Derivatives of 1,2,3,4-Tetramethylcyclobutene. Stable Cations in Sulfuric Acid[1]

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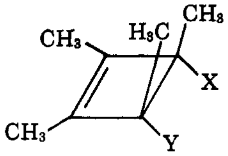
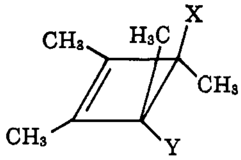
The synthesis of several ester derivatives of *cis*- and *trans*-1,2,3,4-tetramethylcyclobutene-3,4-diol is presented. It is found that solution of these esters in 97% sulfuric acid and other acidic media produces stable bridged cations with structures analogous to those proposed as intermediates in reactions proceeding with neighboring ester group participation.

Sometime ago a study of the solvolysis of 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (**1**) was initiated but not pursued because the high reactivity of **1** limited the range of acceptable solvents.[3] To circumvent this difficulty a series of more slowly solvolyzing benzoate and *p*-nitrobenzoate esters were prepared and examined. As part of their study several of these esters were dissolved in sulfuric acid and the solutions examined by n.m.r. spectroscopy for the presence of stable cations. This paper reports the preparation of these esters and the n.m.r. studies on their sulfuric acid solutions.

Synthesis of Esters.—The key starting material for all of the ester syntheses was the dichloride (**1**), which is now readily prepared by the excellent procedure of Criegee and Moschel.[4] As described by Criegee and Louis[5] **1** could be hydrolyzed to either the *cis*- or *trans*-diol (**2a** or **3a**). When the *cis*-diol (**2a**) was treated in ether with one equivalent each of sodium hydride and benzoyl chloride, the *cis*-hydroxybenzoate (**2b**) was obtained in 21% yield. The *cis*-hydroxy-*p*-nitrobenzoate (**2c**) was obtained in 22% yield in an analogous fashion. The parent tetramethylcyclobutene skeleton was demonstrated to be present in both of these esters by their conversion to **1** in *ca.* 50% yield on dissolving them in a solution of hydrochloric acid in acetic acid.



2a, $X = OH$; $Y = OH$
b, $X = OH$; $Y = OCOC_6H_5$
c, $X = OH$; $Y = OCOC_6H_4\text{-}p\text{-}NO_2$
d, $X = Y = OCOC_6H_5$



3a, $X = OH$; $Y = OH$
b, $X = Y = OCOC_6H_5$

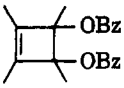
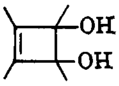
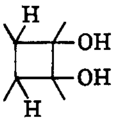
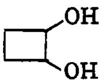
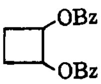
A similar approach to the *trans*-hydroxybenzoate failed. In both ether and tetrahydrofuran at room temperature the *trans*-diol (**3a**) failed to react with sodium hydride and in the mixed solvent of dimethyl sulfoxide and ether the only material isolated was benzoic anhydride.

Both of the hydroxy esters (**2b** and **2c**) decomposed in the presence of strong bases so that the alkoxide route to the diesters failed. Treatment of the dichloride (**1**) with silver benzoate in dry acetonitrile afforded a mixture of three benzoate esters. The major product, obtained in 25–35% yield and melting at 130°, was identified as either the *cis*- or *trans*-dibenzoate (**2d** or **3b**) by its infrared and n.m.r. spectra, elemental analysis, and its reconversion to **1** in 56% yield on shaking with a solution of concentrated hydrochloric acid in acetic acid. Another solid, m.p. 105–106°, was obtained in 4% yield and was identified as the isomeric diester by its infrared and n.m.r. spectra, elemental analysis, and reconversion to **1** in 65% yield on treatment with hydrochloric acid in acetic acid.

The stereochemistry of the higher melting isomeric diester was assigned tentatively as *trans* by analogy to the melting point relations existing among closely related *cis–trans* pairs (see Table I). For each pair the *trans* isomer melts higher than the *cis* isomer. An attempt to verify this assignment by reduction of the diesters with lithium aluminum hydride failed and apparently resulted in ring cleavage. The diesters did not take up hydrogen in cyclohexane over platinum oxide. The *trans*-ester could be hydrogenated in acetic acid and subsequently reduced with lithium aluminum hydride; however, a mixture of four alcohols including both the *cis*- and *trans*-saturated diols was obtained. Hydrogenation in absolute ethanol followed by lithium aluminum hydride reduction gave pure *trans*-diol and cyclohexylcarbinol which could be isolated in 50 and 52% yields, respectively, by g.l.c. In a control experiment it was established that the *trans*-diester did not rearrange in absolute ethanol at the temperature of the

TABLE I

MELTING POINT RELATIONS AMONG SOME *cis–trans* CYCLOBUTANE DERIVATIVES

Structure	M.p., *cis*, °C.	M.p., *trans*, °C.
 OBz OBz	105[a]	130[a]
 OH OH	91[b]	133[b]
 H OH OH H	61[c]	101[c]
 OH OH	12[d]	72[d]
 OBz OBz	61[d]	112[d]

[a] Present work. [b] Ref. 5. [c] Ref. 6. [d] Ref. 7.

