Anal. Calcd. for $C_{16}H_{10}O_5$: C, 68.02; H, 3.58. Found: C, 67.68; H, 3.96.

The hydrolysis product was identical by infrared analysis with an authentic sample of diphthalyllactonic acid[22] obtained by the alkaline hydrolysis of biphthalyl[21]; on heating above 240° the colorless product turned yellow and biphthalyl was regenerated,[22] as identified by its infrared spectrum.

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO]

Condensed Cyclobutane Aromatic Compounds. XXVII. 1,2-Dimethylenebenzocyclobutene and Related Substances[1]

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RECEIVED FEBRUARY 20, 1963

Benzocyclobutadienoquinone (III) has been converted into 1-keto-2-carbomethoxymethylenebenzocyclobutene (V), 1,2-dicarbomethoxymethylenebenzocyclobutene (IX), and 1,2-dimethylenebenzocyclobutene (I). Some chemical and physical properties of these compounds are described.

The delocalization energies of a number of methylenecyclobutenes and ketocyclobutenes have been calculated by the molecular orbital method.[3] According to these calculations, 1,2-dimethylenebenzocyclobutene (I) and 1-keto-2-methylenebenzocyclobutene (II) have delocalization energies of 3.15β and 3.17β, respectively. These values are of the same order of magnitude as that (3.13β) predicted for benzocyclobutadienoquinone (benzocyclobutenedione, III), a known compound of considerable stability.[4] We now wish to report in detail the synthesis and properties of 1,2-dimethylenebenzocyclobutene (I) and its 1,2-dicarbomethoxy derivative IX, and of the carbomethoxy derivative (V) of 1-keto-2-methylenebenzocyclobutene (II).

Reaction of Benzocyclobutadienoquinone with Wittig Reagents.—The most direct approach to the synthesis of diene I appears to be the reaction of dione III with triphenylphosphinemethylene (VI).[5] However, the only isolable product of this reaction is triphenylphosphine. After the successful synthesis of diene I by another route (see below), this reaction was repeated and it was shown by gas chromatography that I is not produced, even in trace amounts. When Wittig reagent VI was replaced by the much less nucleophilic triphenylphosphinecarbomethoxymethylene (VII), olefin formation took place cleanly in methylene chloride at room temperature, and the reaction could be controlled to give either the mono- or the diolefinic product. By the slow addition of one equivalent of reagent VII to dione III, 1-keto-2-carbomethoxymethylenebenzocyclobutene (V), m.p. 87–88°, was obtained in 93% yield. The keto ester V exhibits strong bands in the infrared at 5.62, 5.83, and 5.92 μ, characteristic of a carbonyl in a four-membered ring, an ester carbonyl, and the conjugated exocyclic olefin function, respectively. The ultraviolet spectrum showed only one broad maximum in ethanol at 246 mμ (log ϵ 4.55). The ketonic carbonyl of V reacted with 2,4-dinitrophenylhydrazine to give a normal derivative (VIII), m.p. 235° dec. In addition, it reacted readily with Wittig reagent VII to give 1,2-dicarbomethoxymethylenebenzocyclobutene (IX), m.p. 123–124°, also obtainable directly and in 85% yield from dione III and two equivalents of VII. Diester IX shows ester car-

bonyl absorbtion at 5.80 μ, as well as a strong band at 6.04 μ attributed to the conjugated diene system. Its ultraviolet spectrum in ethanol is characterized by a very strong broad band (log ϵ 4.64) centered at 256 mμ and a second, weaker, but broad band at 290.5 mμ (log ϵ 410). The diene system of IX was quite stable under both basic and acidic conditions as evidenced by the alkaline hydrolysis of IX to the corresponding dicarboxylic acid X, m.p. 313–315°, and the re-esterification of X to IX with methanol containing a drop of sulfuric acid. A number of attempts were made to decarboxylate diacid X to dimethylenebenzocyclobutene by pyrolyzing it in the presence of soda lime, barium oxide, or quinoline containing copper sulfate.[6]
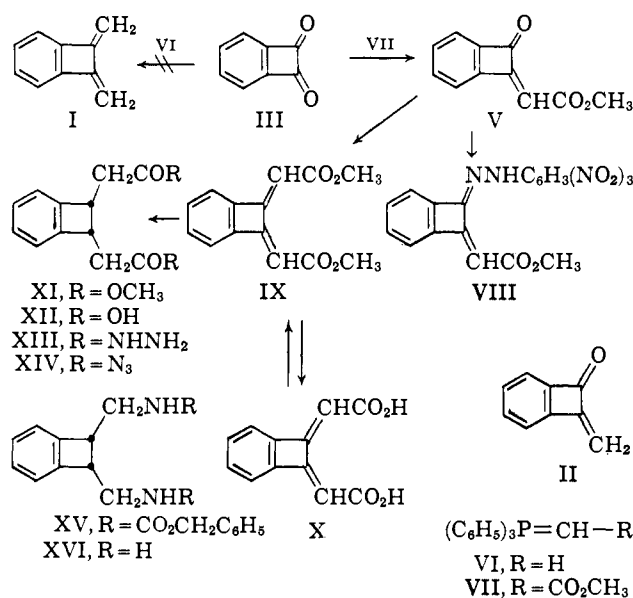
In all cases only a trace of volatile material was obtained, although under the latter conditions at 200–210° the theoretical amount of carbon dioxide was evolved during one hour.

