the residue provided material that was chromatographed on neutral alumina. That fraction eluted with chloroform and crystallized from acetone–ether; m.p. 194–197° was not depressed on mixed m.p. with II obtained from cortisone acetate (I). The infrared spectra of the two samples were identical.

RAHWAY, N. J.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

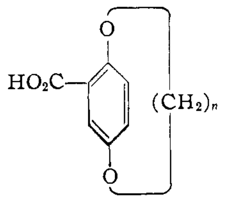
Many-membered Carbon Rings. XVII. A Paracyclophane Possessing Two *gem*-Dimethyl Groups[1,2]

BY A. T. BLOMQUIST AND F. JAFFE[3]

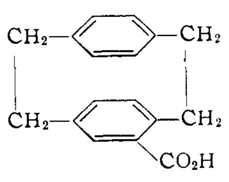
RECEIVED JANUARY 28, 1958

The acyloin cyclization of dimethyl *p*-phenylene-bis-(β,β-dimethylvalerate) has given 3,3,8,8-tetramethyl-5-keto-6-hydroxy[10]paracyclophane in 31% yield, together with a dimeric cyclic acyloin (*ca.* 10% yield). The dimethyl ester named above was synthesized from benzene and other simple intermediates.

Our general concern with the chemistry of many-membered carbon rings has included, among other things, a particular interest in the stereoisomerism attendant with certain kinds of these carbocycles. For example, we have indicated previously that the conformations of molecules such as cyclononane and *trans*-cyclononene are dissymmetric[4,5] and suitable derivatives of these should, under the circumstances of restricted rotation at room temperature, be resolvable into optical antipodes. It is also true that certain *o*-substituted paracyclophanes would possess molecular dissymmetry as a consequence of restricted rotation of the benzene nucleus with respect to the polymethylene bridge. Molecular dissymmetry arising from such circumstances has in fact been demonstrated by Lüttringhaus in his resolution of the polymethylene ethers of gentisic acid (I and II).[6] Further, a similar kind of origin of molecular dissymmetry was shown by Cram in his resolution of the paracyclophanecarboxylic acid III.[7]

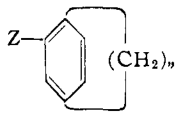


I, $n = 8$
II, $n = 9$

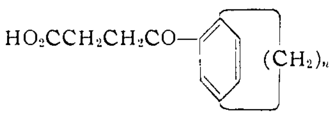


III

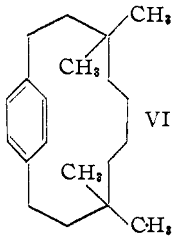
From a consideration of modern molecular models one would expect to be able to resolve suitable derivatives of nuclearly-substituted paracyclophanes such as IV provided the polymethylene bridge had a chain of eight to ten carbon atoms. Accordingly, studies were carried out to test this thesis. The first work done toward this end, synthesis and attempted resolution of the acids V,[8] was not encouraging. It seemed desirable therefore to develop the synthesis of a very highly hindered paracyclophane such as VI and to then attempt resolution of suitable *o*-substituted derivatives of it.



IV, n = 8, 9 and 10



V, n = 9 and 10



VI

While the study of syntheses leading to VI was in progress it was discovered in this Laboratory[9] that the discouraging results obtained with the acids V were due to the fact that the compounds V were not at hand at all and that the succinoylation of [9]- and [10]paracyclophane rearranged the *para*-polymethylene bridge to a *meta*-polymethylene bridge. The development of syntheses leading to VI was nevertheless continued and the results obtained in the synthesis of the acyloin precursor for VI are presented in this article. A subsequent account will be given of the resolution studies of this hydrocarbon.

A condensed outline of the total synthesis of 3,3,8,8-tetramethyl-5-keto-6-hydroxy[10]paracyclophane (XII) is given.

The acylation of benzene with β,β-dimethylglutaric anhydride, reported to give an almost

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[1] For the preceding paper in this series see A. T. Blomquist and Y. C. Meinwald, THIS JOURNAL, **80**, 630 (1958).

[2] For a discussion of the "cyclophane" system of nomenclature for bridged benzene rings see W. M. Schubert, W. A. Sweeney and H. K. Latourette, *ibid.*, **76**, 5462 (1954), and D. J. Cram and J. Abell, *ibid.*, **77**, 1179 (1955).

