pentanol. A sample having bp 90–91° (97 mm) and $n^{25}D$ 1.3861 was analyzed.

Anal. Calcd for $C_5H_2Br_2F_8O$: Br, 40.00; F, 38.98. Found: Br, 40.46, 40.43, 40.68; F, 38.24.

Nmr examination of both of the products above indicated that they were alcohols (strong unsplit resonance with chemical shift moved by trifluoroacetic acid) containing another proton (complex splitting).

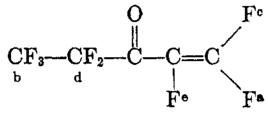
1,2-Dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone.—A 300-ml, four-necked flask fitted with a stirrer, thermometer, dropping funnel, and condenser was charged with 83.7 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanol and 23 ml of concentrated sulfuric acid. A solution prepared from 65.5 g of sodium dichromate dihydrate, 92 ml of water, and 38 ml of concentrated sulfuric acid was added from a dropping funnel during 15 min. The mixture was stirred and heated on a steam bath for 24 hr. Concentrated sulfuric acid, 90 ml, was added and liquid products were evaporated with vacuum into a Dry Ice cooled receiver. Phosphorus pentoxide was added to the distillate, and it was vacuum-distilled into the receiver of a Vigreux column. Phosphorus pentoxide (15 g) was added and the mixture was distilled. There was obtained 66.3 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone, bp 112–116.5°. A sample, bp 116.5°, $n^{25}D$ 1.3587, was analyzed.

Anal. Calcd for $C_2Br_2F_8O$: Br, 41.20; F, 39.17. Found: Br, 40.33, 40.56; F, 38.08.

Pentafluoroethyl Trifluorovinyl Ketone.—The pot of a small spinning band still with a side arm closed by a serum stopper was charged with 30 ml of sodium-dried dioxane and 20 g of zinc dust. The mixture was stirred and heated and 5 ml of dioxane was distilled. The column was set to a slow take off and 4.8 g of 1,2-dibromo-1,1,2,4,4,5,5,5-octafluoro-3-pentanone was added from a syringe through the serum stopper in small portions. A vigorous reaction occurred and distillate boiling at 85–100°, about 20 ml in all, was collected. Gas chromatography indicated the presence of a new compound in the material, and a quantity of this material was collected by large scale gas chromatography on a 20 ft × 3/8 in. column of Dow Corning silicone 200 oil on 48–65 mesh firebrick. The pentafluoroethyl trifluorovinyl ketone had bp 62° and was pure.

Anal. Calcd for C_5F_8O: C, 26.33; F, 66.66. Found: C, 25.85; F, 66.62.

The ultraviolet spectrum was similar to that of the methyl compound having λ_{max} 242 mμ (ϵ_{max} 5500) and λ_{max} 318 mμ (ϵ_{max} 27). Infrared bands at 5.6 and 5.9 μ were characteristic. The structure was confirmed by F^{19} nmr.



$$\underset{b}{CF_3}-\underset{d}{CF_2}-\overset{O}{\overset{\|}{C}}-\underset{F^e}{\underset{|}{C}}=C\begin{matrix}F^c\\F^a\end{matrix}$$

The resonance due to a, a pair of doublets, was centered at 680 cps from symmetrical tetrachlorodifluoroethane; that due to b, a doublet, was centered at 990 cps; that due to c, a pair of resonances, each of which was overlapping triplets, was centered at 1397 cps; that due to d, a pair of doublets, was centered at 3253 cps; the resonance due to e, a pattern of 21 lines formed by the overlapping of a pair of triplets split to quadruplets, was centered at 7029 cps. Coupling constants were 36 for ae, 12 for ac, 7 for be, 113 for ce, 8 for cd, and 22 cps for de.

Debromination of 22.5 g of dibromo ketone followed by gas chromatography of the product afforded 7.27 g, or 45% yield, of pentafluoroethyl trifluorovinyl ketone, about 98% pure according to gas chromatography. It had a boiling point of 62° with some decomposition.

