The Secondary Deuterium Isotope Effect on the Diels–Alder Reaction

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To gain further insight into the bond-forming processes of the Diels–Alder reaction and also to investigate the effect of slight reactant modification on the size of an α-deuterium isotope effect, competitive kinetics of maleic anhydride and maleic anhydride-d_2 with butadiene, cyclopentadiene, and anthracene were determined. The values of k_D/k_H per deuterium at 25° are, respectively, 1.01, 1.03, and 1.05. The isotope effects (k_D/k_H) in the reaction of maleic anhydride with 1,3-butadiene-1,1,4,4-d_4 and anthracene-9,10-d_2 are 1.07 and 1.06 on a per deuterium basis at 25°. The results are consistent with a four-center transition state which lies only a short distance along the reaction coordinate from the reactants.

I. Introduction

The use of α-secondary deuterium isotope effects in detailing the structure of transition states has gained steadily in popularity since Streitwieser, Jagow, Fahey, and Suzuki[1] demonstrated the applicability of the technique to solvolysis reactions and offered a theoretical explanation for the effect. Other investigators[2,3] had previously shown that β-deuterium substitution lowered the rate of solvolytic reactions. Seltzer,[4] in particular, has expanded the application of the α-effect to free-radical processes and has also tabulated[5] some literature data on α-isotope effects in solvolysis reactions. Other types of reactions which have been investigated from the standpoint of α-deuterium isotope effects include the thiocyanate-catalyzed maleic-fumaric acid isomerization,[6] base-catalyzed deuterium exchange from hydrocarbons,[7] and addition of various reagents to double bonds.[8,9] A general review of secondary isotope effects has been recently published.[10]

In a previous communication[11] it was reported that a small but significant inverse $(k_H/k_D < 1)$ isotope effect was observed in the Diels–Alder reaction between cyclopentadiene and maleic anhydride-d_2. Seltzer[12] has recently described the deuterium isotope effect for the retro Diels–Alder reaction of maleic anhydride with 2-methylfuran. To add detail to the knowledge of the bond-forming processes in the Diels–Alder reaction, we have measured the deuterium isotope effect for three cases where the dienophile is deuterated and for two cases where the deuterium has been incorporated in the diene. A comparison of the numbers is also expected to give additional insight into the practical problem of how the magnitude of the isotope effect varies with changes of reactant substrate.

II. Experimental

A. **Materials.**—Maleic anhydride-d_2 was synthesized by the procedure described by Seltzer[6] where the second alternative ("method II," catalytic deuteriogenation of dimethyl acetylene-

(1) A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958).

(2) V. J. Shiner, *ibid.*, **75**, 2925 (1953).

(3) E. S. Lewis and C. E. Boozer, *ibid.*, **76**, 791 (1954).

(4) S. Seltzer, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 20–22, 1964, p. 4C.

(5) S. Seltzer, *J. Am. Chem. Soc.*, **83**, 2625 (1961).

(6) S. Seltzer, *ibid.*, **83**, 1861 (1961).

(7) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 254 (1962).

(8) D. B. Denney and N. Tunkel, *Chem. Ind.* (London), 1383 (1959).

(9) M. Matsuoka and M. Swarc, *J. Am. Chem. Soc.*, **83**, 1260 (1961).

(10) E. A. Halevi in "Progress in Physical Organic Chemistry," Vol. I, edited by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, Inc., New York, N. Y., 1963, p. 109.

(11) D. E. Van Sickle, *Tetrahedron Letters*, **No. 19**, 687 (1961).

(12) S. Seltzer, *ibid.*, **No. 11**, 457 (1962); *J. Am. Chem. Soc.*, **85**, 1360 (1963).

dicarboxylate) was employed. The mass spectrum indicated the material to be 89.6% d_2, 7.7% d_1, and 2.7% d_0.

