tained after two recrystallizations from acetone was 0.32 g. (65%). It melted at 242–243° and rotated $[\alpha]^{22}D$ −39.1° ($CHCl_3$, c 0.904, l 2). The reported[5] melting point and rotation for the enantiomorph were 242–243° and $[\alpha]^{20}D$ +38.6° ($CHCl_3$), respectively.

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MONTREAL, CANADA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

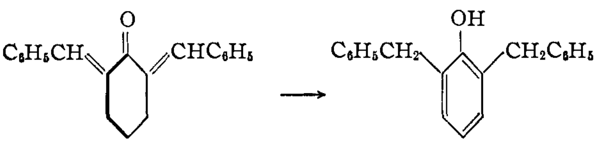
Tropolones by Isomerization. I. 3,7-Dibenzyltropolone[1]

BY NELSON J. LEONARD AND GENE C. ROBINSON[2]

RECEIVED OCTOBER 27, 1952

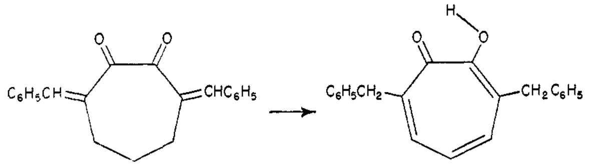
A new synthesis of tropolones is here described, represented by the isomerization of 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone with hydrogen bromide–acetic acid. The generation of the tropolone nucleus was demonstrated in the physical and chemical properties of the product. Moreover, the structure of the substituted tropolone was verified by an independent synthesis proceeding through 3,7-dibenzyl-1,2-cycloheptanedione. Certain evidence bearing on the mechanism of the conversion has been accumulated by a study of variations in the reaction conditions and by the behavior of possible bromine-containing intermediates.

The consideration of tropolone as an aromatic system[3] and the known aromatization of 2,6-dibenzylidenecyclohexanone (I) to 2,6-dibenzylphenol (II) by means of hydrogen bromide–acetic acid[4,5] suggested that 3,7-dibenzyltropolone (IV) might be obtained similarly from 3,7-dibenzylidene-1,2-cycloheptanedione (III). We have indeed been able to effect the isomerization of III to IV by hydrogen bromide in acetic acid, thus providing a new route for the synthesis of substituted tropolones.



I II

IIa, OAc in place of OH



III IV

The intermediate in the seven-membered ring aromatization, 3,7-dibenzylidene-1,2-cycloheptanedione (III), was obtained by condensation of benzaldehyde with 1,2-cycloheptanedione in ethanol solution containing piperidine. This yellow compound, m.p. 189–190°, had ultraviolet (Fig. 1) and infrared (Fig. 2) absorption spectra characteristic of the α,β-unsaturated carbonyl systems present. Conversion to a colorless isomer, m.p. 118–119°, was effected in 46% yield by treatment of III with hydrogen bromide in acetic acid at 60°. The ultraviolet absorption spectrum of the product (Fig. 1) was similar to that of representative tropolones.[6] The infrared absorption spectrum in chloroform solution (Fig. 2) showed a peak at 2990 cm.$^{-1}$, the form of which was characteristic of a strongly bonded hydroxyl group, and at 1605 cm.$^{-1}$, indicative of the carbonyl in a tropolone.[7,8] Finally, the dark green color obtained with alcoholic ferric chloride solution was characteristic of a tropolone.[6] All of the accumulated evidence thus indicated that the structure of the isomerization product of 3,7-dibenzylidene-1,2-cycloheptanedione (III) was 3,7-dibenzyltropolone (IV).

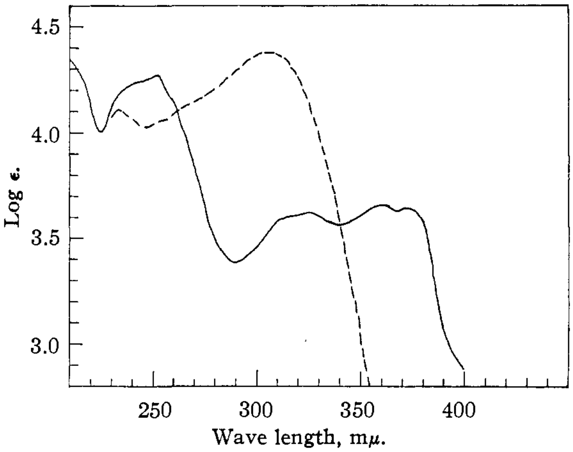


Fig. 1.—Ultraviolet absorption spectra: ———, 3,7-dibenzyltropolone; - - - 3,7-dibenzylidene-1,2-cycloheptanedione (in cyclohexane).