Catalytic reduction of diester IX took place readily at room temperature in the presence of palladium-on-charcoal to give *cis*-dicarbomethoxymethylbenzocyclobutene (XI) as an oil which was hydrolyzed by base to the corresponding dicarboxylic acid (XII), m.p. 189–190°. The reduced diester XI was characterized in the ultraviolet by the band triplet (λ_{max} 259, 265, and 271 mμ) typical of the unconjugated benzocyclobutene chromophore.[7] Several attempts were made

(1) For preliminary communications of portions of this investigation, see M. P. Cava and R. J. Pohl, *J. Am. Chem. Soc.*, **82**, 5242 (1960); M. P. Cava, M. J. Mitchell and R. J. Pohl, *Tetrahedron Letters*, **No. 18**, 825 (1962).

(2) Fellow of the Alfred P. Sloan Foundation, 1958–1962.

(3) S. L. Manatt and J. D. Roberts, *J. Org. Chem.*, **24**, 1336 (1959).

(4) (a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 3606 (1957); (b) M. P. Cava, D. R. Napier and R. J. Pohl, *ibid.*, **85**, 2076 (1963).

(5) G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954).

(6) C. Walling and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **69**, 852 (1947).

(7) M. P. Cava and D. R. Napier, *ibid.*, **80**, 2255 (1958).

to convert XI or XII into the unknown diamine XVI, which might serve as a starting material for the synthesis of diene I *via* the Hoffmann method. When diester XI was heated with hydrazine hydrate in refluxing ethanol, the crystalline dihydrazide XIII, m.p. 211–214°, was obtained in almost quantitative yield. The reaction of XIII with nitrous acid afforded the corresponding diazide XIV which was decomposed thermally, without purification, in the presence of benzyl alcohol to give the bisbenzylurethan XV, m.p. 153–155°. The identical urethan XV was obtained from the dicarboxylic acid XII *via* the acid chloride and azide XIV. Neither acid hydrolysis nor catalytic reduction according to Bergmann[8] was successful in converting XV into a definite, characterizable product. Further investigations in this series were abandoned at this point in favor of a different approach to I.

Reaction of Benzocyclobutadienoquinone with Methylmagnesium Bromide.—A study of the reaction of dione III with methylmagnesium bromide led eventually to a successful synthesis of 1,2-dimethylenebenzocyclobutene. Two colorless crystalline compounds of composition $C_{10}H_{12}O_2$ were obtained in good yield from this reaction. Since treatment of dione III with phenylmagnesium bromide gave only 1,2-diphenylisobenzofuran,[4b] it seemed possible that methylmagnesium bromide had also given ring cleavage products, namely the *cis* and *trans* isomers of hemiketal XVII. The hemiketal structures were readily eliminated, however, on the basis of nuclear magnetic resonance spectra.[9] The spectrum of each isomer shows only a single sharp methyl peak, whereas a compound of structure XVII should show two distinctly different methyls, one of which would be split into a doublet. It was concluded, therefore, that the methyl Grignard products were indeed the normal dimethyldiols XVIII and XIX. Assignment of configuration to the isomers was made possible by a study of their rates of oxidation with lead tetraacetate.[10] The isomer of m.p. 122–123° had a rate constant of 116 and was assigned the *trans* configuration XIX; the isomer of m.p. 157° had a rate constant greater than 30,000, similar to that found for *cis*-1,2-benzocyclobutenediol,[4b] and it was assigned the *cis* configuration XVIII. Although both isomers showed the triplet typical of an unconjugated benzocyclobutene in the ultraviolet, the extinction coefficients for the maxima of the *trans* compound were significantly less than those of the *cis* product. The same ultraviolet absorption pattern was followed by the dinitrate esters XXIVa and XXIVb of *cis*- and *trans*-1,2-benzocyclobutenediols[4b]: the absorption maxima were essentially the same, but the extinction coefficients of the *trans*-ester were lower than those of the *cis* analog. These results, summarized in Table I, are suggestive of a general effect on the electronic spectra of *cis*- and *trans*-1,2-disubstituted benzocyclobu-

TABLE I

ULTRAVIOLET COMPARISON OF 1,2-DIOXYGENATED
BENZOCYCLOBUTENE DERIVATIVES

Benzocyclobutene deriv.	λ_{max} mμ (log ϵ)		
cis-Dinitrate XXIVa[4b]	258.5 (3.03)	265 (3.17)	271 (3.14)
cis-Dimethyldiol XVIII	258 (3.02)	264 (3.18)	270.5 (3.14)
cis-Diol XXV[4b]	259 (3.03)	265 (3.19)	272 (3.12)
trans-Dinitrate XXIVb[4b]	258 (2.96)	264 (3.10)	270.5 (3.04)
trans-Dimethyldiol XIX	258 (2.98)	264 (3.15)	270.5 (3.09)

(8) M. Bergmann and L. Zervas, *J. Biol. Chem.*, **113**, 341 (1936).

