bonate solution was added. The loss of water from the trans-diol VIII gave the anthrolate directly and these rate samples were treated in the same manner as with the cis-dibenzoate. The reaction samples taken of the other compounds were transferred into dilute alcoholic acetic acid to neutralize the base, and the optical density at the appropriate wave length was determined in the acidic solution.

The rate calculations were all made on the basis of the reactions being first order in base and first order in the compound studied. No base was assumed to be used up in the loss of water from the trans-hydroxy benzoate, and one equivalent of base was assumed to be consumed in the eliminations from the trans-dibenzoate and from the trans-diol by the formation of the anthrolate ion.

The rates with the cis-dibenzoate were complicated by the fact that the major product with base was the diol given by saponification. At 22 and 62° the reaction was followed until anthraquinone production appeared to cease. This was found to be at 3.3 and 7% reaction, respectively. The cis-diol was isolated from the reaction mixtures at both temperatures. Rate constants for the elimination reactions were calculated by multiplying the fraction of the reaction observed to be elimination by the appropriate factor (30 in the 22° case) to convert to total fraction reaction and plotting the usual logarithmic function of this, assuming two equivalents of base consumed per mole of dibenzoate, against time (Fig. 2). The rate constant thus obtained when divided by the same conversion factor gave the rate constant for elimination. The 4% deviation between the two runs at 22° seems surprisingly good in view of the very minor extent of the elimination reaction and the consequential small optical densities to be determined (less than 0.1).

The unexpected loss of water, and not benzoic acid, from the trans-hydroxy benzoate was shown to take place both from the spectra of the rate samples being identical to that of 1,5-dichloroanthryl benzoate and the isolation of the pure product from the reaction mixture.

The rate constant given in Table I for the loss of water from the cis-diol was calculated from one point obtained 25 hours after the saponification of the cis-dibenzoate had gone to completion. Correction was made for the 7% elimination from the dibenzoate and for the base used up in the initial fast reactions.

Most of the spectral measurements were obtained with a Beckman model DU spectrophotometer, but some runs were measured with a Coleman model 14 universal spectrophotometer. The latter instrument had a poorer resolving power and spectral curves of products had to be measured for comparison.

Procedure for trans-1,8,9,10-Tetrachloro-9,10-dihydroanthracene.—Solutions were prepared as described in the previous section, but the samples withdrawn from time to time were added to excess standard hydrochloric acid. The excess acid was back titrated with standard sodium hydroxide, using rosolic acid as indicator.

Saponification of 1,5-Dichloroanthryl Benzoate (IXb) and Acetate (IXa).—Solutions were prepared and handled as described above. The extent of reaction was estimated spectrophotometrically from the extent of disappearance of the light absorption maximum in the 370–380 mμ range.

Calculations of Rate Constants.—The form of the second-order rate equation used was

$$d \log \frac{1 - xa\varphi/b}{1 - \varphi} \Big/ dt = \frac{b - xa}{2.303} k$$

where a is initial substrate concentration, b is initial hydroxide concentration, φ is fraction of substrate reacted at time t and k is the specific reaction rate constant. The term x represents the moles of base consumed per mole of substrate reacted and was equal to 1 for the trans-diacetate IVa and dibenzoate IVb (formation of anthryl acetate IXa or benzoate IXb and acylate ion), for the trans-diol VIII (formation of the anthroxide), as well as for the tetrachloro compound, was equal to 2 for the cis-dibenzoate (formation of two moles of benzoate ion) and for the saponification of the anthryl acetate IXa and benzoate IXb, and was equal to 0 for elimination from the trans-monobenzoate VIb.

BOULDER, COLORADO

The Preparation of Stereoisomeric Epoxy Ketones Related to Chalcone Oxide[1,2]

BY HARRY H. WASSERMAN AND NORMAN E. AUBREY

The usual methods for the preparation of α-epoxy ketones involving reaction of α,β-unsaturated ketones with alkaline hydrogen peroxide lead to products whose configurations are not necessarily related to those of the starting olefins. A stereospecific method for the preparation of epoxy ketones in the present work involves reduction of the carbonyl group of the cis or trans unsaturated ketone to the alcohol, epoxidation with perbenzoic acid, and then reoxidation of the epoxy alcohol to the ketone by means of chromic anhydride–pyridine complex. In this way the hitherto unknown cis-chalcone oxide has been prepared. Correlations between the configuration and the ultraviolet absorption spectra of a number of cis-and trans-epoxy ketones have been made.