A study of the isomerization conditions was undertaken to obtain evidence bearing on the mechanism of the conversion. The isomerization is not induced by acid alone, since perchloric, sulfuric and hydrochloric acid in acetic acid were ineffectual in bringing about the conversion. The temperature employed seemed to be a critical factor governing the yield, and the optimum reaction temperature was about 60°. The reaction time appeared not to be as critical a factor, but the best yield was obtained after about 11 hours. The singular effec-

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(1) Presented at the 122d National Meeting of the American Chemical Society, Altantic City, N. J., September 15, 1952.

(2) Monsanto Chemical Company Fellow 1951–1952.

(3) M. J. S. Dewar, *Nature*, **155**, 50 (1945).

(4) R. Weiss and J. Ebert, *Monatsh.*, **65**, 399 (1935).

(5) We have found that the procedure of Weiss and Ebert[4] can be simplified by conducting the isomerization at atmospheric pressure in an open vessel. Addition of acetic anhydride to the hydrogen bromide–acetic acid provides for the formation of 2,6-dibenzylphenyl acetate (IIa) in excellent yield.

(6) J. W. Cook and J. D. Loudon, *Quart. Revs.*, **5**, 99 (1951).

(7) H. P. Koch, *J. Chem. Soc.*, 512 (1951).

(8) G. P. Scott and D. S. Tarbell, THIS JOURNAL, **72**, 240 (1950).

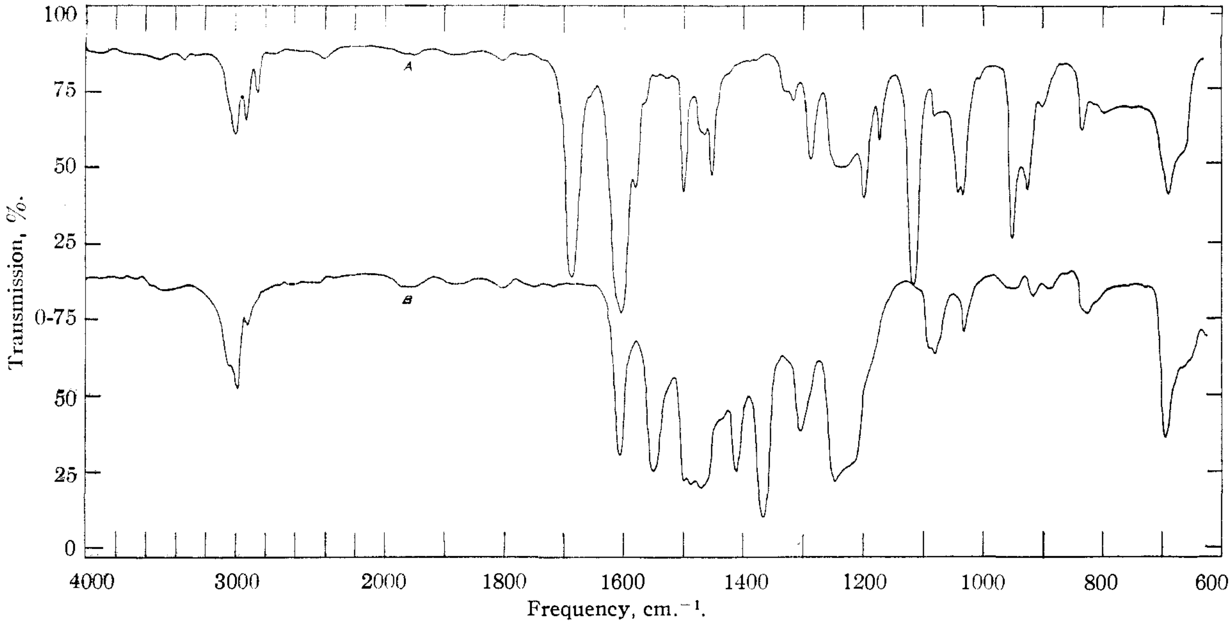
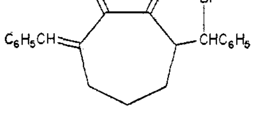


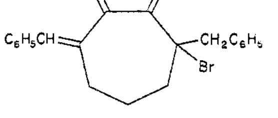
Fig. 2.—Infrared absorption spectra: A, 3,7-dibenzylidene-1,2-cycloheptanedione; B, 3,7-dibenzyltropolone (in chloroform).

