in 10 ml. of methanol was cooled to 0° and 30% hydrogen peroxide (10.2 g., 90 mmoles) was added over a period of 30 min. The solution was allowed to come to room temperature and stand for 24 hr., at the end of which time it was neutral to Universal Indicator. To the solution there was then added 0.25 g. of platinum asbestos, and stirring was continued for 24 hr. The slurry was filtered and the filtrate was subjected to vacuum distillation. The water and methanol were removed at 30–40° (10–100 mm.) resulting in a viscous sirup. The temperature was then carefully raised to 130–140° (3–4 mm.) at which point decomposition ensued. The pyrolysate was distilled under reduced pressure giving 0.6 g. (15%) of water-white liquid, b.p. 55° (0.10 mm.), $n^{25}D$ 1.5625. An infrared spectrum of the product showed strong N-vinyl absorption at 1645 cm.$^{-1}$.

Anal. Calcd. for C_5H_7NOS: C, 46.49; H, 5.46; N, 10.84; S, 24.82. Found: C, 46.40; H, 5.60; N, 10.89; S, 24.80.

B. From V.—To freshly prepared sodium sand (11.5 g., 0.50 g.-atom) suspended in 800 ml. of anhydrous tetrahydrofuran there was added 51.6 g. (0.50 mole) of II in 300 ml. of tetrahydrofuran at such a rate that the temperature did not rise above 40°. When the exotherm had subsided there was added all at once 143.4 g. (1.0 mole) of 1-bromo-2-chloroethane. After the initial mild exotherm had subsided, the reaction mixture was refluxed for 24 hr. The slurry was vacuum filtered and the filter cake was washed with additional solvent. The combined filtrates were concentrated under vacuum; the residue was distilled under reduced pressure. The fraction distilling at 100–110° (0.5 mm.) was collected and used as such, 29 g. (35%). To a solution of 52 g. (0.31 mole) of N-(2-chloroethyl)-2-thiazolidinone dissolved in 100 ml. of absolute *t*-butyl alcohol and warmed to 60° there was slowly added a previously prepared solution of 13 g. (0.33 g.-atom) of potassium metal in 600 ml. of *t*-butyl alcohol. The reaction mixture was heated at reflux overnight, neutralized with glacial acetic acid, and filtered. The filter cake was washed with ether and the combined filtrates were concentrated under vacuum. The residue was distilled under reduced pressure to give 14 g. (35%) of product with physical constants and infrared spectrum identical to that obtained *via* the Cope degradation of IV.

Poly(N-vinyl-2-thiazolidinone). A. Polymerization in Bulk.—A thick-walled, Pyrex, cappable tube was charged with 10 g. (0.08 mole) of freshly distilled N-vinyl-2-thiazolidinone and 50 mg. (0.5 wt. %) of α,α'-azobisisobutyronitrile. The polymer tube was alternately evacuated and flushed with dry nitrogen three times and then sealed under vacuum. The charged tube was maintained at 60° in an oil bath for 24 hr. The resultant polymer plug, which was triturated with ethanol to separate unreacted monomer, was dissolved in 50 ml. of dimethylformamide, reprecipitated by adding dropwise to a 10:1 excess of methanol, filtered, and dried under vacuum. The product, 9.7 g. (97%), was a white solid: softening range 265–285°; $[\eta]$ 0.35, determined in dimethylformamide at 29.2°.

Anal. Calcd. for $(C_5H_7NOS)_n$: C, 46.49; H, 5.46; N, 10.84; S, 24.82. Found: C, 46.20; H, 5.50; N, 10.81; S, 24.59.

B. Solution Polymerization.—A solution of 1.0 g. of IV in 5.0 ml. of anhydrous benzene was polymerized at 60° with 5 mg. of α,α'-azobisisobutyronitrile as initiator. After a 3-hr. period, polymer had precipitated from solution. The insoluble material was filtered and washed with benzene. "Work-up" was effected as described to yield 0.55 g. (55%), η_{rel} (1% in dimethylformamide) 1.25.

