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The Chemistry of Photodimers of Maleic and Fumaric Acid Derivatives. II.[1a] The Preparation of *cis,trans,cis*- and *trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane; the Acid Chlorides of 1,2,3,4-Tetracarboxycyclobutanes

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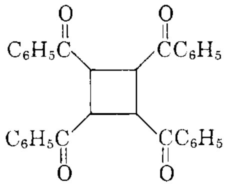
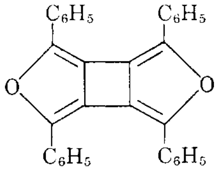
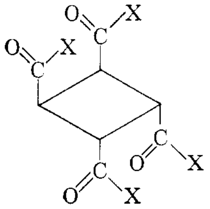
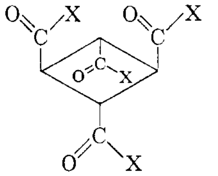
The acid chlorides of *cis,trans,cis*- and *trans,trans,trans*-1,2,3,4-tetracarboxycyclobutane have been prepared and employed as precursors for several symmetrically 1,2,3,4-tetrasubstituted cyclobutane derivatives including tetraaminocyclobutane, tetrabenzoylcyclobutane and cyclobutanetetraacetic acid.

Although the direct photodimerization of either *cis*- or *trans*-1,2-dibenzoylethylene to 1,2,3,4-tetrabenzoylcyclobutane has proved difficult to effect,[2] the anticipated isomers have been synthesized by an independent route from dimethyl fumarate dimer in order to facilitate the paper chromatographic detection of trace quantities of the dimers in the irradiation mixtures. Furthermore, it was hoped that *cis,trans,cis*-tetrabenzoylcyclobutane Ia might be induced to close to the bis-furan II, a biphenylene analog. Such a molecule, aside from being interesting in its own right, could formally lead to a cyclobutadiene derivative on reaction with a dienophile in the normal Diels–Alder manner.[3]


Ia, *cis,trans,cis*
b, *trans,trans,trans*


II

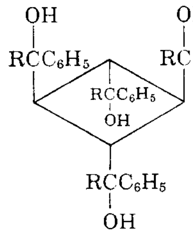

IIIa, X = OH
b, X = Cl

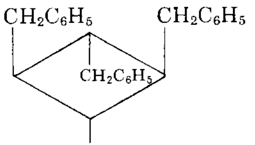

IVa, X = OH
b, X = Cl
c, X = OCH_3
d, X = OC_6H_5

On treatment with phosphorus pentachloride, the tetrabasic acids IIIa and IVa[1,4] react smoothly, affording the corresponding solid tetraacid chlorides IIIb (m.p. 76–77°) and IVb (m.p. 63–65°). These acid chlorides were isolated by distillation in 60% and 83% yields, respectively. Each was reconverted to the corresponding 1,2,3,4-tetracarbomethoxycyclobutane on treatment with methanol. The tetraesters had been independently characterized[1,4] and thus isomerization or rearrangement during the rather drastic treatment with phosphorus pentachloride and subsequent distillation is precluded.

Attempts to prepare the tetrabenzoyl derivative Ib by the conventional method of treating the acid chloride with diphenylcadmium proved unavailing. Synthesis of both tetraketones Ia and Ib was ultimately accomplished by allowing the respective acid chlorides to react with benzene in the presence of anhydrous aluminum chloride. As would be expected, the ketone Ia (m.p. 259–261°) is readily isomerized with acid or base to Ib (m.p. 254–256°), the thermodynamically more stable isomer. Furthermore, the infrared spectra, mass spectra, elemental analyses and Rast molecular weights are all consistent with the structures proposed for these products. Treatment of Ia with a variety of reagents, including polyphosphoric acid and sulfuric acid in acetic anhydride, in an attempt to obtain ring closure to II has up to this time proved unrewarding.