Registry No.—**1a,** 15322-89-1; **1b,** 15322-70-0; **2a,** 15152-24-1; **2b,** 2070-67-9; **3a,** 15448-32-5; **3b,** 15448-33-6; **4a,** 15448-34-7; **4b,** 15448-35-8.

The Chemistry of Photodimers of Maleic and Fumaric Acid Derivatives. VI[1]

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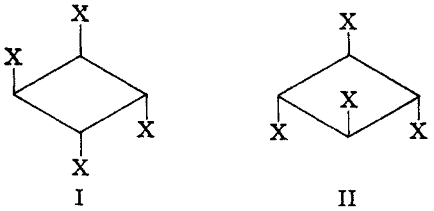
A number of 1,2,3,4-tetrasubstituted cyclobutanes have been prepared from *cis,trans,cis-* and *trans,trans,trans-*1,2,3,4-tetracarbomethoxycyclobutane. Two of these compounds, *cis,trans,cis-* and *trans,trans,trans-*1,2,3,4-tetraiodomethylcyclobutane, undergo an unexpected Grob-type cleavage with lithium aluminum hydride. A novel tricyclic system, namely, the bis anhydride of *trans,trans,trans-*1,2,3,4-cyclobutanetetracarboxylic acid, has also been prepared.

In earlier communications[1] it was reported that tetramethylenecyclobutane could be generated from a variety of substrates, including the 1,2,3,4-tetraiodomethyl- and tetrabromomethylcyclobutanes. At this time we wish to describe the synthesis of these precursors, as well as a variety of related compounds which are of interest in connection with independent studies of small ring systems.



I II

a, $X = CO_2CH_3$
b, $X = CO_2H$
c, $X = CH_2OH$
d, $X = CH_2Br$
e, $X = CH_2I$
f, $X = CH_2OTs$
g, $X = CH_3$
h, $X = COCH_3$
i, $X = COCHN_2$
j, $X = CH_2CO_2H$

The 1,2,3,4-tetrahydroxymethylcyclobutanes Ic and IIc were initially prepared by catalytic reduction of their respective methyl esters Ia and IIa at 250°.[5] Considerable isomerization and ring opening were encountered in the preparation of the *cis,trans,cis* isomer Ic under the rather drastic catalytic reduction conditions. Lithium aluminum hydride was subsequently found to provide homogeneous samples of Ic and IIc in high yields.

The tetraols Ic and IIc were converted into their respective tetrabromides Id and IId with phosphorus tribromide. The nmr spectrum of the *cis,trans,cis*-tetrabromide Id showed peaks at τ 6.35 (eight protons) and 7.25 (four protons). A similar spectrum was observed for the *trans,trans,trans* isomer IId (τ 6.44, eight protons

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[1] For the last paper in this series, see G. W. Griffin and L. I. Peterson, *J. Amer. Chem. Soc.*, **85**, 2268 (1963).

[2] National Institutes of Health Fellow, 1960–1962.

[3] National Institutes of Health Fellow, 1959–1960.

[4] Author to whom inquiries regarding this paper should be addressed: Louisiana State University in New Orleans, New Orleans, La. 70122.

[5] G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Amer. Chem. Soc.*, **83**, 2725 (1961).

and 7.79, one proton). The corresponding tetraiodides Ie and IIe[6] were prepared from their respective alcohols using red phosphorus and iodine.

p-Toluenesulfonyl chloride in pyridine converted the alcohols Ic and IIc into the tosylates If and IIf, respectively. The nmr spectrum of If exhibited signals at τ 5.95 (CH_2O, eight protons) and 7.55 (CH_3 and tertiary hydrogen, sixteen protons), in addition to the characteristic tosyl aromatic quartet centered at τ 2.40. The isomeric *trans,trans,trans* ester IIf showed signals at τ 6.10 (CH_2O), 7.56 (CH_3), 7.91 (tertiary cyclobutyl), and 2.40 (tosyl aromatic quartet).

