THE JOURNAL OF Organic Chemistry®

VOLUME 29, NUMBER 9 SEPTEMBER 11, 1964

Chemistry of Cycloheptatriene. IV. Hydrogen Abstraction from Cycloheptatriene[1]

CHARLES M. ORLANDO, JR., AND KARL WEISS[2]

W. H. Nichols Chemical Laboratory, New York University, New York 53, New York

Received April 7, 1964

The reaction of the 2,4,6-tri-*t*-butylphenoxy radical with cycloheptatriene in benzene solution produces the corresponding phenol, ditropyl, tropone, and oxidation products derived from the phenoxy radical. The latter arise from the presence of a limited amount of oxygen. Ditropyl is considered to result from the dimerization of tropyl radicals, and tropone formation is postulated to involve a hydroperoxide or peroxide of cycloheptatriene.

The application of the simple molecular orbital method to the cycloheptatrienyl (tropyl) radical indicates its resonance energy to be comparable with that of the cycloheptatrienyl cation.[3] However, further considerations predict the radical to be unstable in the chemical sense.[4] Apart from the theoretical implications, the tropyl radical has been detected by physical methods in pyrolysis,[5] radiolysis,[6] photolysis,[7] and reductive processes.[8] The intermediacy of this radical has been postulated in several reactions of cycloheptatriene and its derivatives,[9] and the preparation of three related radicals has recently been reported.[10] Previous reactions which involve the radical have employed either heterogeneous systems or at least moderately energetic processes. We wish to report evidence for the intermediacy of the tropyl radical in a hydrogen abstraction reaction from cycloheptatriene which proceeds readily in solution at room temperature. The 2,4,6-tri-*t*-butylphenoxyradical (I) was used as the abstracting reagent.

Results

The phenoxy radical was prepared by treatment of a benzene solution of 2,4,6-tri-*t*-butylphenol with alkaline potassium ferricyanide under an atmosphere of high purity nitrogen.[11] The resulting dried blue solution was stirred with excess cycloheptatriene at room temperature. After 36 hr., the color of the solution had changed from deep blue to light green, and analysis indicated that 97% of the radical had been consumed. Chromatography on alumina of the green liquid remaining after solvent evaporation furnished seven fractions from which the products shown in Chart I were isolated. Approximately 80% of the total material isolated appeared as a mixture of two compounds in the initial fractions which were eluted with pentane. This solid proved to be mostly the phenol (IV, 82.0%)[12] admixed with the dimer, ditropyl (II, 9.5%). These components were separated by vacuum sublimation at room temperature. The bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) 1-peroxide (VIII, 6.4%) was identified by comparison with an authentic sample, which was prepared by the air oxidation of the radical. Elution with ether provided a dark oil which was identified as tropone (III) by its characteristic infrared spectrum. Three crystalline solids were obtained in small quantities: 2,6-di-*t*-butyl-1,4-benzoquinone (V, 2.9%), 4,6-di-*t*-butyl-1,2-benzoquinone (VI, 0.8%), and 2,4,6-tri-*t*-butylcyclohexa-3,5-dien-1-on-4-ol[13] (VII, 1.8%).

The products isolated account for 94% of the initially present phenoxy radicals. However, the material balance for seven-membered ring compounds is not so

---

[1] Support of this work by a Frederick Gardner Cottrell Grant from Research Corporation is gratefully acknowledged.

[2] To whom enquiries should be addressed at the Department of Chemistry, Northeastern University, Boston 15, Mass.

[3] J. D. Roberts, A. Streitwieser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

[4] *Cf.* A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 279.

[5] (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5592 (1960); (b) H. J. Dauben, Jr., Abstracts. 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963.

[6] S. Arai, S. Shida, and K. Yamaguchi, *J. Phys. Chem.*, **37**, 1885 (1962).

[7] (a) B. A. Thrush and J. J. Zwolenik, *Bull. soc. chim. Belges*, **71**, 642 (1962); (b) B. A. Thrush and J. J. Zwolenik, *Proc. Chem. Soc.*, 339 (1962).

[8] J. Dos Santos-Verga, *Mol. Phys.*, **5**, 639 (1961).