Addition of four moles of phenylmagnesium bromide to *trans,trans,trans*-1,2,3,4-tetrabenzoylcyclobutane (Ib) affords the carbinol Va, identical in all respects to the product obtained when *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane (IVc) was allowed to react with eight moles of phenylmagnesium bromide.[1] The tetraalcohol Va exhibits a marked tendency to eliminate benzophenone under a variety of dehydration conditions. *trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib) was converted smoothly to the tetraol Vb with lithium aluminum hydride. Our dehydration studies on Va and b will be reported at a later date.[5] Catalytic reduction of either the tetraol Vb or the


Va, R = C_6H_5
b, R = H


VI

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[1] (a) For the first paper in this series, see G. W. Griffin, A. Vellturo and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961). (b) N.I.H. Fellow, 1960–1962.

[2] The isomeric 1,2-dibenzoylethylenes are reluctant to straighten under conditions where dimethyl fumarate, maleic anhydride and fumaronitrile react readily (see G. W. Griffin, J. Basinski, A. Vellturo, *Tetrahedron Letters*, **No. 3**, 13 (1960)). A small yield of an uncharacterized higher molecular weight product, however, was obtained when the dibenzoylethylenes were subjected to irradiation in the solid state with a 150 w. General Electric reflector flood lamp. The nature of the product is currently under investigation.

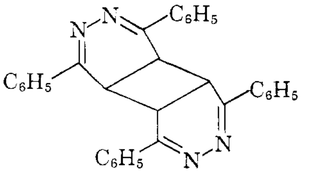
[3] A similar but unsuccessful approach to the synthesis of a cyclobutadiene derivative has been published; see A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **79**, 5316, 1957).

[4] R. Criegee and H. Höver, *Ber.*, **93**, 2521 (1960).

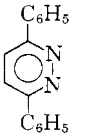
[5] G. W. Griffin, A. Vellturo and R. B. Hager, in press.

"all-*trans*" tetraketone Ib in ethanol over copper chromite catalyst at 250° affords *trans,trans,trans*-1,2,3,4-tetrabenzylcyclobutane (VI) which, unlike the precursor ketone, has the advantage of being soluble in conventional n.m.r. solvents. The n.m.r. spectrum of this material is completely consistent with the assignment of structure VI and attests to the fact that the cyclobutane skeleton has been retained throughout the entire course of the reaction sequence originating with IVa. Unequivocal evidence for the retention of the cyclobutane ring as well as the stereochemistry during the aluminum chloride-catalyzed acylation reaction for the preparation of Ia and Ib was obtained from the results of Baeyer–Villiger oxidation of a *homogeneous* sample of Ib. Although, as might be expected, in this case the oxidation affords a mixture of products, it was possible to isolate by fractional crystallization from benzene in 10% yield, an ester IVd identical in all respects to that obtained on treating the acid chloride IVb (of unquestionable structure) with sodium phenoxide.

Hydrazine hydrate reacts with the tetraketone Ia to give a solid product that melts at 221–222° after sublimation. This sublimate is identical in all respects with an authentic sample of 1,6-diphenylpyridazine (VIII) prepared independently from *cis*-dibenzoylethylene and hydrazine.[6] An attempt is being made to isolate the presumed intermediate VII to employ as a precursor for the 2,0,0,2-tricyclooöctane system. The thermal scission of the cyclobutane ring to give the aromatic system VIII is apparently rapid under the reaction conditions (100°) and is not without analogy. For example, the reversal of the dimerization of anthracene[7] and acenaphthylene[8] may be achieved thermally.

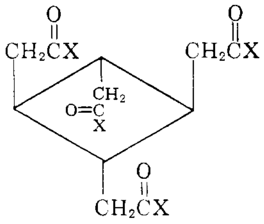


VII

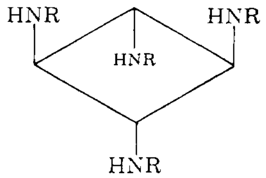


VIII

Conversion of the "all-*trans*" acid chloride IVb to *trans,trans,trans*-1,2,3,4-cyclobutanetetraacetic acid (IXa) was accomplished by the Arndt–Eistert technique.[9] Treatment of Ib with diazomethane in ether affords the tetradiazoketone (94%) which upon decomposition with silver oxide in methanol smoothly eliminated nitrogen (66%) providing the extended ester IXb. The infrared and n.m.r. spectra of this ester are completely consistent with the assignment of structure. Hydrolysis of the ester to cyclobutanetetraacetic acid IXa was effected in almost quantitative yield under acid conditions. This tetrabasic acid was shown to be identical to the ozonolysis product of *trans,trans,trans*-1,2,3,4-tetrabenzylcyclobutane (VI), thus confirming the structure of the acid IXa.