[3] This article is an abstract of part of the dissertation presented by F. Jaffe in September, 1957, to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] A. T. Blomquist, L. H. Liu and J. C. Bohrer, THIS JOURNAL, **74**, 3643 (1952).

[5] A. T. Blomquist, E. S. Wheeler and Y. Chu, *ibid.*, **77**, 6307 (1955).

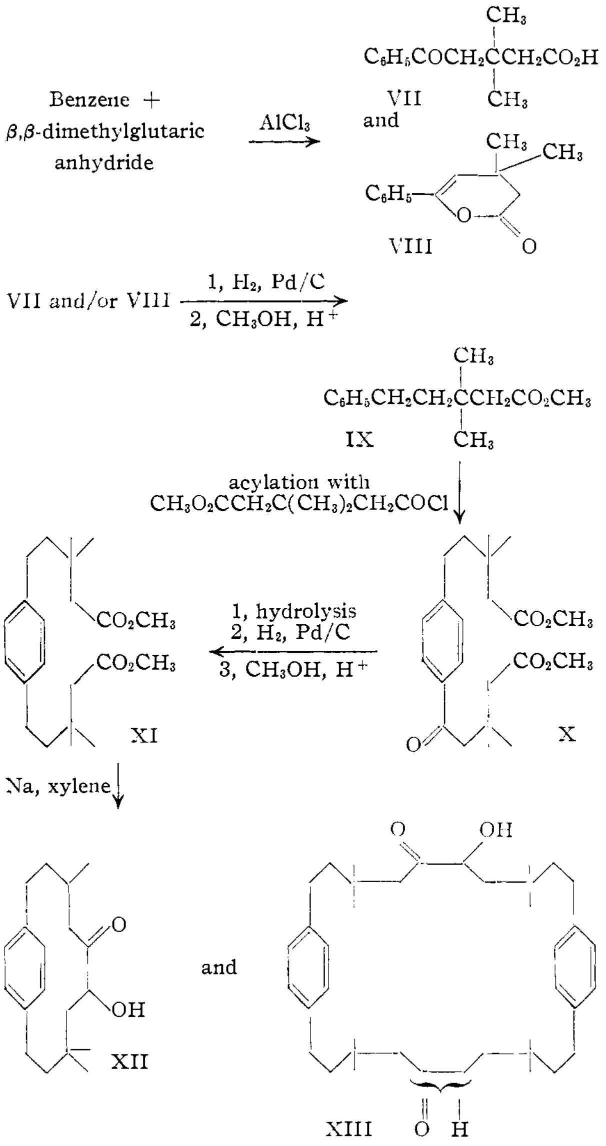
[6] A. Lüttringhaus and H. Gralheer, *Ann.*, **557**, 108, 112 (1947); A. Lüttringhaus and G. Eyring, *Angew. Chem.*, **69**, 139 (1957); *Ann.*, **604**, 111 (1957).

[7] D. J. Cram and N. L. Allinger, THIS JOURNAL, **77**, 6289 (1955).

[8] R. E. Stahl, Thesis, Cornell University, Ithaca, N. Y., 1954; K. L. Lockwood, Thesis, Cornell University, Ithaca, N. Y., 1955.

[9] A. T. Blomquist and Y. C. Meinwald, unpublished results.

quantitative yield of the keto acid VII (b.p. 115° (35 mm.)[10]), actually gave VII (b.p. 141.5–144.5° (0.12 mm.)) and the lactone VIII in varying ratio which depended upon the rate of the final distillation of the product. A slow careful distillation favored the conversion of VII to VIII. The infrared absorption spectrum of the pure acid VII showed bands at 5.87 μ (—CO_2H) and 5.93 μ (C_6H_5CO—) while a similar spectrum of VIII showed absorption at 5.67 μ (vinyl ester[11,12]) and 6.02 μ (double bond[13]) together with several strong peaks in the 7–10 μ region absent in the spectrum of VII. The lactone VIII was insoluble in cold 10% aqueous sodium hydroxide but dissolved readily on warming. Acidification of the alkaline solution gave the acid VII. The acid VII was converted quantitatively to VIII by refluxing with acetic anhydride in the presence of a trace of sulfuric acid. Esterification of the keto acid VII with methanol and sulfuric acid afforded the expected methyl ester of VII together with the lactone VIII.