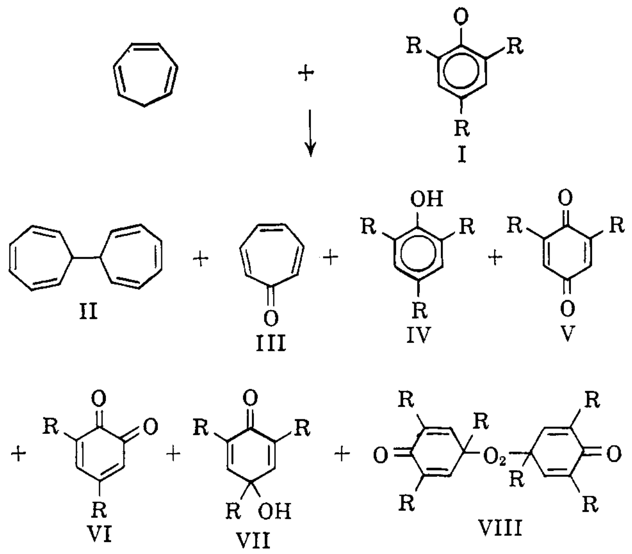
[9] (a) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **79**, 352 (1957); (b) K. Weiss and M. Lalande, *ibid.*, **82**, 3117 (1960); (c) K. Weiss and C. M. Orlando, Jr., *J. Org. Chem.*, **27**, 4714 (1962); (d) G. Juppe and A. P. Wolf, *J. Am. Chem. Soc.*, **83**, 337 (1961).

[10] (a) Heptaphenylcycloheptatrienyl radical: M. A. Batiste, *ibid.*, **84**, 3780 (1962). (b) 1-Phenyltribenzocycloheptatrienyl and 1-phenyl-2,3,6,7-dibenzocycloheptatrienyl radicals: G. Wittig, E. Hahn, and W. Tochtermann, *Chem. Ber.*, **95**, 431 (1962). However, in contrast with the planar tropyl radical (*cf.* ef. 5b), these radicals may be nonplanar owing to steric interactions.

[11] C. C. Cook and R. C. Woodworth, *J. Am. Chem. Soc.*, **75**, 6242 (1953).

[12] Yield % indicated after each product is based on the phenoxy radical.

CHART I



R = *t*-butyl

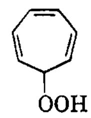
satisfactory. Thus the consumption of 74 mmoles of the phenoxy radical is accompanied by the disappearance of 32 mmoles of cycloheptatriene, as was determined by iodometric titration and gas chromatography, respectively. The isolated tropone (15.7 mmoles) and ditropyl (3.6 mmoles) account for 23 mmoles of cycloheptatriene, and for 39 mmoles of the phenoxy radical if it is assumed that the formation of each mole of these products requires 2 moles of the radical. About 9 mmoles of the phenoxy radical is incorporated in products (V, VI, VII, and VIII) derived from reactions with oxygen, which was unavoidably introduced during a transfer stage and during the work-up. Since no other compounds derived from cycloheptatriene could be isolated, it must be concluded that the missing 9 mmoles of cycloheptatriene participated in complex reactions involving several moles of radical per mole of olefin, which led to the tarry and possibly polymeric fractions which were obtained at various stages of the chromatography.

Discussion

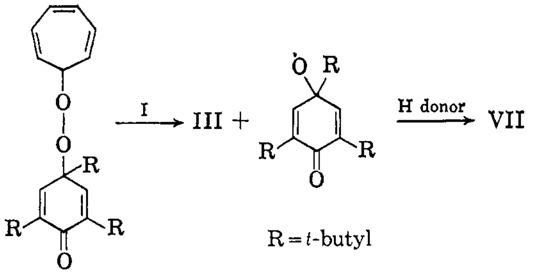
The major reaction path of radicals in the gas phase is dimerization. However, in solution radical dimerizations occur primarily with the low reactivity benzylic systems, whereas the more reactive radicals (*e.g.*, methyl and phenyl) undergo hydrogen abstraction reactions with the solvent. The difference in reactivity, and hence in mode of reaction, is generally attributed to the more extensive electron delocalization associated with benzylic radicals. As expected, the tropyl radical, which is isomeric with the benzyl radical, follows the pattern of the stabilized radicals. In several reactions which are considered to involve the seven-membered ring radical, ditropyl is a major product. These include the reduction of the tropylium ion with zinc metal[9a] and with titanium trichloride,[14] and the hydrogenolysis of seven-substituted cycloheptatrienes.[9c] Although in the gas phase the isomerization of tropyl to benzyl radicals is estimated to be exothermic by about 20 kcal./mole,[5a] no products from the latter were detected in these reactions.

The formation of ditropyl from the 2,4,6-tri-*t*-butylphenoxy radical and cycloheptatriene demonstrates that tropyl radicals can be generated in homogeneous solution under conditions where complicating surface-stabilizing effects are eliminated. This product is considered to arise by hydrogen abstraction from cycloheptatriene and subsequent dimerization. The abstraction step, which is reminiscent of the corresponding ionic reaction, *i.e.*, cycloheptatriene with trityl salts to produce triphenylmethane and tropylium salts,[15a] evidently also occurs with the triphenylmethyl radical, although no ditropyl could be isolated from this reaction.[15b] The relatively low yield of ditropyl coupled with the extensive conversion of the phenoxy radical to the phenol in the presence of excess olefin suggests that ditropyl may be a more effective hydrogen donor than cycloheptatriene.