Butadiene-1,1,4,4-d_4 was prepared as described by Cope, Berchtold, and Ross[13] by deuterium exchange of butadiene sulfone followed by thermal decomposition to the hydrocarbon. Mass spectral studies of the deuterated butadiene indicated that it was 97.9% d_4 and 2.1% d_3. This analysis was confirmed by n.m.r. examination of the deuterated butadiene sulfone where the area of the residual hydrogen at the α-position was compared with the area of the doublet produced by C-13 splitting of the vinyl protons.

A transmetalation on 9,10-dibromoanthracene followed by quenching the reaction mixture with deuterium oxide was found to be a convenient procedure for preparation of anthracene-9,10-d_2 and to compare favorably with a previous method.[14] The 9,10-dibromoanthracene (25 g., 0.074 mole) was dissolved in 200 ml. of anhydrous ether, and 110 ml. of 1.4 M butyllithium in ether was added. The mixture was stirred under nitrogen for 15 min. at room temperature and then 5.0 g. of 99.5% deuterium oxide was added slowly with vigorous stirring. After refluxing for 2 hr. the ether was allowed to boil away on a steam bath. The residue was extracted with boiling benzene until no more yellow color remained on the residue. Evaporation of the extracts followed by washing of the crystals with $ca.$ 50 ml. of cold benzene yielded 7.3 g. (55%) of crude anthracene-9,10-d_2. The material was purified by recrystallization from toluene followed by sublimation to yield white crystals, m.p. 216°. The mass spectrum of the material indicated it to be 86.8% d_2, 12.0% d_1, and 1.2% d_0, and had no significant amount of material with more than two deuterium atoms per molecule. Combustion analyses[15] gave the atom fraction deuterium as 0.1867 and 0.1876 in duplicate runs. The composition assignment used in the calculations was based on the d_1/d_2 ratio from the mass spectrum and total deuterium content from the combustion analysis: d_2, 0.8756; d_1, 0.1208; d_0, 0.0036.

The solvents used in the experiments, methylene chloride and toluene, were of reagent grade and were kept over Drierite and sodium wire, respectively.

B. **Procedure. 1. Maleic Anhydride-d_2–Cyclopentadiene.** —A known mixture of maleic anhydride–maleic anhydride-d_2 was prepared by taking 4.995 g. of the deuterated material, 4.928 g. of the protio species (Matheson Coleman and Bell, resublimed before use) and making up to 50.00 ml. at 20° with methylene chloride. An analysis of the sublimed residue from an evaporated aliquot of this solution was: atom-fraction deuterium, 0.4659, 0.4668; d_1/d_2, 0.0856 (mass spec.); assigned composition, d_2, 0.4472; d_1, 0.0384; d_0, 0.5144. Five-ml. aliquots of this solution were placed in 50-ml. stoppered flasks stored in a desiccator. After being brought to 0°, a known amount of cyclopentadiene sufficient to form adduct with 40 to 70% of the maleic anhydride was added. The cyclopentadiene was measured out by passage through a Beckman GC-2 gas phase chromatography apparatus, condensation of the effluent hydrocarbon at −80°, and quantitative transfer with 10 ml. of precooled methylene chloride to the flasks containing the maleic anhydride solution. Estimation of the cyclopentadiene delivered was by a previously calibrated recorder chart peak area.

The solutions in tightly stoppered flasks were allowed to stand at 0° for sufficient length of time to ensure 99.9% reaction,[16]

(13) A. C. Cope, G. A. Berchtold, and D. L. Ross, *ibid.*, **83**, 3859 (1961).

(14) V. Gold and F. A. Long, *ibid.*, **75**, 4543 (1953).

(15) Combustion analyses (falling drop method) for deuterium by Josef Nemeth, Urbana, Ill.

the solvent was removed on a rotary evaporator, and the residue separated into adduct and residual maleic anhydride by fractional sublimation of the latter at 50°. The adduct was further purified by recrystallization from toluene followed by sublimation. Melting points of the samples submitted for deuterium analysis by combustion ranged from 158 to 162°.