(9) Details are given in the Experimental section. We are very grateful to Dr. H. E. Simmons (E. I. du Pont de Nemours and Co., Inc.) for providing us with these spectra, which were run in deuterioacetone.

(10) See ref. 4b and papers by Criegee, *et al.*, cited therein. Units are in l./mole/min.
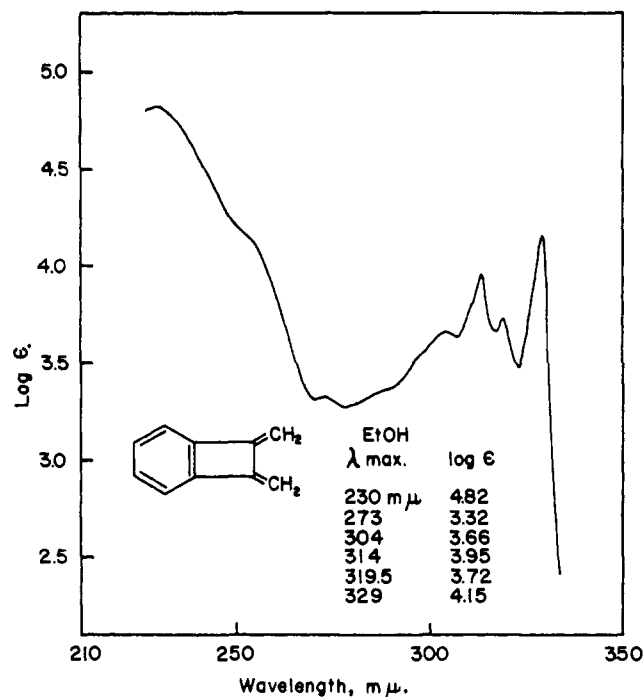

Figure 1.

tenes when substituents such as oxygen functions are present on the cyclobutene ring. Such functions which bear unshared electron pairs may be capable of interacting with the π-orbitals of the aromatic ring, thus giving rise to the observed variation of absorption intensity in each *cis–trans* pair.

Despite the fact that the dimethyldiols XVIII and XIX are formally tertiary benzylic alcohols, neither compound showed any tendency to undergo dehydration when heated with pyridine containing acetic anhydride. Instead, each reacted slowly at steam-bath temperatures to give first a monoacetate (XX and XXI) and then a diacetate (XXII and XXIII) in good yield. In no instance did both the *cis*- and *trans*-diols give the same monoacetate or diacetate, thus ruling out the possibility that acetate formation took place *via* a common dehydration product (*e.g.*, XXVI) which then added the elements of acetic acid.

Synthesis and Properties of 1,2-Dimethylenebenzocyclobutene.—The diol diacetates XXII and XXIII proved to be surprisingly stable to pyrolysis. When the *cis*-diacetate XXII was passed over Sterchamol firebrick at 300°, however, cracking occurred to give the desired 1,2-dimethylenebenzocyclobutene (I) in 27% yield. Diene I was a colorless liquid of characteristic odor, which froze in an ice-bath to give crystals, m.p. 15–16°. Although more stable in the solid state, it polymerized to a thick gum at room temperature after a few hours. It could be purified by gas chromatography at 150° on a special column impregnated with *t*-butylcatechol, although considerable losses were encountered through polymerization during the operation. The ultraviolet spectrum of I (Fig. 1) is complex and consists of six well defined bands between 230 and 329 mμ. The infrared spectrum of I (Fig. 2) is dominated by the strong methylene absorbtion bands at 11.42 μ, and at 5.92 and 5.95 μ. The n.m.r. spectrum is consistent with the assigned structure[11] and shows only aromatic and vinyl protons.

Diene I readily absorbs two equivalents of hydrogen in the presence of palladium to give *cis*-1,2-dimethyl-

