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The Oxidation of Hydrocarbons. Part II. The Oxidation of Cyclopentene, 3-Methylcyclohexene and Tetralin in Acetic Anhydride Solution

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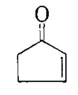
The oxygen oxidation of three hydrocarbons in acetic anhydride solution under free-radical initiation has been studied. Cyclopentene gave the acetate of 2-oxa-3-cyclohexene-1-ol; 3-methylcyclohexene gave a mixture of the acetates of 2-oxa-5-methyl-3-cyclohepten-1-ol and 1-methyl-2-oxa-3-cyclohepten-1-ol; tetralin gave the acetate of 2-oxa-3:4-benzcycloheptanol. The yield in each case was small.

In an earlier publication[2] it was shown that when cyclohexane is oxidized in acetic anhydride and in propionic anhydride there are obtained the acetate and propionate of 2-oxa-3-cycloheptene-1-ol in 25 and 22% yield, respectively.

Oxidation by oxygen and with free-radical initiation has been extended to a number of unsaturated and saturated hydrocarbons from among which we are now able to report our results on cyclopentene, 3-methylcyclohexene and tetralin. The oxidations were carried out in an ultraviolet reactor such as that described earlier.[3] The products of reaction were separated by fractional distillation under reduced pressure and were identified by reactions leading to known compounds.

Oxidation of Cyclopentene.—From this were obtained 2-cyclopentene-1-one (I) and 2-oxa-3-cyclohexenyl acetate (II). The identity of II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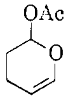
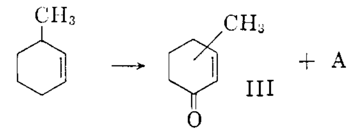


II

was established by elemental analysis and also by treatment with 2,4-dinitrophenylhydrazine, during which hydrolysis and cleavage at the 1,2-bond occurred to give the known derivative of glutaraldehyde.

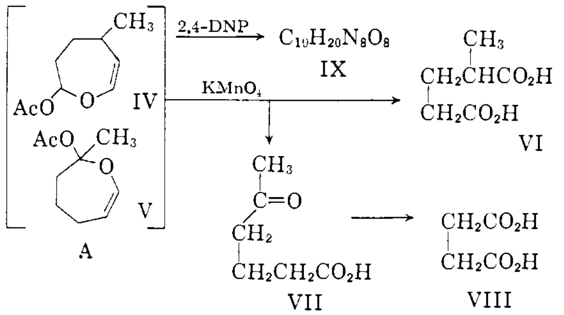
Oxidation of 3-Methylcyclohexene.—This hydrocarbon underwent much more extensive oxidation than cyclohexene under the same conditions. Products obtained were a ketone, III, (either 3-methyl- or 4-methyl-2-cyclohexene-1-one) and a mixture, A, of 2-oxa-5-methyl-3-cycloheptenyl acetate (IV) and 1-methyl-2-oxa-3-cycloheptenyl acetate (V).



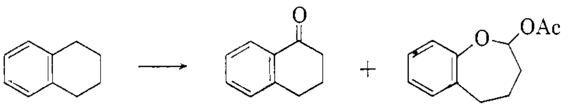
The two acetates in A were identified by elemental analysis af A and by reactions as follows.

Oxidation of A with neutral potassium permanganate gave 2-methylglutaric acid (VI), 5-ketocaproic acid (VII) and some succinic acid (VIII). The acid VI arises from the oxidation at the double bond of IV followed by further oxidation, while VII and VIII are obtained from V.

After the treatment of A with acidified 2,4-dinitrophenylhydrazine solution the derivative (IX) of a heptanedione was isolated. It is not known whether this is the derivative of 3-methyladipaldehyde (from IV) or of 6-ketoheptanal (from V); the derivatives of these are not recorded in the literature.

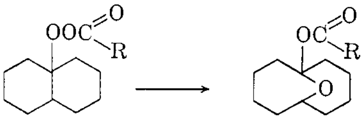


Oxidation of Tetralin.—From this there were obtained α-tetralone (X) and the nicely crystalline 2-oxa-3:4-benzocycloheptyl acetate (XI). The product XI was identified by elemental analysis



and by treatment with acidified 2,4-dinitrophenylhydrazine leading to hydrolysis of the 1,2-bond and formation of the derivative of *o*-hydroxyphenylbutyraldehyde.