tiveness of hydrogen bromide was suggestive of a free radical process at some stage in the isomerization. In order to test this hypothesis, the effect of added peroxides and antioxidants was studied. Irradiation with ultraviolet light or the addition of benzoyl peroxide did not improve the yield, but the presence of the peroxide in the reaction mixture did allow for easier isolation of the pure 3,7-dibenzyltropolone. By contrast, the addition of antioxidants had a marked effect on the yield. Hydroquinone reduced the yield to 26% and *p*-thiocresol, to 4%. The by-products of the isomerization as carried out in hydrogen bromide–acetic acid could not be isolated in pure form, but on the basis of solubility behavior alone, there appeared to be at least three constituents of the crude reaction product in addition to IV. Accordingly, any hypothesis as to possible intermediates in the reaction must be confined to those which could lead to the known reaction product, 3,7-dibenzyltropolone.

The free radical step in the isomerization may be the addition of hydrogen bromide to the unsaturated system in III. It has been found in the past that addition of hydrogen bromide to α,β-unsaturated ketones proceeds in a "conjugate" manner,[9,10,11] yet it is difficult to see how such an adduct (V) of III could lead to 3,7-dibenzyltropolone (IV) by any plausible reaction sequence. By contrast, a free radical addition of hydrogen bromide to the olefinic double bond, with the phenyl group controlling the direction of addition, would lead to VI, from which a logical series of changes can be evoked leading to the tropolone IV. Although the direction of addition of hydrogen bromide leading to VI is not generally encountered,[12] credence in the postulate is supported by analogies: (1) the formation of ω-bromoacetophenone by the addition of hydrogen bromide to cinnamic acid in the presence of oxygen,[13] (2) the coupling of diazonium salts with the α-carbon of cinnamic ester types,[14] and (3) addition of butyraldehyde to mesityl oxide in the presence of benzoyl peroxide to give some of the 1,3-diketone along with the 1,4-diketone, the major product.[15] There remains the possibility, although more remote, that 1,4-addition of hydrogen bromide occurs initially to give V, which then undergoes transformation to VI, in the manner of the rearrangement of ethyl α-bromoacetoacetate to ethyl γ-bromoacetoacetate.[16,17]



V



VI

A second and more conventional route to 3,7-dibenzyltropolone (IV) was investigated which provided α,α'-dibromo intermediates. The diethyl α,α'-dibenzylpimelate (VII) required for this synthesis was obtained by the general Perkin method[18,19] starting with the sodium salt of diethyl benzylmalonate and trimethylene bromide. The acyloin ring closure was effected with sodium in refluxing xylene using high speed stirring and high dilution conditions. The yield of 3,7-dibenzylpimeloin (VIII) was 87%, as compared with the yield (52%) of unsubstituted pimeloin obtained from

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(9) F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

(10) C. Walling, M. S. Kharasch and F. R. Mayo, THIS JOURNAL, **61**, 2693 (1939).

(11) A. Michael and G. H. Shadinger, *J. Org. Chem.*, **4**, 128 (1939).

(12) Weiss and Ebert[4] postulated reverse addition of hydrogen bromide to explain the formation of 2,6-dibenzylphenol (II) from 2,6-dibenzylidenecyclohexanone (I).

(13) O. Shimamura and M. Takahashi, *Bull. Chem. Soc. Japan*, **22**, 60 (1949).

(14) C. F. Koelsch and V. Boekelheide, THIS JOURNAL, **66**, 412 (1944).

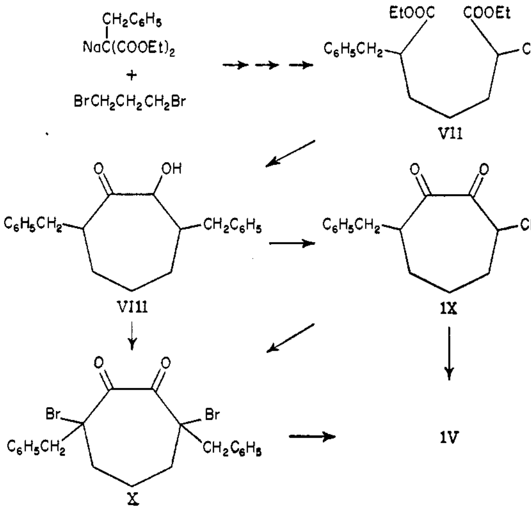
(15) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1269 (1952).

(16) M. S. Kharasch, E. Sternfeld and F. R. Mayo, THIS JOURNAL, **59**, 1655 (1937).

(17) F. Kröhnke and H. Timmler, *Ber.*, **69**, 614 (1936).