It should be noted that the cyclobutyl proton signals of the compounds in the *trans,trans,trans* series appear at higher field than the corresponding protons in the *cis,-trans,cis* isomers.[7] This tendency has been observed in five such isomer pairs when the spectra are taken in carbon tetrachloride or deuteriochloroform. With few exceptions (*e.g.*, the tosylates) the melting points of the *trans,trans,trans* isomers are lower than those of the related centrosymmetric *cis,trans,cis* forms.

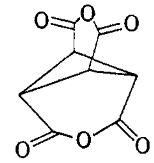
Two of the four possible isomeric 1,2,3,4-tetramethylcyclobutanes, the *cis,cis,cis* and *cis,cis,trans* forms, have been prepared by catalytic reduction of the *cis*- and *trans*-1,2,3,4-tetramethylcyclobutenes.[8] In connection with studies on the reduction of tetramethylenecyclobutane, it was of interest to synthesize the remaining isomers of 1,2,3,4-tetramethylcyclobutane, namely, Ig and IIg.

In our initial attempts to prepare the two unknown isomers of tetramethylcyclobutane, lithium aluminum hydride was allowed to react with the tetraiodides Ie and IIe. The desired tetramethylcyclobutane could not be detected upon attempted reduction of either iodide. The reduction products consisted entirely of terminally unsaturated hydrocarbons. In each instance a significant amount of 3,4-dimethyl-1,5-hexadiene was isolated. This diene was presumably formed by Grob-type cleavage[9] of the cyclobutane ring and nucleophilic attack by hydride ion on the iodomethyl groups. The numerous products formed in these reactions apparently arise from three competing processes, namely, Grob-type cleavage, E2 elimination, and nucleophilic substitution. Attempts to prepare the isomeric tetramethylcyclobutanes by lithium aluminum hydride reduction of the tetratosylates If and IIf were also unsuccessful.

trans,trans,trans-1,2,3,4-Tetraacetylcyclobutane (IIh) was prepared from the tetradiazo ketone (IIi) by the action of hydroiodic acid in chloroform. This convenient method for the conversion of acids into methyl ketones by way of the acid chloride and diazo ketone, originally reported by Wolfrom and Brown,[10] does not seem to have found widespread synthetic acceptance. The infrared spectrum of IIh shows the characteristic carbonyl frequency[11] at 1698 cm^{-1} and the nmr spectrum exhibits peaks at τ 6.68 and 7.95 in the expected ratio of 1:3. The gross structure of the "all-*trans*" tetraketone was confirmed by comparison of the tetramethyl ester of acid IIb formed by sodium hypobromite oxidation of IIh with an authentic sample of IIa. Some difficulty was encountered when an attempt was made to utilize the aforementioned diazo ketone technique for the preparation of *cis,trans,cis*-1,2,3,4-tetraacetylcyclobutane (Ih) from the tetradiazo ketone Ii. Alternate routes for the preparation of Ih involving the use of dimethyl cadmium and ethoxymagnesium diethylmalonate have also been tried without success.

A superior route to the extended acid IIj, which had been prepared and reported earlier,[12] has been developed and employs the tetrabromide IId as a precursor. Treatment of the bromide IId with potassium cyanide under reflux in ethanol provided the tetranitrile. The latter was subsequently hydrolyzed with base directly without isolation to the tetrabasic acid which was identical in all respects with that obtained earlier.