IXa, X = OH
b, X = OCH$_3$



Xa, R = H
b, R = CO—C$_6$H$_5$

The reaction of IVb with sodium azide represents still another example which illustrates the ease with which the tetraacid chloride IVb can be made to react at all four centers. The resulting tetraazide, which was not isolated, was rearranged directly to the polyisocyanate, employing typical Curtius reaction conditions.[10] Immediate hydrolysis of the tetraisocyanate was effected with hydrochloric acid providing 1,2,3,4-tetraaminocyclobutane as the hydrochloride salt. Trituration of this salt with sodium hydroxide, followed by sublimation, gave the extremely hygroscopic free amine Xa as a crystalline solid. Presumably the stereochemistry of the amine Xa, like that of the precursor acid chloride IVb, is *trans,trans,trans*.[11] The hygroscopic nature of the free amine made elemental and infrared analyses difficult to obtain. Benzoylation, however, provided the more tractable 1,2,3,4-tetrabenzamidocyclobutane (Xb), whose infrared spectrum and elemental analysis is consistent with the structural assignment Xb. Furthermore, the n.m.r. spectra of both the amine hydrochloride (D_2O) and the amide Xb ($DCCl_3$) are also consistent, the former showing only one peak in addition to the peak for residual water. The n.m.r. spectrum of Xb has two unsplit peaks having approximately the expected relative areas at τ = 6.12 and 1.46 in addition to a complex group in the aromatic region of the spectrum. The use of Xa and the corresponding *cis,trans,cis* isomer as complexing agents will be investigated since formally they may be considered closely related to ethylenediamine.

Experimental[12,13]

Preparation of *cis,trans,cis*-1,2,3,4-Tetrabenzoylcyclobutane (Ia).—To the dried acid prepared from 22 g. (0.076 mole) of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane[1] was added 63.2 g. (0.304 mole) of phosphorus pentachloride. The resulting mixture was allowed to stand until it liquefied and then was heated under reflux for 3 hours. Most of the phosphorus oxychloride was removed on an evaporator and the crude acid chloride was diluted with 50 ml. of anhydrous benzene. The resulting solution was added dropwise with stirring to a suspension of 40.4 g. (0.304 mole) of aluminum chloride in 300 ml. of benzene. After 2.5 hours of stirring, the reaction mixture was decomposed by pouring it onto

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[6] H. Keller, R. Pasternak and H. Halban, *Helv. Chim. Acta*, **29**, 512 (1946).

[7] A. Mustafa, *Chem. Revs.*, **51**, 18 (1952).

[8] K. Dziewonski and C. Paschalski, *Ber.*, **46**, 1986 (1913).

[9] B. Eistert, "Newer Methods of Preparative Organic Chemistry," English Ed., Interscience Publishers, Inc., New York, N. Y., 1948, p. 545.

[10] P. Smith, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 373.

[11] A. Campbell and J. Kenyon, *J. Chem. Soc.*, 25 (1946).

[12] All melting points and boiling points are uncorrected and unless otherwise indicated the infrared spectra were determined in potassium bromide on a Perkin–Elmer model 21B spectrophotometer with sodium chloride optics. All n.m.r. spectra were obtained at 60 megacycles.

[13] Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

500 ml. of 10% hydrochloric acid cooled with ice. After an hour of stirring, the hydrolysis mixture was filtered and the solid which collected on the filter was washed with ethanol. The dry ketone was then placed in a Soxhlet thimble and continuously extracted for 36 hours with 200 ml. of chloroform. The pure tetrabenzoylcyclobutane Ia which precipitated from the chloroform was collected on a filter and melted at 259–261° (7.5 g., 21%). The infrared spectrum shows aromatic carbonyl absorption at 5.96 μ. Other significant bands in the spectrum appear at 8.23(s), 10.94(m), 12.75(m), 13.05(m), 14.32(s) and 14.44(s) μ. The mass spectrum of the ketone shows the expected parent mass (M/e = 472) and the fragmentation pattern is consistent with the proposed structure.[14]

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 81.47; H, 5.16.