In connection with the determination of the configurations of cis- and trans-γ-halo-α-epoxy ketones,[3] recently shown[4-6] to be the products of a Darzens-like condensation of the phenacyl halides with sodium methoxide, methods were sought for the conversion of α,β-unsaturated ketones of known configuration to the corresponding cis- and trans-epoxides. The general method commonly employed in the formation of α-epoxy ketones from

α,β-unsaturated ketones involves treatment with alkaline hydrogen peroxide, the method of Weitz and Scheffer.[7] This method is, however, limited by the fact that the configuration of the starting olefin is not necessarily preserved in the process of epoxide formation. Thus, as has recently been shown,[8] both the cis and trans isomers of chalcone[9] react with alkaline hydrogen peroxide to yield the same epoxy ketone, m.p. 90°, while under the same reaction conditions the known form of dypnone, which is assumed to have the trans configuration, reacts[5] to form two epoxy ketones, m.p. 94 and 164°. It has been found[5] furthermore that in the preparation of epoxy ketones related to dypnone oxide, the product which is formed initially, is con-

(1) Taken from a thesis submitted to the Graduate School of Yale University by N. E. Aubrey in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1954.

(2) Presented, in part, at the 124th Meeting of the American Chemical Society, Chicago, Ill., Sept. 6 to 11, 1953.

(3) O. Widman, Ann., 400, 86 (1913).

(4) J. Berson, THIS JOURNAL, 74, 5175 (1952).

(5) H. H. Wasserman, N. E. Aubrey and H. E. Zimmerman, ibid., 75, 96 (1953).

(6) C. L. Stevens, R. J. Church and V. J. Traynelis, J. Org. Chem., 19, 522 (1954).

(7) E. Weitz and A. Scheffer, Ber., 54, 2327 (1921).

(8) W. B. Black and R. E. Lutz, THIS JOURNAL, 75, 5990 (1953).

(9) R. E. Lutz and R. H. Jordon, ibid., 72, 4090 (1950).

verted, in part, to the isomeric oxide, merely by standing in alcoholic base.
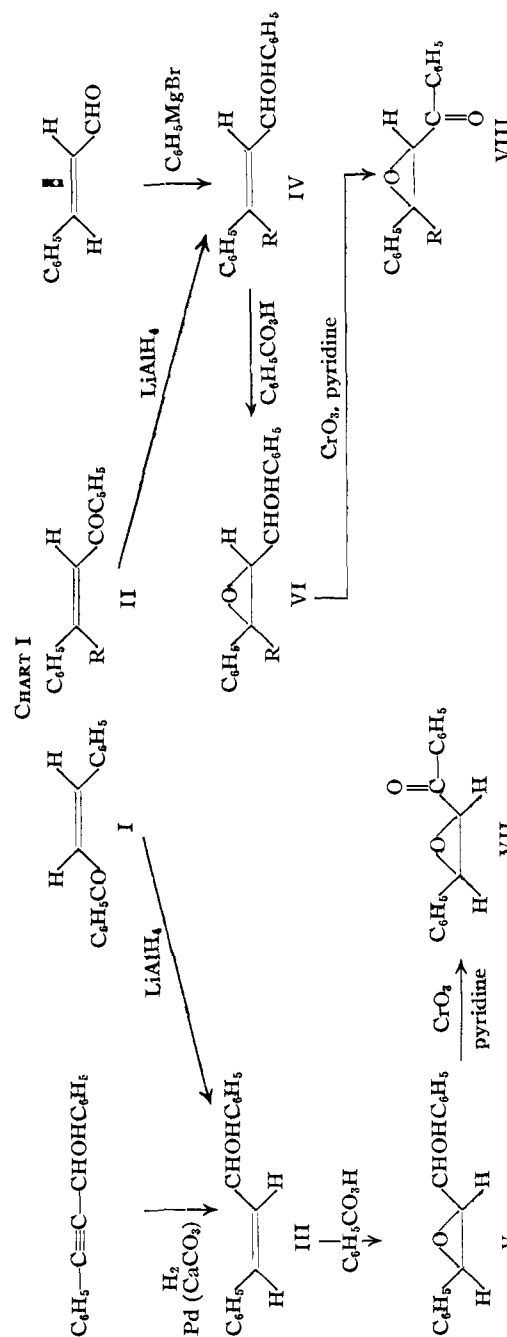
On the other hand, the reaction of perbenzoic acid with unsaturated systems leads to epoxides having the same configuration as the original olefin.[10] This method would be applicable to the formation of the desired cis and trans epoxy ketones in the present work were it not for the fact that the reaction, involving attack of an electron-deficient fragment, is not useful when electron-withdrawing groups are attached to the double bond.[11,12] In order to make use of this reagent, therefore, the electron-withdrawing carbonyl group of the unsaturated ketone was first reduced to the alcohol, which was then subjected to perbenzoic acid oxidation, followed by reoxidation to the ketone under mild conditions. By this process, as is described below, and outlined in Chart I, trans-chalcone was converted to trans-chalcone oxide,[13] cis-chalcone, to the hitherto unknown cis-chalcone oxide, and dypnone, to the corresponding trans-dypnone oxide.[5]