2. Maleic Anhydride-d_2-Butadiene.—The maleic anhydride solution of B1, which had been kept in storage at 10° approximately 10 months, was evaporated to dryness and the residual maleic anhydride sublimed. A sample was resubmitted for analysis for comparison in this series of experiments; results were: atom fraction deuterium, 0.4655, 0.4640; d_1/d_2, 0.0864 (mass spec.). Weighed amounts of the mixed maleic anhydrides and 10 ml. of methylene chloride were placed in 50-ml. flasks which were attached to a vacuum line, cooled to −190°, and degassed. Known amounts of butadiene (Phillips Research Grade, 99.81 mole %) were delivered to the flasks using a calibrated volume on the vacuum line; the PVT relationships for butadiene as reported by the National Bureau of Standards[17] were used. Dry nitrogen was then admitted to the flasks which were tightly stoppered and placed in the 25.0° thermostated bath.

The solutions were allowed to stand 100 hr. at 25.0° ensuring completion of the reaction[18] before the solvent was removed on a rotary evaporator. Isolation of the adduct from the unreacted maleic anhydride and purification of the adduct were similar to the cyclopentadiene experiments. The adducts submitted for analysis had melting points ranging from 95 to 97°.

3. Butadiene-1,1,4,4-d_4-Maleic Anhydride.—The synthesized butadiene-d_4 (1.9966 g.) was mixed with normal material (2.1709 g.) in a 20-ml. steel tank equipped with a valve and standard taper joint. Combustion analyses proved impractical and composition was assigned directly from mass spectral data and weights: d_4, 0.452; d_3 0.0097; d_0, 0.539. The mixture was stored at −20° until needed. The technique of mixing the butadienes with a limiting amount of maleic anhydride and isolation and purification of product were essentially the same as described in B2: The volume of methylene chloride used was 18 ml. Analysis of the product was again by combustion.

TABLE I

ANALYSIS OF REACTION PRODUCTS

Reaction	Init. amt. reactants, mmoles		Adduct composition, atom fraction deuterium[16]
	Diene	Dienophile	
Maleic anhydride-d_2 + cyclopentadiene	3.92	10.02	0.1189
	5.08	10.02	.1196
	5.85	10.02	.1188
	6.82	10.02	.1185
Maleic anhydride-d_2 + butadiene	3.465	9.88	.1168
	5.185	9.96	.1166
	6.866	9.84	.1169
Maleic anhydride-d_2 + anthracene	1.40	2.80	.0797
Butadiene-d_4 + maleic anhydride	18.53	12.20	.2482
	18.77	9.49	.2522
	18.50	7.00	.2552
Anthracene-d_2 + maleic anhydride	2.80	1.40	.0805

4. Anthracene-9,10-d_2-Maleic Anhydride.—A solution of 0.2495 g. (1.40 mmoles) of normal anthracene (Rutgerswerke, recrystallized from toluene and sublimed), 0.2520 g. (1.40 mmoles) of the synthesized anthracene-d_2, and 0.1373 g. (1.40 mmoles) of maleic anhydride was made up with 25.0 ml. of toluene and kept at 100.0° in a tightly stoppered flask for 48 hr. Investigation of the rate and equilibrium position of this reaction (see B6) showed that this condition leads to kinetic control of the product. The adduct crystallized from the solution upon

(16) The data of D. Craig, J. J. Shipman, and R. B. Fowler, *J. Am. Chem. Soc.*, **83**, 2885 (1961), predict 76 1./mole/hr. for the second-order rate constant for cyclopentadiene and maleic anhydride at 0°.

(17) C. H. Meyers, C. S. Cragoe, and E. F. Mueller, *J. Res. Natl. Bur. Std.*, **39**, 507 (1947).

(18) B. Eisler and A. Wasserman, *J. Chem. Soc.*, 1943 (1953), give 0.14 1./mole/hr. for the second-order rate constant of butadiene-maleic anhydride reaction at 25°.

cooling and was collected by filtration. The material was powdered and pumped to constant weight; m.p. 271–272° The product was then sublimed and submitted for analysis.