(11) Details will be discussed in a forthcoming publication (G. Fraenkel, M. J. Mitchell and M. P. Cava) on the n.m.r. analysis of a number of benzocyclobutene derivatives.
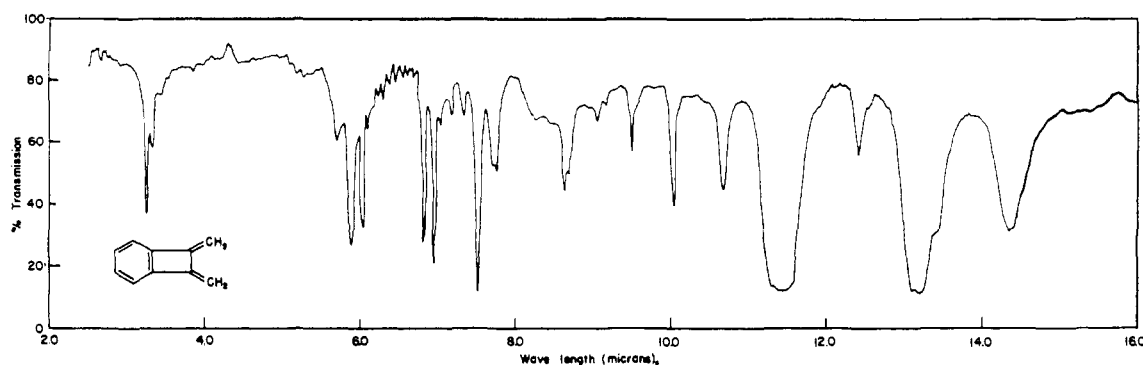
Figure 2.

benzocyclobutene (XXVII). Pyrolysis of I in the gas phase over a nichrome wire at 700° caused isomerization to naphthalene. When a solution of I in benzene was treated with tetracyanoethylene, an orange color developed which was suggestive of complex formation. However, no stable complex could be isolated; when the mixture was allowed to stand until hydrocarbon I had disappeared, the reaction products appeared to be polymeric in nature. In contrast, almost all of the much more stable dicarbomethoxy derivative (IX) of I was recovered unchanged after being heated for 24 hours with tetracyanoethylene at 110°, thereby showing no tendency on the part of IX to give either a benzocyclobutadiene derivative or a cycloaddition product.[12]
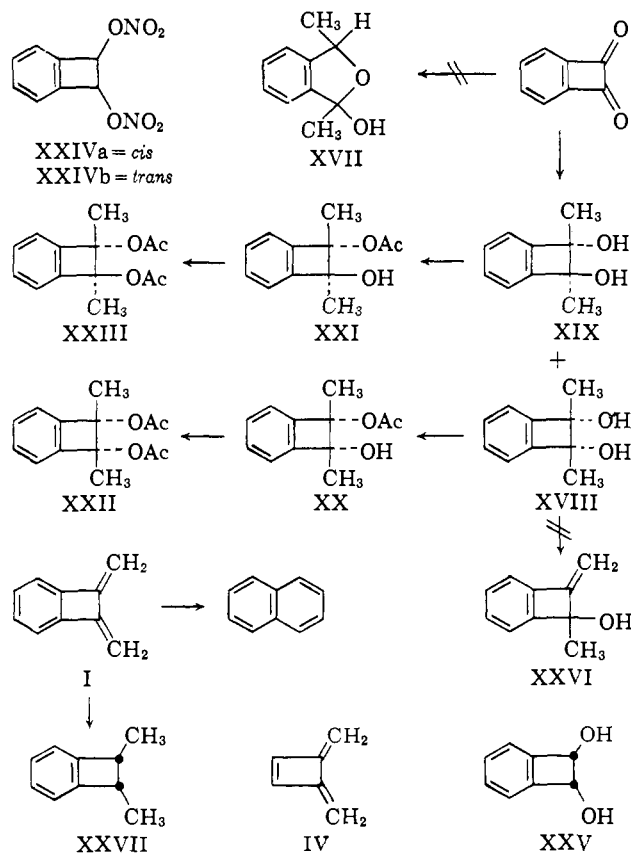
In conclusion, the dimethylenebenzocyclobutene system appears to possess a reasonable amount of delocalization energy, as predicted by theoretical calculations.[3] The unsubstituted hydrocarbon I, however, probably has high free valence character at the methylene carbons. In this respect it resembles the recently

(12) Cycloaddition of TCNE to 1,2-diphenyl-3,4-dimethylenecyclobutene has been observed: A. T. Blomquist and Y. C. Meinwald, J. Am. Chem. Soc., **81**, 667 (1959).

reported 3,4-dimethylenecyclobutene (IV),[13] which also polymerizes with great ease and which gives only indefinite products with tetracyanoethylene.

Experimental[14]

1-Keto-2-carbomethoxymethylenebenzocyclobutene (V).—A solution of triphenylphosphinecarbomethoxymethylene (VII, 0.759 g., 2.27 mmoles)[15] in methylene chloride (25 ml.) was added dropwise at room temperature during 8 hr. to a stirred solution of dione III (0.300 g., 2.27 mmoles) in methylene chloride (10 ml.). After allowing the mixture to stand for an additional 8 hr. at room temperature, the solvent was evaporated and the residue was dissolved in benzene (3 ml.). Chromatography on acid-washed alumina (Merck) with benzene afforded the crystalline keto ester V (0.393 g., 93%), m.p. 87–88°.

Anal. Calcd. for $C_{11}H_8O_3$: C, 70.21; H, 4.29. Found: C, 69.91; H, 4.65.

