

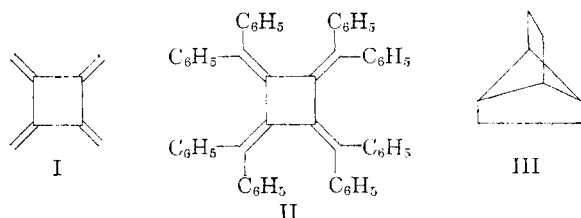
[CONTRIBUTION NO. 1652 FROM THE STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY, NEW HAVEN, CONN.]

The Chemistry of Photodimers of Maleic and Fumaric Acid Derivatives.<sup>1</sup> I. Dimethyl Fumarate DimerBY G. W. GRIFFIN, A. F. VELLTURO<sup>2</sup> AND K. FURUKAWA

RECEIVED JANUARY 24, 1961

Irradiation of dimethyl fumarate in the solid state affords a dimer, *cis,trans,cis*-1,2,3,4-tetracarboxymethoxycyclobutane, whose stereochemistry can be rationalized in terms of direct bond formation between nearest neighbor molecules in the crystal lattice of the monomer. Isomerization of this dimer to the thermodynamically more stable *trans,trans,trans*-tetracarboxymethoxycyclobutane is readily achieved thermally. The reduction of the *trans,trans,trans*-isomer and the hydrolysis of both isomers as well as their reactions with phenylmagnesium bromide were also studied.

In the course of studies directed toward the synthesis of the elusive 1,2,3,4-cyclobutanetetracarboxylic acids<sup>3-7</sup> to be employed as possible precursors for the unknown tetramethylenecyclobutane (I),<sup>8</sup> tetrakis-(diphenylmethylene)-cyclobutane (II)<sup>9</sup> as well as the tricyclic system III, we have irradiated several derivatives of maleic and fumaric acid in the solid state with formation of the corresponding cyclobutane derivatives.<sup>1</sup>



Although numerous examples of solid state olefin photodimerizations appear in the literature,<sup>10</sup> no broad study of the scope of this method for the preparation of substituted cyclobutanes has been reported. The primary purpose of the work presented in this report is to determine the structure and study the properties of the dimer obtained from dimethyl fumarate. However, it is hoped that these data coupled with crystallographic studies and results obtained with a series of related olefins will shed some light on the more general problem of the mechanism of olefin photodimerizations in the solid state. Of particular interest is the significance of monomer lattice geometry (*i.e.*, intermolecular distances and relative orientations) in allowing dimer formation and dictating product stereochemistry.<sup>11</sup>

(1) For a preliminary communication on this subject, see G. W. Griffin, J. E. Basinski and A. F. Vellturro, *Tetrahedron Letters*, No. 3, 13 (1960).

(2) Predoctoral N.I.H. Fellow, 1960-1961.

(3) Y. Shibata, *Ber.*, **43**, 2619 (1910).

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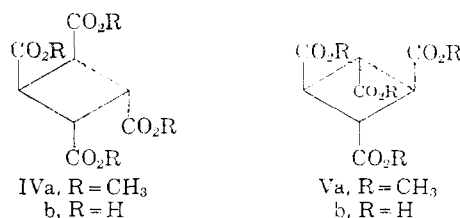
(8) J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

(9) H. Shechter and R. O. Uhler have recently published data which indicate that the photodimer of tetraphenylbutatriene possesses this structure; see *Dissertation Abstr.*, **21**, 765 (1960).

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(11) For a preliminary report on a study of the effect of monomer crystal structure in determining the course of solid state reactions, see G. M. J. Schmidt, Abstracts, 4th International Congress, International Union of Crystallography, Montreal, July, 1957, p. 65. It is reported that the dimerizations of the alpha and beta modifications of *trans*-cinnamic acid to  $\alpha$ -truxillic and  $\beta$ -truxinic acids, respectively, may be