The ready formation of the lactone VIII is not too unexpected. Cyclization of open chain systems is known to be favored by the presence of *gem*-dimethyl groups[14,15] and further there are other instances of δ-aldehydo- and δ-keto acids which readily form cyclic enol lactones.[16]

The catalytic method of Horning and Reisner[17] was used to reduce both VII and VIII to δ-phenyl-β,β-dimethylvaleric acid.[18] Friedel–Crafts acylation of the ester IX with γ-carbomethoxy-β,β-dimethylbutyryl chloride gave the keto dicarboxylic ester X (72%). This ester X was converted to the substituted *p*-phenylene-bis-(valeric ester) XI by (a) hydrolysis of X to its keto-dicarboxylic acid, (b) catalytic hydrogenolysis of the keto-dicarboxylic acid to the simple dicarboxylic acid and (c) esterification of the latter to the dimethyl ester XI. The *para*-attachment of the two valeric acid groups to the benzene nucleus in the dicarboxylic acid which gave XI was demonstrated by (a) the infrared absorption spectrum of the latter, for it included a band at 6.59 μ, characteristic of *para* aromatic substitution[19] and (b) chromic acid oxidation of the dicarboxylic acid which gave an 85% yield of terephthalic acid.

The cyclic acyloin XII, m.p. 116.5–118.5°, prepared from the dicarboxylic ester XI by the conventional acyloin cyclization method was realized in 31.4% yield only if a twofold excess of sodium was used. If the normal ratio of sodium to dicarboxylic ester were employed the maximum yield of XII was 25%. In the cyclization reaction there always was formed an appreciable quantity (*ca.* 10%) of a dimeric product of m.p. 199–205°. On the basis of the data available this compound is considered to be the di-acyloin XIII. Both XII and XIII gave positive tests for the α-hydroxycarbonyl group[20] and their infrared absorption spectra showed bands expected for the acyloin function.

The monomeric acyloin XII was characterized by its conversion (1) to a *p*-nitrobenzoate derivative and, further, *via* its related α-diketone (2) to a quinoxaline derivative.

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[10] A. Ali, R. D. Desai, R. F. Hunter and S. M. M. Muhammad, *J. Chem. Soc.*, 1013 (1937).

[11] R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publ. Corp., New York, N. Y., 1944, p. 72.

[12] J. Meinwald, THIS JOURNAL, **76**, 4571 (1954).

[13] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1954, pp. 33, 36.

[14] See ref. 5.

[15] C. K. Ingold, *J. Chem. Soc.*, **119**, 305 (1921). For a discussion of Ingold's "*gem*-dimethyl effect" see G. S. Hammond in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 460 ff.

[16] (a) M. Quadrat-I-Khuda, *J. Chem. Soc.*, 201 (1929); (b) S. M. McElvain, R. B. Bright and P. R. Johnson, THIS JOURNAL, **63**, 1558 (1941); S. M. McElvain and E. J. Eisenbraun, *ibid.*, **77**, 1599 (1955); (c) R. B. Turner, *ibid.*, **72**, 579 (1950); (d) R. Ya. Levina, N. P. Shusherina and M. Yu Lur'e, *Zhur. Obshchei Khim.*, **24**, 1439 (1954) [*C. A.*, **49**, 10277 (1955)].

[17] E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

[18] It should be noted that the hydrogenolysis of the methyl ester of the keto acid VII also afforded the free acid named above and not the methyl ester IX.

[19] L. J. Bellamy, ref. 13, pp. 55, 60–61.

[20] W. Rigby, *J. Chem. Soc.*, 793 (1951).

