taining 10 g. of *p*-toluidine. The solution was cooled to 8° and filtered. The precipitate was taken up in 100 ml. of warm water and an additional 24 ml. of the water–hydrochloric acid solution containing 5 g. of *p*-toluidine was added. The solution was warmed until all was in solution, treated with Norit filtered hot, and cooled to 8° to precipitate the *p*-toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 177–182°. After recrystallization from 75 ml. of hot water, there was obtained 8.0 g., 27.5% of the theoretical amount, of the pure toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 182–183°. This recrystallized salt was used in all of the following experiments.

Anal. Calcd. for $C_{15}H_{17}NO_3S$: C, 61.80; H, 5.88; S, 11.0; neut. equiv., 291.35. Found: C, 61.90; H, 5.99; S, 11.12; neut. equiv., 289.

Potassium *p*-Vinylbenzenesulfonate.—Five grams of the dry *p*-toluidine salt of *p*-vinylbenzenesulfonic acid, m.p. 182–183°, was dissolved in 30 ml. of water and 14.25 ml. of 1.2 *N* potassium hydroxide. This solution was extracted with three 50-ml. portions of ether and evaporated to dryness. The crude salt thus obtained was dissolved in 1–1 methanol–water and cooled to −20° to precipitate 1.35 g., 42.8% of the theoretical amount, of dry potassium *p*-vinylbenzenesulfonate. Salt thus obtained was used in the preparation of polymers B, C and D.

Anal. Calcd. for $C_8H_7KO_3S$: C, 43.22; H, 3.18. Found: C, 43.07; H, 3.25.

A 1.0-g. sample of potassium *p*-vinylbenzenesulfonate was oxidized with potassium permanganate and converted to the sulfonamide. The product was hydrolyzed with alkali to remove any carboxamide. There resulted 0.16 g., 17% of the theoretical amount, of *p*-carboxybenzenesulfonamide, m.p. 276-277° dec.; reported m.p. 280° dec.[1a]

Attempts to isolate the barium and lead salt and the free acid have thus far been unsuccessful.

Polymerization of Potassium *p*-Vinylbenzenesulfonate.—Polymer A was prepared by polymerization of a solution of the potassium salt obtained by neutralization of the toluidine salt and extraction of the toluidine. To 3.5 g. of the dry *p*-toluidine salt was added 10 ml. of 1.2 *N* potassium hydroxide. This solution was extracted three times with 50-ml. portions of ether. Seventeen ml. of water was added and the extraction repeated. To this solution were added 0.06 g. of potassium persulfate (2.7% based on monomer) and 0.03 g. of sodium bisulfite (1.33% based on monomer). After 5 hours at 45° under oxygen-free nitrogen the solution was neutralized and evaporated to dryness. The polymer was dried under vacuum for 24 hours.

Polymers B, C and D were prepared from recrystallized potassium *p*-vinylbenzenesulfonate with different concentrations of the monomer in water and different amounts of initiator. Polymer D was prepared from a 25.3% solution of 1.35 g. of the salt in 3 ml. of water. This solution was placed in a flask fitted with a stirrer and flushed with oxygen-free nitrogen. A solution of 0.018 g. of potassium persulfate (1.33% based on monomer) and 0.009 g. (0.67% based on monomer) of sodium bisulfite in one ml. of water was added as initiator. This solution (*p*H 7–8) was stirred under nitrogen for five hours. The *p*H, now 4–5, was adjusted to 7–8 by adding a few drops of dilute potassium hydroxide solution. The solution was evaporated to dryness and dried in a vacuum. Polymer C was prepared following this procedure using twice as much persulfate (2.7%) and bisulfite (1.33%) for the same amount of monomer. Polymer B was prepared similarly using twice as much persulfate (2.7%) and bisulfite (1.33%) for a 7.6% solution of 1.35 g. of salt in 16.5 ml. of water except that the solution was not stirred during the polymerization. The thoroughly dried polymer is quite hygroscopic and has the unusual property of decrepitating as it absorbs water.

Anal. Calcd. for $(C_8H_7KO_3S)_x$: C, 43.22; H, 3.18. Found: C, 39.48, 39.75; H, 3.67, 3.48.