It is interesting to note that Criegee[4] reports that whereas the decalyl peresters XII rearranged to the oxa compounds XIII, tetralyl perbenzoate



gave only α-tetralone. The product XI is the acetate corresponding with the benzoate which one would have expected to be formed from rearrangement of tetralyl perbenzoate.

Experimental[5]

Oxidation of Cyclopentene.—A solution of 200 g. (2.94 moles) of cyclopentene in 459 g. (4.5 moles) of acetic

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[1] Department of Chemistry, Texas Technological College, Lubbock, Tex.

[2] H. J. Shine and R. H. Snyder, THIS JOURNAL, **80**, 3064 (1958).

[3] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

[4] R. Criegee, *Ann.*, **560**, 127 (1948).

[5] Analyses by Schwarzkopf Laboratories, Woodside 77, N. Y. All melting points uncorrected.

anhydride was placed in the ultraviolet vessel.[3] Oxygen was bubbled continuously for 24 hr. through the solution at 50°. Fractional distillation under reduced pressure gave 2-oxa-3-cyclohexenyl acetate (II), 16.5 g. (4% yield), b.p. 47–49° (3 mm.), $n^{20}\text{D}$ 1.4532, d^{25}_{4} 1.107.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.04. Found: C, 59.34; H, 6.90.

The compound II has been made by other workers[6] from vinyl acetate and acrolein; the physical constants given were: b.p. 77–78° (20 mm.), $n^{20}\text{D}$ 1.4596, d^{20}_{4} 1.1178.

Treatment of II with acidified 2,4-dinitrophenylhydrazine gave the yellow derivative of glutaraldehyde, m.p. 189–90° (nitrobenzene) (literature 186–187°[7]; 192°[6]).

2-Cyclopentene-1-one was identified in the lower boiling fractions by its 2,4-dinitrophenylhydrazone, m.p. 166.5–167.5° (literature[8] 166°).

Oxidation of 3-Methylcyclohexene.—The 3-methylcyclohexene was prepared from 3-bromocyclohexene and methylmagnesium iodide.[9]

Oxidation of 192 g. (2 moles) in 408 g. (4 moles) of acetic anhydride was carried out at 55–65° for 40 hr. Fractional distillation of this yellow solution under reduced pressure gave 65 g. of products and 185 g. of undistillable residue. Further fractional distillation of the 65 g. of products gave the ketonic product III, b.p. 45–47° (2 mm.), $n^{20}\text{D}$ 1.4646, and 19.75 g. (5.8% yield) of the hemi-acetal ester mixture boiling between 58–66° (2 mm.) and having a range of $n^{20}\text{D}$ of 1.4578 to 1.4589. Of this material 6.2 g., b.p. 61–62° (2 mm.), $n^{20}\text{D}$ 1.4583, comprised the product A.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 63.72; H, 7.96.

A 2,4-dinitrophenylhydrazone, m.p. 170–172°, was obtained from III. This was the derivative of either 3-methyl- or 4-methylcyclohex-2-en-1-one.[10]

Identification of A.—Addition of acidified 2,4-dinitrophenylhydrazine solution gave an orange deposit, m.p. 175–185°. Extraction with hot ethyl alcohol left the yellow derivative IX of a heptanedione; recrystallization from nitrobenzene gave m.p. 202–203°.

Anal. Calcd. for $C_{19}H_{20}N_8O_8$: C, 46.70; H, 4.12; N, 22.95. Found: C, 46.82; H, 3.88; N, 22.71.

The ethanol extract gave two red derivatives, m.p. 105–170° and m.p. 60–70°, which could not be purified.

A portion of A, 0.9 g., was shaken overnight with 1.5 g. of potassium permanganate in 50 ml. of water. The colorless solution was filtered, acidified with hydrochloric acid and distilled to dryness under reduced pressure. The dry residue was extracted with hot ethyl acetate. The ethyl acetate was removed at reduced pressure, leaving a sirupy residue.

A portion of the sirup gave a semicarbazone. Recrystallization from hot water gave m.p. 169.5° (literature[11] 168–169°).

Anal. Calcd. for $C_7H_{13}N_3O_3$: C, 44.95; H, 6.95; N, 22.45. Found: C, 44.68; H, 7.04; N, 22.44.