The 2,4-dinitrophenylhydrazone (VIII) of V was prepared in the usual manner from V. It crystallized from ethyl acetate as yellow-orange needles, m.p. 235° dec.

Anal. Calcd. for $C_{17}H_{12}N_4O_6$: C, 53.93; H, 3.40; N, 15.73. Found: C, 53.89; H, 3.13; N, 15.22.

1,2-Dicarbomethoxymethylenebenzocyclobutene (IX). A. From Dione III.—A solution of dione III (5.07 g., 38.5 mmoles) in methylene chloride (60 ml.) was added at room temperature, over a 30-min. period, to a stirred solution of triphenylphosphinecarbomethoxymethylene (VII, 25.82 g., 77 mmoles) in methylene chloride (60 ml.). The reaction mixture was stirred for 12 hr., the solvent was then removed *in vacuo*, and the residue was dissolved in boiling methanol (40 ml.). The resulting solution was concentrated to 30 ml., cooled to 10°, and filtered to give crude crystalline product IX (6.96 g.). Evaporation of the filtrate to dryness and extraction of the residue with ether (3 × 20 ml.) gave an extract from which additional crude IX (0.94 g.) was obtained by removal of the ether followed by methanol crystallization of the residue. Recrystallization of the total material from methanol afforded diester IX (7.79 g., 85%) as colorless needles, m.p. 124–125°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.01; H, 4.95.

B. From Keto Ester V.—A solution of keto ester V (0.124 g., 9.4 mmoles) in methylene chloride (3 ml.) was added to a solution of the phosphinemethylene VII (0.314 g., 9.4 mmoles) in methylene chloride (3 ml.). After standing for 12 hr. at room temperature, the reaction mixture was evaporated to dryness *in vacuo* and the residue was crystallized from a small amount of methanol to give diester IX (0.185 g., 81%) as colorless crystals, m.p. 122–124°. This material was identical with that obtained in method A, as determined by infrared and mixture melting point evidence.

Treatment of IX with Tetracyanoethylene.—The diester IX was recovered in 93% yield after it was heated for 24 hr. with tetracyanoethylene in boiling toluene.

1,2-Dicarboxymethylenebenzocyclobutene (X).—A mixture of diester IX (0.488 g., 2.0 mmoles), methanol (10 ml.), sodium hydroxide (0.170 g.) and water (10 ml.) was refluxed for 30 min. The reaction mixture was cooled and poured into a mixture of ice (20 g.) and concentrated hydrochloric acid (5 ml.). The crude precipitate was crystallized from acetone to give, in two crops, diacid X (0.420 g., 99%), m.p. 313–315° dec.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.66; H, 3.73. Found: C, 66.39; H, 3.98.

(13) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).

(14) Melting points are uncorrected. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

(15) O. Isler, H. Gutman, M. Montavon, R. Ruegg, C. Ryser and P. Seller, *Helv. Chim. Acta*, **40**, 1242 (1957).

Esterification of Diacid X.—A mixture of diacid X (0.061 g.), methanol (5 ml.) and concentrated sulfuric acid (1 drop) was refluxed for 5 hr. The product was worked up in the usual way to give diester IX (0.063 g., 92%), identical in melting point and infrared spectrum with material prepared from dione III.

cis-1,2-Dicarbomethoxymethylbenzocyclobutene (XI).—Diester IX (6.29 g., 25.6 mmoles), dissolved in ethanol (200 ml.), was hydrogenated under 32 p.s.i. initial hydrogen pressure in the presence of 10% palladium-on-charcoal catalyst (0.5 g.). When the uptake of hydrogen had ceased, the reaction mixture was filtered through zeolite to remove the catalyst, the filtrate was evaporated in vacuo to remove the solvent, and the residue was chromatographed on alumina (Woelm, neutral grade IV) in ether solution. Evaporation of the ether in vacuo afforded the pure diester XI (5.76 g., 92%) as an oil, $n^{22.5}$D 1.5190.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.61; H, 6.70.

cis-1,2-Dicarboxymethylbenzocyclobutene (XII).—A mixture of diester XI (1.80 g., 7.2 mmoles), methanol (10 ml.), sodium hydroxide (0.58 g.) and water (10 ml.) was refluxed for 1 hr. The reaction mixture was cooled and poured into a mixture of ice (30 g.) and concentrated hydrochloric acid (5 ml.). The crude precipitate was crystallized from methanol to give diacid XII (1.45 g., 91%), m.p. 183–185°. The ultraviolet spectrum, like that of its ester precursor XI, was typical of that of a saturated benzocyclobutene.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.49; H, 5.49. Found: C, 65.52; H, 5.74.

Synthesis of Bisbenzylurethan XV. A. From Diester XI.—A mixture of dimethyl ester XI (2.48 g., 0.01 mole), hydrazine hydrate (8 ml.) and ethanol (5 ml.) was refluxed for 8 hr. after cooling the solution, the white precipitate of hydrazide was filtered, washed well with water and with a small amount of ether and dried. The crude hydrazide XIII (2.42 g., 98%), m.p. 211–215°, was not further purified.