Viscosity Determinations.—The viscosities were determined on successive dilutions of aqueous solutions of the polymers in modified Ostwald viscometers at 30°. The data are presented in Fig. 1. The comparative values of the specific viscosity for solutions of 1.0 g. of the polymer in 100 ml. of solution are: A, 0.731; B, 0.453; C, 0.999; and D, 2.63.

LOUISVILLE, KENTUCKY

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION]

The Preparation and Reactions of Methyl 9-Oxo-14-hydroperoxydehydroabietate

BY PAUL F. RITCHIE, THOMAS F. SANDERSON AND LANE F. MCBURNEY

RECEIVED AUGUST 14, 1953

Methyl 9-oxodehydroabietate, prepared by chromic acid oxidation of methyl dehydroabietate, has been oxidized with molecular oxygen to mixtures containing methyl 9-oxo-14-hydroperoxydehydroabietate. The hydroperoxide has been converted to four new phenanthrene derivatives and the structures of the compounds have been proved.

The primary attack of molecular oxygen upon the dehydroabietic acid nucleus[1] occurs at the 9-position, as was shown in previous communications.[1,2] It was demonstrated[2] that reaction also occurs at the 14-position but products of this secondary reaction were not isolated. In the present research a derivative of dehydroabietic acid in which the 9-position was not readily available for further oxidation, that is, methyl 9-oxodehydroabietate (II), was oxidized in the molten state at 90° in the presence of a benzoyl peroxide initiator. Oxidation was accomplished by continuously circulating oxygen through the reaction mixtures at atmospheric pressure while following the course of the reaction by measuring the volume of oxygen absorbed. The major initial product of this oxidation proved to be methyl 9-oxo-14-hydroperoxydehydroabietate (III) which was not isolated but was converted to four new, isolable phenanthrene derivatives (IV, V, VI and VII).

The methyl 9-oxodehydroabietate used in these experiments was prepared by a procedure hitherto unreported. Methyl dehydroabietate was oxidized with acetic acid solutions of chromic acid at temperatures of 30–50° to mixtures from which, after chromatographic adsorption on alumina, was obtained crystalline methyl-9-oxodehydroabietate in yields of 30–35%. An alternative method of isolating the ketone consisted of countercurrent extraction of the oxidation mixtures with isoöctane and methanol containing 5% of water as the solvent pair and by crystallization of the fraction recovered from the aqueous methanol phase. The ketone was isolated in yields comparable to those cited above but, even after repeated recrystallization resulting in apparent high purity, contained oxida-

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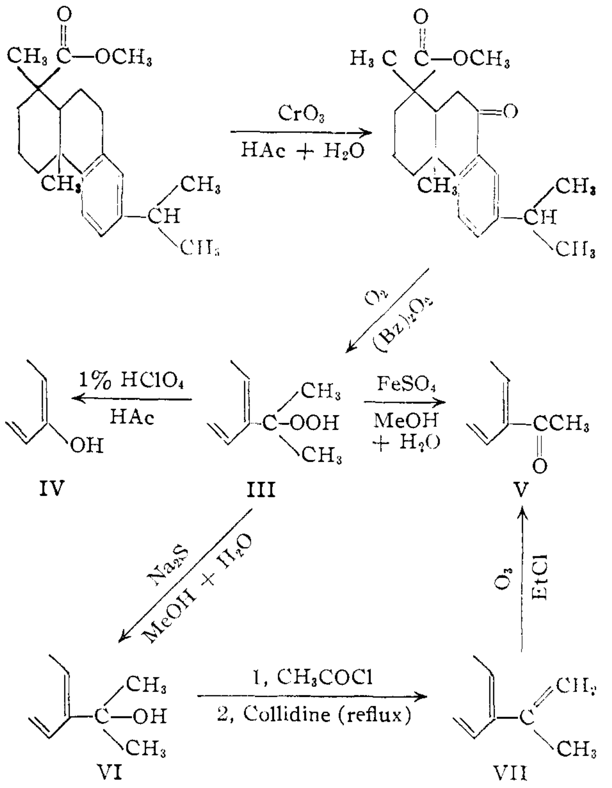
(1) A. E. Drake (to Hercules Powder Co.), U. S. Patent 2,434,643 (Jan. 20, 1948).

(2) P. F. Ritchie, T. F. Sanderson and L. F. McBurney, THIS JOURNAL, **75**, 2610 (1953).



tion inhibitors which necessitated chromatography in order to obtain material most suitable for our oxidation studies.

