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Synthesis of Substituted Tropolones

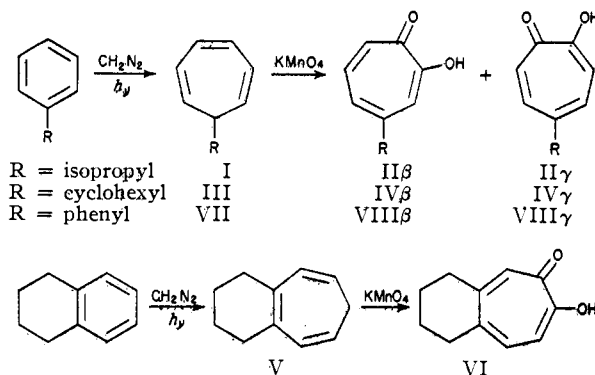
BY W. VON E. DOERING¹ AND LAWRENCE H. KNOX

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By the method of photochemically decomposing diazomethane in a substituted benzene and oxidizing the resulting tropilidene with potassium permanganate, β - and γ -isopropyl, β - and γ -cyclohexyl, 4,5-tetramethylene and β - and γ -phenyltropolone have been synthesized and have been assigned structures, in part on the basis of rearrangement to the related benzoic acids.

Of the several methods now available for the synthesis of tropolones, that developed by Nozoe, *et al.*,² and Cook, *et al.*,³ in which a cycloheptandione-1,2 is dehydrogenated with bromine or *N*-bromosuccinimide (in some cases accompanied by bromination and necessitating subsequent debromination), has been applied to the synthesis of tropolone,^{2a,3a} β -isopropyltropolone,^{2b,d,3b} α -isopropyltropolone^{2c,3b} (both workers obtaining 2-isopropylcycloheptanone by ring enlargement with diazoisobutane), γ -isopropyltropolone,^{3b,2d} β -methyltropolone,^{2e} β -ethyltropolone,^{2e} *t*-butyltropolones of unassigned structure^{2f} and 3,4-benzotropolone.^{3c} Catalytic dehydrogenation of the appropriate diketone has led to the synthesis of 3,4-benzotropolone,^{3c} 1',2',3'-trimethoxy-3,4-benzotropolone⁴ and 2',3'-dimethoxy-3,4-benzotropolone.⁵ The synthesis of tropolone has also been accomplished by the brominative dehydrogenation of cycloheptanone to 2,4,7-tribromotropone which is hydrolyzed and debrominated^{2g} and by the brominative dehydrogenation of 2-hydroxycycloheptanone.⁶ The general method where an *o*-dimethoxybenzene is treated with ethyldiazoacetate⁷ has resulted in syntheses of stiptic acid^{7a} and a tropolone carboxylic acid.^{7b} The syntheses of β -methyltropolone^{8a,c} and tropolone^{8b,c} by degradation of (synthetic) purpurogallin⁴ and the synthesis of 4,5-benzotropolone from phthalaldehyde and hydroxyacetone⁹ by a condensation of the Thiele type are the only examples of presumably limited methods.

Doering and Knox¹⁰ have made tropolone by the permanganate oxidation of tropilidene, the latter having been synthesized by the photochemical reaction of diazomethane and benzene. Extension of this sequence to the synthesis of substituted tropolones is limited mainly by the characteristics of the photochemical step. As a consequence of the fact that the intermediate fragment, methylene, reacts not only with a double bond or aromatic ring by addition, but with undecomposed diazomethane to form nitrogenous by-products and with many other functions including the carbon-hydrogen bond,¹¹ the irradiation is effected in high dilution with the aromatic compound itself serving as solvent for optimum results. This step is therefore convenient only with readily available starting materials. The actual materials chosen for conversion to tropolones were isopropylbenzene, starting material for the naturally occurring thujaplicins and hinokitiol, cyclohexylbenzene, tetrahydronaphthalene, as an example of a fused ring system, and biphenyl, a solid which has to be irradiated in a solvent.



The substituted tropilidenes, I, III, V and VII, have not been obtained pure by distillation in a 35-plate column, presumably because the crude products are contaminated by the difficultly separable methyl homologs. Even in the reaction with benzene, separation of toluene, formed in smaller amount (9% of the theoretical yield based on *N*-methyl-*N*-nitrosourea) and tropilidene, the major product (32%), in a pure state required fractionation in a 100-plate column.¹² The ultraviolet

(10) W. von E. Doering and L. H. Knox, *ibid.*, **72**, 2305 (1950); **73**, 828 (1951).

(11) Cf. H. Meerwein, H. Rathjen and H. Werner, *Ber.*, **75**, 1610 (1942), and W. von E. Doering and L. H. Knox, "Abstracts of Papers," 119th Meeting, American Chemical Society, Boston, Mass., April 1, 1951, p. 2M.

(12) This unpublished observation of W. von E. Doering, L. H. Knox and F. L. Detert differs from that of H. Van de Vloed, Dissertation, Marburg, Germany, 1946 (kindly sent by Dr. H. Meerwein, Marburg) who claims that the crude irradiation product contains no toluene and is a mixture of norcaradiene and cycloheptatriene.

(1) Sterling Chemistry Laboratory, Yale University, New Haven 11, Conn.

(2) (a) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**(7), 38 (1950); (b) T. Nozoe, S. Seto, K. Kikuchi, T. Mukai, S. Matsumoto and M. Murase, *ibid.*, **26**(7), 43 (1950); (c) T. Nozoe, Y. Kitahara and S. Ito, *ibid.*, **26**(7), 47 (1950); (d) T. Nozoe, S. Seto, K. Kikuchi and H. Takeda, *ibid.*, **27**(3), 146 (1951); (e) T. Nozoe, T. Mukai and S. Matsumoto, *ibid.*, **27**(2), 110 (1951); (f) T. Nozoe, H. Kishi and A. Yoshikoshi, *ibid.*, **27**(3), 149 (1951); (g) T. Nozoe, Y. Kitahara, T. Ando and S. Masamune, *ibid.*, **27**(8), 415 (1951).

(3) (a) J. W. Cook, A. R. Gibb, R. A. Raphael and A. R. Somerville, *Chemistry & Industry*, 427 (1950); *J. Chem. Soc.*, 503 (1951); (b) J. W. Cook, R. A. Raphael and A. I. Scott, *ibid.*, 695 (1951); (c) J. W. Cook and A. R. Somerville, *Nature*, **163**, 410 (1949); J. W. Cook, A. R. M. Gibb, R. A. Raphael and A. R. Somerville, *J. Chem. Soc.*, 603 (1952).

(4) D. Caunt, W. D. Crow, R. D. Haworth and C. A. Vodoz, *Chemistry & Industry*, 149 (1950); *J. Chem. Soc.*, 1631 (1950).

(5) J. A. Barltrop, A. J. Johnson and G. D. Meakins, *ibid.*, 181 (1951).

(6) J. D. Knight and D. J. Cram, *THIS JOURNAL*, **73**, 4136 (1951).