Anal. Calcd. for $C_{12}H_{16}N_4O_2$: N, 22.70. Found: N, 22.44.

A solution of sodium nitrite (3.95 g., 57.2 mmoles) in water (ca. 2 ml.) was added dropwise to a cold (0°), stirred mixture of ether (100 ml.) and a solution of hydrazide XIII (7.03 g., 28.6 mmoles) in 0.1 N hydrochloric acid (60 ml.). The temperature of the mixture was not allowed to rise about 10° during the addition of the nitrite. The ethereal layer containing azide XIV was washed with aqueous sodium bicarbonate, dried over sodium sulfate, and added to a solution of benzyl alcohol (7.02 g., 65 mmoles) in dry toluene (50 ml.). The ether was distilled off, and the remaining toluene solution was heated on the steam-bath for 8 hr., during which time nitrogen was steadily evolved. Evaporation of the solvent in vacuo left a gelatinous mass which crystallized from ethanol to give urethan XV (7.40 g., 60%) as a white powder, m.p. 153–154°.

Anal. Calcd. for $C_{26}H_{26}N_4O_2$: C, 72.54; H, 6.08; N, 6.50. Found: C, 72.74; H, 5.99; N, 6.62.

B. From Diacid XII.—A mixture of diacid XII (0.30 g., 1.3 mmoles), thionyl chloride (5 ml.) and pyridine (1 drop) was heated for 1 hr. on the steam-bath. After removal of excess thionyl chloride in vacuo, the residual oil was dissolved in dry acetone (10 ml.) and a solution of sodium azide (0.20 g., 3 mmoles) in water (0.5 ml.) was added rapidly. The mixture was diluted with water (25 ml.) and extracted with ether (3 × 10 ml.). The dried ether extract was added to a solution of benzyl alcohol (1 ml.) in benzene (10 ml.). The ether was boiled off and the remaining benzene solution was heated at 70° until no more nitrogen was evolved. Evaporation of the benzene left a gelatinous residue which was crystallized from ethyl acetate to give urethan XV (0.30 g., 53%), m.p. 153°, identical by infrared comparison with material obtained as described in method A above.

cis- and trans-1,2-Dimethylbenzocyclobutenediols (XVIII and XIX).—A solution of dione III (2.46 g., 20 mmoles) in 1:1 ether–benzene (100 ml.) was added dropwise to a stirred solution of methylmagnesium bromide (90 mmoles) in ether. When all of the solution of III had been added, the reaction mixture was stirred for an additional hour and was then hydrolyzed with aqueous ammonium chloride solution. The resulting inorganic precipitate was removed by filtration and was washed with ether (3 × 25 ml.). The organic filtrate was dried over sodium sulfate, concentrated in vacuo to one-fourth of its original volume, cooled to 20° for 1 hr., and then filtered to give cis-diol XVIII (1.62 g., 49%) as colorless rhombs, m.p. 157°. The melting point was not raised by recrystallization from ether. The n.m.r. spectrum[9] in deuterioacetone showed only singlets at 8.40 τ (CH_3) and 5.28 τ (OH), as well as an aromatic band centered at 2.25 τ.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36. Found: C, 73.18; H, 7.35.

The filtrate from the crystallization of the cis-diol was evaporated to an oil in vacuo. Crystallization of the oil from methylene

chloride afforded trans-diol XIX (1.30 g., 39%) as plates, m.p. 113–118°. The analytical sample, m.p. 122–123°, was obtained after two recrystallizations from methylene chloride. The n.m.r. spectrum[9] in deuterioacetone showed only singlets at 8.35 τ (CH_3) and 5.37 τ (OH), as well as an aromatic band centered at 2.34 τ.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.15; H, 7.36. Found: C, 73.35; H, 7.19.

Lead Tetraacetate Oxidation Rates of Diols XVIII and XIX.—The oxidation rates were obtained by the standard procedures of Criegee.[16] The glacial acetic acid used was distilled from chromic oxide, the first portion of distillate being discarded. The lead tetraacetate used was recrystallized from acetic acid. For the cis-diol XVIII Criegee's fast method[16] was employed. The rates found are: cis-diol XVIII, $k_{21.8}$ = 30,000 l./mole/min.; trans-diol XIX, $k_{20.6}$ = 116 l./mole/min.

As a check on the procedure, a sample of trans-9,10-dimethyl-9,10-dihydro-9,10-phenanthrenediol was oxidized. The rate found ($k_{21.8}$ = 248) compares very well with that calculated ($k_{21.8}$ = 251) from the experimentally determined rates for this diol at 20 and 30°.[17]

Acetylation of cis-Diol XVIII. A. Monoacetate XX.—A mixture of cis-diol XVIII (0.70 g., 4.2 mmoles), acetic anhydride (3 ml.) and pyridine (0.5 ml.) was heated for 1 hr. on the steam-bath. The reaction mixture was evaporated to dryness in vacuo at 50°. The residue was dissolved in ether (25 ml.) and the resulting solution was washed with water (5 × 10 ml.), dried over sodium sulfate and evaporated in vacuo. Crystallization from petroleum ether afforded cis-monoacetate XX (0.83 g., 96%), m.p. 85–86°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.53; H, 6.90.