The bis anhydride III was prepared in 65% yield by treatment of *trans,trans,trans*-1,2,3,4-tetracarboxycyclobutane (IIb) with acetic anhydride. This is the last of three possible anhydrides of the 1,2,3,4-cyclobutanetetracarboxylic acids which remained to be synthesized. The *trans*-bis anhydride of *cis,trans,cis*-1,2,3,4-tetracarboxycyclobutane (Ib) and the *cis*-bis anhydride of the "all-*cis*" tetrabasic acid have been reported earlier.[5,13]



III

Experimental Section[14]

Preparation of *trans,trans,trans*-1,2,3,4-Tetrahydroxymethylcyclobutane (IIc). Method A. Catalytic Reduction.—To 100 ml of ethanol contained in a 250-ml steel bomb, was added 10 g (0.35 mole) of the "all-*trans*" tetraester IIa and 1.5 g of "copper chromite" catalyst.[15] Hydrogenation in a rocking autoclave at 250° required 8 hr. The initial pressure was 2000 psi, and this increased to 3200 psi during the course of the reaction. Removal of the catalyst by filtration and evaporation of the solvent under reduced pressure afforded the crude alcohol IIc in 98% yield. The tetrol, initially an oil, crystallized on standing.

The nmr spectrum of this compound, determined in deuterium oxide, exhibited signals at 68.7 and 170 cps (2:1) at higher field from water.

To 0.075 g (0.425 mmol) of the tetraol in 3 ml of pyridine was added 1 ml of benzoyl chloride. The resulting suspension was warmed at 80° for 2 min and then poured into 10 ml of water. The hydrolysis mixture was then extracted with ether and the combined organic phases dried over calcium sulfate. The volatile solvents were removed under reduced pressure and the residual oil was dissolved in ethanol. The ethanol solution upon cooling deposited 0.15 g (60%) of the tetrabenzoate of IIc: mp 87–88.5°; $\nu_{max}^{CCl_4}$ 3070, 3040, 2950, 2890, 1732 (s), 1450, 1312, 1272 (s), 1180, 1110, 1098, 1072, 1030, 710 (s) cm^{-1}.

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(6) R. Criegee and H. Hover, *Chem. Ber.*, **93**, 2521 (1960).

(7) An exception is made for the isomeric tetrahydroxymethylcyclobutanes Ic and IIc where the reverse is true. In this case, intramolecular hydrogen bonding and/or solvent effects (D_2O) may be responsible for the apparent atypical behavior.

(8) R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).

(9) C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955); C. Grob (Kekulé), "Symposium on Theoretical Organic Chemistry," Butterworth and Co. Ltd., London, 1959, p 114.

(10) M. L. Wolfrom and R. L. Brown, *J. Amer. Chem. Soc.*, **65**, 1516 (1943).

(11) L. J. Bellamy, *ibid.*, **65**, 132 (1943).

(12) G. W. Griffin, R. B. Hager, and D. F. Veber, *ibid.*, **84**, 1008 (1962).

(13) G. W. Griffin and D. F. Veber, *ibid.*, **82**, 6417 (1960).

(14) All melting points are uncorrected and were obtained using a stirred, Thomas–Hoover silicone oil bath. Infrared spectra were measured in a Perkin-Elmer Model 221 double-beam instrument and the proton magnetic resonance spectra were obtained using the Varian A-60 apparatus with tetramethylsilane as an internal standard. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(15) H. Adkins, E. Burgoyne, and H. Schneider, *J. Amer. Chem. Soc.*, **72**, 2626 (1950).

Anal. Calcd for $C_{36}H_{32}O_8$: C, 72.96; H, 5.44. Found: C, 73.12; H, 5.32.

The nmr spectrum determined in carbon tetrachloride shows absorption in the expected regions. Two doublets are present at τ 2.12 and 2.60, the characteristic region for aromatic protons. Peaks at τ 5.65 and 7.54 are consistent in area and position for that expected for $-CH_2O-$ and *t*-cyclobutyl hydrogens, respectively. The infrared spectrum determined in carbon tetrachloride shows a carbonyl band at 1732 (s) cm^{-1}.

Essentially the same procedure described above for the preparation of the *trans,trans,trans*-tetraol IIc was employed for the preparation of the *cis,trans,cis* isomer Ic.