A plausible path for the formation of tropone is *via* the cycloheptatrienyl hydroperoxide (IX), which can arise from the interaction of tropyl radicals with oxygen. Schenck has recently shown that the photosensitized addition of oxygen to cycloheptatriene produces this compound, which is unstable and readily converts to tropone.[16] Hydrogen abstraction from other oxygenated cycloheptatrienyl compounds can also account for the production of tropone. For example, the peroxide X can furnish tropone and the hydroxy compound VII (eq. 1).



IX



X

(1)

The peroxide VIII arises from the reaction of the phenoxy radical with oxygen.[11] Its thermal decomposition at 200° furnishes, among other products, the quinone V.[17] This compound has also been observed as a product in the reaction of the phenol IV with oxygen in the presence of 2,2′-azobisisobutyronitrile.[18] In this case quinone formation can reasonably be ascribed

---

(13) Compound VII was prepared by H. R. Gersmann and A. F. Bickel, *J. Chem. Soc.*, 2711 (1959). The only physical property reported was the melting point (126–130°). The material isolated from this reaction, which was assigned the structure VII, had m.p. 125.5–127.5°. Except for a strong free hydroxyl band at 2.85 μ, the infrared spectrum of this compound was almost identical with that of the peroxide VIII.

(14) C. M. Orlando, Jr., and K. Weiss, unpublished results.

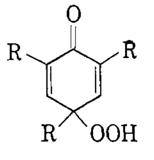
(15) (a) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957); (b) H. J. Dauben, Jr., private communication.

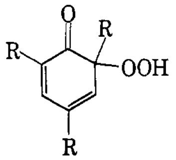
(16) G. O. Schenck, E. von Gustorf, B. Kim, G. v. Bünau, and G. Pfundt, *Angew. Chem., Intern. Ed. Engl.*, **1**, 516 (1962).

(17) C. D. Cook, R. C. Woodworth, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 4159 (1956).

(18) A. F. Bickel and E. C. Kooyman, *J. Chem. Soc.*, 3211 (1953).

to loss of isobutene and water from the intermediate hydroperoxide XI. It is clear that, under the conditions of our experiment, the peroxide VIII cannot be the precursor of quinone V. If the formation of peroxide VIII is viewed as the addition of oxygen to the phenoxy radical which is followed by reaction with another phenoxy radical, it may be assumed that hydrogen donors present in the solution can compete effectively with phenoxy radicals in the second step. The decomposition of hydroperoxides XI and XII generated in this manner can then give rise to quinones V and VI, respectively.


XI


XII

Experimental

All the solvents used were of C.P. grade. The melting points reported are corrected, and boiling points are uncorrected. Ultraviolet spectra were determined in cyclohexane with a Beckman Model DK-2 spectrophotometer, and infrared spectra were measured in KBr disks with a Baird Model 4-55 recording infrared spectrometer. Gas chromatographic analyses were carried out with a Perkin-Elmer vapor fractometer, Model 154, and an F and M Model 500 linear programmed temperature gas chromatograph. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

Purification of Cycloheptatriene.—Cycloheptatriene (500 g., 91% pure, Shell Chemical Co.) was distilled through a Heligrid-packed Podbielniak column. Fractions containing 99.8% cycloheptatriene and 0.2% toluene (analyzed by gas chromatography) amounted to 87 g. and had b.p. 115–116° at 760 mm., n^{18}_{D} 1.5254 (lit.[9a] b.p. 114° at 760 mm., n^{25}_{D} 1.5215).

2,4,6-Tri *t*-Butylphenoxy Radical.[11,19]—A solution of 2,4,6-tri-*t*-butylphenol (26.0 g., 0.099 mole) in 1.2 l. of benzene was stirred with a suspension of potassium ferricyanide (130.0 g., 0.51 mole) in 650 ml. of a 2 *N* potassium hydroxide solution for 2.5 hr. Precautions taken to exclude air from the radical solution during its preparation and during its reaction with cycloheptatriene included operating under an atmosphere of higher purity nitrogen, and deaerating the solvents before use. Titration of 10-ml. aliquots of the dark blue organic layer with standard sodium thiosulfate solution indicated a 91.9% yield of 2,4,6-tri-*t*-butylphenoxy radical. The radical solution was dried over freshly fused potassium carbonate before use.

Reaction with Cycloheptatriene.—Cycloheptatriene (8.37 g., 0.090 mole, 99.8% pure) was added under nitrogen to 1.0 l. of the phenoxy radical solution (19.76 g., 0.076 mole) and the resulting solution was stirred at room temperature for 24 hr. During this time the color changed from dark blue to light green. Comparison of the gas chromatogram of this solution with that of the initial mixture indicated that 0.032 mole of cycloheptatriene had been consumed. No further change occurred on the addition of another 1.0 g. of cycloheptatriene and stirring for an additional 12 hr. Analysis of an aliquot showed that 97% of the phenoxy radical had reacted. The solvent was evaporated, leaving a green liquid. Chromatography of this material on 625 g. of Merck acid-washed alumina afforded seven major fractions.