B. Diacetate XXII.—A mixture of cis-diol XVIII (2.54 g., 15.5 mmoles), acetic anhydride (20 ml.) and pyridine (3 ml.) was refluxed gently for 4 hr. under nitrogen. The reaction mixture was cooled and evaporated to dryness in vacuo. The residue was dissolved in benzene (25 ml.) and the resulting brown solution was washed with water (3 × 5 ml.), dried over magnesium sulfate, and chromatographed with benzene on a column of grade III neutral alumina (Woelm, 4 × 10 cm.). Evaporation of the eluate afforded diacetate XXII (2.72 g., 17%) of sufficient purity (m.p. 82–85°) for conversion into 1,2-dimethylenebenzocyclobutene. The analytical sample, m.p. 94.5–95.0°, was obtained by crystallization from petroleum ether (30–60°) containing 10% methylene chloride.

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50. Found: C, 67.90; H, 6.37.

Acetylation of trans-Diol XIX. A. Monoacetate XXI.—The trans-diol XIX (0.50 g., 3 mmoles) was acetylated by the procedure employed in the synthesis of the cis-monoacetate XX (see above). The trans-monoacetate XXI (0.53 g., 83%) was obtained as an oil which could not be crystallized.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.97; H, 6.47.

B. Diacetate XXIII.—The trans-diol XIX (0.61 g., 37 mmoles) was acetylated by the procedure employed in the synthesis of the cis-diacetate XXII (see above). The crude product, an oil, was subjected to molecular distillation in a micro apparatus at 100° (0.5 mm.) to give a solid distillate (0.68 g., 74%) of trans-diacetate XXIII. The analytical sample, m.p. 86.5–88.5°, was obtained by crystallization from petroleum ether (30–60°).

Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.71; H, 6.50. Found: C, 68.07; H, 6.52.

1,2-Dimethylenebenzocyclobutene (I).—cis-1,2-Dimethyl-1,2-diacetoxybenzocyclobutene (XXII, 0.497 g., 2.0 mmoles) was pyrolyzed at 300 ± 5° in five equal portions of ca. 100 mg. each in a pyrolysis tube (1.5 × 60 cm.) which was packed with Sterchamol firebrick (0.2–0.4 mm. mesh), through which a steady stream of nitrogen was passed. The pyrolysis product (caught in a Dry Ice trap) was mixed with 0.25 ml. of petroleum ether (b.p. 35–40°) and the resulting solution was washed successively with two 0.5-ml. portions of water and with one 0.5-ml. portion of 5% aqueous sodium bicarbonate solution. The organic layer was dried over magnesium sulfate; the volatile components were evaporated at room temp. and condensed at −78° in a small all-glass inverted U-tube still. Vapor phase chromatography of the volatile components on a special t-butylcatechol–Apiezon M column (Sterchamol, 0.2–0.4 mm. mesh, 0.25 inch × 3 ft.) with nitrogen (3.0-cm. inlet pressure) at 150° gave 1,2-dimethylenebenzocyclobutene (I, 0.069 g., 27%) as a clear, colorless liquid, m.p. 15–16°.

Anal. Calcd. for $C_{10}H_8$: C, 93.71; H, 6.29. Found: C, 93.40; H, 6.57.

(16) R. Criegee, *Ann.*, **495**, 211 (1932).

(17) R. Criegee, E. Höger, H. Huber, P. Kruck, F. Marktscheffel and H. Schellenberger, *ibid.*, **599**, 81 (1956).

The ultraviolet spectrum of I is complex: λ_{max}^{EtOH} 230 mμ (log ϵ 4.82), 273 (3.32), 304 (3.66), 314 (3.95), 319.5 (3.72), 329 (4.15). The infrared spectrum exhibits bands at 3.29(m); 3.36, 5.73(w); 5.92 and 5.95(doublet, s); 6.07; 6.86, 7.55, 8.66(s); 9.54(m); 10.08, 10.67, 11.42(s); 12.43(m); 13.10, and 14.38(s) μ.

Hydrogenation of 1,2-Dimethylenebenzocyclobutene.—A sample of the diolefin I was prepared from 0.721 g. (2.87 mmoles) of diacetate XXII as described above, except that the purification by v.p.c. was omitted. Instead, the total material obtained in the distillation step was subjected directly to hydrogenation at atmospheric pressure in the presence of palladium-on-charcoal catalyst (0.05 g.) suspended in methanol (5 ml.). The hydrocarbon absorbed 40.0 ml. (S.T.P.) of hydrogen during 11 min. The reaction mixture was filtered through Celite to remove the catalyst and was poured into water (20 ml.). Extraction of the resulting suspension with 1 ml. of petroleum ether (b.p. 35–40°) followed by gas chromatography of the extract [15% Apiezon M on Sterchamol (0.2–0.4 mm. mesh), 0.25 inch × 6

ft., nitrogen at 160°] gave crude cis-1,2-dimethylbenzocyclobutene (XXVII, 0.060 g.). The analytical sample was obtained by a second pass of the crude material through the same gas chromatography column.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.86; H, 8.91.