(7) (a) J. Bartels-Keith, A. W. Johnson and W. I. Taylor, *Chemistry & Industry*, 337 (1951); *J. Chem. Soc.*, 2852 (1951); (b) J. R. Bartels-Keith and A. W. Johnson, *Chemistry & Industry*, 677 (1950).

(8) (a) R. D. Haworth, B. P. Moore and P. L. Pauson, *J. Chem. Soc.*, 1045 (1948); (b) R. D. Haworth and J. D. Hobson, *Chemistry & Industry*, 441 (1950); (c) R. D. Haworth and J. D. Hobson, *J. Chem. Soc.*, 561 (1951).

(9) D. S. Tarbell, G. P. Scott and A. D. Kemp, *THIS JOURNAL*, **72**, 379 (1950).

spectra of I, III and V are almost identical with that shown in Fig. 1 (curve 1) of pure tropilidene. The spectrum of impure phenyltropilidene (VII, Fig. 1, curve 2) has been considerably displaced and is similar (but not completely identical) to that of a phenyltropilidene prepared by Cope and D'Addieco from tropinone.¹³ As reported for tropilidene itself,¹⁴ the four substituted tropilidenes have been converted to crystalline maleic anhydride addition products. Although the structures of the tropilidenes are not known, one possible structure is included in the diagram for convenience' sake.

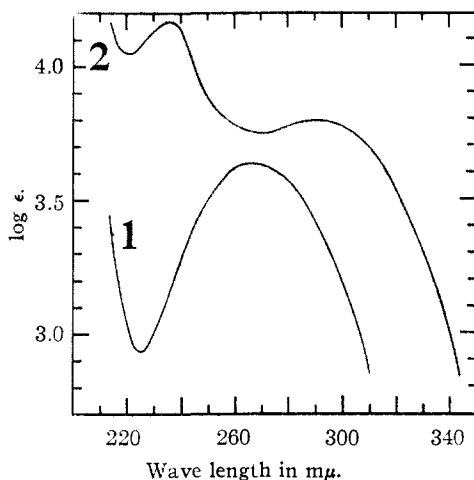


Fig. 1.—Ultraviolet spectra of tropilidene (curve 1) and phenyltropilidene (VII, curve 2).

The oxidation of the impure tropilidenes with potassium permanganate gives rise to mixtures of tropolones in about 4% of the theoretical yield, from which pure isomers can be separated in quite low over-all yield (0.1–0.6% of the theoretical based on N-methyl-N-nitrosourea).¹⁵ The pure tropolones prepared in this way are β (II β)- and γ (II γ)-isopropyl, β (IV β)- and γ (IV γ)-cyclohexyl, 4,5-tetramethylene (VI) and β (III β)- and γ (VIII γ)-phenyl. The relative positions of the substituents and oxygen atoms have been established by rearrangement to known aromatic acids. It is interesting that the method gives no isolable quantity of the α -substituted isomers.

Our samples of II β and II γ , the structures of which are firmly established,¹⁶ are identified by melting point,^{2b,16b,c} preparation of the crystalline octahydro derivative of II γ ,^{16b} ultraviolet absorption spectra,^{16b,17a} dibromo derivative^{2,b,d,18} and alkaline rearrangement of the corresponding chloro-

(13) A. C. Cope and A. A. D'Addieco, *THIS JOURNAL*, **73**, 3419 (1951).

(14) E. P. Kohler, M. Tishler, H. Potter and H. T. Thompson, *ibid.*, **61**, 1057 (1939).

(15) By way of comparison, β - and γ -isopropyltropolone, prepared by this method in 0.48 and 0.21% of theory, were obtained by Nozoe, *et al.*,^{2d} in 1.5 and 0.65% and by Cook, *et al.*,^{2b} in 0.06 and 0.61% of theory, respectively, based on 4-isopropylcyclohexanone.

(16) (a) H. Erdtmann and J. Gripenberg, *Nature*, **161**, 719 (1948); (b) *Acta Chem. Scand.*, **2**, 625 (1948); (c) A. B. Anderson and J. Gripenberg, *ibid.*, **2**, 644 (1948).

(17) (a) G. Aulin-Erdtmann, *ibid.*, **4**, 1031 (1950); (b) G. Aulin-Erdtmann and H. Theorell, *ibid.*, **4**, 1490 (1950).

(18) T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **25**(8), 19 (1950).

tropolones¹⁹ to *m*- and *p*-isopropylbenzoic acids, respectively. The infrared spectra are reported in Fig. 2 and are in the main identical with the less complete, published spectra.^{17b,20}

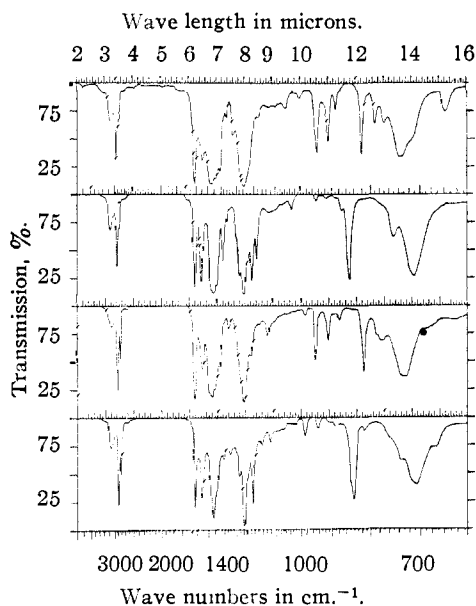


Fig. 2.—Infrared absorption spectra of β -isopropyltropolone (II β , top curve), γ -isopropyltropolone (II γ , upper middle curve), β -cyclohexyltropolone (IV β , lower middle curve) and γ -cyclohexyltropolone (IV γ , bottom curve).

The structures of IV β and IV γ are established by the methoxide-catalyzed rearrangement of their methyl ethers to *m*-cyclohexylbenzoic acid,²¹ and *p*-cyclohexylbenzoic acid,²² respectively. Both IV β and IV γ are characterized by ultraviolet (Fig. 3) and infrared (Fig. 2) absorption spectra, by *p*-nitrobenzoate derivatives and, in the case of IV γ , by a crystalline methyl ether (ultraviolet spectrum, Fig. 6).

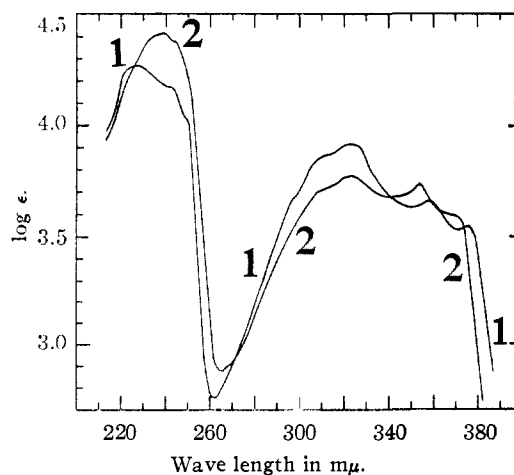


Fig. 3.—Ultraviolet spectra of β -cyclohexyltropolone (IV β , curve 2) and γ -cyclohexyltropolone (IV γ , curve 1).