Methyl 9-oxodehydroabietate, containing 2.5 mole per cent. of benzoyl peroxide as an initiator, absorbs oxygen rapidly at 90° until 40–60 mole per cent. of oxygen is absorbed. The oxidates obtained under these conditions contain 40–50 mole per cent. of hydroperoxide as shown by analysis. These oxidates resisted crystallization but the presence of methyl 9-oxo-14-hydroperoxydehydroabietate was demonstrated by the isolation of acetone after acid cleavage[2] in yields approximately corresponding to the hydroperoxide content of the crude oxidates. Extraction with dilute caustic of the non-volatile residue from the acid treatment afforded a crystalline compound in 30–35% yield.

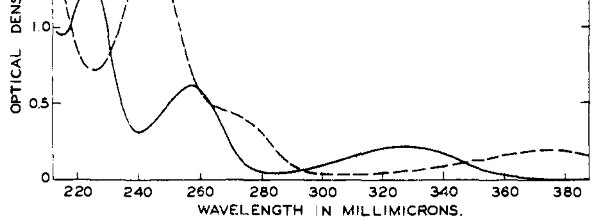


Fig. 1.—Ultraviolet absorption spectrum of methyl 1,4a-dimethyl - 7 - hydroxy - 9 - oxo - 1,2,3,4,4a,9,10,10a - octahydro-1-phenanthrene carboxylate (IV): 1, —, concn. 0.02 g./l. in 3A alcohol; 2, ---, concn. 0.02 g./l. in 3A alcohol + KOH.

The analysis of the crystalline compound and derivatives, the ultraviolet absorption spectrum (curve 1, Fig. 1), of the crystalline compound and the bathochromic shift[3] observed upon salt formation (curve 2, Fig. 1) are all consistent with the structure 1,4a-dimethyl-1-carbomethoxy-7-hydroxy-9 - oxo - 1,2,3,4,4a,9,10,10a - octahydrophenanthrene (IV).

Treatment with aqueous methanolic solutions of ferrous sulfate[2] of the reaction mixtures obtained by oxidation of methyl 9-oxodehydroabietate resulted in products from which could be isolated, by chromatography on alumina, a crystalline diketone in 8–10% yield. This diketone gave a positive iodoform test. Analysis of the compound and its derivatives and the ultraviolet absorption spectrum (curve 1, Fig. 2) indicated structure V, 1,4a-dimethyl-1-carbomethoxy-9-oxo-7-acetyl-1,-2,3,4,4a,9,10,10a-octahydrophenanthrene.

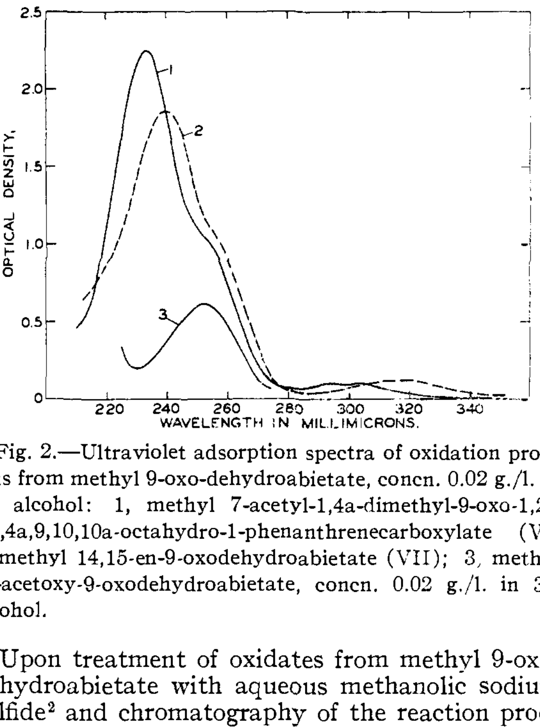


Fig. 2.—Ultraviolet adsorption spectra of oxidation products from methyl 9-oxo-dehydroabietate, concn. 0.02 g./l. in 3A alcohol: 1, methyl 7-acetyl-1,4a-dimethyl-9-oxo-1,2,-3,4,4a,9,10,10a-octahydro-1-phenanthrenecarboxylate (V); 2, methyl 14,15-en-9-oxodehydroabietate (VII); 3, methyl 14-acetoxy-9-oxodehydroabietate, concn. 0.02 g./l. in 3A alcohol.