The technique used in the dimerization of dimethyl fumarate consisted of irradiating a thin layer of the monomer on the inner surface of a glass tube with a light source which had been inserted into the tube. The dimethyl fumarate was deposited from solution on the inner surface of the tube by evaporation of solvent under a nitrogen stream. The system was thermostated at 25° and the irradiation was continued for a period of 1-5 days. Under these conditions dimethyl fumarate undergoes a 59% conversion to a stereoisomer of 1,2,3,4-tetracarboxymethoxycyclobutane (m.p. 144-145°). It is noteworthy that only one product could be isolated from the irradiation although four isomers are possible. On inspecting the X-ray crystallographic data for dimethyl fumarate<sup>12</sup> it appeared that the most reasonable structure for the dimer was the *cis,trans,cis* or "chair" form (IVa). Professor R. Criegee and co-workers<sup>13</sup> have recently synthesized three of the four possible isomeric 1,2,3,4-cyclobutanetetracarboxylic acids and their methyl esters by ozonolysis of cinnamic acid dimers of known stereochemistry. The fourth isomer possessing *cis,cis,cis* stereochemistry (m.p. 203-205°) was obtained in our laboratories from *cis*-heptacyclicene, an acenaphthylene dimer, by ozonolysis.<sup>14,15</sup> We are indebted to Professor Criegee for confirming by mixture melting point and infrared determinations that the dimethyl fumarate dimer does indeed possess the "chair" structure IVa.



IVa, R = CH<sub>3</sub>  
b, R = H

Va, R = CH<sub>3</sub>  
b, R = H

The *cis,trans,cis*-isomer is thermally stable up to 200° and for short periods at 250°, but undergoes thermal isomerization at 300° in 50% yield rationalized in terms of the packing arrangement of nearest neighbor molecules in the crystal structure of the monomer.

(12) I. E. Knaggs and K. Lonsdale, *J. Chem. Soc.*, 417 (1942).

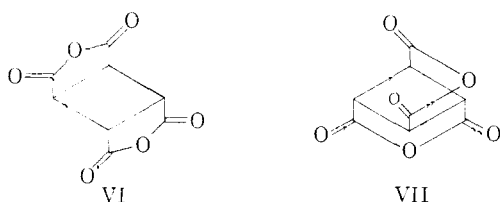
(13) R. Criegee, Private Communication; R. Criegee and H. Höver, *Ber.*, **93**, 2521 (1960).

(14) G. W. Griffin and D. Veber, *J. Am. Chem. Soc.*, **82**, 6417 (1960).

(15) Professor Criegee has recently been successful in obtaining *cis,cis,cis*-tetracarboxymethoxycyclobutane by ozonolysis of peritruxillic acid anhydride and subsequent esterification of the oxidation product with diazomethane. This compound has an infrared spectrum identical in all respects to that of our product.

to an isomeric ester, m.p. 126–127°. The thermally rearranged product was assigned structure Va, having the *trans,trans,trans* stereochemistry, on the basis of melting point and infrared data for authentic Va supplied by Professor Criegee.<sup>13</sup> Further confirmation of this assignment was obtained by n.m.r. analysis. The rearrangement of IVa to the more stable isomer can also be effected with sodium methoxide, albeit in much lower yields (18%).

Essentially quantitative hydrolysis of the tetramethyl esters to IVb and Vb can be achieved with concentrated hydrochloric acid. Esterification of IVb with diazomethane to IVa established that the less stable isomeric ester IVa does not rearrange under these hydrolysis conditions. When heated at its melting point in a sublimator the tetrabasic acid IVb loses water and affords a dianhydride which has been assigned the *trans* structure VI. Conversion of IVb to VI can be accomplished more effectively with thionyl chloride. The assignment



of structure is supported by the infrared spectrum of VI which exhibits the characteristic unconjugated anhydride peaks at 5.38 and 5.60 $\mu$ .<sup>16</sup> Furthermore, this anhydride is identical in all respects to the dimer obtained from the *solid state* irradiation of maleic anhydride.<sup>1</sup> It is interesting, however, that the "all-*trans*" isomeric tetrabasic acid Vb undergoes thermal isomerization and dehydration at 265° under reduced pressure to form VI. As yet conditions have not been found which allow isolation of the pure *trans,trans,trans*-dianhydride VII, although its formation from the "all-*trans*" acid and acetyl chloride is indicated by infrared analysis.