5. Maleic Anhydride-d_2-Anthracene.—A solution of 0.2495 g. (1.40 mmoles) of anthracene and 0.2771 g. (2.80 mmoles) of the mixed maleic anhydrides used in B2 was made up with 25.0 ml. of toluene and thermostated at 100° for 48 hr. as described in B4. The product which crystallizes out upon cooling to 25° was collected, pumped dry, and sublimed; m.p. 271–272°.

Data for the runs described in B1, 2, 3, 4, and 5 are summarized in Table I.

6. Kinetics and Equilibrium of Anthracene–Maleic Anhydride at 100°.—A Beckman DU spectrophotometer was calibrated at 380 mμ by plotting log (I/I_0) vs. anthracene concentration of standard solutions. Beer's law is obeyed and an excellent straight line is obtained. The rate of the maleic anhydride–anthracene reaction was determined by mixing 253.5 mg. (1.42 mmoles) of anthracene with 203.5 mg. (2.07 mmoles) of maleic anhydride and 25.0 ml. (at 25°) of toluene, thermostating at 100°, and removing samples at intervals to determine the residual anthracene concentration. Dilutions were necessary for the first points during the run. Concentrations of materials at 100° were calculated using d_{25} 0.861 and d_{100} 0.788 for toluene.[19]

A standard second-order plot of the form

$$\log \left(\frac{b - x}{a - x} \right) = \frac{k(b - a)}{2.303} t - \log (a/b) \quad (1)$$

where a and b are the initial concentrations of anthracene and maleic anhydride and x is the amount reacted at time t gave a good straight line for points up to 30 hr. with slope yielding 4.64 1./mole/hr. for the value of k. Thus the extent of reaction, x/b, of experiment B4 is about 0.999995.

The value of the equilibrium constant for the reaction

$$K = \frac{[\text{adduct}]_e}{[\text{anthracene}]_e [\text{maleic anhydride}]_e} \quad (2)$$

was obtained by determining [anthracene]$_e$ from points of the kinetic run at t = 54 and 70 hr. using the equation[20]

$$\log \frac{[b - a]}{b[a_x - a_e]} = \frac{k[b - a]t}{2.303} \quad (3)$$

where the symbols have the same meaning as before with a_e = [anthracene]$_e$ and a_x = amount of anthracene remaining at time t. The value of [anthracene]$_e$ was also determined directly by allowing 256.0 mg. (1.42 mmoles) of anthracene, 208.7 mg. (2.13 mmoles) of maleic anhydride, and 25.0 ml. of toluene to equilibrate for 190 hr. at 100° followed by spectrophotometric measurement of the anthracene concentration. The values of the equilibrium constant in eq. 2 obtained by the two methods were 1.04 and 1.05 × 10⁵ 1./mole. The calculated rate constant for the unimolecular dissociation reaction is, then, 4.64/1.05 × 10⁵ = 4.42 × 10⁻⁵ hr.⁻¹ and the half-life for dissociation is 653 days.

C. Calculations.—In all cases it was assumed that the reaction proceeded quantitatively and that the limiting amount of reactant gave the extent of reaction. Also, since the isotope effects are small, it was assumed that the ratio of d_2 to d_1 (in the cases of maleic anhydride and anthracene) or d_4 to d_3 (butadiene) was the same in the adducts as in the reactants. From the assigned compositions of reactant and product and the known quantities of starting materials, appropriate substitution was made in the equation[21]

$$k_D/k_H = \frac{\log (a_D/a_D^0)}{\log (a_H/a_H^0)} \quad (4)$$

(19) G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, American Chemical Society, Monograph Series No. 78, Reinhold Publishing Corp., New York, N. Y., 1946, p. 48.