The remainder of the sirup was neutralized with sodium hydroxide and boiled for 1 hr. with alcoholic *p*-bromophenacyl bromide. Fractional recrystallization of the product gave the bis-ester of succinic acid, m.p. 206–208° (melting point undepressed by authentic specimen, m.p. 208–209°), and the bis-ester of 2-methylglutaric acid, m.p. 96–99°.

Anal. Calcd. for $C_{22}H_{20}O_6Br_2$: C, 48.00; H, 3.70; Br, 29.55. Found: C, 48.07; H, 3.97; Br, 29.93.

Repeated crystallization from absolute ethyl alcohol failed to change the melting point. The bis-ester prepared from authentic 2-methylglutaric acid[12] had the same range of melting point. The melting point of a mixture of the esters was 96–99°.

Oxidation of Tetralin.—A solution of 331 g. (2.5 moles) of redistilled tetralin in 383 g. (3.75 moles) of acetic anhydride was oxidized at 50–55° for 21 hr. and then at 70–73° for 17 hr. Fractional distillation of the amber solution under reduced pressure gave 42 g. of α-tetralone, 2,4-dinitrophenylhydrazone m.p. 256–257° (literature[13] 259–260°), and 81 g. (15.7% yield) of 2-oxa-3,4-benzcycloheptyl acetate (XI) as an oily solid. Several crystallizations from aqueous ethanol gave colorless plates, m.p. 60–61°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.85. Found: C, 69.93; H, 7.17.

Treatment of XI with acidified 2,4-dinitrophenylhydrazine gave the golden yellow derivative of *o*-hydroxyphenylbutyraldehyde, m.p. 143–144° (literature[14] 149°).

WAYNE, N. J.

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[6] C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, **73**, 5270 (1951).

[7] R. H. Hall and B. K. Howe, *J. Chem. Soc.*, 2480 (1951).

[8] G. N. Chelnokova and V. V. Korshak, *Sbornik, Statei Obshchei Khim.*, **2**, 1070 (1953); *C. A.*, **49**, 5297 (1955).

[9] R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

[10] (a) The following melting points are to be found for the 3-methyl-derivative: 172.5–173°, C. S. Marvel, THIS JOURNAL, **60**, 280 (1938); 173°, A. J. Birch, *J. Chem. Soc.*, 430 (1944); 173–174°, A. J. Birch, *J. Chem. Soc.*, 593 (1946); 170–171°, M. Mousseron, *Bull. soc. chim. France*, 462 (1952); 178–179°, M. S. Newman, *J. Org. Chem.*, **17**, 577(1952); 177–178°, G. F. Woods, THIS JOURNAL, **71**, 2028 (1949); 175–177°, M. W. Cronyn, THIS JOURNAL, **75**, 1247 (1953). (b) The 4-methyl-derivative is given as 173–174°, A. J. Birch, *J. Chem. Soc.*, 593 (1946); 172–173°, M. Mousseron, *Bull. soc. chim. France*, 1246 (1954).

[11] G. T. Tatevosyan, *et al.*, *Bull. Armenian branch Acad. Sci. USSR*, **5–6**, 37 (1944); *C. A.*, **40**, 3398 (1946).

[12] Kindly supplied by Prof. C. G. Overberger.

[13] F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952).

[14] A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Concerning the Mechanism of the Reaction of Phosphorus Pentachloride with Ketones

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A mechanism for the reaction of phosphorus pentachloride with ketones is presented, the main feature of which involves the formation of a chlorocarbonium ion. The known reactions of ketones with phosphorus pentachloride are explained by the proposed mechanism.

Although phosphorus pentachloride has been used for a long time as a reagent which attacks the carbonyl group in aldehydes and ketones, there has been little discussion of possible mechanisms for these reactions. Because of an unexpected result in the reaction of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I) with phosphorus pentachloride[1] we became interested in the mechanism of reaction of phosphorus pentachloride with carbonyl-containing compounds in general and with I and the analogous 4-methyl-4-trichloromethyl-2,5-cyclohexadienone[2] (II) in particular. Much work must be done before any mechanism can be considered to be established, but the scheme below accounts so well for a number of facts that it seems worthwhile to present at this time.

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[1] M. S. Newman and L. L. Wood, Jr., *J. Org. Chem.*, **23**, 1236 (1958).

[2] K. von Auwers and W. Julicher, *Ber.*, **55**, 2167 (1922).