(18) W. H. Perkin, *J. Chem. Soc.*, **65**, 572 (1894).

(19) W. H. Perkin and B. Prentice, *ibid.*, **59**, 818 (1891).



diethyl pimelate under the same conditions by Knight and Cram.[20] 3,7-Dibenzyl-1,2-cycloheptanedione (IX) was obtained from 3,7-dibenzylpimeloin in 86–90% yield by oxidation with cupric acetate in 70% acetic acid.[21] These compounds (VIII and IX) were characterized by elemental analysis and by infrared absorption. The general method of diketone to tropolone conversion of Cook and his co-workers[22] was applied to 3,7-dibenzyl-1,2-cycloheptanedione (IX). The 3,7-dibenzyltropolone (IV) obtained in 82% yield by the action on IX of bromine in acetic acid at 55° was identical with the isomerization product from 3,7-dibenzylidene-1,2-cycloheptanedione (III). Both methods of synthesis of 3,7-dibenzyltropolone offer satisfactory routes to this compound, but the isomerization method is the more convenient.

It seems likely that the conversion of IX to IV proceeds through the 3,7-dibromo-3,7-dibenzylcycloheptanedione (X). Corresponding to the two isomers (*cis* and *trans*) of this structure, we have isolated two compounds having the correct composition for $C_{21}H_{20}Br_2O_2$. The isomer of m.p. 130–133° (may not be isomerically pure) was obtained from the bromination of 3,7-dibenzyl-1,2-cycloheptanedione (IX) in carbon tetrachloride. The isomer of m.p. 159–160.5° was obtained from the bromination of 3,7-dibenzylpimeloin (VIII) in acetic acid at 55°. Since neither isomer gave the color with alcoholic ferric chloride that would be characteristic of an enolizable diketone, both were regarded as 3,7-dibromo compounds. It was possible to assign stereochemical structures to these isomers on the basis of their infrared absorption spectra and a study of the scale molecular models of the *cis* (*meso*) and *trans* (racemic) forms of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanedione (X). The use of infrared as a means of distinguishing between the *cis* and *trans* forms was made possible by the findings of Jones, Ramsay, Herling and Dobriner[23] on the spectra of the α-brominated ketosteroids. They found that when the α-bromine atom occupied an equatorial position on the six-membered ketonic ring of a steroid molecule (*i.e.*, the C–Br bond was essentially coplanar with the carbonyl group), the carbonyl peak was shifted about 20 cm.$^{-1}$ toward higher frequency, and when the α-bromine occupied a polar position (*i.e.*, the C–Br and C=O dipoles were essentially perpendicular), there was no shift in frequency of the carbonyl absorption peak from that of the ketone lacking bromine. The carbonyl absorption peak we found for 3,7-dibenzylpimeloin (VIII) was at 1698 cm.$^{-1}$ and that (unconjugated C=O) for 3,7-dibenzyl-1,2-cycloheptanedione (IX) was at 1700 cm.$^{-1}$. The infrared spectrum of the low-melting isomer (A) of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanedione exhibited a broad peak at 1717–1720 cm.$^{-1}$, and that of the high-melting isomer (B), peaks at 1698 and 1715 cm.$^{-1}$ (Fig. 3).

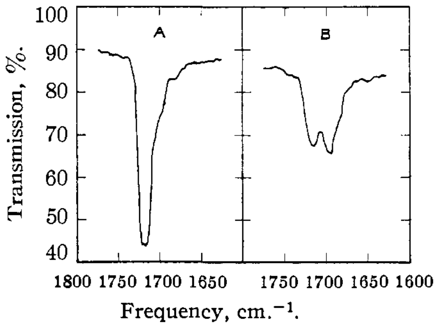


Fig. 3.—Infrared absorption spectra of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanediones: A, m.p. 130–133°; B, m.p. 159–160.5° (in Nujol mull).