(20) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., p. 186, give a description of unimolecular dissociation with reversibility. Equation 3 may be obtained by a similar procedure and making the assumption that, toward the end of the reaction, a and $b \gg a_x$ and a_e.

(21) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p. 49.

where $a_D{}^0$ and $a_H{}^0$ are initial concentrations of deuterio and protio reactants and a_D and a_H are the amounts of reactant remaining after an extent of reaction; that is

a_D = (initial moles reactant-d) − (moles adduct-d)
    = $a_D{}^0$ − (extent of reaction)(total moles normal and deuterated reactants)(fraction adduct-d)

III. Discussion

Table II summarizes the results of individual kinetic

TABLE II

SUMMARY RESULTS OF ISOTOPE EFFECTS

	Temp., °C.	$(k_D/k_H)_T$, individual runs	$(k_D/k_H)_{200}$, per deuterium[a]
Maleic anhydride-d_2 + cyclopentadiene	0	1.05	1.03
		1.07	
		1.05	
		1.06	
Maleic anhydride-d_2 + butadiene	25	1.014	
		1.009	1.00₇
		1.022	
Maleic anhydride-d_2 + anthracene	100	1.08	1.05
Butadiene-d_4 + maleic anhydride	25	1.31	1.07
		1.31	
		1.30	
Anthracene-d_2 + maleic anhydride	100	1.10	1.06

[a] Obtained from the equation $\dfrac{RT}{n} \ln \dfrac{k_D}{k_H} = \Delta(\Delta F)$ using average value of k_D/k_H.

runs and also gives the average value for the isotope effect corrected to 25° on a per deuterium basis. All of the effects are inverse; that is, the deuterated species react faster than the protio analogs. Theory[1] predicts this result, of course, since the reactant carbons to which the deuterium is bonded begin at an sp^2 hybridization and incur partial change toward sp^3 in passing to the transition state.

Three main features of the data of Table II warrant discussion; they are: (1) in all cases, the effect per deuterium would be classified as "small"; (2) the effect of isotope substitution when incorporated in the diene is greater than if incorporated in the dienophile; (3) the magnitude of the isotope effect with deuteriomaleic anhydride smoothly increases in changing the diene from butadiene to cyclopentadiene to anthracene.

On the first point, we do not believe that the small magnitude of the effect should be construed to indicate a two-step mechanism for the Diels–Alder reaction.[22] "Normal" magnitudes for secondary deuterium isotope effects have been asserted to be near 1.12 per deuterium[5] (at 105°) but these numbers refer to bond *breaking* processes at the isotopically substituted center whereas we are here dealing with bond *forming* processes. Data for isotope effects on reactions of this category are less complete but indicate that smaller effects are the rule. In particular, Matsuoka and Swarc[9] observed a small effect (~1.05 based on only the two β-deuteriums affecting the rate) in the addition of the methyl radical to styrene-α,β,β-d_3, and Takahasi and Cvetanovic[23] obtained a similarly low number for hydrogen

atoms adding to propylene-d_6. In the case of thiocyanate ion adding to the double bond[6] of maleic acid-d_2, where temperature dependence studies indicate the progression along the reaction coordinate is nearly halfway to a fully formed bond, the effect may be of greater magnitude. The measured ratio of rate constants for -2,3-d_2 to -2,3-d_0 is 1.17 (at 25°) and this would be the appropriate value on a per deuterium basis if it is assumed that no significant change is imposed on one carbon–deuterium center by attack of thiocyanate on the other. In any event, we would like to interpret the low k_D/k_H values as indicating a small change in hybridization of the four centers of reaction, implying that the Diels–Alder reaction transition state lies only a little way along the reaction coordinate from the reactants.