Preparation of *cis,trans,cis*-1,2,3,4-Tetrahydroxymethylcyclobutane (Ic). Method B. Lithium Aluminum Hydride Reduction.—*cis,trans,cis*-1,2,3,4-Tetracarbomethoxycyclobutane (Ia) (12.0 g, 0.042 mol) dissolved in 320 ml of ether and 320 ml of benzene was reduced in the inverse manner by adding 4.0 g (0.11 mol) of lithium aluminum hydride. A superior procedure for accomplishing this consists of extracting the reducing agent into the stirred ether solution from a Soxhlet thimble with the hot solvent. After heating under reflux overnight, the reaction mixture was hydrolyzed with 40 ml of 50% aqueous methanol. The resulting mixture was filtered and the solid material subsequently extracted for 24 hr with methanol. After removal of the volatile solvents under vacuum the semicrystalline residue was dried over phosphorus pentoxide, (6.43 g, 87%). The nmr spectrum of Ic in D_2O exhibits resonance at 72.0 and 156 cps upfield from water in the expected 2:1 ratio.

The tetraol was characterized as its benzoate and after recrystallization from 1-butanol melted at 104–105°:[16] ν_{max}^{KBr} 3020, 2925, 1721 (s), 1312, 1268, 1179, 1118 (s), 1066, 1027, 955, 852, 830, 806 cm^{-1}.

The yields of the "all-*trans*" tetrabromomethyl derivative (IId), mp 54–55.5° (ethanol), were somewhat higher (10.2 g, 71%): ν_{max}^{KBr} 2961, 2937, 2922, 1435, 1317, 1252, 1232 (s), 1210 (s), 1100, 1075, 1060, 982, 900, 830, 818, 650 (s), 615 (s) cm^{-1}.

Anal. Calcd for $C_8H_{12}Br_4$: C, 22.45; H, 2.83; Br, 74.72. Found: C, 22.67; H, 3.16; Br, 74.45.

The nmr spectrum of the *cis,trans,cis* isomer (Id) determined in deuteriochloroform shows peaks at τ 6.35 and 7.25 (2:1) while that of the *trans,trans,trans* isomer (IId) exhibits signals at τ 6.44 and 7.79 (2:1).

Preparation of *trans,trans,trans*-1,2,3,4-Tetraiodomethylcyclobutane (IIe).—Molten *trans,trans,trans*-1,2,3,4-tetrahydroxymethylcyclobutane (10.0 g, 0.057 mol) was added with the aid of an infrared lamp to a mixture of iodine (63.3 g, 0.25 mol) and red phosphorus (5.15 g, 0.17 mol) which previously had been heated to 70° for 1 hr. The alcohol was added at such a rate that each drop reacted completely. The resulting solution was stirred at 120° for 5 hr. The reaction mixture was diluted with 50 ml of benzene and cooled to 0° and the excess phosphorus triiodide decomposed by adding ice water. The hydrolysis mixture was then extracted five times with 50-ml portions of benzene. The combined benzene extracts were washed with an aqueous solution of sodium sulfite to remove iodine and was dried over anhydrous calcium sulfate. The benzene was then removed under vacuum and the residual solid was recrystallized from cyclohexane to give colorless crystals of the tetraiodide (17.0 g, 48%, mp 102–102.5°): ν_{max}^{KBr} 2951, 2929, 1422, 1418, 1315, 1307, 1240, 1215, 1175 (s), 1085, 928, 800, 790, 610 cm^{-1}.

Anal. Calcd for $C_8H_{12}I_4$: C, 15.71; H, 1.32; I, 82.97. Found: C, 15.61; H, 1.50; I, 83.05.