A study of the Fisher–Taylor–Hirschfelder models showed that in the *trans*-dibromo compound, the two carbonyl groups are in identical environments and that each of the carbon–bromine bonds is nearly coplanar with the opposite carbonyl group. The spectrum with the single broad peak shifted about 20 cm.$^{-1}$ toward higher frequency from the normal carbonyl peak (as in VIII, IX) would therefore be representative of the *trans* isomer. A model of the *cis*-dibromo compound showed that the two carbonyl groups here are in very different environments: one of the C=O groups is nearly at right angles to both of the C–Br bonds, while the other is in the same plane with both C–Br bonds. The spectrum with the normal peak at 1698 cm.$^{-1}$ and the shifted peak at 1715 cm.$^{-1}$ would therefore be representative of the *cis* isomer. Accordingly, the low-melting isomer (A) can be assigned the *trans* structure and the high-melting isomer (B), the *cis* structure of X. The *trans* isomer was readily converted to the tropolone (IV) by hydrogen bromide in acetic acid. By contrast, the *cis* isomer was isolated from an acetic acid solution containing hydrogen bromide. Yet another route to the 3,7-dibenzyltropolone (IV) was reaction of 3,7-dibenzyl-1,2-cycloheptanedione (IX) with N-bromosuccinimide,[24,25] followed by heating the unstable, partially brominated product in acetic acid.

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[20] J. D. Knight and D. J. Cram, THIS JOURNAL, **73**, 4136 (1951).

[21] P. Ruggli and P. Zeller, *Helv. Chim. Acta*, **28**, 741 (1945).

[22] J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 503 (1951); *Chem. and Ind.*, 427 (1950).

[23] R. N. Jones, D. A. Ramsay, F. Herling and K. Dobriner, THIS JOURNAL, **74**, 2828 (1952).

[24] Ng. Ph. Buu-Hoï, *Experientia*, **2**, 310 (1946).

[25] T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, No. 7, 38 (1950); *C. A.*, **45**, 7098e (1951).

Experimental[26]

Absorption Spectra.—The infrared absorption spectra were obtained with a Perkin–Elmer automatic recording infrared spectrometer, model 21. The ultraviolet absorption spectra were determined using a Cary recording spectrophotometer, model 11.

Isomerization of 2,6-Dibenzylidenecyclohexanone (I). 2,6-Dibenzylphenyl Acetate (IIa).—The procedure was a modification of that of Weiss and Ebert[4] in that the isomerization was conducted at atmospheric pressure in an open vessel. A mixture of 10 ml. of glacial acetic acid saturated with hydrogen bromide, 5 ml. of acetic anhydride and 5 g. of 2,6-dibenzylidenecyclohexanone[27] was heated at 70° for 12 hr. protected from moisture. Dilution of the reaction mixture with water caused the separation of 4.2 g. (84%) of solid, which melted at 75–77° after one recrystallization from aqueous acetic acid (reported 76–77°).

3,7-Dibenzylidene-1,2-cycloheptanedione (III).—A mixture of 0.5 g. (4 millimoles) of 1,2-cycloheptanedione,[28] 1.7 g. (16 millimoles) of benzaldehyde and 5 drops of piperidine[29] with 2 ml. of absolute ethanol was heated under reflux on a steam-bath for 6 hr. Dilution with ethanol followed by cooling caused the separation of 0.41 g. (34%) of crude product. After recrystallization from ethanol and a subsequent recrystallization from acetone, the 3,7-dibenzylidene-1,2-cycloheptanedione was obtained as yellow needles, m.p. 189–190°.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.65; H, 6.28.

The infrared spectrum in chloroform solution showed strong absorption at 1683 cm.$^{-1}$, indicative of a conjugated carbonyl, and at 1605 cm.$^{-1}$, indicative of a conjugated carbon–carbon double bond.

The conditions described above represent the optimum among the many tried for effecting the condensation between benzaldehyde and 1,2-cycloheptanedione.

3,7-Dibenzyltropolone (IV).—To 20 ml. of glacial acetic acid saturated with hydrogen bromide at 30° was added 0.50 g. (1.65 millimoles) of 3,7-dibenzylidene-1,2-cycloheptanedione and 0.01 g. of benzoyl peroxide. The reaction mixture was heated at 60° for 11 hr. while protected from moisture and then poured into 150 ml. of water. Chloroform was used repeatedly for extraction until the aqueous solution was colorless. The chloroform extracts were combined and washed once with water, and the chloroform was evaporated on a steam-bath. The residue was extracted repeatedly with petroleum ether (b.p. 40–60°); these extracts were combined, concentrated to 10 ml., and cooled in an ice-box. The crude product (0.23 g., 46%) which separated was recrystallized twice from methanol with decolorization; colorless needles, m.p. 118–119°. See Fig. 1 for ultraviolet and Fig. 2 for infrared absorption spectra.

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.73; H, 6.09.

When the isomerization was carried out under similar conditions using larger amounts of material, the yield was somewhat lower. Irradiation of the reaction mixture did not boost the yield. If the benzoyl peroxide was omitted, the crude product was less readily purified. Addition of hydroquinone or *p*-thiocresol diminished the yield. The conditions described represent the optimum so far as temperature and time variants were tried. No isomerization was realized by treatment of 3,7-dibenzylidene-1,2-cycloheptanedione with other acids (HCl, H_2SO_4, $HClO_4$).