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[1] Taken from the dissertation submitted by D. L. Nealy in partial fulfillment of the requirements for the Ph.D. degree, Cornell University, June, 1963.

[2] National Science Foundation Predoctoral Fellow, 1959–1963.

[3] Some of the initial work is reported in the Ph.D. dissertation of M. P. Stevens, Cornell University, 1961.

[4] R. Criegee and A. Moschel, *Ber.*, **92**, 2181 (1959).

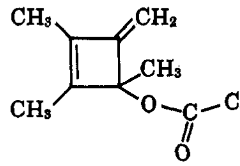
[5] R. Criegee and G. Louis, *ibid.*, **90**, 417 (1956).

[6] R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

[7] R. Criegee, E. Hoger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *ibid.*, **599**, 81 (1956).

hydrogenation. Because of possible rearrangement in the presence of catalyst or on reduction with lithium aluminum hydride, the main argument for the *cis-trans* assignment rests on the relative melting points.

The third ester, a liquid isolated in 10–15% yield from the silver benzoate reaction, was identified as 3-methylene-1,2,4-trimethylcyclobuten-4-ol benzoate, (**4**).[8] The molecular formula of this liquid ester was established by its elemental analysis, its saponification equivalent, and its reasonably low boiling point. The presence of an *exo*-methylene group was indicated by its infrared absorption at 1620 and 850–860 cm.$^{-1}$; it rapidly decolored a solution of bromine in carbon tetrachloride in contrast to the solid diesters. Confirmation of its structure was obtained by n.m.r. spectroscopy. The nonequivalent methylene protons appeared as a pair of singlets at 5.06 and 5.58 τ so that they had the usual[9] very small coupling constant. The three methyl groups gave rise to three distinct singlets at 8.18, 8.25, and 8.43 τ, and the aromatic protons gave a typical pattern of absorption at 2.0–2.8 τ. The relative integrated n.m.r. peak areas were in accord with the assigned structure. The dienebenzoate (**4**) regenerated **1** in 61% yield on treatment with hydrochloric acid in acetic acid.



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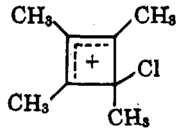
Reaction of the dichloride (**1**) with silver *p*-nitrobenzoate afforded a low yield of bis-*p*-nitrobenzoate ester. The stereochemistry of this diester was not investigated.

N.m.r. Spectra and Discussion

The n.m.r. spectrum of a solution of dichloride (**1**) in 97% sulfuric acid at room temperature showed a single peak at 7.43 τ. Katz[10] observed that the n.m.r. spectrum of **1** in liquid sulfur dioxide at −63° with added silver hexafluoroantimonate displayed three peaks in the ratio of 2:1:1, which he assigned to the methyls of the monochloro cation (**5**). The average position (weighted in the ratio of 2:1:1) of the peaks in the Katz spectrum was 7.26 τ. The excellent correspondence between this value and the single peak observed in sulfuric acid indicates that under the present conditions cation **5** is formed also, but that the methyl groups are being equilibrated rapidly. By combination of the low-temperature Katz data[10] with the present results the barrier to methyl equilibration can be estimated to lie near the range of 9 to 12 kcal.[11]



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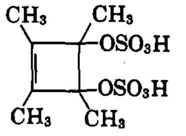
An n.m.r. spectrum of the hydroxybenzoate (**2b**) in sulfuric acid gave a *single* sharp peak at 8.13 τ. The only other absorption was in the low field region, which displayed a complex pattern at 1.8–2.5 τ that appeared identical with the spectrum of a sulfuric acid solution of benzoic acid (protonated in this medium). The ratio of high and low field peak areas was 12:5. A significant difference between the sulfuric acid spectra of the dichloride and the hydroxybenzoate is the position of the averaged methyl absorption. The higher field absorption ($\Delta\tau$ 0.70) of the hydroxybenzoate spectrum in sulfuric acid indicates that its methyl groups on average are exposed to much less positive charge.[12] This small shift combined with the apparent identity of the low field spectrum with that of protonated benzoic acid suggests that the major species in sulfuric acid has one of the following structures.