Conversion of 1,2-Dimethylenebenzocyclobutene (I) into Naphthalene.—1,2-Dimethylenebenzocyclobutene (0.071 g., 0.55 mmole) was passed over a hot nichrome wire coil (ca. 700°) in a vacuum apparatus. The product (trapped on a cold-finger at −78°) was dissolved in 1 ml. of cyclohexane and the resulting solution was subjected to vapor phase chromatography (3 ft. × 0.25-inch column, 15% silicone grease on firebrick, nitrogen at 150°) to give naphthalene (0.013 g.), identical in melting point and infrared spectrum with authentic material.

The Copper-Catalyzed Reaction of Peresters with Hydrocarbons[1]

BY CHEVES WALLING AND ANDREAS A. ZAVITSAS

Experiments are described intended to test a mechanism for copper-catalyzed perester decompositions similar to that proposed by Kochi. Major steps are reduction of perester by Cu^I to yield t-butoxy radicals, attack of t-butoxy radicals on hydrocarbon substrates, and oxidation of the resulting hydrocarbon radicals by Cu^{II} to carbonium ions. Relative reactivities of seven hydrocarbons are shown to be the same in t-butyl peracetate and perbenzoate reactions as in t-butyl hypochlorite chlorination. The distributions of allylic acetates obtained from reaction of t-butyl peracetate and a number of alkenes are in good agreement with Kochi's findings, and it is suggested that the result is more consistent with an electron transfer process to give a relatively "free" carbonium ion than with ligand transfer. Products from perester reactions with allylbenzene and β-methylstyrene are shown to have undergone allylic rearrangements, although isomer distributions are different from the two alkenes. Examples of what appear to be carbonium ion rearrangements are found in the reaction of t-butyl peracetate with 6,6-dimethyl-1,3-cyclohexadiene to give o-xylene, and in the decomposition of 2,4,4-trimethyl-2-pentyl hydroperoxide to give isopentenes. The importance of side reactions in the perester decomposition which fail to regenerate Cu^I is pointed out, and some limiting kinetic expressions are shown to be consistent with the kinetic data available.

The effect of traces of heavy metal ions on the decomposition of organic peroxides has long been recognized and finds important application in autoxidation processes and oxidation–reduction-initiated polymerization. Numerous synthetic applications have also appeared recently, and an understanding of the mechanisms of such reactions has obvious bearing on aerobic biochemical processes involving metal-containing enzymes.[2] A very interesting group of such metal-catalyzed reactions were described by Kharasch and his students in a series of papers beginning in 1958.[3] These investigators found that traces of copper (usually as cuprous chloride or bromide), and to some extent other transition metals, profoundly altered the course of reaction between organic peroxides and a variety of organic substrates, typical being the reaction of t-butyl perbenzoate with cyclohexene.[3d] In the presence of copper, high yields of 3-benzoyloxycyclohexene and t-butyl alcohol are produced, while in its absence the reaction is slower and yields a rather indiscriminate mixture of products including bicyclohexenyl and benzoic acid. The reaction has had considerable synthetic elaboration.[4–10] Allylic substitution occurs with

a variety of olefins, although addition is observed with conjugated dienes and olefins lacking allylic hydrogen. Hydrogens α to N (t-amines), O (alcohols, aldehydes and ethers) and S (thioethers) are attacked, and recently Story[7] has reported an interesting synthesis of 7-t-butoxynorbornadiene from norbornadiene and t-butyl perbenzoate. With t-hydroperoxides in place of peresters, labile hydrogens are said to be replaced by t-alkyl peroxy groups. Early reports also claimed that reaction of peresters with 1-olefins, allylbenzene and β-methylstyrene yielded allylic esters without shift of double bonds.[3,11] and Story[7] noted that the point of substitution in norbornadiene was not that anticipated in a normal radical process.

In part to account for this sort of specificity, Kharasch and Fono in 1959[3b] proposed a mechanism proceeding through a series of copper-stabilized radical-peroxide complexes, and similar "complex" mechanisms have been advanced by Denney,[11] and, in connection with a recent kinetic study, by Barnard and Yang.[12]

An alternative scheme not involving complexes and

(1) Taken from the Ph.D. Dissertation of Andreas A. Zavitsas, Columbia University, 1962. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

(2) For a general discussion of earlier literature, cf. C. Walling, "Free Radicals in Solution" John Wiley and Sons, Inc., New York, N. Y., 1957, Ch. 9 and 11.

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