(19) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **74**, 5683 (1952).

(20) G. P. Scott and D. S. Tarbell, *ibid.*, **72**, 240 (1950).

(21) C. S. Marvel, H. W. Johnson, J. W. Meier, J. W. Martin, J. Whitson and C. M. Himel, *ibid.*, **66**, 914 (1944).

(22) H. A. Mayes and E. E. Turner, *J. Chem. Soc.*, 500 (1929).

Emphasizing the generalization that permanganate oxidation of substituted tropilidenes leads to no α -isomer is the fact that only 4,5-tetramethylenetropolone (VI) is formed from tetramethylenetropolidene (V). VI is characterized by ultraviolet (Fig. 4) and infrared (Fig. 5) spectra, an octahydro derivative and a *p*-nitrobenzoate. The structure follows from the rearrangement of the corresponding methyl ether to 5,6,7,8-tetrahydro-2-naphthoic acid, previously prepared by Coulson.²³

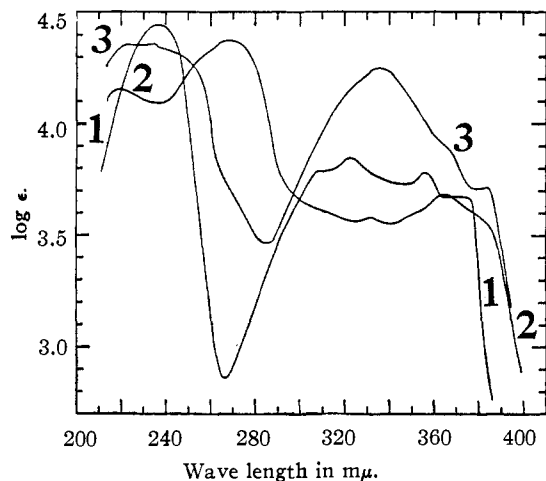


Fig. 4.—Ultraviolet spectra of 4,5-tetramethylenetropolone (VI, curve 1), β -phenyltropolone (VIII β , curve 2) and γ -phenyltropolone (VIII γ , curve 3).

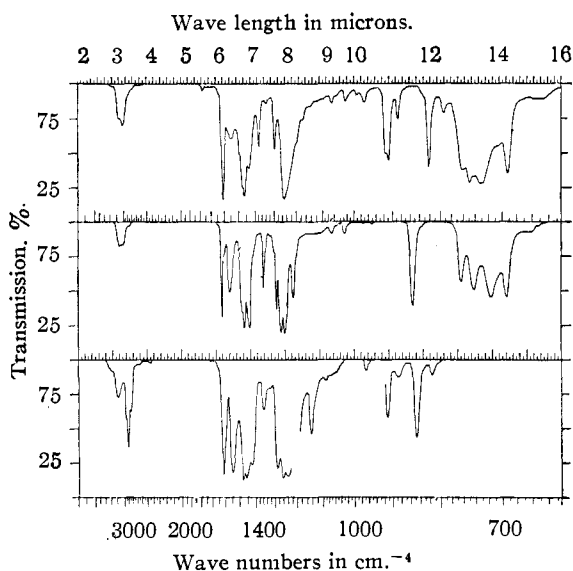


Fig. 5.—Infrared spectra of β -phenyltropolone (VIII β , top curve), γ -phenyltropolone (VIII γ , middle curve) and 4,5-tetramethylenetropolone (VI, bottom curve).

The necessity of irradiating diphenyl in the solvent, dioxane, led to a decreased yield of phenyltropolidene but was otherwise satisfactory. The two isomeric tropolones, VIII β and VIII γ , are characterized by ultraviolet (Fig. 4) and infrared (Fig. 5) spectra, by the formation of crystalline octahydro and *p*-nitrobenzoyl derivatives and, in the case of γ -phenyltropolone, by conversion to a

methyl ether (ultraviolet spectrum: Fig. 6) and 2-chloro-5-phenyltropolone. Rearrangement, effected by way of the corresponding chlorotropolones, led to diphenyl-3- and diphenyl-4-carboxylic acids, respectively.

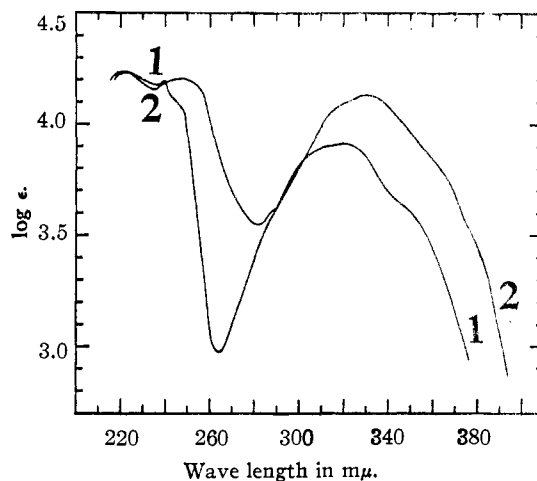


Fig. 6.—Ultraviolet spectra of γ -cyclohexyltropolone methyl ether (curve 1) and γ -phenyltropolone methyl ether (curve 2).

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Experimental²⁴

General Procedure for the Preparation of Tropilidenes.—To a mixture of from 2 to 2.5 l. of the substituted benzene derivative and 210 ml. of 45% potassium hydroxide cooled to 0°, 105 g. (1 mole) of nitrosomethylurea was added in small portions with vigorous stirring as rapidly as the solid dissolved. The resulting deep yellow solution of diazomethane in the hydrocarbon was decanted, dried for 2 hr. over potassium hydroxide pellets at 0°, and irradiated in a round-bottom, Pyrex flask clamped in an inclined position to permit cooling with running water. Two General Electric Reflector Sunlamps were employed as the light source. Evolution of nitrogen began almost immediately and was complete in 18–42 hr. depending upon the hydrocarbon employed and the age of the lamps. The bulk of the hydrocarbon was removed from the practically colorless reaction product by distillation through a 17-plate column and treated again with diazomethane. The residues from several runs were combined and fractionated through a 4-ft. column packed with single-turn, glass helices (35 plates) to yield the respective tropilidenes in an impure state.

When freshly distilled, the tropilidenes are colorless liquids which, in contact with air, rapidly acquire a yellow color changing slowly to orange and finally deposit a viscous yellow-orange, resinous material. They may be kept indefinitely with little discoloration when sealed under nitrogen.

(24) All melting points are corrected. Analyses are by the Schwarzkopf Microanalytical Laboratory, Middle Village, Long Island, New York. The ultraviolet spectra were measured in isoctane solution in a Beckman Model DU spectrophotometer. The infrared spectra were obtained with a Baird Associates Double Beam Infrared Recording Spectrophotometer, model B, with sodium chloride optics and are composites of spectra in 10% carbon tetrachloride and 10% carbon disulfide solution with the exception of VI which was measured in 1,2-dichloroethane, cell thickness being 0.1 mm.

(23) E. A. Coulson, *J. Chem. Soc.*, 77 (1935).