3,7-Di-(α-bromobenzyl)-3,7-dibromo-1,2-cycloheptanedione.—To 0.50 g. (1.65 millimoles) of 3,7-dibenzylidene-1,2-cycloheptanedione in 5 ml. of chloroform was added 0.53 g. (3.3 millimoles) of bromine in 5 ml. of carbon tetrachloride. The reaction mixture became a light straw color in 8 minutes. The solvent was removed *in vacuo* and the residual yellow oil was heated in glacial acetic acid at 60° for 7 hours. Faintly yellow prisms were deposited which, after two recrystallizations from *n*-butyl bromide, melted at 190° with decomposition.

Anal. Calcd. for $C_{21}H_{18}Br_4O_2$: C, 40.55; H, 2.92; Br, 51.39. Found: C, 40.74; H, 3.03; Br, 51.04.

The tetrabromo compound gave no color reaction with ethanolic ferric chloride. Infrared absorption maxima were observed at 1714 and 1724 cm.$^{-1}$ for the Nujol mull.

Regeneration of 3,7-dibenzylidene-1,2-cycloheptanedione was effected by boiling the 3,7-di-(α-bromobenzyl)-3,7-dibromo-1,2-cycloheptanedione with methyl ethyl ketone. Hydrogen bromide was evolved, and a yellow solid was recovered from the methyl ethyl ketone. After recrystallization from acetone, the solid melted at 186–190° and a mixture with 3,7-dibenzylidene-1,2-cycloheptanedione (III) melted at 187–190°.

When conversion of the 3,7-di-(α-bromobenzyl)-3,7-dibromo-1,2-cycloheptanedione to a tropolone was attempted by heating in acetic acid saturated with hydrogen bromide at 60° for 24 hr., followed by the usual isolation procedure (see above), no crystalline product could be isolated, but the crude product gave first a red, then a dark green color with ethanolic ferric chloride.

Diethyl α,α'-Dibenzylpimelate (VII).—To a solution of 21 g. (0.89 gram atom) of sodium dissolved in 1 l. of absolute ethanol was added 223 g. (0.89 mole) of diethyl benzylmalonate. The mixture was stirred vigorously under gentle reflux while 88.8 g. (0.44 mole) of trimethylene bromide was added during 30 minutes. The reaction mixture was heated under reflux for 2 hours (the yield would probably be improved by a longer heating period), and the precipitated sodium bromide was removed by filtration. The solvent was removed from the filtrate by distillation, and the residual mixture of esters was heated under reflux for 2 days with a solution of 600 ml. of acetic acid, 250 ml. of sulfuric acid and 250 ml. of water. The hydrolysis mixture was diluted to 5 l. with water and extracted with four 250-ml. portions of ether. The combined ether extracts were dried, and the material boiling below 150° was removed by distillation. The residual crude α,α'-dibenzylpimelic acid was esterified by heating under reflux for 30 minutes with 320 ml. of absolute ethanol, 160 ml. of toluene and 0.8 ml. of sulfuric acid. The reaction mixture was distilled until the temperature of the distillate rose 5°. To the residue was added 300 ml. of absolute ethanol, and this mixture was refluxed for 18 hours, cooled, and poured into 1.5 l. of ice-water. The crude ester was separated by extraction with three 100-ml. portions of ether. The combined ether extracts were washed with water, 10% aqueous sodium carbonate, and water again. The extracts were dried, the ether was removed, and the residue was fractionally distilled *in vacuo*. The diethyl α,α'-dibenzylpimelate was collected at 210–215° (1.8 mm.), $n^{20}D$ 1.5172, yield 48 g. (14% overall).

Anal. Calcd. for $C_{25}H_{32}O_4$: C, 75.72; H, 8.14. Found: C, 75.70; H, 8.13.

α,α'-Dibenzylpimelic Acid.—A mixture of 1 g. of diethyl α,α'-dibenzylpimelate and 2 g. of potassium hydroxide in 45 ml. of 30% aqueous ethanol was heated under reflux for 3.5 hours. The reaction mixture was poured into 1 *N* hydrochloric acid, and the oil which separated solidified on standing. After recrystallization from cyclohexane, the colorless needles melted at 135–137° (reported[19] 120°).

Anal. Calcd. for $C_{21}H_{24}O_4$: C, 74.09; H, 7.11. Found: C, 74.16; H, 7.04.