Alternately, the *trans,trans,trans*-tetraiodide IIe may be prepared from the corresponding tetrabromide IId. *trans,trans,trans*-1,2,3,4-Tetrabromomethylcyclobutane (0.203 g, 4.7 mmol) and 0.31 g (20.5 mmol) of sodium iodide were dissolved in 50 ml of dry acetone and heated under reflux for 6 hr. The precipitated sodium bromide was separated by filtration and the solvent was removed under vacuum. Recrystallization of the residual material from cyclohexane gave 0.19 g (65%) of the tetraiodide (mp 102°) whose infrared spectrum was identical with that of the product obtained from the reaction of phosphorus triiodide with the *trans,trans,trans*-tetraalcohol IIc.

Preparation of *cis,trans,cis*-1,2,3,4-Tetraiodomethylcyclobutane (Ie).—Essentially the same procedure was employed as described earlier for the preparation of the *trans,trans,trans* isomer. The product obtained in 30% yield melted at 140° after recrystallization from cyclohexane: ν_{max}^{KBr} 2946, 2925, 1439, 1429, 1420, 1360, 1262, 1238, 1230, 1200 (s), 1185, 1175, 1140, 1115, 1035, 803, 669, 635 cm^{-1}.

Anal. Calcd for $C_8H_{12}I_4$: C, 15.71; H, 1.32; I, 82.97. Found: C, 15.71; H, 1.45; I, 83.25.

The *cis,trans,cis*-tetraiodide Ie was also prepared from the corresponding tetrabromide. *cis,trans,cis*-1,2,3,4-Tetrabromomethylcyclobutane (Id) was heated under reflux with sodium iodide in acetone. A 53% yield of the tetraiodide Ie (mp 139–140°) was obtained upon work-up in the manner described for the *trans,trans,trans* isomer prepared in this fashion. The iodide was shown to be identical with that obtained upon treatment of the *cis,trans,cis*-tetraol Ic with phosphorus triiodide by comparison of infrared spectra.

Preparation of the Tetratosylate (IIf) of *trans,trans,trans*-1,2,3,4-Tetrahydroxymethylcyclobutane.—*trans,trans,trans*-1,2,3,4-Tetrahydroxymethylcyclobutane (1.0 g, 6.25 mmol) was added in portions to a stirred solution of *p*-toluenesulfonyl chloride (4.8 g, 25.0 mmol) in 40 ml of dry pyridine. The temperature was maintained below 0° during the course of addition. After being stirred for 24 hr at 0°, the reaction mixture was poured into 90 ml of 10% hydrochloric acid solution at 0°. The oil which separated slowly solidified and was recrystallized from absolute ethanol to give 0.5 g (10%) of the colorless crystalline tetratosylate, mp 142–143°.

Anal. Calcd for $C_{36}H_{40}O_{12}S_4$: C, 54.53; H, 5.08. Found: C, 54.03; H, 4.98.

Preparation of the Tetratosylate (If) of *cis,trans,cis*-1,2,3,4-Tetrahydroxymethylcyclobutane.—Essentially the same procedure was employed which is described above for the preparation of the *trans,trans,trans* isomer IIf. The melting point of the *cis,trans,cis* tetratosylate If was 124.5–125° after recrystallization from absolute ethanol. Only a 10% yield of the product could be obtained.

Anal. Calcd for $C_{36}H_{40}O_{12}S_4$: C, 54.53; H, 5.08. Found: C, 54.02; H, 4.85.

The infrared spectra of If and IIf show absorption bands at 1357 and 1185 cm^{-1} characteristic of sulfonic acid esters.[17]

Conversion of *cis,trans,cis*-1,2,3,4-Tetratosylmethylcyclobutane (If) into *cis,trans,cis*-1,2,3,4-Tetraiodomethylcyclobutane (Ie).—*cis,trans,cis*-1,2,3,4-Tetratosylmethylcyclobutane (If) (1.00 g, 1.25 mmol) and sodium iodide (0.80 g, 5.33 mmol) were dissolved in 50 ml of dry acetone and heated at the reflux temperature for 6 hr. The precipitated sodium *p*-toluenesulfonic acid was collected by filtration and the volatile solvents were removed from the filtrate under vacuum. The residual white solid was recrystallized from cyclohexane to give 0.25 g (32%) of *cis,trans,cis*-1,2,3,4-tetraiodomethylcyclobutane, mp 139–140°. The infrared spectrum of this material was identical with that of the tetraiodide obtained from the reaction of *cis,trans,cis*-1,2,3,4-tetrahydroxymethylcyclobutane with phosphorus triiodide.