trans-Chalcone (II, R = H) was reduced by lithium aluminum hydride to the corresponding trans-alcohol (IV, R = H), in 76% yield, accompanied by 10% of 1,3-diphenyl-1-propanone.[14] This alcohol had been prepared previously, among other methods,[15,16] by the reaction of trans-cinnamaldehyde with phenylmagnesium bromide, assignment of configuration having been made on the basis of mode of formation.[17] A similar reduction of cis-chalcone (I) by lithium aluminum hydride yielded an oil (III) whose infrared spectrum was distinctly different from that of the trans-alcohol but consistent with the same gross structure. This alcohol had been prepared previously[17] by the partial hydrogenation of 1,3-diphenyl-2-propyne-1-ol. The hydrogenation was repeated and the product found to be identical with that obtained by reduction of cis-chalcone.

Both unsaturated alcohols were then treated with perbenzoic acid. The product in the trans case (VI, R = H) was an oil which appeared to polymerize upon distillation. It was therefore used generally in the crude state.[18] The cis-epoxy alcohol V was obtained as a crystalline solid in yields of 65–70%. No trace of the isomeric trans-epoxy alcohol was found in the latter residual reaction mixture.

Oxidation of the trans-epoxy alcohol with chromic anhydride–pyridine complex[19] gave a 60% yield of a crystalline product, m.p. 89°, which was identical with the epoxide obtained by treatment of chal-

cone with alkaline hydrogen peroxide, or by the condensation of benzaldehyde with phenacyl bromide. No isomeric epoxy ketone was found. Since all of the steps in the conversion of the trans unsaturated ketone to the α,β-epoxy ketone were carried out under conditions which would not affect the configurations of the carbon atoms forming the ethylene oxide ring, the oxide, m.p. 89°, is assigned a trans structure (VIII, R = H).

CHART I

(10) D. Swern, THIS JOURNAL, 70, 1235 (1948).

(11) J. Boeseken, Rec. trav. chim., 45, 838 (1926).

(12) D. Swern, THIS JOURNAL, 69, 1692 (1947).

(13) N. H. Cromwell and M. A. Graff, J. Org. Chem., 17, 414 (1952).

(14) This product apparently arose either from 1,4-reduction of the unsaturated system (cf. R. E. Lutz and D. F. Hinkley, THIS JOURNAL, 72, 4091 (1950)), or from rearrangement of the unsaturated alcohol (cf. H. Nomura, Bull. soc. chim., 37, 1245 (1925)).

(15) H. Meerwein and R. Schmidt, Ann., 444, 221 (1925).

(16) W. L. Truett and W. N. Moulton, THIS JOURNAL, 73, 5913 (1951).

(17) K. Campbell, B. Campbell and M. McGuire, Proc. Indiana Acad. Sci., 50, 87 (1940).

(18) No appreciable amount of impurity was discovered in subsequent reactions using the crude product.

(19) G. Poos, G. Orth, R. Orth, R. Beyler and L. Sarett, THIS JOURNAL, 75, 428 (1953).

Oxidation of the cis-alcohol V under conditions similar to those described above, yielded a crystalline material (70%), m.p. 97°, which was not identical with trans-chalcone oxide. That it was, in fact, an isomeric α-epoxy ketone, was shown by its elementary analysis, infrared spectrum, ultra-

violet spectrum (Table I), and ready reaction with potassium iodide in glacial acetic acid. This compound, the only product isolated in the oxidation of V, is assigned the *cis*-chalcone oxide structure VII.