Copolymerization of N-Vinyl-2-thiazolidinone with N-Vinylpyrrolidone.—The monomers were freshly distilled and weighed directly in the polymerization tubes which were then immersed in an acetone–Dry Ice bath and evacuated by means of an oil pump while intermittently flushing with dry nitrogen gas. The tubes were sealed under vacuum and then placed in a constant temperature bath (65°). α,α'-Azobisisobutyronitrile was employed as the free-radical source in a concentration of 0.3–0.4% by weight in each case. The contents of each tube was diluted to approximately one half its initial volume with anhydrous benzene. The polymers were precipitated by addition to cold anhydrous ether. Purification was effected by reprecipitation from dimethylformamide with the same precipitating nonsolvent. The purified polymers were dried under vacuum to constant weight, and the compositions were determined by elemental analysis. The reactivity ratios were calculated using the method of Mayo and Lewis.[17]

Acknowledgment.—The authors gratefully acknowledge the support of this work from the U. S. Army Medical Research and Development Command, Office of the Surgeon General under Contract No. DA-49-193-MD-2032.

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trans,trans-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene[1]

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Received April 17, 1964

trans,trans-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene (**7**) has been prepared and characterized. It can be obtained in *ca.* 15% yield by zinc fragmentation of a mixture of 9,10-dibromo-*trans,syn,trans*-perhydroanthracenes.

We are here reporting a synthesis of *trans,trans*-2,8-*trans*-bicyclo[8.4.0]tetradecadiene (**7**), a study of which may contribute to our knowledge of the stereochemistry of acid-catalyzed cyclizations of 1,5-dienes.[2] It was anticipated that, unlike *trans,trans*-1,5-cyclodecadiene,[3] **7** would be thermally stable through degeneracy of the Cope rearrangement,[4] and the 1,5-cyclodecadiene moiety of **7** would therefore be susceptible to investigation under conditions not otherwise feasible. A discussion of the reactions of **7** will follow.

The projected synthesis was based on the possibility of fragmenting a 9,10-dibromo-*trans,syn,trans*-perhydroanthracene (*e.g.*, **4** → **7**) in a manner analogous to that reported for *cis*- and *trans*-1,4-dibromocyclohexanes, using metals, notably zinc.[5] Control over the stereochemistry of the double bonds formed in the fragmentation was anticipated from the choice of stereochemistry of the disubstituted perhydroanthracene.[5] Our preconception of the mechanism of fragmentation involved the formation of intermediate **6**[6] which is most simply derived from the corresponding *trans*(*e,e*) dibromide. The *cis*(*e,a*) dibromide **4** can also lead directly to **7** if the axial (but not the equatorial) bromine is replaced by zinc.[6] A convenient route to one or both of these dibro-

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[1] This investigation was supported by Public Health Service Research Grant GM 09759 from the Division of General Medical Sciences, U. S. Public Health Service, and by a National Institutes of Health Predoctoral Fellowship to R. A. K. Acknowledgment is also made of National Science Foundation Grant G19108 which contributed to the purchase of the n.m.r. spectrometer used in this research.

[2] For reviews see W. S. Johnson, *Pure Appl. Chem.*, **7**, 317 (1963); A. Eschenmoser, D. Felix, M. Gut, J. Meier, and P. Stadler, *Ciba Found. Symp. Biosyn. Terpenes Sterols*, 217 (1959).

[3] C. A. Grob, H. Link, and P. W. Schiess, *Helv. Chim. Acta*, **46**, 483 (1963).

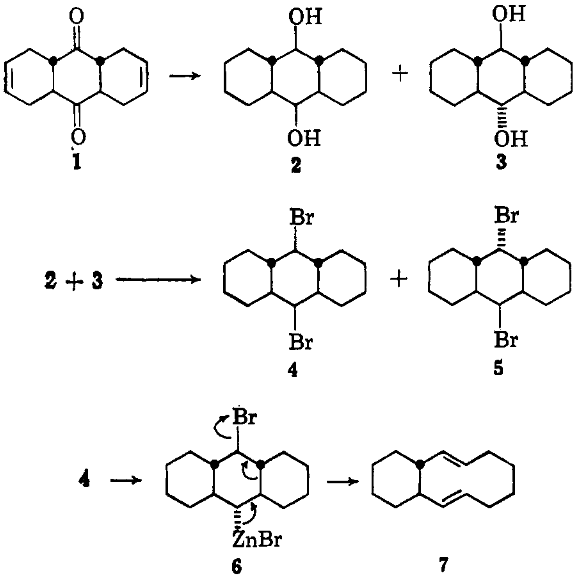
[4] Several examples of this phenomenon are discussed by W. von E. Doering and W. R. Roth, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963).