Preparation and Isolation of the Acid Chloride IIIb from ***cis,trans,cis*-1,2,3,4-Tetracarboxycyclobutane (IIIa).**—A mixture of 22.1 g. (0.095 mole) of the tetrabasic acid IIIa and 79.2 g. (0.381 mole) of phosphorus pentachloride was allowed to stand until the gas evolution had subsided. The reaction mixture, after being refluxed for 3 hours, was then distilled, first at atmospheric pressure to remove phosphorus oxychloride and finally at 0.7 mm. The slightly yellow fraction boiling at 149–150° was collected (17.5 g., 60.4%) and on standing solidified. Purification was effected by dissolving the acid chloride in warm carbon tetrachloride and reprecipitating with *n*-hexane; m.p. 76–77°.

On treatment with methanol the acid chloride afforded a tetraester identical in all respects to that of *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane.

Preparation and Isolation of the Acid Chloride IVb from ***trans,trans,trans*-1,2,3,4-Tetracarboxycyclobutane (IVa).**—A mixture of 20 g. (0.086 mole) of the tetrabasic acid IVa[1] and 72.5 g. (0.35 mole) of phosphorus pentachloride on shaking underwent a smooth reaction in 0.25 hour affording a homogeneous solution which was subsequently heated under reflux for 5 hours. Distillation of the resulting reaction mixture first at atmospheric pressure to remove phosphorus oxychloride and finally at 0.2 mm. gave a total of 21.6 g. (83%) of a colorless liquid, b.p. 120–124°, which on standing solidified, m.p. 63–65°. Treatment of this acid chloride IVb with methanol afforded the previously characterized *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane (m.p. 126–127°) in quantitative yield.

Preparation of ***trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib).**—A solution of 8.5 g. (0.028 mole) of the acid chloride IVb in 120 ml. of dry benzene was added over 0.25 hour to a suspension of 15.8 g. (0.12 mole) of aluminum chloride in 30 ml. of benzene which had been cooled to 5°. The resulting mixture was stirred for 6 hours while the temperature was gradually allowed to rise to 20°. The reaction mixture was then decomposed by pouring it onto a mixture of 350 g. of ice and 115 ml. of concentrated hydrochloric acid. When the resulting solid phase was collected, dried in a rotary evaporator and finally continuously extracted in a Soxhlet apparatus with benzene for 24 hours, the solid which deposited from the benzene after recrystallization from toluene melted at 254–256° (10 g., 76%). The infrared spectrum exhibits a band at 6.00(s) μ which is consistent with an aromatic carbonyl absorption. Other significant absorption bands occur at 6.92(m), 8.15(s), 10.36(m), 10.70(m), 13.32(m), 14.32(s) and 14.45(s) μ. The mass spectrum[14] of this material shows a parent peak at M/e 472 in agreement with the molecular weight of the proposed structure Ib. Furthermore, the fragmentation pattern is readily rationalized in terms of this structure.

Anal. Calcd. for $C_{32}H_{24}O_4$: C, 81.34; H, 5.12. Found: C, 80.82; H, 5.32.

Isomerization of ***cis,trans,cis*-1,2,3,4-Tetrabenzoylcyclobutane (Ia) to** ***trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib).**—A mixture of 0.5 g. (0.0011 mole) of the tetraketone Ia and 1 g. of sodium methoxide in 60 ml. of chloroform was heated under reflux for 0.25 hour. After addition of water the solid which deposited was collected on a filter, air-dried and placed in a Soxhlet thimble. Continuous extraction with benzene provided 0.20 g. (40%) of the "all-*trans*" ketone Ib identified by comparison of infrared spectra.

Acid-catalyzed isomerization can also be achieved by heating Ia with a 10% solution of concentrated hydrochloric acid in glacial acetic acid for 2.5 hours (13% yield).