Upon treatment of oxidates from methyl 9-oxodehydroabietate with aqueous methanolic sodium sulfide[2] and chromatography of the reaction products on alumina there was obtained a non-crystalline fraction in 30–35% yield. The same material was obtained in 15–20% yield along with the diketone V as a product of reaction between ferrous sulfate and hydroperoxide-containing oxidates. This product was converted quantitatively to a crystalline acetate the analysis and ultraviolet absorption spectrum of which (curve 2, Fig. 2) were consistent with structure VI, methyl 9-oxo-14-hydroxydehydroabietate, for the parent compound. Dehydration of the non-crystalline fraction followed by chromatography on alumina resulted in isolation of a crystalline compound in about 35% yield. The ultraviolet absorption spectrum (curve 3, Fig. 2) and analysis of the compound and derivatives were consistent with

[3] L. F. Fieser and M. Fieser in "Natural Products Related to Phenanthrene," 3rd Edition, Reinhold Publ. Corp., New York, N. Y., 1949, p. 198.

structure VII, 1,4a-dimethyl-1-carbomethoxy-7-isopropenyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene. Ozonization of the compound and chromatography of the product on alumina resulted in isolation of the diketone for which structure V was indicated previously.

The authors are indebted to Dr. Evelyn V. Cook and staff of the Spectroscopy Laboratory of the Hercules Experiment Station for valuable assistance throughout the course of this research.

Experimental Details

Preparation of Methyl 9-Oxodehydroabietate (II).—Methyl dehydroabietate[2] (78.5 g.) was dissolved in 425 ml. of acetic acid and to the resulting solution was added dropwise a solution of 33.4 g. of chromium trioxide in 25 ml. of water and 75 ml. of acetic acid. The addition extended over a period of 4 hours during which the reaction mixture was maintained at 48–50° and agitated thoroughly. After standing overnight at room temperature, the product (77.9 g.) was recovered by dilution with water and ether extraction. The product containing 52% of methyl 9-oxodehydroabietate was adsorbed on an alumina[4] column (5 cm. × 122 cm.) and eluted exhaustively with hexane to obtain 29.5 g. of methyl dehydroabietate. Subsequent elution of the column with benzene resulted in removal of 39.8 g. of material which was crystallized from isoöctane to obtain 24.1 g. of white prisms of methyl 9-oxodehydroabietate (m.p. 67–68°), $[\alpha]^{22}D$ +15.3° (2% solution in $CHCl_3$).[5]

An oxidate (32.0 g.) prepared in the manner described above and containing 51% of methyl 9-oxodehydroabietate[6] was fractionated by discontinuous countercurrent extraction in separatory funnels with isoöctane and methanol containing 5% of water as the solvent pair. The diamond pattern of phase separation and combination was that discussed by Bush and Densen.[7] The material recovered from the isoöctane phase (15.6 g.) was essentially unchanged methyl dehydroabietate. The fraction recovered from the aqueous methanol (16.2 g.) was crystallized from aqueous methanol to obtain 10.7 g. of methyl 9-oxodehydroabietate (m.p. 63–65°).

Oxidation of Methyl 9-Oxodehydroabietate (III).—Methyl 9-oxodehydroabietate (10.0 g.) containing 0.50 g. of benzoyl peroxide was oxidized with molecular oxygen in the special apparatus previously described.[8] The progress of the reaction was followed by measuring the oxygen absorption at frequent intervals. After 29 hours reaction was essentially complete, 424 ml. (60.5 mole per cent.) of oxygen had been absorbed, and a sample of the reaction mixture contained 49% of hydroperoxides.[9] The remainder of the oxidate (9.5 g.) was treated at 70° for one hour with 1.0 g. of trichloroacetic acid. During the treatment, a stream of nitrogen was passed slowly through the mixture and into a series of three traps containing an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride. The precipitate recovered from the traps (2.06 g.) was crystallized from alcohol and melted at 124–126°. The melting point was unchanged after admixture of the crystals with the 2,4-dinitrophenylhydrazone of acetone.