Applying the lead dioxide bis-decarboxylative technique of Doering and co-workers<sup>17</sup> to the dianhydride VI could formally lead to cyclobutadiene; however up to the present time experiments along these lines have proved unrewarding. Although more than one mole of carbon dioxide was liberated when the anhydride VI was heated with active lead dioxide, no products could be collected in the low temperature traps and no precipitation occurred when the effluent nitrogen carrier gas was passed through a concentrated silver nitrate solution.<sup>18</sup> The use of lead tetraacetate in pyridine as a milder decarboxylative agent for the tetrabasic acid IVb also proved ineffectual, probably because of the low solubility of the polybasic acid in acetonitrile and benzene which were used as solvents.<sup>19</sup>

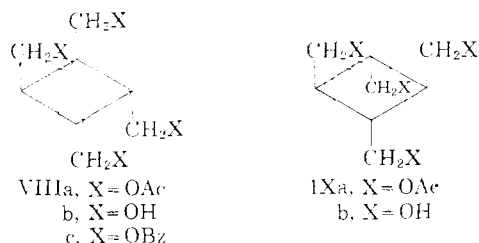
(16) The doublet for the anhydride from *cis,cis*-3-methylcyclobutane-1,2-dicarboxylic acid is at 5.41 and 5.63 $\mu$ . See H. N. Cripps, J. K. Williams, V. Tullio and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 4904 (1959).

(17) W. v. E. Doering, M. Farber and A. Sayigh, *ibid.*, **74**, 4370 (1952).

(18) M. Avram, E. Marica and C. D. Nenitzescu, *Ber.*, **92**, 1088 (1959).

(19) C. A. Grob, M. Ohta and A. Weiss, *Angew. Chem.*, **70**, 343 (1958).

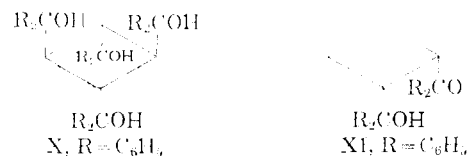
Conversion of the tetraester IVa to the corresponding tetraacetate VIIIa was accomplished in a one-step process designed to avoid the problems associated with isolating the water-soluble alcohol VIIIb from an aqueous system. In this procedure the alcoholate obtained from the reduction of IVa with lithium aluminum hydride in the inverse manner was treated directly with acetyl chloride. The resulting tetraacetate VIIIa after purification by distillation, was converted to the benzoate



VIIIc by basic hydrolysis and subsequent treatment with benzoyl chloride. The results of a study on the pyrolysis of the tetraacetate and the preparation of IXa and IXb will be reported at a later date.

In connection with studies on the tetraacetate VIIIa it is noteworthy that an isomer (m.p. 104–105°) tentatively assigned a cyclobutane structure was obtained by Raphael<sup>20</sup> as a by-product from the partial catalytic hydrogenation of 1,4-diacetoxycyclobutane-2. On the basis of physical properties it is clear that if this product is indeed a cyclobutane derivative, it does not possess the stereochemistry of VIIIa. A preliminary examination, however, indicates that the n.m.r. spectrum of the tetrabenzoate obtained by Raphael from the tetraacetate is too complex to arise from a cyclobutane structure such as VIIIc.<sup>21</sup>

Further studies on the tetraesters IVa and Va included their reactions with phenyl Grignard reagent and with sodium metal. The inverse addition of phenylmagnesium bromide to the 1,2,3,4-tetracarboxymethoxycyclobutane possessing the "chair" stereochemistry afforded a compound which exhibited both carbonyl and hydroxyl bands in its infrared spectrum. In contrast, the corresponding Grignard reaction with the "all-*trans*" isomer Va gave a compound possessing no carbonyl absorption in its spectrum. The latter product has been assigned the "all-*trans*" structure X on the basis of its infrared and combustion analysis.<sup>22</sup> The difference in behavior shown by the two esters

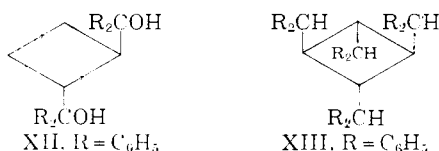


(20) R. A. Raphael, *J. Chem. Soc.*, 401 (1952).