The same sequence of reactions was then carried out in the dypnone series. Here, however, only one isomer of the starting unsaturated ketone was available. Dypnone[20] (*trans* II, R = CH₃) was reduced with lithium aluminum hydride to give a clear, viscous liquid which could not be distilled without polymerization. This product, 1,3-diphenyl-2-butene-1-ol (IV, R = CH₃) was treated with perbenzoic acid in chloroform to yield a crystalline oxide (VI, R = CH₃) which decomposed readily upon standing in solution, or in the solid state.[21] It was, in fact, necessary to work up the perbenzoic acid reaction mixture somewhat before completion of the reaction (as indicated by consumption of perbenzoic acid), since the yields of oxide declined sharply on longer standing. The epoxy alcohol was oxidized with chromic anhydride–pyridine complex in the usual manner.[19] A 60% yield of crystalline material, m.p. 93°, was thus obtained which was identical with the low-melting form of dypnone oxide.[5] This is then the *trans* form of dypnone oxide (VIII, R = CH₃), while the higher-melting isomer, m.p. 160°, obtained along with the *trans* form in the alkaline epoxidation of dypnone,[5] must be assumed to have the *cis* configuration.

Correlation of Configuration with Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the isomeric dypnone and chalcone oxides, whose configurations now have been established by synthesis, have been studied further in this work. It has been found (Table I) that in both series, the *cis* isomers absorb at a somewhat lower wave length and with less intensity than the *trans* compounds, a result which parallels findings in the ethyleneimine ketone series.[22] Cromwell[13] has explained the latter results in terms of a steric inhibition of hyperconjugation in the *cis* isomers and has suggested that this effect may be generalized to include epoxy ketones and cyclopropyl carbonyl compounds as well. In Table II are listed the ultraviolet absorption maxima of a number of epoxy ketones whose configurations have not yet been established by chemical means. Where two isomers of a given ketone are available, the one which has the higher wave length of maximum absorption and the higher molar absorptivity has been assigned the *trans* configuration. The assignment of configuration on the basis of ultraviolet absorption spectra, as outlined above, is in complete agreement with the configurational assignments made in the case of the related γ-halo-α-epoxy ketones (the so-called

(20) This material is a liquid, apparently consisting of one pure isomer. Successive fractions taken during its distillation do not vary in refractive index, and its ultraviolet absorption spectrum (λmax 287 mμ, ε 18700) shows no appreciable absorption in the region where the *cis* isomer would be expected to absorb.[5]

(21) The stability of the product varied greatly from one batch to another. It is suggested that the decomposition may have taken place by an autoxidation similar to that reported by Kohler (THIS JOURNAL, **53**, 205 (1931) who isolated an unstable peroxide from the corresponding triphenyl epoxy alcohol.

(22) N. H. Cromwell and co-workers, THIS JOURNAL, **73**, 1044 (1951).

chloro- and bromodiphenacyls.) The stereochemistry of the epoxy ketones in the latter series was established independently on the basis of their stereospecific reactions with basic reagents.[23a,b] Among these compounds (Table I, X = CH₂Cl, CH₂Br) the *trans* isomers show absorption at longer wave lengths with greater intensity.[6]

TABLE I

ULTRAVIOLET ABSORPTION SPECTRAL DATA (ABSOLUTE ETHANOL SOLUTIONS)

$$C_6H_5-\overset{\overset{\displaystyle O}{\diagup\!\diagdown}}{\underset{X\quad H}{|\quad|}}-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \qquad A$$

Epoxy ketone A, X =	M.p., °C.	Configuration	λmax, mμ	ε × 10⁻³
H	89–90	*trans*	250.5	17.2
H	96–97	*cis*	248	12.9
CH₃	94–95	*trans*	249	16.6
CH₃	163–164	*cis*	247	13.3
CH₂Cl	122–124	*trans*	251.5	16.1
CH₂Cl	151–152	*cis*	250	13.0
CH₂Br	135–136[5]	*trans*	252	16.6
CH₂Br	162–163	*cis*	250	13.3