1,4a-Dimethyl-1-carbomethoxy-7-hydroxy-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (IV).—Oxidized methyl 9-oxodehydroabietate (9.5 g., 49% hydroperoxides) was dissolved in 30 ml. of glacial acetic acid. A solution of 1 ml. of perchloric acid (70% aqueous solution) in 20 ml. of glacial acetic acid was added in small portions at room temperature. After one-half hour the solution contained no hydroperoxides. The product was recovered and an ether solution of it extracted with 1% potassium hydroxide solution. Upon recovery of the alkali-soluble fraction and crystallization from aqueous acetic acid there was obtained 2.5 g. of white needles melting at 195–196.5°. After recrystallization from the same solvent the needles melted at 196–197°, $[\alpha]^{22}D$ −8.3° (2% solution in $CHCl_3$).

Anal. Calcd. for $C_{18}H_{22}O_4$: C, 71.50; H, 7.34. Found: C, 71.64; H, 7.44.

The crystals gave a positive phenol test with ferric chloride. The ultraviolet absorption spectrum of the material was characterized by maxima at 224 mμ (α, 64), 257 mμ (α, 29.5), and 328 mμ (α, 9.5).

A reversible shift of the spectrum, typical of phenolic compounds, was observed in alkaline solution to give maxima at 244 mμ (α, 74), 278 mμ (α, 18), and 375 mμ (α, 8.6). A *p*-nitrobenzoate was prepared from the product and was crystallized from a mixture of benzene and petroleum ether to constant melting point 208.5–209.5°.

Anal. Calcd. for $C_{25}H_{25}O_7N$: N, 3.69; C, 66.51; H, 5.58. Found: N, 3.61; C, 66.75; H, 5.68.

A sample (0.50 g.) of the phenol was dissolved in 20 ml. of diethylene glycol containing 0.50 g. of potassium hydroxide, and the solution was heated under reflux for 1.5 hours. After recovery there was obtained 0.45 g. of product which was crystallized from benzene to a constant melting point of 267–269°.

Anal. Calcd. for $C_{17}H_{20}O_4$: C, 70.83; H, 6.94. Found: C, 71.11; H, 6.83.

1,4a-Dimethyl-1-carbomethoxy-7-acetyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (V).—A sample of oxidized methyl 9-oxodehydroabietate (10.2 g.) containing 35.0 mole per cent. of hydroperoxides was dissolved in 400 ml. of methanol. To this solution was added at room temperature with stirring 10 g. of ferrous sulfate dissolved in 200 ml. of 1:1 water–methanol over a period of 2 hours. The mixture was heated to reflux temperature and boiled for one hour. After recovery there was obtained 10.1 g. of material which was dissolved in 50 ml. of benzene and adsorbed on a column of alumina 3.5 cm. in diameter and 105 cm. high. Exhaustive elution with benzene afforded 4.1 g. of unchanged methyl 9-oxodehydroabietate. After elution of the column with methylene chloride and evaporation of the solvent, 1.8 g. of material was obtained. This product was recrystallized from methanol to a constant melting point of 144–145°, $[\alpha]^{22}D$ +30.8° (2% solution in $CHCl_3$).

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37. Found: C, 73.30; H, 7.59.

A sample of the crystals gave a positive iodoform test. The ultraviolet absorption spectrum of the material is characterized by maxima at 234 mμ (α, 112), 295 mμ (α, 3.1), and 304 mμ (α, 2.0) and an inflection point at 255 mμ (α, 46). A sample (0.43 g.) of the compound was saponified by boiling in 15 ml. of ethanol containing 0.15 g. of potassium hydroxide for seven hours. The free acid was recovered (0.34 g.) and recrystallized to constant melting point (189–190°) from aqueous methanol.

Anal. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.06; neut. equiv., 314. Found: C, 72.29; H, 7.25; neut. equiv., 312.