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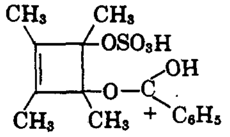

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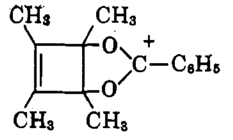

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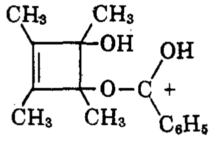

8

Structure **6** can be eliminated by the observation that addition of benzoic acid to a solution of dichloride (**1**) in sulfuric acid causes a gradual diminution of the peak at 7.43 and simultaneous appearance and growth of the peak at 8.13 τ. This implicates benzoic acid as being involved in the species formed from hydroxybenzoate and it also demonstrates the existence of a facile exchange between the two cationic species.[13] Strong evidence against both **6** and **7** comes from the rapid production of the 8.13-τ peak on passing boron trifluoride through a solution of hydroxybenzoate (**2b**) in chloroform thereby demonstrating that the essential components of the sulfuric acid cation are present in the starting material. Another experiment leading to the same conclusion involved the addition of a slight excess of perchloric acid (70% solution) to a chloroform solution of the hydroxybenzoate (**2b**) and the production of a single sharp peak at 8.17 τ (see the Experimental for the complicating details).

The choice between **8** and **9** was made in part from the observation that both dibenzoates and the hydroxybenzoate in 97% sulfuric acid gave an identical 8.13-τ peak. This suggests that a hydroxyl group is absent in the cation so that its structure is represented by **9**.

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[8] The formation of an acetate corresponding to **4** in the acetolysis of **1** has been proposed by Criegee and Noll.[6]

[9] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Ltd., London, 1959, p. 85.

[10] T. J. Katz, J. R. Hall, and W. C. Neikam, *J. Am. Chem. Soc.*, **84**, 3199 (1962).

[11] The solvents are quite different in these two measurements so that some deviation from this range is possible.

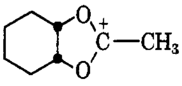
[12] Compared to the parent uncharged hydroxybenzoate (in carbon tetrachloride) the shift in methyl absorption is very small (*ca.* 0.2 τ). Compared to the dichloride the monochloro cation (**5**) has its methyls displaced downfield by *ca.* 1.0 τ.[10]

[13] The exchange reaction was run in the reverse direction by adding lithium chloride to a sulfuric acid solution of benzoate cation. The 8.13-τ peak diminished and the 7.43-τ peak appeared.

More compelling evidence for selecting this bridged cation comes from the production of an identical 8.13-τ peak on passing boron trifluoride through a solution of the *trans*-dibenzoate in *anhydrous* chloroform.

Indirect corroboration for formation of the bridged cation came from the n.m.r. spectrum of a sulfuric acid solution of the bis-*p*-nitrobenzoate. This solution gave every indication that the analogous *p*-nitro cation was formed. At high field there was a single sharp peak at 8.08 τ, representing a shift in peak position that is reasonable for substitution of a *p*-nitro group in **9.** At low field there appeared two closely spaced peaks of nearly identical height. The higher field peak at 1.71 τ corresponded exactly with the single peak observed for a solution of *p*-nitrobenzoic acid in sulfuric acid. The lower field peak at 1.68 τ can be identified with the *p*-nitrobenzoyloxy group of the bridged cation. This identification was verified by adding dibenzoate **3b** to a solution of *p*-nitrobenzoic acid in sulfuric acid. Initially the n.m.r. spectrum consisted of 8.13-τ absorption (methyls of the bridged cation **9**) and a peak at 1.71 τ for protonated *p*-nitrobenzoic acid as well as peaks at 1.8–2.5 τ for the two benzoic acid species (protonated benzoic acid and the benzoyloxy portion of **9**). Over a period of several minutes the 1.71- and 8.13-τ peaks diminished and peaks at 1.68 and 8.08 τ simultaneously developed.