Isopropyltropilidene (I).—The combined residues from the irradiation of cumene with the amount of diazomethane liberated from a total of 1 kg. (10 moles) of nitrosomethylurea was fractionally distilled to give 85.0 g. of material, b.p. 165–172° and 222.0 g. (16.5% based on nitrosomethylurea) of crude isopropyltropilidene (I), b.p. 172–175°, n_D^{25} 1.4932–1.5020, of which a fraction, b.p. 174–175°, absorbed 2.1 molar equivalents of hydrogen in ethanol solution over platinum oxide.

Anal. Calcd. for $C_{16}H_{14}$: C, 89.5; H, 10.5. Found: C, 89.6; H, 10.7.

Maleic Anhydride Adduct of I.—In general, the adducts were prepared from equimolar quantities (0.003 to 0.01 mole) of tropilidene and maleic anhydride in 5–40 ml. of dry benzene by refluxing on the steam-bath for 15–24 hr. The reaction mixture from 1.34 g. of I was concentrated to about 6 ml., diluted with hexane until barely turbid and cooled. Unreacted maleic anhydride separated as colorless needles, 0.120 g., m.p. 50–52°. From the mother liquor, diluted further with hexane and cooled to 0°, 0.406 g. (17% of theory) of the adduct was obtained, m.p. 75–80°. Two recrystallizations from benzene-hexane gave small clusters of needles, m.p. 115–116°.

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.4; H, 6.9. Found: C, 72.3; H, 6.9.

Cyclohexyltropilidene (III).—A solution of diazomethane in phenylcyclohexane, prepared at 5–10°, was irradiated and most of the excess phenylcyclohexane was distilled *in vacuo* (b.p. 125° (25 mm.)). The residues from five runs, utilizing a total of 945 g. (9 moles) of nitrosomethylurea were combined and fractionated to yield 42.3 g. of material, b.p. 121.5–125.5° at 20 mm., and 209.2 g. (13.3%) of impure cyclohexyltropilidene, b.p. 125.5–128° at 20 mm., n_D^{25} 1.5245–1.5300. A fraction, b.p. 128° at 20 mm., absorbed 2.3 molar equivalents of hydrogen in ethanol over platinum oxide.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.6; H, 10.4. Found: C, 89.5; H, 10.1.

Maleic Anhydride Adduct of III.—The reaction mixture from 1.0 g. of III was concentrated to 2 ml. and diluted with 6 ml. of pentane. The brown oil which partially crystallized on standing overnight was centrifuged to give 0.314 g. of discolored needles, which were dissolved in a minimum of hot benzene and diluted with warm heptane until barely turbid and permitted to crystallize until minute clusters of needles began to contaminate the long, slender, colorless needles. Centrifuging at this point gave 0.111 g. of unchanged maleic anhydride, m.p. 50–52°, and a mother liquor from which 0.177 g. (11.3%) of the adduct was obtained on further standing as minute, colorless needles, m.p. 191–196°, raised to 201–202° after two recrystallizations from benzene-heptane.

Anal. Calcd. for $C_{17}H_{20}O_3$: C, 75.0; H, 7.4. Found: C, 75.0; H, 7.4.

1,2-Tetramethylenetropilidene (V).—Fractionation of the mixture obtained by irradiating a solution of diazomethane (liberated from a total of 420 g. (4 moles) of nitrosomethylurea) in Tetralin²⁶ gave recovered Tetralin, b.p. 99.5–101.5° at 30 mm., 14.3 g. of material, b.p. 100–105° at 27 mm., and 117 g. (20.0%) of impure V, b.p. 105–108° at 27 mm., n_D^{25} 1.5525–1.5458. A fraction, b.p. 106–108° at 27 mm., absorbed 2.5 molar equivalents of hydrogen.

Anal. Calcd. for $C_{11}H_{12}$: C, 90.4; H, 9.6. Found: C, 90.1; H, 9.3.

Maleic Anhydride Adduct of V.—The reaction mixture from 0.54 g. of V on cooling and diluting with hexane, deposited a small amount of unreacted maleic anhydride. On further dilution with hexane and cooling to 0°, the adduct slowly crystallized; 0.110 g. (11%), m.p. 82–90° which was raised to 124–125° after two recrystallizations from benzene-hexane.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.7; H, 6.6. Found: C, 73.8, 73.4; H, 7.0, 6.5.

Phenyltropilidene (VII).—Two batches of diazomethane, each prepared at 10–15° from 942 g. of biphenyl dissolved in 1500 ml. of dioxane and 105 g. of nitrosomethylurea, were

united, dried over potassium hydroxide at 10–15° and irradiated until nitrogen ceased to be evolved.

The bulk of the biphenyl was removed by crystallization and progressive concentration of the filtrates on the steam-bath under reduced pressure. The batches of crystallized biphenyl were washed with cold hexane; the combined hexane washings were then concentrated and cooled. In this manner, the reaction mixtures from five irradiations representing a total consumption of 1050 g. (10 moles) of nitrosomethylurea were reduced to a volume of ca. 400 ml. Distillation at 15 mm. afforded a forerun, 12.5 g., b.p. 64–110° and some material consisting mainly of biphenyl, b.p. 110–130°, and the following fractions: (1) b.p. 130–134°; (2) b.p. 134–137°; (3) b.p. 137–140°. Fractions 1 and 2, cooled to –20°, deposited biphenyl which was removed by centrifugation at –20°. Redistillation of the filtrates and fraction 3 gave 148.8 g. (8.9%) of impure phenyltropilidene, b.p. 114–116° at 6 mm., n_D^{25} 1.6164–1.6213. A middle cut, b.p. 116° at 6 mm., n_D^{25} 1.6202, absorbed 3 molar equivalents of hydrogen in ethanol over platinum oxide. A phenyltropilidene, b.p. 100–103° at 1.8–1.9 mm., n_D^{25} 1.6202, has been obtained by Cope and D'Addicco¹³ from 2-phenyl- α -methyltropidene methoxide.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.8; H, 7.2. Found: C, 92.6; H, 7.2.

Maleic Anhydride Adduct of VII.—The reaction mixture from 0.5 g. of VII was diluted with pentane to faint turbidity and cooled to 0°. The adduct, 0.173 g. (22%) slowly crystallized as colorless prisms, m.p. 128–129°, which were recrystallized from benzene-pentane, m.p. 131–132°.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 76.5; H, 5.3.

General Procedure for the Oxidation of Tropilidenes.—Permanganate oxidations of the tropilidenes were carried out essentially as described for tropilidene itself.¹⁰ A solution of the hydrocarbon (0.1 mole) in 1400 ml. of 95% ethanol and 60 ml. of 45% aqueous potassium hydroxide was cooled to –10° and treated with 31.2 g. (6 molar equivalents) of potassium permanganate in 1400 ml. of water over a period of 2–2.5 hr. maintaining the temperature at –5°. The precipitated manganese dioxide was filtered and washed with hot water (1 l.). The washings were added to the filtrate from which ethanol had been removed by distillation on the steam-bath under reduced pressure, and neutral material was extracted with chloroform. The tropolones were liberated by acidification with 6 *N* sulfuric acid, extracted with chloroform, and converted to their copper salts with saturated aqueous cupric acetate. The chloroform solutions of the copper salts, obtained by repeated extractions with warm chloroform, were concentrated and worked as described below for the isolation of the respective tropolones.