(21) We are indebted to R. A. Raphael for a sample of this material and to Nugent Chamberlain of the Humble Oil and Refining Co., Baytown, Tex., for n.m.r. analysis.

(22) The tetraalcohol X has also been prepared from *trans,trans,trans*-1,2,3,4-tetrabenzoxycyclobutane by treatment with phenylmagnesium bromide. The experimental details will be described in a later paper.

is consistent with the observations made by Alberman and Kipping on the reactions of the dimethyl esters of *cis*- and *trans*-1,2-cyclobutanedicarboxylic acids with phenylmagnesium bromide.<sup>23</sup> While the *trans*-diester reacted with four moles of Grignard reagent to give the diol XII which was subsequently converted to the diolefin, the *cis* isomer, presumably because of hindrance, reacted with only three moles affording the ketoalcohol XI. Hydrogenolysis of X to 1,2,3,4-tetrabenzhydrylcyclobutane (XIII) was achieved with copper chromite catalyst in an autoclave at a pressure of 2700 p.s.i. and a temperature of 250°. The simplicity of the n.m.r. spectrum of XIII as well as the splitting and the relative peak areas all attest to the fact that the cyclobutane ring has been preserved in the Grignard reaction and subsequent reduction. Experiments designed to convert X to the tetrakis-(diphenylmethylene)-cyclobutane (II) are now in progress.



Whereas the "all-*trans*" ester Va reacted smoothly with phenyl Grignard reagent, no isolable products were obtained when it was treated with sodium-on-alumina<sup>24</sup> or sodium dispersed in toluene<sup>25</sup> under acyloin conditions.

### Experimental<sup>26</sup>

**Dimerization of Dimethyl Fumarate.**—The solvent from a solution of 10 g. (0.07 mole) of dimethyl fumarate in acetone was evaporated under a nitrogen stream while the container, a 500-ml. graduate cylinder, was rotated in a nearly horizontal position. A Westinghouse 15T8 Germicidal Sterilamp<sup>27</sup> was then inserted and irradiation was continued for a period of 1–5 days. During the course of the irradiation the temperature was maintained at 25–30° by immersing the tube in a large water-bath. After the irradiation was completed the dimer was separated from unreacted dimethyl fumarate and polymer by extraction with benzene, and finally recrystallized from the same solvent (Norit); m.p. 144–145° (60%). A mixture melting point determination showed this product to be identical to an authentic sample of the "chair" form of 1,2,3,4-tetracarboxymethoxycyclobutane (IVa) obtained by Criegee and co-workers from a cinnamic acid dimer of this stereochemistry.

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{16}\text{O}_8$ : C, 50.00; H, 5.60; mol. wt., 288. Found: C, 50.28; H, 5.55; mol. wt., 263 (Rast).

The infrared spectrum of the compound, determined in potassium bromide, shows two bands characteristic of a carbonyl function at 5.74(s) and 5.80(m)  $\mu$ . These bands merge when the spectrum is taken in chloroform. Other significant bands in the spectrum are found at 7.72(s), 8.33(m), 9.79(w), 10.55(w), 11.85(w), and 12.21(w)  $\mu$ . The n.m.r. spectrum determined in deuteriochloroform shows only two types of protons in the expected ratio of 1:3 with the less intense peak at  $\tau = 6.15$  and the other at  $\tau = 6.20$ . The position of the latter peak is consistent with that of the  $-\text{OCH}_3$  protons of methyl acetate ( $\tau = 6.35$ ).<sup>28</sup> The lack of

absorption in the region  $\tau = 3-4$  attests to the absence of vinyl protons. The major peak in the mass spectrum of the dimer is at  $M/e$  257 corresponding to loss of an  $-\text{OMe}$  fragment from the molecule.<sup>29</sup>

The tetrabenzyl ester was prepared by transesterification and was purified by two recrystallizations from benzene-hexane; m.p. 107.5–108.5°. The n.m.r. spectrum is consistent with the proposed structure (three peaks in the ratio of 1:2:5).