Criticism has been leveled by Halevi[10] that "isotopic polarization and polarizability effects on the nonspecific binding between the two moieties" may obscure the significance of the magnitude of the isotope effects observed. However, we do not expect these complications to be of importance in a reaction of the Diels–Alder type. Firstly, the Diels–Alder reaction is essentially nonpolar in character as attested by the relative insensitivity of rate to solvent.[24] Therefore, little charge formation is expected at the transition state and the isotope effect observed should be purely that of hybridization change uncomplicated by hyperconjugative or inductive effects. Secondly, although there may be a side equilibrium between diene and dienophile to yield, say, a charge-transfer complex,[25] this is intuitively expected to be important only in the anthracene case. The parallelism of ionization potential with position of charge-complex equilibrium,[26] coupled with the observation that deuterium substitution, at least in simple molecules such as ethylene and acetylene, does not alter their ionization potential,[27] suggests that the effect of deuterium substitution on complexing equilibria will be small. Admittedly, the last criterion does not offer a desirable degree of precision. The data of Keefer and Andrews[25] on the anthracene–maleic anhydride complex association constant predict (in chloroform) approximate thermodynamic parameters of $\Delta H = -2150$ cal. and $\Delta S = -9.5$ e.u. The experimental uncertainty of the electron impact phenomena (0.02 e.v.) could add −460 cal. to the enthalpy term and raise the equilibrium constant predicted for 100° from 0.15 to 0.27 mole^{-1} l. This changes the free anthracene concentration by *ca.* 10%.

However, from a qualitative standpoint, we may argue that the effect of deuterium substitution on complexing is negligible in our case. As a result of the electron-donating character of deuterium relative to hydrogen,[28] the isotopic substitution of the anthracene would be expected to increase the amount of complexing by the electrophile, lessen the amount of free anthracene-d_2, and decrease the deuterium content of the product. Since the opposite effect is observed, with the anthracene product showing the largest relative enrichment of the reactions studied, the in-

(22) (a) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959); (b) C. Walling and H. J. Schugar, *J. Am. Chem. Soc.*, **85**, 607 (1963); (c) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).
(23) M. Takahasi and R. J. Cvetanovic, *Can. J. Chem.*, **40**, 1037 (1962).

(24) A. Wasserman, *Trans. Faraday Soc.*, **34**, 128 (1938).
(25) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **77**, 6284 (1955).
(26) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).
(27) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, p. 214.
(28) E. A. Halevi, M. Nussim, and A. Ron, *J. Chem. Soc.*, 866 (1963).

fluence on complexing must be negligible. With ring deuteration only and no alkyl substituents, it is unlikely that any hyperconjugative effect is present which would act in the opposite direction.[29]

On the difference in isotope effect between diene and dienophile, we would like to suggest that this represents only a different degree in hybridization change at the transition state for the diene relative to the dienophile. In other words, the bonding in the diene appears to change without a complementary change in the dienophile. At this point we would prefer not to speculate on what kind of transition-state structures could accommodate this observation.

The third feature of our data, the increase in isotope effect in proceeding from butadiene to cyclopentadiene to anthracene, is the most difficult to rationalize. Fundamentally this indicates that the amount of hybridization change of the dienophile (maleic anhydride) in going from reactant to transition state is dependent on the diene under attack. This obviously does not parallel the reactivity of the diene which is cyclopentadiene > butadiene > anthracene. A parallelism of isotope effect to the entropy of activation of each reaction seems to exist (more negative ΔS^* corresponds to lower k_D/k_H), but lack of precision in the data of

(29) E. A. Halevi and M. Nussim, J. Chem. Soc., 876 (1963).

kinetic parameters for these reactions excludes a quantitative correlation.

In conclusion, the isotope effects observed in the forward Diels–Alder reaction are consistent with a one-step mechanism which is the microscopic reverse of that observed in the retro reaction.[12] In the forward reaction, the amount of bond formation is small with the transition state lying only a short distance along the reaction coordinate from the reactants. While the transition state need not be completely symmetrical and may involve differences in degree of hybridization change between diene and dienophile, the reaction can still be formally classed as four centered. The sensitivity of the isotope effect to moderate deuterium positional and structural changes in the reactants emphasizes the difficulties attendant in calculating an "expected" effect from the appropriate statistical mechanical equations and assumed values for vibration frequencies, or, more fundamentally, bond force constants of transition states.