TABLE II

ULTRAVIOLET ABSORPTION SPECTRAL DATA (ABSOLUTE ETHANOL SOLUTIONS)

$$P-\!\!\underset{Q}{\diagup\!\!\diagdown}\!\!-\overset{\overset{\displaystyle O}{\diagup\!\diagdown}}{\underset{H\quad H}{|\quad|}}-\overset{\overset{\displaystyle O}{\|}}{C}-C_6H_5 \qquad B$$

Epoxy ketone B P	Q	M.p., °C.	Probable configuration	λmax, mμ	ε × 10⁻³
NO₂	Hᵃ	124–125	*cis*	253.5	17.8
NO₂	Hᵃ	151–152	*trans*	257.5	19.4
H	NO₂ᵇ	113–114	*trans*	252.5	20.6
H	NO₂ᶜ	176 dec.	*cis*	251.5	18.8

ᵃ See reference 24a. ᵇ See reference 24b.

Experimental

trans-1,3-Diphenyl-2-propene-1-ol.—Twenty grams (0.096 mole) of benzalacetophenone was dissolved in 210 ml. of anhydrous ether and cooled to −10°. A solution of lithium aluminum hydride (50 ml.) containing 0.029 mole of active reagent was added at such a rate that the solution temperature did not rise above −7°. As soon as all the reagent had been added, water was dropped in slowly until the hydride was decomposed completely. The ether solution was decanted, the residue extracted, and the combined extracts washed with 10% sulfuric acid, and then with water. Recrystallization of the crude reaction product from high boiling ligroin gave 15.1 g. (75%) of *trans*-1,3-diphenyl-2-propene-1-ol, m.p. 55–57°. Evaporation of the filtrates and recrystallization of the residue from ethanol gave 1.9 g. of 1,3-diphenyl-1-propanone (m.p. 66–70.5°; oxime, m.p. 83.5°).

This alcohol was identical (mixed m.p., and infrared spectra) with the product prepared by the method of Campbell and co-workers from cinnamaldehyde and phenylmagnesium bromide.[17]

trans-1,3-Diphenyl-2,3-epoxy-1-propanol.—To a solution of 2.59 g. (0.012 mole) of *trans*-1,3-diphenyl-2-propene-1-ol in 100 ml. of chloroform was added 25 ml. of a solution containing 0.015 mole of perbenzoic acid. The mixture was shaken intermittently at 8° for 18 hours. Titration of an

(23) (a) H. H. Wasserman and J. B. Brous, *J. Org. Chem.*, **19**, 515 (1954); (b) C. L. Stevens and V. J. Traynelis, *ibid.*, **19**, 533 (1954).

(24) (a) S. Bodforss, *Ber.*, **49**, 2795 (1916); (b) *ibid.*, **51**, 192 (1918).

aliquot of the reaction mixture at the end of that time indicated virtually complete reaction. The solution was washed twice with 8% sodium hydroxide, twice with water, the chloroform solution dried and the solvent removed *in vacuo.* Distillation of the residue (150° at 0.02 mm.) was accompanied by some decomposition of the product and did not seem to effect further purification as indicated by the infrared spectrum. The material was generally used in crude form. The yield of crude material was quantitative; n^{25}D 1.5729.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.21; H, 6.24.

trans-1,3-Diphenyl-2,3-epoxy-1-propanone.—One and one-tenth grams (0.049 mole) of *trans*-1,3-diphenyl-2,3-epoxy-1-propanol was dissolved in 11 ml. of reagent grade pyridine. The chromic anhydride-pyridine complex[16] was prepared by adding 1.23 g. (0.012 mole) of chromic anhydride in small portions, with shaking and cooling, to 10 ml. of pyridine. The solution of the alcohol was added to the suspension of the complex, and the mixture was allowed to stand at room temperature for eight hours with occasional shaking. It was then diluted with water and extracted with ether. The ether extracts were washed with water, dilute hydrochloric acid and finally sodium carbonate solution. Upon removal of the ether, 0.90 g. of crude material remained. One recrystallization from ethanol gave 0.67 g. (61%) of crystals, m.p. 77–83°, whose infrared spectrum was identical with that of the known chalcone oxide, m.p. 89–90°.[18] Further purification of this product as well as investigation of the filtrate of the above recrystallization yielded no trace of the isomeric epoxy ketone.