Addition of Phenylmagnesium Bromide to ***trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib).**—A solution of 1.0 g. (0.0021 mole) of the ketone in 40 ml. of dry tetrahydrofuran was added over a 0.25-hour period to the Grignard reagent prepared from 2.7 g. (0.017 mole) of bromobenzene and 0.48 g. (0.018 mole) of magnesium turnings in 25 ml. of dry tetrahydrofuran. The mixture was heated under reflux for 1.5 hours after which time the tetrahydrofuran was displaced with benzene. The cooled reaction mixture was then decomposed with 10% aqueous ammonium chloride solution and allowed to stand 7 hours. The solid product was collected on a filter after centrifuging, then washed with water and finally air-dried. This product was extracted from a Soxhlet thimble first with pentane (0.5 hour) to remove diphenyl, then benzene (0.5 hour) to eliminate starting material and by-products, and finally tetrahydrofuran (12 hours). The tetrahydrofuran, when cooled, afforded 0.25 g. (15%) of a crystalline material (m.p. > 330°) whose infrared spectrum was superimposable on that of an authentic sample of Va prepared independently from *trans,trans,trans*-1,2,3,4-tetracarbomethoxycyclobutane.[1]

Reduction of ***trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib) with Lithium Aluminum Hydride.**—To a solution of 0.15 g. (0.0039 mole) of lithium aluminum hydride in dry tetrahydrofuran was added 1.0 g. (0.0021 mole) of the tetraketone Ib. This inverse addition was accomplished by continuously extracting the ketone from a Soxhlet thimble into the boiling hydride solution, a process requiring 8 hours. Final hydrolysis of the reaction mixture was achieved by stirring with 50 ml. of a 10% ammonium chloride solution. The organic phase was then separated and dried over anhydrous calcium sulfate. Removal of volatile solvents on a rotary evaporator provided 0.98 g. of a yellowish solid which after recrystallization from 50% ethanol melted at 256–258° (0.85 g., 83%). The infrared spectrum shows absorption at 3.0 μ characteristic of a hydroxyl function. Other significant bands appear at 6.70(m), 6.90(m), 9.62(m), 10.35(m), 13.4(m) and 14.45(s) μ.

Anal. Calcd. for $C_{32}H_{32}O_4$: C, 79.97; H, 6.71. Found: C, 80.51; H, 6.84.

Preparation of ***trans,trans,trans*-1,2,3,4-Tetrabenzylcyclobutane (VI).**—One gram of the tetracarbinol Vb, 1.0 g. of copper chromite catalyst[15,16] and 100 ml. of ethanol were placed in a 250-ml. steel bomb at an initial hydrogen pressure of 2000 p.s.i. The bomb was then heated to 250° and maintained at this temperature with shaking for a period of 8 hours. The reaction mixture, after cooling, was filtered to remove the catalyst and the filtrate subsequently treated with Norit and concentrated on an evaporator. The crystals which deposited were recrystallized from ethanol, m.p. 123–124° (0.5 g., 78%).

Anal. Calcd. for $C_{32}H_{32}$: C, 92.26; H, 7.74. Found: C, 92.06; H, 7.95.

The tetraketone Ib may also be reduced directly to the hydrocarbon VI under essentially the same conditions. The infrared spectrum of the product has significant bands at 6.27(w), 6.73(m), 6.90(m), 9.42(m), 9.75(w), 13.35(m) 13.57(s) and 14.47(s) μ. The n.m.r. spectrum shows three peaks in the proper ratio (5:2:1) at τ = 3.03 (aromatic), τ = 7.80 ($-CH_2-$) and τ = 8.34 (3° C–H). It is of interest that the two peaks at high field position are unsplit.

Reaction of ***cis,trans,cis*-1,2,3,4-Tetrabenzoylcyclobutane (Ia) with Hydrazine Hydrate.**—A 0.67-g. (0.0014 mole) sample of the tetraketone Ia was heated for 15 hours on a steam-bath with 15 ml. of hydrazine hydrate. The solid material was then collected on a filter washed with ethanol and sublimed at 200° (0.15 mm.). The sublimate after recrystallization from acetone melted at 221–222.5° (0.15 g., 22.8%). This material is identical in all respects to an authentic sample of 3,6-diphenylpyridazine prepared from hydrazine and *cis*-dibenzoylethylene.