[5] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

[6] Assuming configurational lability of the carbon-zinc bond.

mides was available starting from dione **1**,[7] of established stereochemistry.[8]

Hydrogenation of **1** in the presence of Raney nickel yielded a mixture of saturated diols **2** and **3** in 64% yield (first crop of crystals), m.p. 240–247°. As the diol mixture was not very soluble in most organic solvents its composition was determined by quantitative conversion to a mixture of diacetates which was crystallized from alcohol. Only two of the three possible isomers were isolated, each accounting for approximately one-half of the mixture. Their n.m.r. spectra identified the lower melting as the diacetate of *cis*(*e*,*a*) diol **2** and the higher melting as the diacetate of *trans*(*e*,*e*) diol **3** on the basis of the distinctive chemical shifts and coupling constants associated with the low-field protons.[9]



Treatment of the diol mixture with phosphorus tribromide gave a crude product in 39% yield containing 90% of the bromine calculated for $C_{14}H_{22}Br_2$. Although the crude mixture decomposed on standing, it was possible to isolate two pure dibromides by crystallization, albeit in low yield. Their n.m.r. spectra identified[9] the lower melting as *cis*(*e*,*a*) dibromide **4** and the higher melting as *trans*(*a*,*a*) dibromide **5**. A comparison of spectra of mixtures indicated that these two bromides constituted over one-half of the crude mixture. The apparent absence of the *trans*(*e*,*e*) dibromide is consistent with inversion in the substitution and the absence of the requisite *trans*(*a*,*a*) isomer in the diol mixture. Moreover, the conversion of equatorial alcohol to axial bromide may be expected to be more efficient than that of axial alcohol to equatorial bromide, elimination predominating in the latter case.[10]

Treatment of *cis* dibromide **4** with zinc in boiling dimethoxyethane for 18 hr. led to the loss of 96% of the organically bound bromine. The organic product, obtained in 94% yield after distillation, consisted of a mixture of C_{14} hydrocarbons absorbing strongly at 10.3 μ, a hopeful sign that much **7** had been formed. Separation of **7** from the mixture turned out to be straightforward when it was found that aqueous silver nitrate[11] removed about one-half of the distillate and the hydrocarbon residue showed no 10.3-μ absorption. The hydrocarbon extracted by silver nitrate was recovered and sublimed, yielding almost pure **7**, m.p. 46–48°, in 37% over-all yield from dibromide. Final purification to m.p. 48–49° could be effected by crystallization from aqueous alcohol or repetition of the silver nitrate–sublimation sequence.

Characterization of the diene was straightforward. The expected elemental composition was confirmed by microanalysis. The n.m.r. spectrum revealed absorptions due to saturated and olefinic C–H in the ratio of 18:4, corresponding to the presence of two disubstituted double bonds. The positions of the double bonds and *trans* nature of the ring fusion were confirmed by ozonolysis. After an oxidative work-up, the acidic products were esterified with diazomethane and the esters subjected to vapor phase chromatography. Dimethyl *trans*-1,2-cyclohexanedicarboxylate and dimethyl adipate were identified by comparison of retention times and infrared spectra with corresponding data from authentic samples. A third ester was resolved by vapor phase chromatography but not identified. Infrared spectra show that both double bonds of the diene are *trans*. The molar intensity of absorption at 10.3 μ is roughly twice that of the corresponding absorption of *trans*-cyclodecene[12] and no absorption is evident at *ca.* 14 μ corresponding to a *cis*-disubstituted double bond.

The difficulty involved in isolating pure *cis* dibromide **4** combined with the ease of separating diene **7** from coproducts suggested that treating the total crude dibromide mixture with zinc might be a more practical method for preparing quantities of **7**. This desirable simplification proved to be very effective, **7** being recovered in a yield of 14% based on crude dibromide or 6% based on starting diol mixture **2** and **3**, thus making it readily available for further study.