The bridged benzoate cation (**9**) is analogous to the bridged acetate cation (**10**) employed by Winstein and co-workers[14] to account for the formation of *cis*-2-hydroxycyclohexyl acetate from solvolysis of 2-acetoxycyclohexyl derivatives in *wet* acetic acid. Sulfuric acid solutions of *cis*- and *trans*-dibenzoates were allowed to flow through a capillary tube into a rapidly stirred, cold, concentrated, aqueous solution of sodium hydroxide and potassium nitrate[15] in the presence of petroleum ether. The product from either ester, isolated in 70% yield, was essentially pure *cis*-hydroxybenzoate (**2b**).[16] The formation of *cis* product can be rationalized (see Scheme I) by the same sequence of reactions suggested by Winstein and co-workers[14] for their cyclohexyl system.



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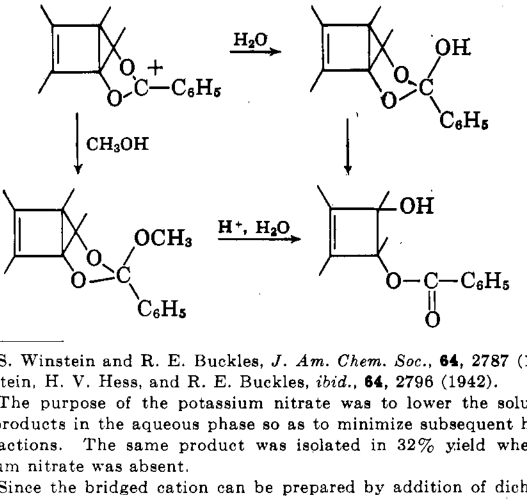
SCHEME I



Ethanolysis[17] of *trans*-2-acetoxycyclohexyl tosylate gives a cyclic ortho ester. This reaction was used to demonstrate the intermediacy of **10.** A chloroform solution of cation **9** formed by passing boron trifluoride through a solution of *trans*-dibenzoate was run into cold (−70°) methanol containing 20% pyridine. The major product, isolated in 60% yield, was a solid, m.p. 68°, having an elemental composition of $C_{16}H_{20}O_3$. This solid showed no hydroxyl or carbonyl absorption in its infrared spectrum. Its n.m.r. spectrum was consistent with the ortho ester structure shown in Scheme I. The ortho ester was found to be sensitive to aqueous acid which caused conversion to the *cis*-hydroxybenzoate (**2b**).

The possible mechanisms and significance of the methyl equivalency in the cations and the exchanges of groups between the cations will be discussed in a following paper.

Experimental[18]

cis-**1,2,3,4-Tetramethylcyclobutene-3,4-diol Monobenzoate (2b).**—Dichloride 1, prepared by the method of Criegee and Moschel,[4] was converted into the *cis*-diol (**2a**) by the procedure of Criegee and Louis,[5] m.p. 91.0–91.8°, lit.[5] m.p. 91.5–92°. To a solution of 1.00 g. of *cis*-diol in 70 ml. of ether was added 0.46 g. of 52% sodium hydride dispersion in mineral oil. When the calculated volume of hydrogen gas (340 ml.) had been collected, a solution of 1.21 g. of benzoyl chloride in 30 ml. of dry ether was added. After the mixture had been stirred at room temperature for 30 min., it was filtered and the filtrate evaporated to dryness. This material was extracted with pentane and the pentane extract was washed with 5% aqueous sodium carbonate and dried over magnesium sulfate. The pentane solution was cooled to 0° and the resulting precipitate collected to give 0.36 g. (21% yield) of monobenzoate, m.p. 93.8–94.2°.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15, H, 7.37. Found: C, 73.21; H, 7.52.

The monobenzoate showed infrared absorption at 3380 (O–H), 1690 (C═O), and weak absorption at 1580–1600 cm.$^{-1}$ (phenyl C═C). An n.m.r. spectrum consisted of a pair of multiplets at 1.9 to 2.8, a singlet at 7.54, and three singlets at 8.30, 8.44, and 8.66 τ. These peaks had relative integrated areas of 5.3:1.0: 2.9:5.9:3.2 and are assigned, respectively, to phenyl hydrogens, hydroxyl hydrogen, and to four methyl groups, two of which are not resolved.

trans-**1,2,3,4-Tetramethylcyclobutene-3,4-diol Dibenzoate (3b).**—To a stirred suspension of 65.5 g. (0.286 mole) of silver benzoate[19] in 200 ml. of dry acetonitrile was added slowly a solution of dichloride (**1**) in 80 ml. of dry acetonitrile while the temperature was maintained at 70–75°. The mixture was stirred at this temperature for an additional 90 min. and then cooled and filtered. The solid was washed with 400 ml. of 80% pentane–20% ether. The combined filtrates were extracted several times with water, twice with 5% aqueous sodium carbonate solution, and finally dried over magnesium sulfate. On evaporation of the solution to a volume of about 50 ml. and cooling in a refrigerator overnight, 10.5 g. (27% yield) of *trans*-dibenzoate (**3b**) crystallized, and was collected by filtration, m.p. 129.5-130.0°. An additional 0.35 g. of this ester was isolated from fractions 25–29 of the chromatography described in the next experiment.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found: C, 75.27; H, 6.38.