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(14) We are indebted to Dr. T. Aczel and the Mass Spectral Group of the Research and Development Division of the Humble Oil and Refining Co., Baytown, Tex., for determination and interpretation of mass spectra.

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

(16) T. W. Riener, *ibid.*, **71**, 1130 (1949).

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; mol. wt., 232. Found: C, 82.65; H, 5.12; mol. wt., 222 (Rast).

Peroxidation of *trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib).—A solution of trifluoroperacetic acid[17] was prepared by dropwise addition of 3.8 ml. of trifluoroacetic anhydride to a stirred mixture of 0.040 ml. of 90% hydrogen peroxide in 6 ml. of methylene chloride. The resulting solution was added over a 15-minute period to a stirred heterogeneous mixture of 3.6 g. (0.04 mole) of dibasic sodium phosphate and 1.0 g. (0.0021 mole) of the tetraketone Ib in 60 ml. of methylene chloride. The reaction mixture was heated under reflux for 20 hours and finally poured into 300 ml. of water. The organic layer was separated and after drying over Drierite was evaporated to dryness; 1.0 g. (88%). The crude reaction mixture was digested with benzene and the residual solid (0.16 g.) shown to be starting material. The benzene soluble portion provided a material which after two recrystallizations from benzene melted at 189–193° (0.095 g., 10%). The infrared spectrum of this substance is superimposable on that of an authentic sample of *trans,trans,trans*-1,2,3,4-tetracarbophenoxycyclobutane (IVd) obtained by treating the acid chloride IVb with sodium phenoxide. The spectrum shows absorption at 5.75(s), 6.60(m), 6.73(w), 7.45(w), 8.37(s), 13.00(w) and 13.65(w) μ.

Preparation of *trans,trans,trans*-1,2,3,4-Cyclobutanetetraacetic Acid (IXa).—A solution of 30 g. (0.098 mole) of the acid chloride IVb in [illegible]0 ml. of ether was added dropwise over a 5-minute period to a stirred and ice-cooled solution of 1.2 moles of diazomethane in 2 l. of ether. Stirring was continued for an additional hour at room temperature before concentrating the reaction mixture to 150 ml. The resulting diazoketone which precipitated was collected on a filter, washed with ether and finally air-dried; 30.2 g. (94%). A 30.0-g. (0.0915 mole) sample of this tetradiazoketone was suspended by stirring in 1 l. of methanol at 61° and 3.5 g. of commercial silver oxide was added over a 4-hour period. The nitrogen which was evolved was collected by water displacement in a graduate (66%). The reaction mixture was then treated with Norit, filtered and the volatile solvents removed under reduced pressure. The residue was digested for a few minutes with 150 ml. of boiling ether and then filtered. The fraction boiling at 184–186° was collected (9.8 g., 31%) and crystallized upon standing. Recrystallization of this product from carbon tetrachloride at −10° afforded the pure tetraester IXb (m.p. 59–61°) whose infrared spectrum possessed bands at 3.30(w), 3.38(w), 5.77(s), 6.94(m), 8.60(m) and 10.0(w) μ in agreement with the proposed structure. The n.m.r. spectrum is also consistent and has peaks at $\tau = 6.44$, $\tau = 7.55$ and $\tau = 7.00$ (broad) in approximately the expected ratio.

Anal. Calcd. for $C_{16}H_{24}O_8$: C, 55.80; H, 7.03. Found: C, 55.65; H, 7.[illegible]3.

The ester was hydrolyzed to the acid by warming to 60° for 30 minutes in 20% sulfuric acid. The acid crystallized as white needles, m.p. 310–312° (92%), on cooling the aqueous solution. The infrared spectrum exhibits bands at 2.8–4.0(broad), 5.87(s), 6.95(m), 7.10(m), 7.55(m), 7.95(m), 8.55(m), 10.75(m), 11.15(m) and 14.00(w) μ.

Anal. Calcd. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60. Found: C, 50.04; H, 6.05.