Experimental Part[21]

Materials.—β,β-Dimethylglutaric acid was prepared as described in reference 22. β,β-Dimethylglutaric anhydride and γ-carbomethoxy-β,β-dimethylbutyryl chloride were obtained by the method of Cason, *et al.*[23]

γ-Benzoyl-β,β-dimethylbutyric Acid (VII).—A solution of 50.0 g. (0.352 mole) of β,β-dimethylglutaric anhydride in 150 ml. of anhydrous benzene was added slowly to a stirred suspension of 100 g. (0.75 mole) of anhydrous aluminum chloride in 250 ml. of reagent grade benzene. After the mixture had been refluxed 3 hr. it was carefully hydrolyzed with a solution of 150 ml. of concentrated hydrochloric acid in 150 ml. of water. The benzene layer was washed with saturated sodium chloride solution and extracted with saturated aqueous sodium bicarbonate. Acidification of the alkaline extracts gave an oil which was taken up in ether. After washing and drying in the usual way, the ether solution was distilled rapidly through a 10-cm. Vigreux column to give 64.4 g. (83%) of the keto acid VII which always contained some enol-lactone VIII, b.p. 141.5–144.5° (0.12 mm.), n^{25}_{D} 1.5269.

The oxime derivative of this VII was prepared and after three recrystallizations from ethanol–water was obtained as white needles, m.p. 109.0–110.5°.

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.34; H, 7.29; N, 5.95. Found: C, 66.44; H, 7.43; N, 6.18.

Enol Lactone of VII (VIII). (**A**).—The benzene solution which remained after extraction with bicarbonate solution, as described above, was dried and distilled. There was obtained 2.0 g. of colorless, neutral liquid VIII, b.p. 100–103° (0.15 mm.), n^{25}_{D} 1.5498.

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.16; H, 6.97. Found: C, 77.43; H, 7.26.

The ratio of VIII to VII isolated in the acylation varied widely in different experiments.

(**B**).—A mixture of 2.20 g. (0.010 mole) of VII and 5 ml. of acetic anhydride containing one drop of concentrated sulfuric acid was warmed for 4 hr. and poured into 350 ml. of cold water. The oil which separated was taken up in ether and the resulting solution dried and the ether removed. The residual oil was dried at 60° and 10 mm. to give 2.10 g. (96%) of VIII, n^{25}_{D} 1.5498. The infrared absorption spectra of this VIII and the VIII described in (A) were identical. The infrared absorption spectrum of VIII showed bands at 5.67, 6.02, 7.91, 8.13, 8.44, 8.69 and 8.93 μ.

The lactone VIII was dissolved in 10% aqueous sodium hydroxide upon warming at 90° for 0.5 hr. Acidification of this alkaline solution gave an insoluble colorless liquid which after the usual work-up gave VII having n^{25}_{D} 1.5252. The infrared spectrum of this VII was identical with that of VII obtained directly from the acylation reaction.

Methyl Ester of VII. A.—To a stirred suspension of 39.9 g. (0.30 mole) of anhydrous aluminum chloride in 200 ml. of anhydrous benzene there was added slowly 18.0 g. (0.0942 mole) of γ-carbomethoxy-β,β-dimethylbutyryl chloride. The mixture was refluxed 2 hr., cooled, and poured carefully into a mixture of 80 g. of ice and 80 ml. of concentrated hydrochloric acid. The brown organic layer was separated, washed successively with saturated sodium chloride solution, 10% sodium hydroxide solution, 10% hydrochloric acid solution, saturated sodium chloride solution and finally dried. Distillation *in vacuo* after removal of the benzene gave 18.75 g. of the keto ester having b.p. 113–117° (0.30 mm.) and n^{25}_{D} 1.5078–1.5080. Redistillation gave an analytical sample of the ester which showed b.p. 111–112° (0.50 mm.), n^{25}_{D} 1.5088 and d^{4}_{20} 1.063.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.78; H, 7.74; sapon. equiv., 234.3. Found: C, 71.96; H, 7.97; sapon. equiv., 236.0.

The 2,4-dinitrophenylhydrazone derivative of the keto ester was prepared.[24] After five recrystallizations from ethanol–water it had m.p. 125.0–126.5°.

Anal. Calcd. for $C_{20}H_{22}O_6N_4$: C, 57.69; H, 5.03. Found: C, 57.96; H, 5.35.

(**B**).—A mixture of 5.0 g. (0.0227 mole) of VII, 15 ml. (12.0 g., 0.375 mole) of absolute methanol and 5 drops of sulfuric acid was refluxed overnight. The usual work-up of the reaction mixture gave, after distillation *in vacuo*, 2.81 g. of a single fraction having b.p. 119–122° (0.3 mm.). Infrared analysis of this fraction indicated that it was a mixture of about 60–70% of VIII and 30–40% of the methyl ester of the keto acid. The infrared spectrum showed absorption peaks in the carbonyl region at 5.68, 5.78 and 5.93 μ indicative of both enol lactone and normal methyl ester groups.