This diester showed infrared absorption at 1715 (C═O) and at 1580–1600 cm. (phenyl C═C). The n.m.r. spectrum showed a

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(14) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2787 (1942); S. Winstein, H. V. Hess, and R. E. Buckles, *ibid.*, **64**, 2796 (1942).

(15) The purpose of the potassium nitrate was to lower the solubility of the products in the aqueous phase so as to minimize subsequent hydrolytic reactions. The same product was isolated in 32% yield when the potassium nitrate was absent.

(16) Since the bridged cation can be prepared by addition of dichloride to a solution of benzoic acid in sulfuric acid, this reaction offers an interesting synthetic shortcut to the hydroxybenzoate.

(17) S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **65**, 613 (1943).

(18) All melting points are corrected. Infrared spectra of solids were taken with potassium bromide pellets and those of liquids with the pure liquids unless otherwise noted. N.m.r. spectra were determined on a Varian A-60 analytical spectrometer using the HR 60 magnet. N.m.r. spectra of solids were determined with carbon tetrachloride solutions, and those of liquids with the pure liquid unless otherwise noted.

(19) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

multiplet at 2.2–3.3 and a pair of singlets at 8.27 and 8.30 τ with an integrated area ratio of 10.0:11.7 (low field to high field absorption).

Further identification of this material is given in a later section of experimental.

3-Methylene-1,2,4-trimethylcyclobuten-4-ol Benzoate (4).—The mother liquor from the crystallization of the *trans*-dibenzoate described previously was chromatographed on a 35 cm. × 25 mm. column of Woelm neutral alumina (activity grade I) with pentane and 15–20-ml. fractions collected. Fractions 8 to 12 contained 3.3 g. (13% yield) of diene ester **4**, which was purified by another chromatography on alumina, $n^{25}D$ 1.5300, b.p. 82–83° (0.1 mm.), with partial decomposition.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 79.00; H, 7.04; sapon. equiv., 228. Found: C, 76.03, 78.55; H, 6.99, 7.38; sapon. equiv., 229, 226, 224.

This diene ester, in contrast to the monoene diesters (**2d** and **3b**), rapidly decolorized a solution of bromine in carbon tetrachloride.

Ester **4** showed infrared absorption at 1715 (C=O), at 1620 850–860 (C=CH$_2$), and at 1580–1600 cm.$^{-1}$ (aromatic C=C). An n.m.r. spectrum of **4** showed a multiplet at 2.00–2.90, singlets at 5.06 and 5.57, and three singlets at 8.16, 8.28, and 8.42 τ with integrated areas in the ratio of 5.0:1.9:9.5.

***cis*-1,2,3,4-Tetramethylcyclobutene-3,4-diol Dibenzoate (2d).**—Fractions 14–21 of the chromatography described previously gave 1.4 g. (3.6% yield) of the *cis*-dibenzoate (**2d**), m.p. 105–106°, after recrystallization from pentane.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.40; H, 6.33. Found C, 75.49; H, 6.41.

This ester showed infrared absorption at 1715 (C=O), at 1580–1600 (aromatic C=C), and a pattern of absorption in the 750–1400-cm.$^{-1}$ range generally similar to, but definitely distinct from, that of the *trans* isomer. An n.m.r. spectrum of the *cis*-ester consisted of a typical absorption pattern for phenyl hydrogens at 2.1–2.9 and partially resolved singlets at 8.22 and 8.24 τ assigned to the two pairs of methyl groups. The relative integrated areas were 10.0:11.6 (phenyl to methyl absorption).

1,2,3,4-Tetramethylcyclobutene-3,4-diol Di-*p*-nitrobenzoate.—The procedure was the same as that used to prepare the *trans*-dibenzoate (**3b**) except that the temperature was maintained below 25°, silver *p*-nitrobenzoate was employed, and benzene was used in place of pentane in the isolation of the product. Only 3.5 g. (7.1%) of diester was isolated, m.p. 180–190° dec. (phase transition at 121–123°).