Experimental

Physical Data.—Melting points were taken in capillary tubes in a Thomas-Hoover melting point apparatus calibrated with samples of known melting points. Infrared and n.m.r. spectra were recorded using a Perkin-Elmer Infracord Model 137 and a Varian A-60 spectrometer, respectively. The n.m.r. data refer to tetramethylsilane as an internal standard. Vapor phase chromatographic data were obtained with an Aerograph Model A-90-P2 and accessory Model 201-B Disc chart integrator. Oil pump pressure can be taken to be *ca.* 0.1 mm.

Materials.—The source of a reagent is unspecified when commercially available. Activated zinc was obtained by stirring zinc dust with 1 *N* hydrochloric acid for 15 min. The zinc was then washed with distilled water until the washings were neutral to litmus and further washed three times with absolute alcohol and three times with anhydrous ether before drying at 60° and atmospheric pressure. Dimethoxyethane was freshly distilled from lithium aluminum hydride before use. Authentic samples of dimethyl *cis*- and *trans*-1,2-cyclohexanedicarboxylates[13] were prepared according to the literature. A sample of *trans*-cyclodecene was generonsly supplied by Professor A. C. Cope. Magnesium sulfate was used to dry organic extracts.

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(9) See L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Inc., New York, N. Y., 1959, p. 115.

(10) For a general discussion, see B. Belleau and S. McLean in "Technique of Organic Chemistry," Vol. 11, part 2, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 921.

(11) For examples of medium-ring diene complexes with silver nitrate, see W. O. Jones, *J. Chem. Soc.*, 312 (1954); R. W. Fawcett and J. O. Harris, *ibid.*, 2673 (1954).

(12) See L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 46.

(13) G. J. Fonken and S. Shiengthong, *J. Org. Chem.*, **28**, 3435 (1963).

Mixture of *cis*- and *trans(e,e)*-9,10-Dihydroxy-*trans,syn,trans*-perhydroanthracenes (2 and 3).—A mixture of 340 g. of 1,[7] m.p. 241.5–245°, and 1 l. of absolute alcohol was hydrogenated over *ca.* 44 g. of Raney nickel W-2 at 1900 p.s.i. and 180° for 16 hr. After cooling to room temperature the mush was filtered and the solid obtained was crystallized from pyridine, giving a first crop of 223 g. (64%) of a mixture of **2** and **3** as a white powder, m.p. 240–247°.

***cis*- and *trans(e,e)*-9,10-Diacetoxy-*trans,syn,trans*-perhydroanthracene.**—A solution of 1.009 g. (4.50 mmoles) of diol mixture **2** and **3**, m.p. 240–247°, in 10 ml. of pyridine and 5 ml. of acetic anhydride was boiled for 1 hr. The warm reaction mixture was poured into 30 ml. of cold water and the resulting white precipitate was separated by filtration, washed with 2% hydrochloric acid and then with distilled water, and finally dried, yielding 1.372 g. (99%) of a mixture of diacetates, m.p. 160–208°. Crystallization of 1.054 g. of this mixture from absolute alcohol afforded a first crop of large white needles, 0.442 g., m.p. 217–226°, and a second crop of smaller white needles, 0.544 g., m.p. 152–156°.

Two recrystallizations of the first crop from absolute alcohol gave 0.272 g. of *trans(e,e)* diacetate as large white spars: m.p. 234.5–235.5°; n.m.r. chemical shifts ($CDCl_3$) at τ 5.55 (2H, broad singlet) and 7.93 (6H, singlet). One further crystallization yielded an analytical sample, m.p. 235–235.5°.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.05; H, 9.07.

One recrystallization of the second crop, m.p. 152–156°, from aqueous alcohol and three subsequent recrystallizations from acetonitrile afforded 61 mg. of *cis* diacetate: m.p. 161–162°; n.m.r. chemical shifts ($CDCl_3$) at τ 5.08 (1H, broad singlet), 5.51 (1H, triplet, $J = 8$ c.p.s.), and 7.91 (6H, singlet). An analytical sample, m.p. 162–162.5°, was obtained by crystallization from acetonitrile of material recovered from the n.m.r. determination.

Anal. Calcd. for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 70.01; H, 9.08.