Ozonolysis of *trans,trans,trans*-1,2,3,4-Tetrabenzylcyclobutane (VI).—A slurry of 1.0 g. (0.0024 mole) of the hydrocarbon in 50 ml. of 90% aqueous-acetic acid was treated with ozone at a flow rate of approximately 1.3 g. of ozone per hour for 8 hours at room temperature. The originally hetergeneous system became homogeneous during this period. Oxidative decomposition was achieved by allowing the reaction mixture to stand 2 days at room temperature in a solution of 10 ml. of 30% hydrogen peroxide in 26 ml. of water. The excess peroxide was destroyed with platinum-on-charcoal catalyst. The catalyst was then removed by filtration and the filtrate concentrated to a volume of 5 ml. on a rotary evaporator. Upon standing overnight this solution deposited 0.12 g. (16%) of an acid identical in all respects to IXa prepared directly by the alternate route from the acid chloride IVb and diazomethane.

Preparation of *trans,trans,trans*-1,2,3,4-Tetraminocyclobutane Xa.—To 9.0 g. (0.030 mole) of the acid chloride IVb in 125 ml. of benzene was added to 7.6 g. (0.12 mole) of activated sodium azide.[18] The resulting suspension was heated under reflux overnight. The reaction mixture was then filtered hot and the solid which collected was washed with benzene. The filtrate was treated with 100 ml. of concentrated hydrochloric acid and finally heated under reflux with vigorous stirring for 0.5 hour. The aqueous layer was then separated from the organic phase which was washed once with water. The combined aqueous layers were concentrated to a volume of 25 ml. on a rotary evaporator and the amine hydrochloride which deposited was collected on a filter 3.0 g. (39%). Significant infrared absorption bands in the spectrum of the hydrochloride appear at 3.0–4.5 (broad), 6.41(m), 6.82(s), 8.38(m), 9.00(m), 9.52(s) and 9.77(s) μ.

A 0.050-g. sample of the amine hydrochloride was triturated with sodium hydroxide and the resulting mixture was heated in a sublimator at 100° (0.1 mm.). The white crystals which sublimed were extremely hygroscopic which made infrared analysis of the free amine difficult.

A sample of the amine was therefore benzoylated according to the Schotten–Baumann technique affording 1,2,3,4-tetrabenzamidocyclobutane which after recrystallization from ethanol melted at 308–310°.

Anal. Calcd. for $C_{32}H_{28}O_4N_4$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.55; H, 5.32; N, 10.37.

The n.m.r. spectrum of the amine hydrochloride taken in deuterium oxide shows only one unsplit peak (30.9 c.p.s. upfield from the residual water peak) while that of the benzamido derivative taken in deuteriochloroform has singlet peaks at $\tau = 6.12$ and $\tau = 1.46$ in the expected ratio of 1:1 as well as a complex set in the aromatic region of the spectrum ($\tau = 2.1$–2.5).

Treatment of *trans,trans,trans*-1,2,3,4-Tetrabenzoylcyclobutane (Ib) under Pinacol Conditions.—To 1.05 g. (0.0432 g. atom) of magnesium in 35 ml. of dry tetrahydrofuran was added 3.24 g. (0.0127 mole) of iodine. A spontaneous reaction occurred with the formation within 15 minutes of a fine maroon suspension.[19] To this suspension was added 50-ml. of dry tetrahydrofuran and 1.0 g. (0.0021 mole) of the polyketone Ib. The latter was added over a 24-hour period from a porous thimble by heating the reaction mixture under reflux in a Soxhlet extractor. All operations were conducted under a nitrogen atmosphere. The reaction mixture was then hydrolyzed with 50 ml. of water and allowed to stand 1 hour. Evaporation of the tetrahydrofuran followed by acidification with dilute hydrochloric acid provided a precipitate that was separated from the aqueous phase by extraction with benzene. Removal of the benzene under reduced pressure gave a solid (0.03 g., 88%) which when recrystallized from ethanol melted at 143–144.5° (61%). This product was identical in all respects to an authentic sample of 1,6-dibenzoylethane prepared from dibenzoylethylene according to the procedure of Conant and Lutz.[20]

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