Anal. Calcd. for $C_{22}H_{20}N_2O_8$: C, 60.00; H, 4.58; N, 6.37. Found: C, 59.73; H, 4.63; N, 6.72.

This ester showed infrared absorption at 1720 (C=O), 1610 (aromatic C=C), and 1520 cm.$^{-1}$ (NO$_2$).

Reduction of *trans*-Dibenzoate (3b) to *trans*-1,2,3,4-Tetramethylcyclobutane-1,2-diol (3a).—A solution of 2.0 g. of *trans*-dibenzoate (**3b**) was hydrogenated in 100 ml. of absolute ethanol at room temperature under 2–3 atm. of hydrogen in the presence of 0.2 g. of Adams' catalyst. About 4–5 mole of hydrogen per mole of ester was absorbed during 20 hr. The solution was filtered and the solvent removed by evaporation under vacuum at room temperature. The residue, weighing 2.2 g., was reduced directly with 0.5 g. of lithium aluminum hydride in refluxing ether for 24 hr. Water (1.0 ml.) was added cautiously and the mixture, after stirring for an additional hour, was filtered. The solid was washed with three small portions of methanol; the combined filtrate and washings were evaporated to a volume of about 2 ml. The concentrate was separated into two components by g.l.c. using a 5 ft. × 0.5 in. column of 20% SF-96 silicon oil on Chromosorb W. The first component eluted was 0.60 g. (52%) of a liquid, $n^{25}D$ 1.4623, which was identified as cyclohexylcarbinol by comparison of its infrared spectrum and g.l.c. retention time with those of a known sample. The second component was 0.40 g. (50%) of a solid, m.p. 105–106°, which was identified as *trans*-1,2,3-tetramethylcyclobutane-1,2-diol (lit.[6] *trans*-diol m.p. 100–101°; *cis*-diol m.p. 60–61°) by its analysis, its negative test for unsaturation and its n.m.r. spectrum. The n.m.r. spectrum of a solution of the solid diol in deuterated acetone consisted of a singlet at 6.82, a multiplet at 8.02, singlets at 8.76 and 8.90, and a set of four peaks of equal intensity at 9.10–9.25 τ with relative peak areas of 2:2:3:3:6. The 6.82 peak was assigned to the hydroxylic protons, the 8.02 multiplet to the pair of tertiary hydrogens, the singlets at 8.76 and 8.90 to the methyl groups adjacent to hydroxyls, and the remaining pair of doublets in the 9-τ region to the methyl groups adjacent to the tertiary hydrogens.

As a control experiment 1.0 g. of *trans*-dibenzoate (**3b**) in 50 ml. of ethanol was allowed to stand for 3 days. Isolation in the identical manner described previously gave 0.98 g. of **3b**.

When the hydrogenation was carried out in acetic acid a mixture of four alcohols including both the *cis*- and *trans*-saturated diols was obtained.

Reduction of 3-methylene-1,2,4-trimethylcyclobuten-4-ol Benzoate (4).—A solution of 3.3 g. of **4** in 60 ml. of dry cyclohexane was hydrogenated in presence of 0.5 g. of 5% palladium on charcoal at room temperature under atmospheric pressure. It absorbed 106% of the amount of hydrogen calculated for one double bond per molecule and then the rate of hydrogen absorption decreased markedly. The solution was filtered and evaporated to yield 3.00 g. (82 % yield) of a liquid ester, $n^{25}D$ 1.5083. An infrared spectrum of this ester was essentially identical with that of the starting material (1715, 1580–1600) except that the bands at 1620 and 850 cm.$^{-1}$ (C=CH$_2$) had disappeared. An n.m.r. spectrum of this liquid showed a pair of multiplets at 1.9–2.6, a poorly resolved multiplet at 7.5, sharp singlets of unequal intensity at 8.28, 8.46, and 8.60, and a symmetrical doublet at 8.82 τ (J = 6 c.p.s.). These data are indicative of a mixture of the two geometric isomers of 1,2,3,4-tetramethyl-2-cyclobuten-1-ol benzoate.

N.m.r. Spectra of Cations.—Sulfuric acid solutions of cations derived from dichloride **1**, the solid esters **2b**, **2d**, **3b**, and the bis-*p*-nitrobenzoate were made by adding about 0.4 ml. of chilled 97% sulfuric acid to 50–100 mg. of the solid. To each solution was added 5–10 mg. of tetramethylammonium fluoborate as an internal standard[20] and the spectrum determined immediately. All of the solutions except that from the dichloride gave unchanged n.m.r. spectra after 24 hr. at room temperature. The dichloride solution darkened markedly and developed a very complex n.m.r. spectrum after a few hours at room temperature.