1,3-Diphenyl-2-propyne-1-ol.—The method used was that of Campbell and co-workers.[17] The yield of 1,3-diphenyl-2-propyne-1-ol was 76%, b.p. 159° (1.3 mm.), n^{25}D 1.6147 (lit.[17] n^{20}D 1.5842).

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86 35; H, 5.49.

cis-1,3-Diphenyl-2-propene-1-ol (By **Hydrogenation of the Acetylene**).—To a solution of 10.14 g. (0.049 mole) of 1,3-diphenyl-2-propyne-1-ol in 200 ml. of ethanol was added 360 mg. of palladium-on-calcium carbonate, prepared according to the method of Busch and Stove.[25] The mixture was allowed to take up 95% of the theoretical amount of hydrogen under conditions of atmospheric pressure and room temperature. The solvent and catalyst were removed and the residue distilled through a 15-cm. spiral column. The main fraction of material, b.p. 147–150° (1.3 mm.), amounted to 7.2 g. (71%), n^{25}D 1.6011. The refractive index reported by Campbell[17] for his product, prepared using Raney nickel rather than palladium, was n^{20}D 1.5821.

The infrared spectrum of this product was superimposable upon the spectrum of the material obtained by reduction of *cis*-chalcone with lithium aluminum hydride.

cis-1,3-Diphenyl-2-propene-1-ol (By **Reduction of *cis*-Chalcone**).—A solution of 1 g. (0.005 mole) of *cis*-chalcone, in 25 ml. of dry ether, at −11° was treated dropwise with ethereal lithium aluminum hydride (0.002 mole). The reaction mixture was stirred for four minutes after the hydride had been added, and then hydrolyzed with water. The ether solution was washed, dried over sodium sulfate and the ether removed to give 1.05 g. of clear liquid, the infrared spectrum of which was superimposable upon the spectrum of the product obtained by partial hydrogenation of 1,3-diphenyl-2-propyne-1-ol.

cis-1,3-Diphenyl-2,3-epoxy-1-propanol.—A solution of 3.98 g. (0.019 mole) of *cis*-1,3-diphenyl-2-propene-1-ol in 100 ml. of chloroform was treated with 35 ml. (0.020 mole) of perbenzoic acid solution, and the mixture maintained at 8° for 12 hours. At the end of this time, titration of an aliquot indicated that 80% of the theoretical amount of perbenzoic acid had been consumed. The chloroform solution was extracted with 8% sodium hydroxide, washed with water and the chloroform removed. The residue was taken up in warm petroleum ether from which 2.56 g. (60%) of material crystallized, m.p. 81–83°.

Investigation of the filtrate gave further crude material corresponding to the above, but no isomeric epoxy alcohol.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.92; H, 6.75.

(25) M. Busch and H. Stove, *Ber.,* **49,** 1063 (1916).

cis-1,3-Diphenyl-2,3-epoxy-1-propanone.—A solution of 2.35 g. (0.01 mole) of III in 23 ml. of pyridine was added to a suspension of 2.85 g. (0.029 mole) of chromic anhydride in 28 ml. of pyridine. This reaction mixture was maintained at room temperature with agitation for 12.5 hours. The solid was then filtered, the filtrate diluted with water and both solid and solution extracted four times with ether. The combined extracts were washed with water, dilute hydrochloric acid and finally sodium carbonate solution. Removal of the ether left an oil which deposited crystals readily. One recrystallization from ethanol gave 1.55 g. (65%) of white crystals, m.p. 92–96°. This material depressed the melting point of the known chalcone oxide (m.p. 89–90°). Further recrystallization from petroleum ether gave white needles, m.p. 96–97°. From the filtrates of these two recrystallizations no trace of the isomeric epoxy ketone could be found.

Anal. Calcd. for $C_{15}H_{12}O_2$: C, 80.33; H, 5.40. Found: C, 80.37; H, 5.57.

trans-1,3-Diphenyl-2-butene-1-ol.—Dypnone (19.1 g., 0.086 mole, n^{25}D 1.6300) was dissolved in 180 ml. of absolute ether. The solution was cooled in an ice–methanol-bath, while 45.0 ml. of an ether solution of lithium aluminum hydride containing 0.024 mole of active reagent was added dropwise with mechanical stirring. The temperature of the reaction mixture was maintained between −11 and −13°. When the addition of the reducing agent was complete, water was added dropwise until the solution had cleared.