(1) A colorless crystalline solid was eluted with pentane, weighed 18.07 g., and had m.p. 129.5–131°. It was identified as 2,4,6-tri-*t*-butylphenol by comparison of its infrared spectrum with that of an authentic sample.

(2) A colorless crystalline solid, 0.66 g., m.p. 56–58, was obtained by vacuum sublimation of fraction 1 at room temperature. This material was identified as ditropyl (lit.[9a] m.p. 61°) by its infrared spectrum.[20]

(3) Light yellow needles, 1.35 g., m.p. 146–147°, were eluted with pentane–benzene (1:1) and proved to be bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) 1-peroxide (lit.[19] m.p. 147–148°) by infrared analysis.[21]

(4) Orange plates, eluted with pentane–benzene (1:1), weighed 0.48 g. and had m.p. 63.5–67° after vacuum sublimation. The ultraviolet spectrum of this compound has $\lambda_{\max}^{C_6H_{12}}$ 254.5 mμ (log ε 4.38) and a shoulder at 261.5 mμ (log ε 4.30).

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1; mol. wt., 220. Found: C, 76.5; H, 9.4; mol. wt., 250.

Authentic 2,6-di-*t*-butyl-1,4-benzoquinone, prepared according to the method of Yoke, *et al.*,[22] had m.p. 65–67° and ultraviolet and infrared spectra identical with those of the product.

(5) Colorless needles, which were eluted with benzene, weighed 0.37 g. and had m.p. 125.5–127.5° after recrystallization from aqueous alcohol. The infrared spectrum of this compound shows prominent maxima at 2.85, 3.40, 6.02, 6.15, 7.40, 10.00, 10.40, 11.00, and 11.35 μ. The ultraviolet spectrum has $\lambda_{\max}^{C_6H_{12}}$ 276.5 mμ (log ε 4.15) and 242.5 mμ (log ε 4.08).

Anal. Calcd. for $C_{18}H_{30}O_2$: C, 77.7; H, 10.8; mol. wt., 278. Found: C, 78.3; H, 11.0; mol. wt., 276.

(6) Crimson crystals were eluted with ether, weighed 0.14 g., and had m.p. 110.5–111.5 after vacuum sublimation and crystallization from pentane. The ultraviolet spectrum shows $\lambda_{\max}^{C_6H_{12}}$ 385 mμ (log ε 3.45). The infrared spectrum of this compound is identical with that of 3,5-di-*t*-butyl-1,2-benzoquinone.[23]

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.4; H, 9.1. Found: C, 76.3; H, 9.2.

(7) A rapidly darkening oil, also eluted with ether, weighed 1.66 g. The infrared spectrum[24] identified it as almost pure tropone.

---

[19] E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

[20] An authentic sample of ditropyl was prepared according to ref. 9a.

[21] A sample of this peroxide was prepared according to the method of ref. 19.

[22] G. R. Yoke, J. E. Dunbar, R. L. Pedrotti, F. M. Scheidt, F. G. H. Lee, and E. C. Smith, *J. Org. Chem.*, **21**, 1289 (1956).

[23] A sample of 3,5-di-*t*-butyl-1,2-benzoquinone was kindly supplied by Dr. J. J. Conradi, Shell Oil Co., Wood River, Ill.

[24] H. J. Dauben, Jr., and H. J. Ringold, *J. Am. Chem. Soc.*, **73**, 876 (1951); W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

Preparation of Steroidal 3-Haloandrosta-1,3,5-trienes and 1-Halo-4-methylestra-1,3,5(10)-trienes

G. W. MOERSCH, W. A. NEUKLIS, T. P. CULBERTSON, D. F. MORROW, AND M. E. BUTLER

Research Laboratories, Parke, Davis and Company, Ann Arbor, Michigan

Received March 3, 1964

3-Haloandrosta-1,3,5-trienes and 1-halo-4-methylestra-1,3,5(10)-trienes were prepared by the reaction of androsta-1,4-dien-3-ones with oxalyl halides. The 3-haloandrostatrienes were easily isomerized to the aromatic 1-halo-4-methylestratrienes. The mechanisms of this isomerization and of the dienone–phenol rearrangement are discussed.

The reaction of oxalyl chloride and of oxalyl bromide with 3-ketoandrosta-1,4-dienes (I) has led to the preparation of 3-haloandrosta-1,3,5-trienes (II and III). These halotrienes were found to be quite labile, being readily isomerized with acid to 1-halo-4-methylestra-1,3,5(10)-trienes (IV and V). Under suitable condi-