3,7-Dibenzylpimeloin (VIII).—To a fine dispersion of 9.3 g. (0.40 gram atom) of sodium in 1.1 l. of dry xylene, whipped by a high speed stirrer and heated at reflux under nitrogen, was added during 13 hours, through a high dilution head, a solution of 40 g. (0.10 mole) of diethyl α,α'-dibenzylpimelate in 200 ml. of dry xylene. The reaction mixture was heated 7 hours after the addition was complete, cooled, and to it was added 29 ml. of acetic acid with 35 ml. of dry ether. The sodium acetate was separated by filtration and the solvent was removed by distillation through a four-inch helices-packed column until the volume of the solution remaining was about 75 ml. The residual solvent was removed through a Claisen head, and analytically pure 3,7-dibenzylpimeloin was collected by connecting the Claisen head directly to an adapter and receiver, b.p. 200–210° (1.4 mm.), $n^{20}D$ 1.5684, yield 27 g. (87%).

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(26) All melting points are corrected. We are indebted to Miss Emily Davis, Mrs. Katherine Pih, Mrs. Esther Fett and Mr. Joseph Nemeth for microanalyses, and to Miss Helen Miklas and Miss Ella Richards for determination of the absorption spectra.

(27) D. Vorländer and K. Kunze, *Ber.*, **59**, 2082 (1926).

(28) W. V. Haar, R. C. Voter and C. V. Banks, *J. Org. Chem.*, **14**, 837 (1949).

(29) P. Karrer and C. Cochand, *Helv. Chim. Acta*, **28**, 1181 (1945).

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.50; H, 7.85.

The acyloin gave an olive-green color with ethanolic ferric chloride.

The infrared spectrum exhibited absorption maxima at 3440, 1400 and 1072 cm.$^{-1}$, attributable to the hydroxyl groups, and at 1698 cm.$^{-1}$, attributable to carbonyl.

3,7-Dibenzyl-1,2-cycloheptanedione (IX).—A mixture of 5.0 g. (16 millimoles) of 3,7-dibenzylpimeloin and 6.72 g. (34 millimoles) of cupric acetate in 150 ml. of 70% aqueous acetic acid was heated under reflux for 2 hours. The reaction mixture was cooled and diluted with 600 ml. of water. After two extractions with 200-ml. portions of ether, the ethereal solution was washed successively with water, aqueous sodium bicarbonate and water, dried, and the ether was removed. The residue was distilled through a Holzman column,[30] b.p. 210–215° (1.3 mm.), $n^{20}D$ 1.5832, yield 4.26 g. (86%). On standing, the 3,7-dibenzyl-1,2-cycloheptanedione solidified to a mushy yellow solid.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.13; H, 7.45.

The infrared spectrum exhibited maxima at 3360 (OH), 1700 (C=O), 1650 (conjugated C=O) and 1618 cm.$^{-1}$ (conjugated C=C).

In a run on a larger scale, this product was obtained in 60% yield along with a colorless solid in 30% yield. The colorless solid crystallized from ether as clumps of fine needles, m.p. 98–100°.

Anal. Calcd. for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.39; H, 7.17.

This colorless material was probably the keto–enol form of the diketone, since it changed on standing to a mushy yellow solid (diketone–ketoenol equilibrium mixture) identical in appearance with that described above. The equilibrium mixture gave a blue–green color with ethanolic ferric chloride.

3,7-Dibenzyltropolone from 3,7-Dibenzyl-1,2-cycloheptanedione.—The general method of diketone-to-tropolone conversion of Cook and his co-workers[22] was applied. To a solution of 1.0 g. (3.2 millimoles) of 3,7-dibenzyl-1,2-cycloheptanedione in 15 ml. of acetic acid was added 1.05 g. (6.6 millimoles) of bromine. The reaction mixture was heated 8 hours at 55° with the exclusion of moisture and then poured into water. Chloroform was used for extraction until the water layer became colorless. The combined chloroform extracts were washed with water, the chloroform was evaporated, and the residue was recrystallized from methanol. The 3,7-dibenzyltropolone (0.81 g., 82%) separated as dark brown needles, m.p. 112–116°, which on further purification was identical in all properties with the compound obtained by the isomerization of 3,7-dibenzylidene-1,2-cycloheptanedione.