The inorganic residue was extracted with ether and the combined ether solutions washed successively with ammonium chloride solution, dilute hydrochloric acid and finally dilute sodium bicarbonate solution. The ether solution was dried over sodium sulfate and the solvent was removed. The residue, 18.8 g., n^{25}D 1.5989, of colorless oil could not be distilled without polymerization. It was used therefore in crude form.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.58; H, 7.26.

trans-1,3-Diphenyl-2,3-epoxy-1-butanol.—Five grams (0.022 mole) of *trans*-1,3-diphenyl-2-butene-1-ol was dissolved in 100 ml. of chloroform. Fifty-five milliliters of a perbenzoic acid solution containing 0.032 mole of active oxygen was added. The reaction mixture was kept at 8° for 12 hours, at the end of which time it was extracted with sodium carbonate solution, washed with water and dried over sodium sulfate. Removal of the chloroform, and crystallization from ligroin gave 3.0 g. (58%) of solid material. Two recrystallizations from ligroin gave white crystals, m.p. 84.5–86.°

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.93.

trans-1,3-Diphenyl-2,3-epoxy-1-butanone.—A solution of 2.40 g. (0.011 mole) of *trans*-1,3-diphenyl-2,3-epoxy-1-butanol in 25 ml. of pyridine was added to a suspension of chromic anhydride–pyridine complex prepared by the cautious addition of 5.00 g. (0.050 mole) of chromic anhydride to 50 ml. of pyridine. The suspension was allowed to stand at room temperature with occasional shaking for 14 hours. The brown solid which formed was then filtered, the filtrate was diluted with water and then saturated with sodium chloride. Both solid and liquid were extracted with ether. The combined ether extracts were washed with dilute hydrochloric acid and with water, and were dried over sodium sulfate. Removal of the ether and recrystallization from ethanol gave 1.57 g. (60%) of white plates, m.p. 90–93°. This material did not depress the melting point of the low-melting dypnone oxide, prepared from dypnone by treatment with alkaline hydrogen peroxide. The infrared spectra of the two products were identical.

An additional 0.15 g. of the same product in a less pure state was obtained from the mother liquors, but no trace of the isomeric epoxide (m.p. 163–164.5°) could be found.

The Isomeric 1-Phenyl-3-(*p*-nitrophenyl)-2,3-epoxy-1-propanones.—A solution of 10.0 g. (0.0502 mole) of phenacyl bromide and 7.4 g. (0.0490 mole) of *p*-nitrobenzaldehyde (Matheson) in 180 ml. of absolute ethanol was stirred in a water-bath kept at 19–20°. Twenty-nine and two-tenths ml. of a solution of sodium methoxide containing 0.046 mole of base was added dropwise over a period of ten minutes. After an additional five minutes of stirring, the solution was

chilled in an ice-bath and the solid which precipitated was filtered (8.6 g., m.p. 147–150°). The filtrate was diluted with water and an additional batch of solid was filtered (2.2 g., m.p. 102–109°), yield 88%.

One recrystallization of the higher melting material from benzene gave 8.0 g. of pale yellow plates, m.p. 149–150.5°. Two recrystallizations of the low melting product from ethyl acetate gave cubes, m.p. 123–125.5°. Bodforss[24a]

reports the isolation, under similar conditions, of only one compound, m.p. 148°.

The previously unreported isomer, m.p. 123–125.5°, was analyzed.

Anal. Calcd. for $C_{15}H_{11}NO_4$: C, 66.92; H, 4.12; N, 5.20. Found: C, 66.45; H, 4.13; N, 5.20.

New Haven, Conn.

The Synthesis of Bicyclo[2,2,2]-2,5-octadiene[1,2]

By Jack Hine, John A. Brown, Leon H. Zalkow, William E. Gardner and Mildred Hine

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A synthesis is reported for bicyclo[2,2,2]-2,5-octadiene (II), a compound of particular interest because of unusual possibilities for interaction between non-conjugated double bonds. Two syntheses, one involving the dehalogenation of 2,3-dichlorobicyclo[2,2,1]-5-heptene and the other the dehydrohalogenation of 2-chlorobicyclo[2,2,1]-5-heptene, are reported also for the related compound bicyclo[2,2,1]-2,5-heptadiene (I). The preparation of II was accomplished by the dehydrohalogenation of a mixture of monochloro-2-bromobicyclo[2,2,2]octanes. The structures of I and II are proven by their reduction (by two moles of hydrogen) to the corresponding saturated hydrocarbons. In addition, II has been shown to form a crystalline tetrabromide and to yield ethylene and benzene upon pyrolysis. An improved method of preparing 1,3-cyclohexadiene also is reported.