***cis*- and *trans(a,a)*-9,10-Dibromo-*trans,syn,trans*-perhydroanthracenes (4 and 5).**—A suspension of 8.34 g. (37.1 mmoles) of diol mixture **5** and **6**, m.p. 240–247°, in 75 ml. of carbon tetrachloride was cooled to ice-bath temperature and 8.19 g. (30.2 mmoles) of phosphorous tribromide was added over a 1-hr. period with magnetic stirring. The resulting mixture was stirred at room temperature for an additional 23 hr., after which time the mixture consisted of a clear liquid and a gummy white precipitate which had adhered to the side of the reaction flask. The clear solution was decanted from the precipitate and combined with several small portions of carbon tetrachloride which were used to wash the precipitate. The combined solutions were washed twice with 25-ml. portions of 20% potassium carbonate solution, once with water, and then dried. Work-up, followed by removal of residual solvent at room temperature under oil pump pressure overnight, gave 5.03 g. (39%) of a mixture of dibromides, m.p. 54–157° dec., as a slightly gummy white solid. The solid was not contaminated with appreciable amounts of phosphorus compounds (no 8- or 10-μ absorption in the infrared spectrum), and contained 90% of the bromine calculated for dibromides of molecular formula, $C_{14}H_{22}Br_2$.

Crystallization of 4.759 g. of the crude dibromide mixture from acetone yielded 0.978 g. of *trans* dibromide **5** as white crystals: m.p. 220–224° dec.; n.m.r. chemical shifts (CCl_4) at τ 5.80 (2H, singlet) and 8.0–8.6 (20H). Attempted purification by further crystallization from acetone, alcohol, hexane, ether, benzene, and carbon tetrachloride failed to raise the melting point of the solid and, in some cases, lowered it. An analytical sample, m.p. 220–223° dec., was obtained by crystallization from carbon tetrachloride.

Anal. Calcd. for $C_{14}H_{22}Br_2$: C, 48.02; H, 6.33; Br, 45.64. Found: C, 47.96; H, 6.04; Br, 45.91.

In another run crystallization of 29.8 g. of crude dibromide yielded successively 6.48 g. of **5**, m.p. 219.5–222.5° dec., from alcohol; 4.97 g., m.p. 116–141°, from acetonitrile; and 2.51 g., m.p. 113–148°, from aqueous acetonitrile. The second and third crops were combined and successively crystallized from carbon tetrachloride and acetone, yielding 2.41 g. of *cis* dibromide **4** as white needles: m.p. 160–161°; n.m.r. chemical shifts (CCl_4) at τ 5.95 (1H, broad singlet), 6.65 (1H, triplet, $J = 10$ c.p.s.), and 7.3–9 (20H). A small amount of inorganic contaminant was removed by sublimation at 100° and oil pump pressure, and an analytical sample, m.p. 160.5–161.5°, was thereby obtained.

Anal. Calcd. for $C_{14}H_{22}Br_2$: C, 48.02; H, 6.33; Br, 45.64. Found: C, 48.00: H, 6.54; Br, 45.82.

***trans,trans*-2,8-*trans*-Bicyclo[8.4.0]tetradecadiene (7).**—A mixture of 505 mg. (1.44 mmoles) of *cis* dibromide **4**, m.p. 160–161°, and 502 mg. (7.7 mmoles) of activated zinc dust in 25 ml. of dimethoxyethane was refluxed under nitrogen with magnetic stirring for 18 hr. After cooling to room temperature the reaction mixture was filtered and the residue was washed with small portions of chloroform and then water. The combined filtrate and washings were diluted with 50 ml. of water and the resulting mixture extracted with four 20-ml. portions of chloroform. The combined chloroform extracts were washed twice with 20-ml. portions of water and dried. The combined aqueous solutions were filtered and treated with 10 ml. of 10% silver nitrate solution. The resulting precipitate of silver bromide weighed 521 mg. (96%) after filtration, washing, and drying. Removal of solvent from the chloroform solution gave 293 mg. of an oily white crystalline solid which afforded 258 mg. (94%) of a white crystalline solid upon short-path distillation at oil pump pressure (maximum oil bath temperature 150°). The solid was dissolved in 20 ml. of hexane and extracted five times with 20-ml. portions of 20% silver nitrate solution. The combined silver nitrate extracts were washed twice with 25-ml. portions of hexane. Removal of solvent from the combined hexane layers afforded 127 mg. of a slightly yellow oily solid which still showed absorption at 10.3 μ. This solid was therefore re-extracted with aqueous silver nitrate as described above, the 88 mg. of tan-colored solid recovered from the hexane layers now showing no absorption at 10.3 μ. Hydrocarbon was recovered from the silver nitrate extracts by adding them to ice-cold concentrated ammonium hydroxide and extracting the resulting suspension with three portions of hexane. The combined hexane extracts were washed twice with water and dried. From the two successive silver nitrate extracts were recovered 97.1 mg., m.p. 45–48°, and 22.7 mg., m.p. 44–45°. Sublimation of the combined solids at 40° and oil pump pressure yielded 101.4 mg. (37% based on dibromide) of white crystalline solid, m.p. 46–48°. Further purification was effected by repetition of the silver nitrate extraction–sublimation sequence so that approximately one-half of the original sample was extracted. Thus 101 mg. yielded 49 mg., m.p. 48–49°, and this melting point was not raised by further extraction–sublimation which yielded an analytical sample: n.m.r. chemical shifts (CCl_4) at τ 5.31 (4H, unresolved multiplet, width at half-height 11 c.p.s.) and 7.3–9.1 (18H); λ_{max}^{KBr} 3.43, 3.52, 6.01, 6.99, and 10.34 μ.