Photochemistry of Stilbenes. III. Some Aspects of the Mechanism of Photocyclization to Phenanthrenes[1,2]

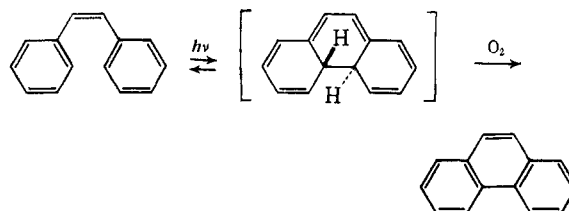BY FRANK B. MALLORY,[3] CLELIA S. WOOD, AND JANICE T. GORDON

With certain exceptions, stilbene derivatives are converted photochemically in good yields to the corresponding phenanthrene derivatives in cyclohexane solution in the presence of oxidants such as dissolved oxygen or iodine. The scope and mechanism of this photoreaction are discussed in detail. The mechanism is believed to involve cyclization of cis-stilbene in its lowest excited singlet state to give an unorthodox dihydrophenanthrene which then undergoes hydrogen abstraction by the oxidant to give phenanthrene. The differences between the course of the photoreaction of stilbene in the vapor phase and in solution are discussed.

Introduction

Irradiation with ultraviolet light of solutions containing cis-stilbene in the presence of a suitable oxidant such as dissolved molecular oxygen has been found to lead to the formation of phenanthrene in good yield.[4] This photoreaction of stilbene or certain substituted stilbenes has also been discovered independently by several other workers,[5] and some limited studies have been carried out.[6] In some of these previous reports

(1) Part II: F. B. Mallory, J. T. Gordon, and C. S. Wood, J. Am. Chem. Soc., 85, 828 (1963).

(2) Taken in part from the Ph.D. Dissertations of (a) C. S. Wood, Bryn Mawr College, 1963, and (b) J. T. Gordon, Bryn Mawr College, 1961.

(3) John Simon Guggenheim Memorial Foundation Fellow 1963–1964.

(4) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, J. Am. Chem. Soc., 84, 4361 (1962).

(5) (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, Chem. Ind. (London), 665 (1957); (d) E. A. Rick, Ph.D. Thesis, Yale University, 1959; (e) E. J. Moriconi, private communication; (f) G. W. Griffin, private communication; (g) D. H. R. Barton, private communication.

(6) (a) P. Hugelshofer, J. Kalvoda, and K. Schaffner, Helv. Chim. Acta, 43, 1322 (1960); (b) G. R. Evanega, private communication; (c) H. Stegemeyer, Z. Naturforsch., 17b, 153 (1962); (d) R. Srinivasan and J. C. Powers, Jr., J. Am. Chem. Soc., 85, 1355 (1963); (e) J. Chem. Phys., 39,

the need for an oxidant was not appreciated and the formation of the phenanthrene occurred as a result of the adventitious presence of dissolved oxygen or other oxidants.[5a,b,6c] In other early reports the identity of the photoproduct was not established as phenanthrene.[7]

As postulated earlier,[4] the reaction is believed to involve as an intermediate the unorthodox dihydrophenanthrene[8] shown below. The postulation of this inter-

580 (1963); (f) M. V. Sargent and C. J. Timmons, J. Am. Chem. Soc., 85, 2186 (1963).

(7) (a) A. Smakula, Z. physik. Chem., B25, 90 (1934); (b) G. N. Lewis, T. T. Magel, and D. Lipkin, J. Am. Chem. Soc., 62, 2973 (1940); (c) G. Oster, G. K. Oster, and H. Moroson, J. Polymer Sci., 34, 671 (1959).

(8) Throughout this paper the name "dihydrophenanthrene" will be used to designate the 4a,4b-dihydrophenanthrene shown above unless specified to the contrary.