Introduction

There have been recently reported several studies of what we shall call *homoconjugation*, in which an olefinic double bond interacts with an atom which is separated from the nearest unsaturated carbon by one saturated carbon atom. These studies include the *i*-cholesteryl rearrangement,[3] rearrangements of dehydronorbornyl compounds to nortricyclene derivatives,[4] the acetolysis of 3-phenyl-2-butyl *p*-toluenesulfonate[5] and related reactions,[6] etc.

We were interested therefore in learning whether the effects of homoconjugation could be detected in the reactions of bicyclo[2,2,1]-2,5-heptadiene (I) and bicyclo[2,2,2]-2,5-octadiene (II).

I   II
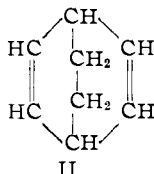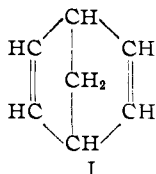
Such homoconjugation might reasonably be expected since the double bonds are so situated that their π-orbitals should overlap somewhat.[7]

We were further interested in learning whether this sort of interaction between double bonds on adjacent bridges of a bicyclic ring system might give aromatic character to bicyclo[2,2,2]-2,5,7-octatriene (III). A view of III from the top suggests that the π-orbitals of the double bonds might overlap enough for the formation of a somewhat cylin-

drical molecular orbital (containing six electrons) around the middle of the molecule.[7]
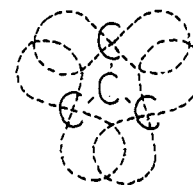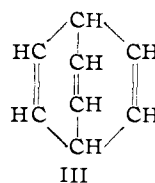
III   Top view of III

However, it may also be seen to be impossible to arrange the π-orbitals in a way which gives all overlapping lobes the same algebraic sign, as is said to be required.[7] Because this is the first case known to us in which the *sign* of an atomic orbital has been of such importance, compound III is of particular interest. While some derivatives of I and II such as the 2- and 3-carboxy compounds are known,[8] any study of interaction between the carbon–carbon double bond in these derivatives would be greatly complicated by the interaction of one of the double bonds with the functional group(s). Triptycene[9] can be thought of as the tribenzo derivative of III but the π-electrons in this compound may be too occupied with the benzenoid resonance to permit much interaction between adjacent bridges, although the difference in absorption spectra between triptycene and triphenylmethane has been attributed to such interaction.[9b]

Since this investigation was begun, Parham, Hunter, Hanson and Lahr have reported the preparation of a small amount of material which was probably the bicycloheptadiene, I.[10] This compound was prepared by the Chugaev degrada-

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) Taken in part from the Ph.D. thesis of John A. Brown, 1954.

(3) C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946); S. Winstein and R. Adams, This Journal, **70**, 838 (1948); R. G. Pearson, L. A. Subluskey and L. C. King, *ibid.*, **70**, 3479 (1948).

(4) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(5) D. J. Cram, *ibid.*, **71**, 3863 (1949).

(6) *Cf.* E. M. Kosower, *Science*, **113**, 605 (1951).

(7) For a discussion of π-orbitals and their interactions to form multiple bonds and aromatic rings see C. A. Coulson, "Valence," Oxford University Press, London, 1952, Sections 4.7, 8.7 and 9.1.

(8) K. Alder, G. Stein, S. Schneider, M. Liebmann, E. Rolland and G. Schulze, *Ann.*, **525**, 183 (1936); O. Diels, K. Alder and H. Nienburg, *ibid.*, **490**, 236 (1931); K. Alder and H. F. Rickert, *Ber.*, **70B**, 1364 (1937).

(9) (a) P. D. Bartlett, M. J. Ryan and S. G. Cohen, This Journal, **64**, 2649 (1942); (b) P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

(10) W. E. Parham, W. T. Hunter, R. Hanson and T. Lahr, *ibid.*, **74**, 5646 (1952).