Methyl 14-Hydroxy-9-oxodehydroabietate (VI).—Oxidized methyl 9-oxodehydroabietate (10.0 g.) containing 41.6 mole per cent. of hydroperoxide was dissolved in 300 ml. of methanol. To the agitated solution was added dropwise a solution of 10.4 g. of sodium sulfide in 100 ml. of aqueous methanol.[2] After one hour the addition was complete and the reaction mixture was heated at reflux temperature for 2 hours. The product (7.9 g.) was recovered, dissolved in 50 ml. of benzene and adsorbed on a column of alumina 3.5 cm. in diameter and 95 cm. high. Exhaustive elution of the column with methylene chloride yielded 4.1 g. of unchanged methyl 9-oxodehydroabietate. Subsequent elution of the column with 1:1 methylene chloride–ether resulted in isolation of 3.3 g. of material in the form of a light yellow, viscous oil. All attempts to crystallize this product were unsuccessful. A sample (2.8 g.) of the material was dissolved in 40 ml. of dry pyridine containing 20 ml. of acetic anhydride. After standing 6 days at room temperature the solution was diluted with water containing only a slight excess (based on pyridine) of hydrochloric acid. The product (3.1 g.) was recovered by ether extraction and washed free of acid. Upon removal of the ether the product crystallized (m.p. 127–130°). After recrystallization from methanol the white needles melted at 133–134°, $[\alpha]^{22}D$ +21.3° (2% solution in $CHCl_3$).

Anal. Calcd. for $C_{23}H_{30}O_6$: C, 71.48; H, 7.82. Found: C, 71.31; H, 7.92.

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(4) All chromatographic separations were carried out on activated aluminum oxide (Harshaw Chemical Company, 80–200 mesh).

(5) All melting points are corrected.

(6) Analyses for methyl 9-oxodehydroabietate were carried out by the ultraviolet spectrophotometric method.

(7) M. T. Bush and P. N. Densen, *Anal. Chem.*, **20**, 121 (1948).

(8) L. F. McBurney, *Ind. Eng. Chem.*, **41**, 1251 (1949).

(9) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

On heating the crystals above the melting point, acetic acid was evolved. The ultraviolet absorption spectrum corresponded exactly with that of methyl 9-oxodehydroabietate.

1,4a-Dimethyl-1-carbomethoxy-7-isopropenyl-9-oxo-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VII).—A sample of the non-crystalline keto alcohol described above (2.3 g.) was heated under reflux for 6 hours with 50 ml. of acetyl chloride. The acetyl chloride was removed under reduced pressure and the residue treated at reflux temperature with 50 ml. of collidine for 17 hours. The dark, tarry product (2.2 g.) was dissolved in 25 ml. of benzene and adsorbed on an alumina column 2.2 cm. in diameter and 60 cm. high. The column was eluted with five one-liter portions of benzene to obtain five fractions of product. Fractions 4 and 5 (0.82 g.) were crystallized to constant melting point (83–84°), $[\alpha]^{22}D$ +25.0° (2% solution in $CHCl_3$) from methanol.

Anal. Calcd. for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.56; H, 8.07.

The ultraviolet absorption spectrum of the compound is characterized by maxima at 240 mμ (α, 93), and 316 mμ (α, 4.7) and an inflection point at 258 mμ (α, 50). A sample of the compound (0.50 g.) was saponified by boiling in 15 ml. of diethylene glycol containing 0.30 g. of potassium hydroxide for 1.5 hours. The free acid (0.45 g.) was recovered and crystallized from benzene–petroleum ether to a constant melting point of 214–216°.

Anal. Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; neut. equiv., 312. Found: C, 76.67; H, 7.80; neut. equiv., 314.

A sample (1.0 g.) of the compound described above was dissolved in 50 ml. of ethyl chloride and a 4% stream of ozone (22 liters/hour) passed through the solution at −60 to −79°. The ozonization was continued for 30 min. before purging the blue solution with oxygen for a similar period of time. The solution was transferred to a flask connected with a series of traps containing an aqueous solution of 2,4-dinitrophenylhydrazine hydrochloride. A slow stream of nitrogen was passed through the solution until the ethyl chloride had been removed. After removing the ethyl chloride, 100 ml. of 25% acetic acid and 0.3 g. of zinc dust were added. The mixture was heated under gentle reflux as nitrogen was passed through the system. After 2 hours the yellow precipitate was recovered from the traps, dried and found to weigh 0.08 g. (m.p. 155°). Recrystallization from ethanol raised the melting point to 163°. The melting point was not depressed by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of formaldehyde. The non-volatile material from the ozonolysis (0.70 g.) was recovered and crystallized to constant melting point (142–143°) from methanol. The melting point was not depressed by admixture with a sample of the previously prepared 1,4a-dimethyl-1-carbomethoxy-7-acetyl-9-oxo-1,2,3,-4,4a,9,10,10a-octahydrophenanthrene.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