*Anal.* Calcd. for  $\text{C}_{36}\text{H}_{32}\text{O}_8$ : C, 72.96; H, 5.44. Found: C, 73.22; H, 5.28.

**Isomerization of *cis,trans,cis*-1,2,3,4-Tetracarboxymethoxycyclobutane (IVa).**—A Pyrex tube containing 1.0 g. (0.004 mole) of the dimer IVa was sealed at a pressure of 0.1 mm. The tube was then heated in a muffle furnace at 300° for 20 hours. After cooling, the dark solid was recrystallized twice from benzene (Norit) to give Va in 50% yield, m.p. 123–125° (reported<sup>13</sup> 127°).

Stereochemical equilibration was also effected by heating the dimer 0.28 g. (0.001 mole) with 0.3 g. (0.006 mole) of sodium methoxide in methanol for 2 hours. The resulting reaction mixture, after treatment with 10 ml. of a 10% ammonium chloride solution, was evaporated to dryness. The organic material was separated from the inorganic solids by sublimation at 80° (0.01 mm.) and subsequently purified by recrystallization from water; m.p. 127° (18%).

The infrared spectrum of this substance determined in potassium bromide shows absorption at 3.36(w), 5.77(s) and 8.25(s)  $\mu$ . The n.m.r. spectrum has bands at  $\tau = 6.67$  and  $\tau = 6.28$  in the proper ratio of 1:3, respectively.

**Hydrolysis of *cis,trans,cis*-1,2,3,4-Tetracarboxymethoxycyclobutane (IVa).**—Five grams (0.017 mole) of the dimer IVa was heated on a steam-bath with concentrated hydrochloric acid until complete solution was attained. The mixture was then evaporated to dryness under reduced pressure. The resulting solid after recrystallization from acetone-hexane lost water at 220–225°; reported<sup>13</sup> m.p. 226° dec. Treatment of the acid with diazomethane in ether provided the original dimer demonstrating that no isomerization had occurred during the hydrolysis stage.

**Hydrolysis of *trans,trans,trans*-1,2,3,4-Tetracarboxymethoxycyclobutane (Va).**—A mixture of 0.28 g. (0.001 mole) of the dimer and 5 ml. of concentrated hydrochloric acid was heated on a steam-bath until a homogeneous solution was obtained. This solution was then evaporated to dryness under reduced pressure. The residual solid was crystallized from either acetic acid-hexane or tetrahydrofuran-hexane solvent pairs; m.p. 261–264° dec., reported<sup>13</sup> 261–264° dec. Sublimation of a sample of this tetrabasic acid Vb at 265° (0.05 mm.) afforded a mixture of starting material and the "chair" dianhydride.

**Dehydration of *cis,trans,cis*-1,2,3,4-Tetracarboxycyclobutane (IVb).**—A 0.10-g. (0.0005 mole) sample of the tetracarboxycyclobutane was heated with 5.0 ml. of thionyl chloride for 3 hours. The excess thionyl chloride was removed by distillation under reduced pressure and the residue after being washed with hexane was collected on a filter and finally purified by sublimation.

The tetrabasic acid may also be dehydrated thermally by heating at 225–230° in a sublimator at 0.05 mm. A second sublimation is needed in order to free the anhydride from acid which also sublimes.

The infrared spectrum exhibits the characteristic anhydride doublet at 5.38 and 5.60  $\mu$  and is identical to the spectrum of the product obtained from the photodimerization of maleic anhydride in the solid state.

**Attempted Bis-decarboxylation of the Dianhydride VI.**—An intimate mixture of 0.50 g. of the dianhydride, 2.50 g. of active lead oxide and 10 g. of powdered pyrex glass was heated at 250° for 0.25 hour while being stirred in a stream of nitrogen. The effluent gases were passed in turn through silver nitrate and barium hydroxide traps. Although carbon dioxide was generated, there was no indication of any reaction occurring in the silver nitrate trap and repeated extraction of the residual material with solvents yielded no soluble organic products.

man, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 50.