Anal. Calcd. for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.35, 88.46; H, 11.85, 11.85.

In practice **7** is best prepared without isolating *cis* dibromide **4**. Thus 5.552 g. of crude dibromide obtained in 43% yield from diol mixture **2** and **3**, m.p. 240–247°, yielded 592 mg. (20%) of slightly oily white crystals of crude diene which afforded 418 mg. (14%) of large white plates, m.p. 46.5–48°, after one crystallization from aqueous alcohol.

Ozonolysis of 7.—A solution of 54.5 mg. (0.286 mmole) of diene **7**, m.p. 47–48°, in 10 ml. of methylene chloride (freshly distilled from phosphorus pentoxide) was cooled to Dry Ice–acetone temperature and 50 ml. of a 0.0218 *M* solution of ozone (1.09 mmoles) in methylene chloride, also at Dry Ice–acetone temperature, was added. The mixture was allowed to warm to room temperature and 1 ml. of 40% peracetic acid was added. After this stood at room temperature for 19 hr., 27 mg. of 30% palladium on carbon was added and the mixture was allowed to stand until gas evolution ceased. The mixture was dried and solvent was then removed under reduced pressure, yielding 92.7 mg. of a tan-colored residue (101% of theoretical yield of dicarboxylic acids). The residue was suspended in a mixture of 3 ml. of ether and 2 ml. of methanol and then treated with an excess of ethereal diazomethane. After this stood at room temperature for 2 hr., solvent was removed with a stream of nitrogen, leaving 98.4 mg. of a yellow oil. Distillation under reduced pressure of 34 mg. of this oil yielded 27 mg. of a clear light yellow liquid which was analyzed by vapor phase chromatography on a 5-ft. column of 5% Carbowax 20M on Teflon at 150°. Two major peaks were observed with retention times of 10.9 and 19.5 min. with relative areas of 1:2. A minor peak was observed with a retention time of 7.8 min. Material corresponding to each peak was collected, using undistilled product. Too little material corresponding to the first peak was collected for positive identification although the infrared spectrum showed strong carbonyl absorption (5.80 μ). A comparison of retention times showed that it was neither dimethyl glutarate nor dimethyl succinate. The infrared spectra of material corresponding to the second and third peaks were identical with those obtained from authentic dimethyl adipate and dimethyl *trans*-1,2-cyclohexanedicarboxylate, respectively. The identities of these components were further checked by addition of authentic esters to the reaction product. Vapor phase chromatography of the new mixture did not show broadening or resolution of the original second and third peaks. Vapor phase chromatography of the individual and mixed authentic dimethyl esters of *cis*- and *trans*-1,2-cyclohexanedicarboxylic acids showed that the retention time of the *cis* diester differed from the *trans* by 0.7 min., thereby excluding the possibility that *cis* diester was present in the mixture of esters arising from ozonolysis.

