, **16**, 146 (1961); (b) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2806 (1961); (c) G. J. Fonken, *Tetrahedron Letters*, 549 (1962).

(6) Photodimerization to tetraphenylcyclobutane is negligible if the stilbene concentration is 10^{-2} M or less.

(7) A jacketless 100-watt General Electric H100-A4 mercury arc.



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[3g] 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.

[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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RECEIVED OCTOBER 10, 1962

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).

[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.