β -Isopropyltropolone (II β). (a) **Preparation.**—The chloroform solution of the copper salt obtained from the oxidation of 13.4 g. of I concentrated to about 5 ml. and cooled, deposited 1.22 g. of copper salt, m.p. 74–78°, which was recrystallized from chloroform to give 0.760 g. of the green copper salt of II β , m.p. 92–94°. From the mother liquor, an additional 0.229 g., m.p. 89–91°, was obtained. The mother liquors were combined and treated as described below to isolate the γ -isomer.

The recrystallized copper salt (0.760 g.), from which chloroform of crystallization can be completely removed only after long drying in air or *in vacuo*, was treated in chloroform solution with gaseous hydrogen sulfide as described for the isolation of tropolone from its copper salt¹⁰ to yield 0.372 g. of discolored crystals from isohexane. Sublimation at 60–70° and 4 mm. gave colorless II β , 0.362 g., m.p. 50–51°, which was recrystallized from isohexane as prisms, m.p. 51–52° (reported^{2b, 16b, c} m.p. 52–52.5°). From the lower melting copper salt (0.229 g.), 0.119 g. of a colorless sublimate was similarly obtained, m.p. 43–45°. This, combined with the second crops from both isohexane mother liquors, was sublimed and recrystallized to give an additional 0.116 g., m.p. 50–51°, raising the yield to 0.478 g. (2.9%).

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.1; H, 7.4. Found: C, 73.4; H, 7.5.

The ultraviolet absorption spectrum of β -isopropyltropolone in iso-octane solution follows: max. 236 $m\mu$ ($\log \epsilon$ 4.37); min. 268 (2.92); max. 322 (3.72); min. 343 (3.62); max. 353 (3.66); inflection 360 (3.53).

(26) The Tetralin employed was distilled to remove the naphthalene impurity, which otherwise rendered fractionation of the irradiation product troublesome due to crystallization in the still-head.

(b) **II β *p*-Nitrobenzoate.**—In the general procedure, the tropolone (0.028–0.041 g.) was heated on the steam-bath for 2–3 min. with 1.1 molar equivalents of *p*-nitrobenzoyl chloride in 0.15–0.30 ml. of pyridine. In all cases but one the crude product was isolated by diluting with 2 ml. of water, centrifuging, washing with 2 *N* aqueous sodium carbonate and water, drying and crystallizing from absolute ethanol. The ester from II β was obtained in 70% yield, m.p. 117–118° after one crystallization; m.p. 119° after two more.

Anal. Calcd. for C₁₇H₁₅NO₃: C, 65.2; H, 4.8; N, 4.5. Found: C, 65.5; H, 5.1; N, 4.5.

(c) **Bromination.**—II β , 0.041 g., was dissolved in 8 ml. of water with the aid of a little ethanol (1 ml.) and treated with 1.2 ml. of an aqueous solution of bromine (3 molar equivalents) and potassium bromide containing 0.107 g. of bromine per ml. The bromination product separated as an oil which was recovered by ether extraction, and which crystallized after standing several days with occasional scratching. Recrystallization from ethanol gave 0.024 g. (29%) of α,α' -dibromo- β -isopropyltropolone as pale yellow needles, m.p. 122–128°, m.p. 132–133° after two recrystallizations from ethanol. The reported m.p. is 134°. ^{2b,18}

Anal. Calcd. for C₁₆H₁₀Br₂O₂: C, 37.3; H, 3.1; Br, 49.6. Found: C, 37.1; H, 3.5; Br, 49.4.

(d) **Rearrangement.**—A mixture of 0.328 g. of II β , 8 ml. of dry benzene and 0.3 ml. of thionyl chloride was refluxed on the steam-bath until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride (2 hr.). Removal of solvent and excess thionyl chloride on the steam-bath, followed by two evaporative distillations of the residual oil at 95–100° at 2 mm., gave 0.202 g. (50%) of 2-chloro-4(or 6)-isopropyltropolone as a light yellow oil.

Anal. Calcd. for C₁₀H₁₁ClO: C, 65.8; H, 6.1; Cl, 19.4. Found: C, 65.7; H, 5.9; Cl, 19.1.

A crude sample of the material (from 0.164 g. of II β) was rearranged and worked as described above. Evaporative distillation gave 0.063 g. (38%) of β -isopropylbenzoic acid as a light yellow oil which was dissolved in 1 ml. of 2 *N* sodium carbonate solution, diluted with 5 ml. of water, and oxidized on the steam-bath with 0.288 g. of potassium permanganate added in portions over a period of about an hour. Concentration of the filtered reaction mixture to 3 ml., acidification with 6 *N* sulfuric acid, and cooling gave 0.017 g. of isophthalic acid, m.p. 335–338° after recrystallization from ethanol, undepressed in admixture with an authentic sample.

γ -Isopropyltropolone (II γ). (a) **Preparation.**—The combined mother liquors from the isolation and recrystallization of the copper salt of II β were treated in chloroform solution with hydrogen sulfide to give an oil which was triturated with boiling isohexane. Concentration of the isohexane solution to about 4 ml. and cooling gave 0.223 g. of slightly discolored needles. Sublimation at 60–70° and 4 mm. gave colorless γ -isopropyltropolone, 0.213 g. (1.3%), m.p. 78–79°, which was recrystallized from isohexane as long, colorless needles, m.p. 80–81° (reported m.p. 82°^{16a}, 80°^{16b}).

Anal. Calcd. for C₁₀H₁₃O₂: C, 73.1; H, 7.4. Found: C, 73.0; H, 7.1.

The ultraviolet absorption spectrum of γ -isopropyltropolone in isoöctane solution follows: max. 225 μ ($\log \epsilon$ 4.48); inflection 239 (4.30); min. 262 (3.89); inflection 311 (4.00); max. 323 (4.04); min. 349 (3.79); max. 358 (3.83); min. 371 (3.70); max. 375 (3.72).

(b) **Hydrogenation.**—II γ , 0.060 g. was hydrogenated in 95% ethanol over platinum oxide, 4.0 molar equivalents of hydrogen being rapidly absorbed. Filtration and concentration on the steam-bath under reduced pressure left a colorless oil which crystallized when freed of the last traces of solvent *in vacuo*. Recrystallization from hexane gave 0.037 g. (60%) of 5-isopropyl-1,2-cycloheptanediol as colorless crystals, m.p. 78–80°. Two crystallizations from hexane gave material of m.p. 85–86° (reported^{16b} m.p. 87–88°).

(c) **II γ *p*-Nitrobenzoate.**—The ester, obtained in 77% yield, melted at 134–135° after one crystallization and at 135° after two more.

Anal. Calcd. for C₁₇H₁₅NO₃: C, 65.2; H, 4.8; N, 4.5. Found: C, 65.4; H, 4.7; N, 4.3.