δ-Phenyl-β,β-dimethylvaleric Acid (IXa).[25]—The catalytic reduction method described by Horning and Reisner was used.[17] A solution of 64.4 g. (0.292 mole) of VII in 150 ml. of glacial acetic acid was reduced under 2–3 atm. hydrogen pressure at 65° using 4.5 g. of palladium-on-charcoal catalyst. Reduction was complete in 1.5 hr. After removal of the catalyst, the acetic acid solution was poured into 500 ml. of cold water. The colorless oil which separated solidified after long standing. There was obtained 58.5 g. (97%) of crude IXa, m.p. 45–48°. Vacuum distillation of this IXa gave, after a 5.5-g. forerun, 50.3 g. (83%) of pure liquid IXa, b.p. 143–145° (1.5 mm.) and n^{25}_{D} 1.5051. Upon adding a seed crystal this IXa crystallized immediately to give solid IXa, m.p. 52.5–53.8°. The infrared absorption spectra of both liquid and solid (KBr pellet) IXa were identical and showed the expected absorption at 5.88 and 6.25 μ.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.68; H, 8.79. Found: C, 75.50; H, 8.52.

The *p*-bromophenacyl ester of IXa was prepared. After several recrystallizations from methanol–water it showed m.p. 73.9–74.9°.

Anal. Calcd. for $C_{21}H_{23}O_3Br$: C, 62.54; H, 5.75. Found: C, 62.65, 62.74; H, 5.49, 5.52.

Methyl δ-Phenyl-β,β-dimethylvalerate (IX).—A mixture of 108 g. (0.528 mole) of IXa, 200 g. (6.25 moles) of absolute methanol and 0.5 ml. of concentrated sulfuric acid was refluxed for 24 hr. After removal of the excess methanol the residue was worked up in the usual way to give 110 g. (95%) of the ester IX, b.p. 88.5–89.0° (0.2 mm.) and n^{20}_{D} 1.4928. A portion of this IX was redistilled to give a sample of IX for analysis; b.p. 86–91° (0.7 mm.), n^{25}_{D} 1.4908.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.15; H, 8.74.

Methyl γ-[*p*-(δ-Carbomethoxy-γ,γ-dimethylbutyl)-benzoyl]-β,β-dimethylbutyrate (X).—To a thoroughly chilled, stirred mixture of 63.3 g. (0.287 mole) of IX and 55.6 g. (0.289 mole) of γ-carbomethoxy-β,β-dimethylbutyryl chloride in 250 ml. of *sym*-tetrachloroethane was added in portions over a 1.5-hr. period a total of 116.5 g. (0.872 mole) of anhydrous aluminum chloride. After the mixture had been stirred for 11 hr. at room temperature, 250 ml. of ether was added and the mixture chilled in an ice-bath. The mixture was hydrolyzed carefully by adding slowly with stirring a solution of 75 ml. of concentrated hydrochloric acid in 25 ml. of water. The organic layer was separated, washed with dilute hydrochloric acid and saturated sodium chloride solution and finally dried. Distillation, after removal of the solvent, gave 78.4 g. (73%) of the dicarboxylic ester X, b.p. 184–191° (0.26 mm.), n^{25}_{D} 1.5030–1.5034. The infrared absorption spectrum included peaks at 5.75, 5.93, 6.22 and 6.36 μ.

Anal. Calcd. for $C_{22}H_{32}O_5$: C, 70.27; H, 8.57. Found: C, 69.47, 70.51; H, 8.28, 8.94.

The 2,4-dinitrophenylhydrazone derivative of X was prepared and showed m.p. 85–87° after four recrystallizations from methanol–water.

Anal. Calcd. for $C_{28}H_{36}O_8N_4$: C, 61.41; H, 6.52. Found: C, 60.96; H, 6.24.

γ-[*p*-(δ-Carboxy-γ,γ-dimethylbutyl)-benzoyl]-β,β-dimethylbutyric Acid.—The crude undistilled X (103 g.) ob-

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[21] All melting points and boiling points are uncorrected. Infrared absorption spectra were determined with a Perkin–Elmer double beam infrared spectrophotometer, model 21.