(29) We are indebted to A. H. Struck and Miss R. Herberich, Stamford Research Laboratories, American Cyanamid Co., Stamford, Conn., for determination of the mass spectrum.

(23) K. B. Alberman and F. B. Kipping, *J. Chem. Soc.*, 779 (1951).

(24) W. v. E. Doering and P. LaFlamme, *Tetrahedron*, 2, 75 (1958).

(25) A. C. Cope and E. C. Herrick, *J. Am. Chem. Soc.*, 72, 983 (1950).

(26) Unless otherwise indicated all melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y. We are indebted to R. B. Hager and R. Willcott for 60mc. n.m.r. spectra.

(27) Maximum ultraviolet radiation (95%) at 253.7  $\mu$ .

(28) G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958); L. M. Jack-

**Preparation of *cis,trans,cis*-1,2,3,4-Tetraacetoxymethylcyclobutane (VIIIa).**—A 5.8-g. (0.02 mole) sample of the tetraester IVa dissolved in a mixture of 150 ml. of benzene and 150 ml. of dry ether was reduced in the inverse manner by adding 3.0 g. (0.08 mole) of lithium aluminum hydride. A superior procedure for accomplishing this consists of extracting the lithium aluminum hydride into the stirred ester solution from a Soxhlet thimble with the refluxing solvent. After the addition was completed 25 ml. of acetyl chloride in 50 ml. of ether was added dropwise and heating was continued for an additional 12 hours. The reduction mixture was finally decomposed by adding 200 ml. of water followed by 100 ml. of 10% sulfuric acid. The organic layer was removed and the aqueous phase extracted three times with 50-ml. portions of benzene. The combined organic layers were then dried over Drierite and finally concentrated to a dark oil (4.5 g.). Vacuum distillation of this oil (178–180° (0.02mm.)) provided 2.0 g. of the polyacetate VIIIa which slowly solidified on standing. The infrared spectrum of this compound measured in chloroform has bands at 5.80(s) and 8.09(s)  $\mu$ . The n.m.r. spectrum has peaks at  $\tau = 5.88$ ,  $\tau = 7.42$  and  $\tau = 8.00$  in the ratio of 2:1:3 which is consistent with the assigned structure.

*Anal.* Calcd. for  $C_{16}H_{24}O_8$ : C, 55.80; H, 7.03. Found: C, 55.26; H, 7.24.

**Preparation of *cis,trans,cis*-1,2,3,4-Tetrabenzoyloxymethylcyclobutane (VIIIc).**—A solution of 0.90 g. (0.0026 mole) of the tetraacetate VIIIa and 2.0 g. of potassium hydroxide in 50 ml. of methanol was heated under reflux for 2 hours. The methanol was then removed and the residue was heated for 3 hours with 50 ml. of benzoyl chloride. After hydrolysis of the excess benzoyl chloride the reaction mixture was repeatedly extracted with benzene. Removal of the benzene from the organic phase under vacuum afforded an oil which consisted largely of methyl benzoate. This in turn was removed by distillation and the residual oil was dissolved in ethanol and allowed to stand in the freezer. After 2 days crystals were deposited which upon recrystallization from 1-butanol melted at 104–105°. The infrared spectrum of this material determined in potassium bromide has bands at 5.82(s) and 7.90(s)  $\mu$ . The n.m.r. spectrum, determined in carbon tetrachloride, shows absorption at  $\tau = 2.10$ , 2.20, 2.65, 2.75 (aromatic),  $\tau = 5.45$  (—CH<sub>2</sub>—O) and  $\tau = 7.10$  (3° C—H) in the approximate ratio of 5:2:1, respectively.

*Anal.* Calcd. for  $C_{26}H_{32}O_4$ : C, 72.96; H, 5.44; mol. wt., 393. Found: C, 72.91; H, 5.54; mol. wt., 475 (Rast).