(d) **Bromination.**—To a solution of 0.041 g. of II γ in 0.5 ml. of absolute ethanol, 3 molar equivalents of the brom-

inating solution described above were added. The yellow precipitate which separated immediately was centrifuged after standing several hours at 4°, dried (0.074 g.) and crystallized from absolute ethanol to give α,α' -dibromo- γ -thujaplicin as long, slender yellow needles; 0.052 g. (65%), m.p. 144–145°, which was recrystallized twice more from absolute ethanol to give material, m.p. 146°. Nozoe, *et al.*,^{2b,d} report m.p. 148.5°.

Anal. Calcd. for C₁₀H₁₀Br₂O₂: C, 37.3; H, 3.1; Br, 49.6. Found: C, 37.2; H, 3.4; Br, 49.3.

(e) **Rearrangement to Cuminic Acid.**—A mixture of 0.164 g. of II γ , 5 ml. of dry benzene and 0.25 ml. of thionyl chloride, treated as described above, gave 0.073 g. (40%) of the oily 2-chloro-5-isopropyltropolone. A mixture of 0.058 g. of this material and 2 ml. of 10% alcoholic potassium hydroxide was heated under reflux on the steam-bath for 10 min. Ethanol was removed on the steam-bath under reduced pressure, leaving a residue which was dissolved in 2 ml. of water, and acidified with 6 *N* sulfuric acid. The precipitated acid was separated by chloroform extraction and sublimed at 90–100° at 2 mm. The slightly yellow sublimate was crystallized from nitromethane to give 0.009 g. (17%) of cuminic acid as colorless crystals, m.p. 114–116° undepressed in admixture with an authentic sample.

β (IV β)- and γ (IV γ)-Cyclohexyltropolone.—The chloroform solution of soluble copper salts obtained from the oxidation of 17.4 g. of cyclohexyltropolilidene (III) was concentrated to 5–6 ml. and cooled to give 0.935 g. (4%) of a mixture of β - and γ -cyclohexyltropolone copper salts as bright green crystals, m.p. 168–171°, which could not be separated by fractional crystallization from chloroform.

An oily material was obtained from the copper salt on treatment with hydrogen sulfide. Sublimation of this oil at 80–90° and 2 mm. gave 0.601 g. of colorless sublimate, m.p. 63–68° which crystallized from 3–4 ml. of isohexane. Colorless prisms of almost pure γ -cyclohexyltropolone (IV γ), 0.227 g. m.p. 95–97°, rapidly crystallized and were separated by centrifugation before the clusters of flat needles of the β -isomer began to appear. From the filtrate, after warming to effect solution of material that had crystallized during centrifugation, β -cyclohexyltropolone (IV β) slowly crystallized, 0.153 g., m.p. 85–87°. By successive concentrations and coolings an additional 0.102 g. of IV γ , m.p. 94–97°, and 0.058 g. of IV β , m.p. 85–88°, was obtained, raising the yield to 0.329 g. (1.6% based on III; 0.21% based on *N*-methyl-*N*-nitrosourea) and 0.211 g. (1%; 0.13%), respectively.

Recrystallization of the γ -isomer from isohexane raised the m.p. to 97–98°.

Anal. Calcd. for C₁₃H₁₅O₂: C, 76.4; H, 7.9. Found: C, 76.5; H, 8.0.

Recrystallization of the β -isomer from isohexane raised the m.p. to 88–89°.

Anal. Found: C, 76.7; H, 8.0.

β -Cyclohexyltropolone (IV β). (a) **Hydrogenation.**—IV β , 0.050 g., was hydrogenated in 95% ethanol over platinum oxide, four molar equivalents of hydrogen being rapidly absorbed. After the catalyst was filtered, removal of the solvent on the steam-bath under reduced pressure, followed by evaporative distillation of the residue, gave 4-cyclohexyl-1,2-cycloheptanediol as a colorless glass.

Anal. Calcd. for C₁₃H₂₄O₂: C, 73.5; H, 11.4. Found: C, 73.4; H, 11.5.

(b) **IV β *p*-Nitrobenzoate.**—Obtained in 56% yield, this ester melted at 136–137° after one crystallization, and 139–140° after two.

Anal. Calcd. for C₂₀H₁₉NO₃: C, 68.0; H, 5.4; N, 4.0. Found: C, 68.0; H, 5.6; N, 3.9.

(c) **Rearrangement.**—An ether solution of 0.090 g. of IV β containing a few drops of methanol was treated with excess ethereal diazomethane to give the oily methyl ether. Dried *in vacuo* over calcium chloride, this ether was heated for 12 hr. in a sealed tube at 120° with 6 ml. of absolute methanol containing sodium methoxide prepared from 0.10 g. of sodium. The reaction mixture was concentrated on the steam-bath under reduced pressure to a residue consisting of oil and salts which was heated for 2 hr. on the steam-bath with 2 ml. of 6 *N* sodium hydroxide. Acidification with 6 *N* sulfuric acid and chloroform extraction yielded a solid residue which was recrystallized from cyclohexane to

yield 0.029 g. (32%) of *m*-cyclohexylbenzoic acid; m.p. 119–121°, m.p. 123–123.5° after a second crystallization from cyclohexane; reported²¹ m.p. 120–121°.

Anal. Calcd. for C₁₁H₁₆O₂: C, 76.4; H, 7.9. Found: C, 76.7; H, 8.0.

γ -Cyclohexyltropolone (IV γ). (a) **Hydrogenation.**—IV γ , 0.030 g., hydrogenated as described above, similarly absorbed four molar equivalents of hydrogen. Filtration of the catalyst followed by removal of the solvent on the steam-bath under reduced pressure, gave a colorless residue which crystallized. Recrystallization from cyclohexane gave 0.013 g. (42%) of 5-cyclohexyl-1,2-cycloheptanediol as colorless crystals, m.p. 123–125°, raised to 125° by a second recrystallization from cyclohexane.

Anal. Calcd. for C₁₃H₂₄O₂: C, 73.5; H, 11.4. Found: C, 73.3; H, 11.2.

(b) **IV γ *p*-Nitrobenzoate.**—This ester crystallized in 66% yield as clusters of needles; m.p. 157–158°, m.p. 160–161° upon recrystallization.

Anal. Calcd. for C₂₀H₁₉NO₃: C, 68.0; H, 5.4; N, 4.0. Found: C, 68.2; H, 5.1; N, 4.2.

(c) **γ -Cyclohexyltropolone Methyl Ether.**—A solution of 0.153 g. of IV γ in 2 ml. of absolute methanol was treated with an ethereal solution of diazomethane until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride. Evaporation of the solvent and crystallization of the solid residue from cyclohexane gave 0.144 g. (88%) of the methyl ether as colorless needles; m.p. 141–143°, m.p. 142–143° after a second recrystallization from cyclohexane.

Anal. Calcd. for C₁₄H₁₈O₂: C, 77.0; H, 8.3; OCH₃, 14.2. Found: C, 77.0; H, 8.4; OCH₃, 14.3.