Conversion of *trans,trans,trans*-1,2,3,4-Tetratosylmethylcyclobutane (IIf) into *trans,trans,trans*-1,2,3,4-Tetraiodomethylcyclobutane (IIe).—The same reaction with sodium iodide as described above for the *cis,trans,cis* isomer was performed with *trans,trans,trans*-1,2,3,4-tetratosylmethylcyclobutane to give the corresponding *trans,trans,trans*-tetraiodide, mp 102–103° (48%). The identity of the product was again confirmed by direct comparison of the infrared spectrum with the previously obtained *trans,trans,trans*-tetraiodide.

Attempted Synthesis of *cis,trans,cis*- and *trans,trans,trans*-1,2,3,4-Tetramethylcyclobutanes (Ig and IIg).—In each instance 3.0 g (4.9 mmol) of the corresponding tetraiodide was placed in a Soxhlet thimble and extracted with the refluxing solvent into an ether solution (150 ml containing 0.5 g (0.013 mol) of lithium aluminum hydride). After the addition of the iodide was complete, the reaction mixture was cautiously decomposed with water and the ether layer was dried over anhydrous calcium sulfate. The ether was then removed by distillation. Gas chromatography of the higher boiling fractions using a Carbowax 20M column revealed that the mixture contained at least four components, none of which had the properties expected of the desired tetramethylcyclobutane. The infrared spectrum of

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[16] It is noteworthy that an isomeric tetrabenzoate (mp 149–150°) tentatively assigned a cyclobutane structure was reported by Raphael. On the basis of its physical properties it is clear that, if this product is indeed a cyclobutane derivative, it does not possess the stereochemistry of Ic or IIc. See R. A. Raphael, *J. Chem. Soc.*, 401 (1952).

[17] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 364.

each component exhibited strong absorption in the 880–915 cm^{-1} region, characteristic of terminal olefinic groups. Only one of the major components was identified in each instance and this was shown to be 3,4-dimethyl-1,5-hexadiene by comparison of the infrared spectrum with that of the authentic diene.

Preparation of *trans,trans,trans*-1,2,3,4-Tetraacetylcyclobutane (IIh).—A solution of 15 g (0.049 mol) of the acid chloride of *trans,trans,trans*-1,2,3,4-tetracarboxycyclobutane (IIb)[12] in 300 ml of anhydrous ether was added over a period of 30 min to a solution of diazomethane prepared from 90 g of N-nitrosomethylurea.[18] The resulting mixture was stirred for 1 hr after addition was complete. The volatile solvents were then removed under reduced pressure to a volume of 250 ml and the solid tetradiazoketone IIi (16 g, 100%) collected on a filter. The infrared spectrum of this compound possesses bands at 2110 (s) and 1639 (m) cm^{-1} which are characteristic of diazoketones.[19]

The diazo ketone was suspended in 800 ml of chloroform in a separatory funnel and treated with 100 ml of 47% hydriodic acid in portions small enough that the evolution of nitrogen could be controlled. When the reaction had subsided, the funnel was shaken vigorously and the layers separated. The chloroform layer was washed first with 20 ml of water, then with sufficient saturated sodium thiosulfate solution to remove the liberated iodine, and finally with 20 ml of water. The organic phase was then dried over calcium sulfate, treated with Norit, and finally evaporated to dryness under reduced pressure. The residual solid was sublimed at 95° (0.8 mm) and the sublimate recrystallized twice from carbon tetrachloride to yield 5.9 g (75%) of *trans,trans,trans*-1,2,3,4-tetraacetylcyclobutane (IIh): mp 134–137°; $\nu_{\max}^{\text{KBr}}$ 3400, 3006, 2943, 2920, 1698 (s), 1423, 1364, 1327, 1300, 1180 (s), 1068, 900, 600 cm^{-1}.