[22] *Org. Syntheses*, **31**, 40 (1951).

[23] J. Cason, G. Sumrell and R. S. Mitchell, Jr., *J. Org. Chem.*, **15**, 850 (1950).

[24] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 171.

[25] Reduction of the methyl ester of VII using the conditions described above for the reduction of the acid VII gave the free carboxylic acid rather than the ester, in good yield.

tained in an acylation experiment exactly as described above was refluxed with 500 ml. of 20% methanolic potassium hydroxide solution for 24 hr. The cooled alkaline solution was acidified with hydrochloric acid and the crude solid monoketo-dicarboxylic acid which precipitated was filtered and dried. There was obtained 82 g. (86% from IX) which had m.p. 137–141°. Recrystallization of this product from acetic acid–water, after decolorizing with charcoal, gave 71.5 g. (75%) of the monoketo-dicarboxylic acid as pale yellow plates, m.p. 139.5–141.5°. An analytical sample was obtained after several recrystallizations from hot water (1 l. of water per gram of keto acid) which showed m.p. 140.5–142.5°.

Anal. Calcd. for $C_{20}H_{28}O_5$: C, 68.95; H, 8.10; neut. equiv., 174.22. Found: C, 68.84; H, 8.32; neut. equiv., 175.6.

The di-*p*-bromophenacyl ester of this monoketo-dicarboxylic acid was prepared. After nine recrystallizations from ethanol it had m.p. 104.8–106.6°. The infrared absorption spectrum of the monoketo-dicarboxylic acid showed peaks at 5.87, 5.90, 6.22 and 6.36 μ.

Anal. Calcd. for $C_{38}H_{38}O_7Br_2$: C, 58.24; H, 5.16; Br, 21.52. Found: C, 57.77; H, 5.25; Br, 21.32.

***p*-Phenylene-bis-(β,β-dimethylvaleric Acid) (XIa).**—A slurry of 34.8 g. (0.1 mole) of the crude monoketo-dicarboxylic acid described above in 150 ml. of glacial acetic acid was reduced under 2–3 atm. of hydrogen pressure at 65° using 1.5 g. of 10% palladium-on-charcoal catalyst.[17] After reduction was complete sufficient glacial acetic acid was added to the slurry to dissolve all the organic solid on warming to 80°. The catalyst was filtered from the hot acetic acid solution. The solid crystalline XIa which separated from the cooled acetic acid solution was recrystallized from acetic acid–water. There was obtained 26.7 g. (80%) of the dicarboxylic acid XIa, m.p. 184–187.5°, which after five recrystallizations from ethanol–water showed m.p. 188.5–189.5°.

Anal. Calcd. for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04; neut. equiv., 167.23. Found: C, 71.75; H, 9.34; neut. equiv., 167.2, 165.5.

The di-*p*-bromophenacyl ester of XIa was prepared using methanol as a solvent. This derivative had m.p. 137.3–138.8° after several recrystallizations from benzene–ethanol. The infrared absorption spectrum of XIa included peaks at 5.88 and 6.59 μ with a shoulder at 6.20 μ.

Anal. Calcd. for $C_{36}H_{40}O_6Br_2$: C, 59.36; H, 5.54. Found: C, 59.45; H, 5.30.

Oxidation of XIa.—Chromic acid oxidation[26] of 2.0 g. (6.00 mmole) of XIa gave 0.85 g. (85%) of a crude solid which sublimed at 285–305° (lit. value[27] for terephthalic acid, 300°). The infrared spectrum of this substance was identical with that of an authentic sample of terephthalic acid. The crude acid was converted to its dimethyl ester by treatment with phosphorus pentachloride followed by reaction with methanol.[28] After recrystallization from aqueous ethanol the dimethyl ester had m.p. 140.5–141.5° (lit. value[28] for dimethyl terephthalate, 140°). The infrared spectrum of the ester was identical with that of an authentic sample of dimethyl terephthalate.[29]

Dimethyl *p*-Phenylene-bis-(β,β-dimethylvalerate) (XI).—Crude XIa was esterified using excess absolute methanol and sulfuric acid as a catalyst. From 26.5 g. (0.0793 mole) of XIa, m.p. 183–188°, there was obtained 25.6 g. (89%) of the diester XI, b.p. 167–177° (0.08 mm.), $n^{25}\mathrm{D}$ 1.4902–1.4914. A sample redistilled for analysis had b.p. 163–165° (0.05 mm.) and $n^{25}\mathrm{D}$ 1.4902. The infrared absorption spectrum of XI included peaks at 5.75, 6.22 and 6.61 μ.