(d) **Rearrangement of IV γ Methyl Ether with Methoxide Ion.**—IV γ methyl ether, obtained from 0.070 g. of IV γ and ethereal diazomethane, was dissolved in 4 ml. of absolute methanol containing 0.05 g. of sodium methoxide and heated for 12 hr. at 120° in a sealed tube. Treated as in the β -case above, there was obtained *p*-cyclohexylbenzoic acid; 0.039 g. (56%); m.p. 183–188° after one crystallization from isohexane and m.p. 197–198° after two more crystallizations; reported²² m.p. 199°.

Anal. Calcd. for C₁₂H₁₆O₂: C, 76.4; H, 7.9. Found: C, 76.2; H, 7.7.

4,5-Tetramethylenetropolone (VI). (a) **Preparation.**—The chloroform solution of the copper salts obtained from the oxidation of 14.6 g. of V gave, after concentration to about 6 ml., a nicely crystalline, green copper salt which became amorphous on drying in air by losing chloroform of crystallization; 0.790 g., m.p. 287–288°. Concentration of the mother liquor and cooling gave an additional 0.063 g., raising the yield to 0.853 g. (4.1%).

Treatment of the copper salt in chloroform solution with gaseous hydrogen sulfide afforded material which was crystallized from 95% ethanol to yield 0.506 g. of 4,5-tetramethylenetropolone as faintly yellow needles, m.p. 129–130°. Concentration of the mother liquor and cooling gave an additional 0.134 g., raising the yield to 0.640 g. (3.1% based on V; 0.62% based on N-methyl-N-nitrosourea). Sublimation at 100–110° at 4 mm., followed by crystallization from ethanol, gave a colorless product, m.p. 130°.

Anal. Calcd. for C₁₁H₁₂O₂: C, 75.0; H, 6.9. Found: C, 74.7; H, 7.0.

(b) **Hydrogenation.**—VI, 0.088 g., absorbed four molar equivalents of hydrogen in 95% ethanol over platinum oxide. The glycol was isolated in the manner already described as a colorless, viscous oil which partially crystallized. Recrystallization from isohexane gave 0.040 g. (43%) of 4,5-tetramethylene-1,2-cycloheptanediol as colorless rosettes, m.p. 67–71°, and m.p. 74–75° after three recrystallizations from isohexane.

Anal. Calcd. for C₁₁H₂₀O₂: C, 71.7; H, 10.9. Found: C, 71.8; H, 10.7.

(c) **VI *p*-Nitrobenzoate.**—This ester was obtained in 75% yield as orange-yellow octahedral crystals after one crystallization, m.p. 147–149°; m.p. 149–150.5° after two.

Anal. Calcd. for C₁₈H₁₈NO₃: C, 66.5; H, 4.7; N, 4.3. Found: C, 66.4; H, 4.9; N, 4.3.

(d) **Rearrangement.**—VI, 0.106 g., was treated with ethereal diazomethane to give the methyl ether as a viscous

oil which crystallized on standing overnight at 4°. Recrystallization from cyclohexane gave 0.072 g. (63%) of a mixture of the isomeric tetramethylenetropolone methyl ethers, as colorless, dendritic crystals, m.p. 59–65°, unimproved by further recrystallization from cyclohexane or a benzene-hexane mixture.

Anal. Calcd. for C₁₂H₁₄O₂: C, 75.8; H, 7.4; OCH₃, 16.8. Found: C, 75.9; H, 7.4; OCH₃, 16.8.

The mixture of ethers (0.057 g.) was heated for 7 hr. in a sealed tube with 5 ml. of absolute methanol containing 0.19 g. of sodium methoxide. The dark brown reaction mixture was concentrated on the steam-bath under reduced pressure to a dark residue which was heated on the steam-bath for 1.5 hr. with 2 ml. of 6 *N* sodium hydroxide. The dark, tarry product obtained by acidification and extraction with chloroform was sublimed at 130–140° and 2 mm. to give 0.018 g. of a light yellow sublimate. Crystallization from benzene gave 0.013 g. of 5,6,7,8-tetrahydro-2-naphthoic acid as clusters of colorless needles, m.p. 147–150°. Several recrystallizations from benzene raised the m.p. to 153–154°. The m.p. reported for the acid is 154°.²³

Anal. Calcd. for C₁₁H₁₂O₂: C, 75.0; H, 6.9. Found: C, 74.9; H, 7.2.

The derivative, 5,6,7,8-tetrahydronaphthalene-2-carboxamide was prepared according to v. Braun, *et al.*,²⁸ who report m.p. 137–138°, and had m.p. 136–138°.

Preparation of β (VIII β)- and γ (VIII γ)-Phenyltropolone.—The chloroform extract of the acidified aqueous solution obtained in the oxidation of 16.8 g. of VII was concentrated by distillation on the steam-bath. The residual, red oil was dissolved in 250 ml. of ether, extracted twice with 20-ml. portions of 10% aqueous sodium hydroxide giving insoluble sodium salts which were filtered and washed with cold water. A suspension of the yellow sodium salt in 200 ml. of water was acidified with 6 *N* sulfuric acid, liberating the free tropolones which were extracted with chloroform, and converted to the copper salts with aqueous cupric acetate as already described. Concentration of the chloroform solution of the copper salts to 12–15 ml. and cooling gave 0.323 g. (1.4%) of the sparingly soluble, microcrystalline, green copper salt of VIII γ , m.p. 342–345° with dec. The mother liquor was treated as described below for the isolation of the β -isomer.

The solid residue obtained from the copper salt in 25 ml. of chloroform with hydrogen sulfide was sublimed at 100° and 4 mm. to give a slightly yellow crystalline sublimate, 0.236 g., m.p. 113–117°. Recrystallization from 95% ethanol gave 0.204 g. (1.0%; 0.09%) of γ -phenyltropolone (VIII γ) as practically colorless needles, m.p. 124–125°, raised to 125–126° by a second recrystallization from ethanol.

Anal. Calcd. for C₁₃H₁₀O₂: C, 78.8; H, 5.1. Found: C, 79.0; H, 5.0.

The mother liquors from the isolation of the copper salt of γ -phenyltropolone were diluted with a little chloroform and treated with hydrogen sulfide. The dark residue on sublimation at 100° and 4 mm. gave a light yellow sublimate, 0.495 g., m.p. 71–79°. Crystallization from 95% ethanol gave 0.398 g. (2%; 0.18%) of β -phenyltropolone (VIII β) as faintly yellow, long needles, m.p. 92–94°. Resublimation at 80–90° and 4 mm. followed by recrystallization from ethanol gave a colorless product, m.p. 97°.

Anal. Calcd. for C₁₃H₁₀O₂: C, 78.8; H, 5.1. Found: C, 79.0; H, 5.2.

β -Phenyltropolone (VIII β). (a) **Hydrogenation.**—VIII β , 0.050 g., was hydrogenated in 95% ethanol over platinum oxide, four molar equivalents of hydrogen being rapidly absorbed. After filtration of the catalyst and removal of the solvent on the steam-bath under reduced pressure, a colorless, viscous residue was obtained that partially crystallized on standing *in vacuo* over calcium chloride with occasional scratching. Two recrystallizations from cyclohexane gave 0.016 g. (31%) of 4-phenyl-1,2-cycloheptanediol as colorless needles; m.p. 93–97°, m.p. 107–109° after recrystallization from dry benzene.