In an n.m.r. tube was placed a chloroform solution of hydroxybenzoate, a small amount of the tetramethylammonium fluoborate reference, and a slight excess of 70% aqueous perchloric acid. The relative volumes of the chloroform and acid layers were such that the n.m.r. probe sensed only the chloroform solution. Sufficient amounts of the cation and the reference were extracted into the chloroform layer to give an n.m.r. spectrum which consisted of a single sharp peak at 8.17 τ relative to the reference. A similar experiment was carried out with the *trans*-dibenzoate, which gave a single sharp peak at 8.19 τ relative to the reference. When a drop of tetramethylsilane was added to a chloroform solution of *trans*-dibenzoate in contact with 70% perchloric acid, the spectrum (determined immediately) showed a cation peak at 8.12 τ relative to TMS. In view of the complexities introduced by the two-phase system and the change in solvent these values are in acceptable accord with the sulfuric acid spectra.

Hydrolysis of the Bridged Benzoate Cation (9).—A solution of 1.15 g. of *trans*-dibenzoate (**3b**) in 8.0 ml. of 97% sulfuric acid was allowed to flow through a glass capillary into a concentrated aqueous solution of sodium hydroxide and potassium nitrate in the presence of 25 ml. of petroleum ether (b.p. 30–60°) with external cooling and rapid stirring. The mixture was diluted with water and extracted with three 25-ml. portions of petroleum ether. The organic extracts were dried over magnesium sulfate and distilled to dryness under aspirator vacuum. The residue, 0.65 g. of a solid melting at 80–85°, gave an infrared spectrum apparently identical with that of the *cis*-hydroxybenzoate (**2b**). Crystallization of the solid from petroleum ether gave 0.57 g. of crystals, m.p. 95–96°, which did not depress the melting point of an authentic sample of **2b** (m.p. 94°).

Methanolysis of the Bridged Benzoate Cation (9).—A solution of 2.7 g. of *trans*-dibenzoate (**3b**) in 25 ml. of chloroform was cooled to −70° and boron trifluoride gas bubbled through a capillary tube into the solution for about 30 sec. The resulting light yellow solution was passed through another capillary tube (about 1-mm. i.d.) into a well stirred solution of 5 ml. of pyridine in 20 ml. of dry[21] methanol that was maintained at −70°. The reaction mixture was diluted with 60 ml. of carbon tetrachloride and then extracted with 50 ml. of 10% aqueous sodium hydroxide. The organic phase was dried over magnesium sulfate and evaporated under about 50-mm. pressure without heating. The

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[20] The reference standard has been shown by Professor D. G. Farnum of this department to give a single sharp peak at 6.87 τ in aqueous sulfuric acid solutions of 0–100% acid.

[21] H. Lund and J. Bierrum, *Ber.*, **64**, 210 (1931).

residue was diluted with 60 ml. of pentane and washed several times with water to remove residual pyridine, then again dried over magnesium sulfate and evaporated under vacuum. The liquid residue, free of pyridine odor, was dissolved in 10 ml. of pentane and cooled with a mixture of Dry Ice and methylene chloride. After about 2 hr., colorless crystals separated which were collected by filtration, m.p. 55–57°. Further recrystallizations from pentane raised the melting point to 67.5–68.5°. The total weight of solid isolated was 1.23 g. (60%).

Anal. Calcd. for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.60; H, 7.67.

An infrared spectrum of this solid showed no hydroxyl or carbonyl absorptions. An n.m.r. spectrum showed the characteristic phenyl absorption at 2.5–2.9 (area, 5.0), a singlet at 6.70 (area, 3.0), and two sharp singlets at 8.70 (area, 6.2) and 8.80 τ (area, 5.9).

A chloroform solution of 0.52 g. of the ortho ester was shaken for a few minutes with 3 *N* hydrochloric acid and then washed with 5% aqueous sodium hydroxide solution. The organic phase was dried over magnesium sulfate and evaporated to give 0.41 g. of solid, m.p. 90–92°, after recrystallization from pentane. This solid was identified as *cis*-hydroxybenzoate (**2b**) by its infrared spectrum and lack of melting point depression when mixed with an authentic sample.