The Mechanism of Bleaching of Naphthoquinone Imine Dyes in Alkaline Solution

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Received August 6, 1964

The bleaching of alkali-unstable naphthoquinone imine dyes involves initial base-catalyzed hydrolysis of the azomethine linkage to give a *p*-phenylenediamine and a 1,4-naphthoquinone. The quinone subsequently adds water to form a naphthalenetriol which rapidly reduces unhydrolyzed dye to the corresponding leuco base. The hydrolysis step involves reversible addition of OH^- to the azomethine linkage to form a carbinolamine which then collapses to hydrolysis products in a pH-independent step. At sufficiently high pH, the dye can be almost completely converted to the carbinolamine. The proposed mechanism is supported by product and kinetic studies of the bleaching reaction and by a separate kinetic study of the decomposition of the quinone intermediate.

In an earlier paper,[1] a kinetic study of the alkaline bleaching of some unstable naphthoquinone imine dyes established the following facts of mechanistic significance: (1) the bleaching follows an empirical

$$X + OH^- \underset{k_2}{\overset{k_1}{\rightleftarrows}} Z \xrightarrow{k_3} P \qquad (1)$$

$$X + OH^- \xrightarrow{k_4} P \qquad (2)$$

rate law consistent with a general scheme where X represents dye, Z represents an addition complex, and P denotes the product(s) of the irreversible reaction; and (2) the rate of approach to equilibrium between X, OH^-, and Z is slow enough to measure conveniently. The kinetics of bleaching are equally consistent with a scheme in which $k_4 = 0$ (consecutive mechanism) or where $k_3 = 0$ (parallel mechanism). In the consecutive mechanism, the addition complex is an intermediate in the over-all irreversible path. In the parallel mechanism, the addition complex is merely an inert reserve, whereas all irreversible reaction proceeds by way of direct attack of OH^- to give the product. The kinetics of dye bleaching alone cannot distinguish these two mechanisms, and in the earlier work we considered the two as equally likely and evaluated the rate constants as composite constants.

We now report the results of a detailed study of the bleaching of the water-soluble dye I which was used as one of the models in the earlier kinetic study.[1] This dye was selected because bleaching and formation of Z occur in a pH range convenient for measurement and because the suspected intermediate and most of the products are known compounds. The complete bleaching reaction can be divided into two parts: the primary reaction represented by eq. 1 and a secondary reaction involving reduction of dye by the product(s) from the primary reaction. We shall show that in the primary reaction the irreversible part proceeds through the complex Z (consecutive mechanism), the structure of which is suggested. Evidence is given to implicate the reducing agent responsible for the secondary reaction. Kinetic measurements for both the disappearance of dye and the formation of the products as well as some separate product yields are used to support the proposed mechanism. We refer to bleaching as any dark reaction leading to destruction of the dye chromophore and include in this general term hydrolysis, nucleophilic addition, and reduction.

Results and Discussion

The final products of the bleaching reaction are the *p*-phenylenediamine II, 2-acetyl-3-hydroxy-1,4-naphthoquinone (V), and the leuco base VI corresponding to a two-electron reduction of the original dye. Large-scale product isolation studies from concentrated solutions of a number of other naphthoquinone imine dyes have shown that similar products are obtained in every case.[2] The 3-hydroxyquinone (V) was identified in product mixtures by its polarographic wave which was determined from a pure synthetic sample. The leuco base VI was identified by reoxidation to the original dye and comparison of the absorption curve with that of a known sample, and by the identity of the half-wave potential of VI in the product mixtures with that of a pure synthetic sample and of the original dye. The *p*-phenylenediamine II found in the product mixtures was shown to be identical with a known sample by comparison of the properties of dyes formed by oxidative coupling with several substituted α-naphthols.

The quantitative studies of product yields and the kinetic runs were performed on solutions containing I at initial concentrations of 10^{-4} *M* or less. At higher concentrations, deviations from Beer's law and nonlinear dependence of the bleaching rate on the concentration of I indicated that some aggregation of the dye was occurring. The same three products were obtained from bleaching in the very dilute solutions as were isolated from the concentrated solutions. Because of the low concentrations and sensitivity of II and VI to aerial oxidation, all product and most kinetic studies

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(1) R. L. Reeves and L. K. J. Tong, *J. Am. Chem. Soc.*, **84**, 2050 (1962).

(2) D. P. Harnish, unpublished results.