***trans*-3,7-Dibromo-3,7-dibenzyl-1,2-cycloheptanedione.**—A solution of 1.0 g. (3.2 millimoles) of 3,7-dibenzyl-1,2-cycloheptanedione in 10 ml. of carbon tetrachloride was mixed with a solution of 1.0 g. (6.3 millimoles) of bromine in 5 ml. of carbon tetrachloride, with vigorous evolution of hydrogen bromide. The mixture was allowed to stand for 1.5 hours and the solvent was removed *in vacuo*. The residual light brown viscous liquid was extracted with boiling petroleum ether (b.p. 40–60°). When the combined extracts were cooled, a clear viscous liquid layer separated and solidified on standing. Recrystallization from petroleum ether yielded a colorless powder, m.p. 130–133°, yield 0.12 g. (8%).

Anal. Calcd. for $C_{21}H_{20}Br_2O_2$: C, 54.33; H, 4.34; Br, 34.43. Found: C, 54.51; H, 4.52; Br, 32.22.

An ethanolic solution of the product gave no color with ferric chloride. The infrared spectrum, as determined in Nujol mull, showed twin absorption maxima at 1717 and 1720 cm.$^{-1}$ (A in Fig. 3).

***cis*-3,7-Dibromo-3,7-dibenzyl-1,2-cycloheptanedione.**—To a solution of 1.0 g. (3.2 millimoles) of 3,7-dibenzylpimeloin in 15 ml. of acetic acid was added 1.57 g. (9.8 millimoles) of bromine. The reaction mixture was heated 8 hours at 60° while protected from moisture. The mixture was poured into water and extracted with chloroform. The chloroform extract was concentrated and the residue was taken up in methanol. The solid which separated (0.43 g., 29%) when the solution was cooled was recrystallized from methanol; colorless needles, m.p. 159–160.5°, with gas evolution. (The possibility that some 3,7-dibenzyltropolone was also present in the crude product was not eliminated.)

Anal. Calcd. for $C_{21}H_{22}Br_2O_2$: C, 54.10; H, 4.76. Calcd. for $C_{21}H_{20}Br_2O_2$: C, 54.33; H, 4.34. Found: C, 54.08; H, 4.56.

The analysis suggested that the compound was one of the forms of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanedione. It gave a negative ferric chloride test. The infrared absorption spectrum showed two adjacent peaks (C=O) at 1698 and 1715 cm.$^{-1}$, the latter of slightly lower intensity, and a small peak at 3402 cm.$^{-1}$ (B in Fig. 3).

Conversion of *trans*-3,7-Dibromo-3,7-dibenzyl-1,2-cycloheptanedione in Hydrogen Bromide–Acetic Acid.—When a solution of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanedione, m.p. 130–133°, was heated in acetic acid at 60° for 10 hours, followed by the usual isolation procedure, no 3,7-dibenzyltropolone was obtained but only about 10% of the starting material was recovered. When hydrogen bromide–acetic acid was used, 3,7-dibenzyltropolone was obtained. A solution of 151 mg. (0.33 millimole) of 3,7-dibromo-3,7-dibenzyl-1,2-cycloheptanedione in 15 ml. of acetic acid saturated with hydrogen bromide was heated at 60° for 12 hours. The reaction mixture was diluted with water and extracted with chloroform. The chloroform extracts were evaporated and the residue, after one recrystallization from methanol, melted at 114–118°, yield 64 mg. (65%) of slightly impure 3,7-dibenzyltropolone.

Reaction of 3,7-Dibenzyl-1,2-cycloheptanedione with N-Bromosuccinimide.—A solution of 1.0 g. (3.3 millimoles) of 3,7-dibenzyl-1,2-cycloheptanedione, 1.15 g. (6.6 millimoles) of N-bromosuccinimide, and 0.1 g. of benzoyl peroxide in 20 ml. of dry carbon tetrachloride was heated under reflux for 1 hour. The reaction mixture was cooled, and the succinimide was removed by filtration. The solvent was removed under reduced pressure, and the viscous liquid residue was extracted twice with 100 ml. of hot petroleum ether (b.p. 40–60°). The first extract was discarded. The second extract was concentrated *in vacuo* to 20 ml. A light yellow oil separated on cooling in an ice-bath. Recrystallized from petroleum ether by cooling in Dry Ice, the solid material reliquefied at room temperature and soon began to decompose.

Anal. Calcd. for $C_{21}H_{20}Br_2O_2$: C, 54.33; H, 4.34. Found: C, 61.68; H, 5.52.

A portion of the crude, partially brominated product was heated in acetic acid solution at 60° for 14 hours. The mixture was worked up in the usual manner and crude 3,7-dibenzyltropolone was isolated. The same results were obtained when a saturated solution of hydrogen bromide in acetic acid was used.

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(30) G. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.* **20**, 361 (1948).