Solvolytic Studies of *cis*- and *trans*-2,2,4,4-Tetramethylcyclobutane Derivatives[1]

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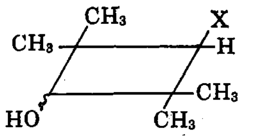
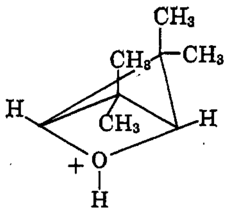
Several 2,2,4,4-tetramethylcyclobutane esters have been solvolyzed and the rates and products determined. No evidence is found for participation of a 3-OH group but the results are consistent with a cyclopropylcarbinyl intermediate. The mechanisms of the solvolyses are discussed and related to the previous work on the dehydration of the 2,2,4,4-tetramethylcyclobutane-1,3-diols.

Recently Hasek, Clark, and Chaudet reported that cleavage of *cis*- and *trans*-2,2,4,4-tetramethylcylobutane-1,3-diols (**1a**) by aqueous acid proceeded at markedly different rates.[3] They proposed that the *trans*-diol reacted with neighboring hydroxyl participation by way of the bicyclic oxonium salt **2** which they felt possessed sufficient stability to account for the higher reactivity of the *trans*-diol.


1a, X = OH

1b, X = *p*-toluenesulfonate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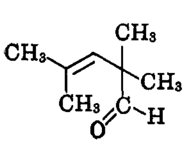
We were interested in examining this system in part because of our general interest in bicyclic systems and in part because of our thwarted attempts to carry out related cyclizations on less strained systems.[4] A quantitative estimate of the relative reactivities of the *cis*- and *trans*-diols seemed difficult to obtain from the dehydration reaction.[5] On the plausible assumption that the *cis*- and *trans*-hydroxy tosylates (**1b**) would possess a similar difference in reactivity these esters were prepared and studied. From the kinetic and product data obtained with these esters combined with similar data for model systems and other derivatives of **1a**, it could be shown that the intermediacy of bicyclic ion **2** is improbable. An alternative mechanism consistent with all data now available will be presented.

Dehydration of the Diols.—The dehydration of *cis*- and *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diol in 4% aqueous sulfuric acid was repeated. In addition to 2,2,4-trimethyl-3-pentenal (**3**), reported to be the major product by previous workers, two other higher boiling materials were isolated. These proved to be the cyclic hemiacetal **4** and the bisacetal **5**.[6] Since these products appear to be formed from **3** rather than **1a** and since their identification involves considerable chemistry not pertinent to the present cyclobutanediol problem, they will be discussed elsewhere.[7] As reported by Hasek, *et al.*,[3] the organic material precipitating from the acid solution was found to be almost pure *cis*-2,2,4,4-tetramethylcyclobutane-1,3-diol. No evidence for other primary rearrangement products was found.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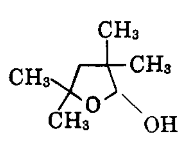
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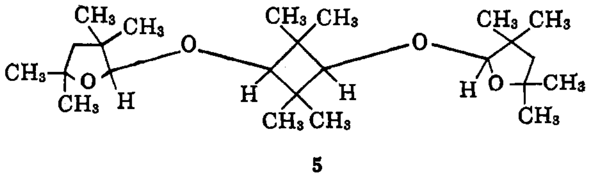
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Synthesis of Esters for Solvolytic Studies.—Treatment of pure *cis*-2,2,4,4-tetramethylcyclobutane-1,3-diol with one equivalent of *p*-toluenesulfonylchloride in pyridine gave a 58% yield of the *cis*-hydroxytosylate and a 10% yield of the *cis*-ditosylate. Pure *trans*-diol when treated in the same manner gave a 35% yield of the *trans*-hydroxytosylate and an 8% yield of *trans*-ditosylate. Because the diesters proved to have such

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[1] Taken from the dissertation submitted by D. L. N. in partial fulfillment of the requirements for the Ph.D. degree, Cornell University, June, 1963.

[2] National Science Foundation Predoctoral Fellow, 1959–1963.

[3] R. H. Hasek, R. D. Clark, and J. H. Chaudet, *J. Org. Chem.*, **26**, 3130 (1961). The *cis*-diol was essentially unchanged by an acid treatment that completely cleaved the *trans*-diol.

[4] C. F. Wilcox, Jr., and S. S. Chibber, *ibid.*, **27**, 2332 (1962).

[5] With the high concentrations employed the dehydrations are heterogeneous. Under conditions where the *trans*-diol reacted completely, the *cis*-diol was recovered unchanged; however, under much more vigorous conditions, the *cis*-diol reacted to give intractable products.

[6] The stereochemistry of the bisacetal **5** is uncertain.

[7] C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3454 (1963).