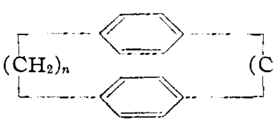
Macro Rings. III. Synthesis and Properties of *p,p'*-Tetramethylene-1,4-diphenylbutane[1]

BY DONALD J. CRAM AND NORMAN L. ALLINGER

RECEIVED AUGUST 20, 1953

The compound in which two benzene rings are joined in the para positions by two four-carbon methylene bridges has been prepared. The method employed is believed to be of general application to the preparation of paracyclophanes, and involves hydrogenation of the benzene rings prior to an acyloin ring closure followed by dehydrogenation at a later stage. The stereochemical structure of the fully hydrogenated paracyclophane is established.

The previous papers of this series[2] reported the preparation of the paracyclophanes (I) in which $n = m = 2$, $n = 2$ and $m = 3$, $n = 2$ and $m = 4$, $n = 3$ and $m = 6$, and $n = 5$ and $m = 6$. Attempts to prepare I in which $n = 1$ and $m = 2$ resulted in a ring twice as large in which four benzene rings were incorporated.[2b] The spectral properties of the paracyclophanes show a gradual progression from normal (compared to open chain models, II) for I in which n and m are large (*e.g.*, $n = 5$, $m = 6$) to abnormal in which n and m are small (*e.g.*, $n = m = 2$). These abnormalities have been attributed to two effects, the distortion of the benzene rings from planarity,[3] and to a trans-annular electronic effect of one benzene on another.[4] The ultraviolet absorption spectrum of I ($n = 3$ and $m = 6$) is slightly abnormal while that of I ($n = 5$ and $m = 6$) is completely normal. Molecular models indicate that I with $n = m = 4$ possesses a geometry which allows the two phenyl groups to be completely planar, but which restricts their rotation with respect to one another. The synthesis of this compound was undertaken for two reasons: to determine the smallest ring size for the paracyclophanes compatible with a normal spectrum; and to develop a synthetic route for those substances (I, $n = m = 3$, $n = m = 4$, $n = m = 5$) whose ring size and symmetry properties were the most amenable to aromatic substitution and restricted rotation studies.



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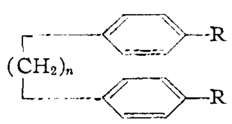

II

The paracyclophanes previously prepared were obtained by either of two procedures.[5] Dibro-

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(1) Research supported in part by the Office of Naval Research.

(2) (a) D. J. Cram and H. Steinberg, THIS JOURNAL, **73**, 5691 (1951); (b) H. Steinberg and D. J. Cram, *ibid.*, **74**, 5388 (1952).

(3) C. J. Brown and A. C. Farthing [*Nature*, **164**, 915 (1949)] have demonstrated by X-ray diffraction analysis of the crystal structure of I with $n = m = 2$ that the 1,4-carbons of each benzene ring are distorted about 11° out of the plane of the other four carbons.

(4) Elsewhere we have used the term interstitial electronic effects (ref. 2a). The general term "trans-annular" has been used to describe the general phenomena of cross-ring reactions. [For rearrangements, see A. C. Cope, S. W. Fenton and C. F. Spencer, THIS JOURNAL, **74**, 5884 (1952); A. C. Cope, A. C. Haven, F. L. Ramp and E. R. Trumbull, *ibid.*, 4867 (1952); V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952); V. Prelog, K. Schenker and W. Kung, **36**, 471 (1953); G. Fodor and K. Nador, *J. Chem. Soc.*, 721 (1953). For elimination reactions see A. C. Cope and G. Holyman, THIS JOURNAL, **72**, 3062 (1950); K. Schenker and V. Prelog, *Helv. Chim. Acta*, **36**, 896 (1953)]. The term might be equally well applied to cross-ring electronic modifications of physical properties such as spectra. Examples of trans-annular electronic interactions are as follows: ref. 2; E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 607 (1949); J. C. Lunt and F. Sondheimer, *ibid.*, 3361 (1950); P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1005 (1950).

(5) Compound I ($n = m = 2$) has also been obtained in trace amount by pyrolysis of *p*-xylene (ref. 3).