Anal. Calcd. for C₁₃H₁₈O₂: C, 75.7; H, 8.8. Found: C, 75.8; H, 8.8.

(b) **VIII β *p*-Nitrobenzoate.**—The chloroform extract of the crude oily ester which precipitated on addition of water

(26) J. v. Braun, G. Kirschbaum and H. Schumann, *Ber.*, **53**, 1155 (1920).

was washed with 2 *N* aqueous sodium carbonate and with water and was concentrated to a residue which crystallized from 95% ethanol to give the ester in 32% yield, m.p. 141–143°, m.p. 144–145° after a second crystallization.

Anal. Calcd. for $C_{20}H_{12}NO_2$: C, 69.2; H, 3.8; N, 4.0. Found: C, 69.4; H, 3.9; N, 4.0.

(c) **Rearrangement.**—A mixture of 0.079 g. of VIII β , 2 ml. of dry benzene, and 0.10 ml. of thionyl chloride was heated on the steam-bath under reflux until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride (25 min.). Removal of solvent and excess thionyl chloride on the steam-bath under reduced pressure afforded 2-chloro-4-phenyltropone as an oil which was rearranged by refluxing with 2 ml. of 10% alcoholic potassium hydroxide for 10 min. on the steam-bath. Removal of ethanol under reduced pressure left material which was dissolved in 2 ml. of water and acidified with 6 *N* sulfuric acid. The filtered precipitate was crystallized from benzene to give 0.060 g. (77% of theory based on VIII β) of diphenyl-3-carboxylic acid, m.p. 164–165°. Recrystallization from benzene raised the m.p. to 165–166°. The reported melting points are 161–162°,^{27a} and 162–164°.^{27b}

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 79.1; H, 5.2.

γ -Phenyltropone (VIII γ). (a) **Hydrogenation.**—VIII γ , 0.050 g., absorbed four molar equivalents of hydrogen when hydrogenated in 95% ethanol with platinum oxide catalyst. The residue crystallized after removal of catalyst and solvent. Recrystallization from cyclohexane gave 5-phenyl-1,2-cycloheptanediol as flat, colorless needles, 0.034 g. (67%); m.p. 93–96°, m.p. 97–98° after two additional recrystallizations from cyclohexane.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 75.7; H, 8.8. Found: C, 75.6; H, 9.0.

(b) VIII γ *p*-Nitrobenzoate.—This ester, obtained in 71%

(27) (a) F. Mayer, *Ber.*, **46**, 2579 (1913); (b) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

yield, m.p. 213–215°, was recrystallized from benzene as needles, m.p. 220–221°.

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 69.2; H, 3.8; N, 4.0. Found: C, 69.6; H, 4.1; N, 3.9.

(c) **γ -Phenyltropone Methyl Ether.**—Treatment of 0.036 g. of VIII γ with ethereal diazomethane, followed by evaporation, and crystallization of the residue from benzene, gave the ether as clusters of faintly yellow needles, 0.027 g., m.p. 140–141°. Sublimation at 100° and 4 mm., followed by recrystallization from benzene gave a practically colorless product, m.p. 141°.

Anal. Calcd. for $C_{14}H_{15}O_2$: C, 79.2; H, 5.7; OCH₃, 14.6. Found: C, 79.2; H, 5.5; OCH₃, 14.5.

(d) **2-Chloro-5-phenyltropone.**—A mixture of 0.079 g. of VIII γ , 2 ml. of dry benzene and 0.10 ml. of thionyl chloride, treated as in the case of the β -isomer above, gave 2-chloro-5-phenyltropone as a yellow solid which crystallized from ethanol in long, light yellow needles, 0.071 g. (83%), m.p. 155–157°. Sublimation at 120–130° and 4 mm., followed by recrystallization from ethanol, raised the m.p. to 158°.

Anal. Calcd. for $C_{13}H_9ClO$: C, 72.1; H, 4.2; Cl, 16.4. Found: C, 72.3; H, 4.1; Cl, 16.3.

(e) **Rearrangement of 2-Chloro-5-phenyltropone with Hydroxide Ion.**—A mixture of 0.071 g. of 2-chloro-5-phenyltropone and 2 ml. of 10% alcoholic potassium hydroxide was rearranged as described above for the β -isomer to give diphenyl-4-carboxylic acid as a yellow precipitate in a yield of 0.057 g. (97%), m.p. 200–210°. Sublimation at 110° and 2 mm., followed by recrystallization from benzene, gave colorless needles; 0.039 g., m.p. 223–224°, m.p. 224.5–226° in admixture with an authentic sample,²⁸ m.p. 225–226°.

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 78.8; H, 5.0.

(28) Kindly supplied by Professor Ernst Berliner, Bryn Mawr College, Bryn Mawr, Pa.

KATONAH, N. Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Synthesis of Phenanthrenes.

IV. 8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene

By RODERICK A. BARNES AND MARK D. KONORT¹

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8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene has been prepared by the cyclization of two isomeric tertiary alcohols. Both cyclizations were stereospecific producing one and the same stereoisomer. When the chlorine atom was replaced by hydrogen the 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene obtained was different from the isomer formed by direct cyclization of the unchlorinated tertiary alcohol.

Previous papers^{2,3} have reported the preparation of octahydrophenanthrenes having substituents in both the 5- and 8-positions. The present work was initiated in order to make available an octahydrophenanthrene with a substituent at the 8-position which might be used for building toward a steroid ring system having no functional group in ring C.

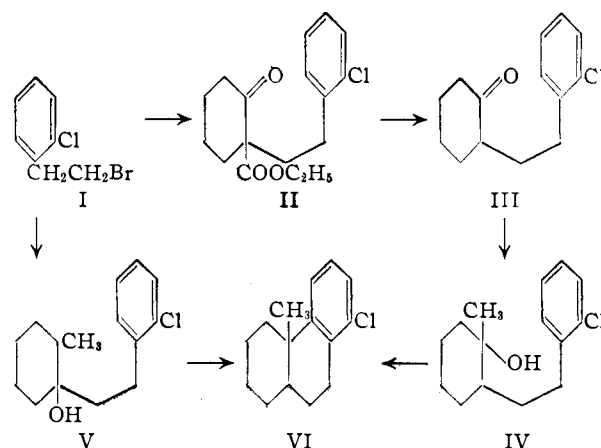
Two procedures for preparing 8-chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene were investigated.

A first attempt to prepare β -2-chlorophenylethyl bromide (I) was unsuccessful because the reaction of *o*-chlorophenylmagnesium iodide with ethylene

(1) Abstracted from a thesis submitted by M. D. Konort to the Graduate Faculty of Rutgers University for the Ph.D. degree, June, 1952.

(2) R. A. Barnes, H. P. Hirschler and B. R. Bluestein, *THIS JOURNAL*, **74**, 32 (1952).

(3) R. A. Barnes, H. P. Hirschler and B. R. Bluestein, *ibid.*, **74**, 4091 (1952).



oxide produced only 0–5% yields of the desired alcohol. The reaction of bromine with silver β -2-