**Condensation of *cis,trans,cis*-1,2,3,4-Tetracarboxymethylcyclobutane (IVa) with Phenylmagnesium Bromide.**—A solution of 0.1 mole of phenylmagnesium bromide in 50 ml. of anhydrous tetrahydrofuran was added dropwise to a solution of 1.0 g. (0.0035 mole) of the tetraester in 200 ml. of boiling tetrahydrofuran. The first 10 ml. of Grignard solution turned the reaction mixture wine-red. After the addition was completed the solution was heated under reflux for 1 hour and then the temperature was raised to 80° by displacing the tetrahydrofuran with benzene. After cooling the reaction mixture to room temperature it was permitted to stand overnight while stirring was continued. Finally, decomposition was achieved by pouring the solution into an ammonium chloride-ice mixture and then allowing it to stand 0.25 hour. The organic layer was removed and the

aqueous phase extracted repeatedly with 50-ml. portions of benzene. After the combined organic layers had been dried over Drierite, the volatile solvents were removed. The residual solid was heated with enough benzene to effect solution. When the benzene was exchanged with methylcyclohexane 0.5 g. of crystals separated, which when recrystallized from benzene melted at 285–287° dec. The infrared spectrum of this compound has bands assignable to a hydroxyl function (3.03  $\mu$ ) and an aromatic carbonyl group (6.07  $\mu$ ).

**Condensation of *trans,trans,trans*-1,2,3,4-Tetracarboxymethylcyclobutane (Va) with Phenylmagnesium Bromide.**—The Grignard reagent prepared in tetrahydrofuran from 16 g. (0.70 g. atom) of magnesium turnings and 72 ml. of bromobenzene (0.70 mole) in 75 ml. of dry tetrahydrofuran was added dropwise to a well stirred solution of the tetraester Va in 250 ml. of tetrahydrofuran. After the addition was completed, the solution was heated under reflux for 2 hours, and then stirred an additional 12 hours at room temperature. The tetrahydrofuran was then displaced with benzene and, after being cooled, the reaction mixture was poured into a solution of ammonium chloride (70 g.) cooled to 0° with ice. After stirring 2–3 hours the resulting suspension was centrifuged and the solid which appeared at the interface was collected by decanting the solvents. This solid was dried, transferred to a Soxhlet thimble and extracted in turn with pentane to remove biphenyl; benzene, to extract hydroxyketones; and finally with tetrahydrofuran. After 3 to 5 hours of extraction, the tetracarbinol X began to crystallize from the boiling tetrahydrofuran and in 10–12 hours the extraction was completed. The product which precipitated when the extract was diluted with absolute ethanol melted above 300°. The infrared spectrum has bands at 3.00(s), 3.10(s) and 3.30(w)  $\mu$ . An n.m.r. spectrum was not obtained on the product because of its low solubility.

*Anal.* Calcd. for  $C_{26}H_{40}O_4$ : C, 85.68; H, 6.13. Found: C, 85.69; H, 6.06.

**Preparation of *trans,trans,trans*-1,2,3,4-Tetrabenzhydrylcyclobutane.**—A mixture of 0.50 g. (0.0006 mole) of the carbinol, 1.0 g. of copper oxide-copper barium chromite catalyst<sup>30,31</sup> and 100 ml. of ethanol was placed in a hydrogenation bomb and heated at 250° for 8 hours. The original hydrogen pressure was 1900 p.s.i. at room temperature. The hydrocarbon was obtained as a crystalline solid, insoluble in hot ethanol and was collected by decantation (0.25 g., 60%). After being recrystallized from methylcyclohexane the product melted at 234–237°. The n.m.r. spectrum has a complex peak in the aromatic region centered at  $\tau = 3.15$ , and two doublets in the aliphatic region at  $\tau = 5.84$  and  $\tau = 7.54$  with a coupling constant of 11.6 c.p.s. These peaks appeared to have the expected ratio 10:1:1, respectively.

*Anal.* Calcd. for  $C_{26}H_{42}$ : C, 93.29; H, 6.71; mol. wt., 721. Found: C, 93.33; H, 6.92; mol. wt., 715 (Rast).

**Acknowledgment.**—The authors are indebted to the Office of Ordnance Research, U. S. Army (Contract No. DA-ORD-31-124-61-G31) the Research Corporation and to the National Institutes of Health for a fellowship (GF-11,801).

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