Anal. Calcd for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.12; H, 7.10.

The nmr spectrum obtained in carbon tetrachloride had two singlet signals at τ 7.95 and 6.88 (3:1).

Hypobromite Oxidation of *trans,trans,trans*-1,2,3,4-Tetraacetylcyclobutane (IIh).—To a solution of sodium hypobromite, prepared by the addition of 0.30 ml (5.58 mmol) of bromine to 0.94 g (23.5 mmol) of sodium hydroxide in 13 ml of water at 5°, was added 100 mg (0.45 mmol) of *trans,trans,trans*-1,2,3,4-tetraacetylcyclobutane (IIh). After the resulting mixture had been stirred for 2 hr an additional 100 ml of water was added, and the bromoform removed by steam distillation. The residual solution was then cooled and acidified with hydrochloric acid. Evaporation of this acidic solution to dryness provided a solid residue which was transformed, by the action of diazomethane in ether, into *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane (IIa) (61.3 mg, 48%).

Preparation of *trans,trans,trans*-1,2,3,4-Cyclobutanetetraacetic Acid (IIj) from the Tetrabromide IId.—To 60 ml of ethanol was added 48 g (0.112 mol) of the "*all-trans*" tetrabromide IId and 37 g (0.56 mol) of potassium cyanide. The resulting solution was heated under reflux for a period of 30 hr. The reaction mixture after first being cooled to 0° was filtered, and the material which collected on the filter was washed with two 100-ml portions of ethanol. The combined filtrates were then concentrated to approximately 75 ml and finally heated for 12 hr with 22.5 g (0.56 mole) of sodium hydroxide in 100 ml of ethanol. The reaction mixture was then cooled, diluted with 200 ml of water, and acidified to pH 2 with hydrochloric acid. After treatment with Norit, the volatile solvents were removed under reduced pressure. When the volume reached, approximately 50 ml 17.8 g (55%) of crystalline solid was deposited, which proved to be identical in all respects to a sample of *trans,trans,trans*-1,2,3,4-cyclobutanetetraacetic acid prepared earlier.[12]

Preparation and Structure Proof of the "Cage" Anhydride (III).—*trans,trans,trans*-1,2,3,4-Tetracarboxycyclobutane (28 g, 0.13 mol) and 900 ml of acetic anhydride were heated under reflux for 5 hr. The resulting solution was then distilled at atmospheric pressure to a residual volume of 200 ml which, upon cooling in an ice bath for several hours, deposited 15 g (63%) of crystalline "cage" anhydride III. Concentration of the mother liquor afforded an additional 3 g of anhydride. Recrystallization of III from acetic anhydride provided cubic crystals: mp >280° dec; $\nu_{\max}^{\text{KBr}}$ 3060, 3050, 3030, 3020, 1820 (s), 1760 (s), 1262, 1220, 1195, 1110, 960, 810, 740 cm^{-1}.

Anal. Calcd for $C_8H_4O_6$: C, 48.99; H, 2.06. Found: C, 49.40; H, 2.32.

A small sample of III was allowed to stand in methanol. After 2 days the anhydride had dissolved and the excess methanol was removed under reduced pressure. Addition of diazomethane in ether to the residue afforded an ester identical in all respects with an authentic sample of *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane (IIa).

Registry No.—Ic, 1128-49-0; Ic tetrabenzoate, 15377-84-1; Id, 15377-85-2; Ie, 15377-86-3; If, 4092-19-5; IIc, 15377-99-8; IIc tetrabenzoate, 15377-88-5; IId, 15377-89-6; IIe, 15523-33-8; IIf, 15523-34-9; IIh, 15377-90-9; III, 15377-91-0.

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