Anal. Calcd. for $C_{22}H_{34}O_4$: C, 72.88; H, 9.45. Found: C, 72.92; H, 9.28.

3,3,8,8-Tetramethyl-5-keto-6-hydroxy[10]paracyclophane (XII).—The apparatus and method used for the acyloin cyclization have been described.[30] A dispersion of 10.6 g. (0.46 g.-atom) of sodium in 200 ml. of dry toluene was prepared. A solution of 20.5 g. (0.0566 mole) of the diester XI in 100 ml. of dry deoxygenated toluene was added slowly over an 11-hr. period. After addition was complete, the mixture was refluxed 15 min. and cooled to −10°. To the cooled mixture there was added 50 ml. of methanol and 100 ml. of 20% acetic acid. The separated water layer was extracted with three 100-ml. portions of toluene. The toluene solutions were combined and washed successively with 100 ml. of saturated sodium bicarbonate solution and two 100-ml. portions of water. The dried toluene solution was distilled to remove the toluene. The residue comprised a white crystalline solid suspended in a yellow liquid. The solid was separated by filtration and washed with methanol. There was thus obtained *ca.* 2.0 g. of the dimeric acyloin XIII which had m.p. 195–200°. This XIII after two recrystallizations from benzene showed m.p. 199–205°, gave a positive acyloin test with bismuth oxide and showed absorption at 2.95 and 5.84 μ in the infrared.

Anal. Calcd. for $C_{40}H_{60}O_4$: C, 79.42; H, 10.00; mol. wt., 604.92. Found: C, 80.08; H, 10.46; mol. wt., 676 (Rast).

The methanol washings from above were evaporated and the residue was combined with the original yellow liquid product of the reaction. Distillation of this through a 30-cm. Podbielniak type column with heated jacket gave 5.27 g. (31.4%) of the acyloin XII as a waxy semi-solid, b.p. 149° (2.0 mm.). After recrystallization from aqueous ethanol this XII showed m.p. 116.5–118.5°. This XII gave a positive test for the acyloin group[30] and its infrared spectrum included peaks at 2.95 and 5.87 μ.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; mol. wt., 302.46. Found: C, 79.69; H, 9.90; mol. wt., 289, 304 (*micro* Rast).

The *p*-nitrobenzoate derivative of XII was prepared. It showed m.p. 135–137° after five recrystallizations from ethanol–water.

Anal. Calcd. for $C_{27}H_{33}O_3N$: C, 71.82; H, 7.37; N, 3.10. Found: C, 71.74; H, 7.46; N, 3.29.

The quinoxaline derivative of the α-diketone derived from the acyloin XII was prepared; XII (0.44 g., 1.50 mmoles) was heated with 0.24 g. (1.94 mmoles) of bismuth oxide in 25 ml. of refluxing acetic acid for 15 min. The mixture was cooled, filtered and poured into water. The organic layer was extracted with benzene. From this benzene solution there was obtained, after drying and removal of benzene, crude yellow liquid diketone (from XII) whose infrared spectrum included peaks at 2.90 and 5.83 μ, with a shoulder at 5.76 μ. The crude yellow colored product was refluxed in 25 ml. of acetic acid with 0.162 g. (0.0015 mole) of *o*-phenylenediamine. The quinoxaline derivative was isolated as light straw-colored plates: m.p. 153–155°, ultraviolet $\lambda_{\max}^{\text{ethanol}}$ 238 mμ (log ε 4.53).

Anal. Calcd. for $C_{26}H_{32}N_2$: C, 83.83; H, 8.66; N, 7.52. Found: C, 83.76; H, 8.70; N, 7.56.

Ithaca, New York

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(26) R. L. Shriner and R. C. Fuson, ref. 24, p. 198.

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