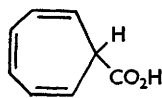


12. The Tropylium Ion. Part III.¹ Oxidation of cyclohepta-2 : 4 : 6-trienecarboxylic Acid.

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Oxidation of cyclohepta-2 : 4 : 6-trienecarboxylic acid by several agents is found to give tropylium salts. The other main product is terephthalic acid. The mechanism of these reactions is discussed.

OXIDATION of the tropylium cation by acidic permanganate to benzaldehyde, reported in Part I¹ of this series, has since been of some use for the detection of tropylium salts in dilute aqueous solutions. However, it was later found that the test is of limited applica-



(I)

tion, for cyclohepta-2 : 4 : 6-trienecarboxylic acid* (I), which is the starting material in the synthesis of the tropylium cation described in Part I, is also oxidised to benzaldehyde under these conditions. This led us to investigate further the oxidation of the acid (I), for from the above experiments the most likely mechanism for the formation of benzaldehyde seemed to involve intermediate formation of the tropylium cation.

Buchner³ first investigated the oxidation of cyclohepta-2 : 4 : 6-trienecarboxylic acid, obtaining a variety of products depending on the conditions used. Thus, oxidation with acidic permanganate gave benzaldehyde, benzoic acid, terephthalic acid, phthalic acid, and *trans*-cyclopropane-1 : 2 : 3-tricarboxylic acid, accounting together for about 10% of the starting material.

We have repeated the oxidation with acidic permanganate and, under suitable conditions, have obtained yields of up to 40% of tropylium salts, together with some of Buchner's products. Tropylium salts were isolated from the aqueous reaction mixture by conversion into ditropyl ether, which was extracted and converted by hydrogen bromide into tropylium bromide. Buchner had presumably also obtained solutions of tropylium salts but since these compound have unusual properties and were then unknown their presence could hardly have been suspected.

The other products isolated in the present instance were benzaldehyde and benzoic acid.

We have also studied the reaction of cyclohepta-2 : 4 : 6-trienecarboxylic acid with a number of other oxidising agents, with the results tabulated. These suggest that two types of oxidation take place. Benzaldehyde and benzoic acid are known to be formed on oxidation of tropylium salts, and in these cases tropylium is probably the primary product;

Oxidant	Products	Oxidant	Products
Acidic KMnO ₄	Tropylium salts, Ph·CHO, Ph·CH ₂ ·CO ₂ H	Alkaline H ₂ O ₂	α -cycloHeptatrienecarboxylic acid
Neutral KMnO ₄	Ph·CHO	Acid H ₂ O ₂	No reaction
Alkaline KMnO ₄	<i>p</i> -C ₆ H ₄ (CO ₂ H) ₂	HNO ₃	BzOH, <i>p</i> -C ₆ H ₄ (CO ₂ H) ₂
Pb(OAc) ₄	Tropylium salts	HIO ₄	Tropylium salts, BzOH, Ph·CHO, <i>p</i> -C ₆ H ₄ (CO ₂ H) ₂
Na ₂ S ₂ O ₈	Tropylium salts, <i>p</i> -C ₆ H ₄ (CO ₂ H) ₂	CrO ₃	<i>p</i> -C ₆ H ₄ (CO ₂ H) ₂
(NH ₄) ₂ Ce(NO ₃) ₆	Tropylium salts		

indeed tropylium salts have been isolated in 20—40% yield from the reactions of cyclohepta-2 : 4 : 6-trienecarboxylic acid with acidic permanganate, ceric ammonium nitrate, or lead tetra-acetate. The formation of terephthalic acid must, however, involve a different mechanism.

The formation of tropylium ions presumably involves an overall two-electron oxidation of the type outlined by Levitt.⁴ Reactions of this kind are well known in the oxidation of acids R·CO₂H when R⁺ is a stable ion, *i.e.*, R·CO₂H \longrightarrow R⁺ + CO₂H⁺ + 2e;

* In Part I¹ we referred to norcaradienecarboxylic acid; recent work² has shown that a cyclohepta-2 : 4 : 6-triene formulation (I) for this compound is more reasonable than the bicyclic structure.

¹ Parts I and II, *J.*, 1956, 2021, 2026.

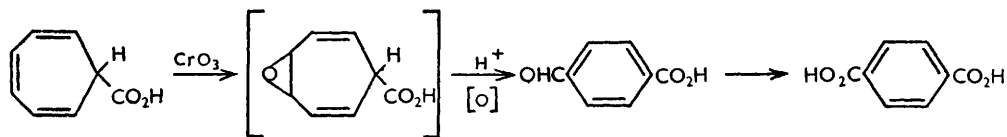
² Doering, Laber, Vorderwahl, Chamberlain, and William, *J. Amer. Chem. Soc.*, 1956, **78**, 5448.

³ Buchner, *Ber.*, 1896, **29**, 106; Braren and Buchner, *Ber.*, 1901, **34**, 995.

⁴ Levitt, *J. Org. Chem.*, 1955, **20**, 1297.

for example, α -amino-acids, $R'CH(NH_2) \cdot CO_2H$, are oxidised to aldehydes *via* the ion $R'CH:NH_2^+$, and triphenylacetic acid to triphenylmethanol *via* the ion Ph_3C^+ . The electrons may of course be removed successively, and ionisation of the acid may precede oxidation.

The formation of terephthalic acid probably involves attack on the 4 : 5-bond of *cycloheptatrienecarboxylic acid*, followed by a Wagner–Meerwein rearrangement, *e.g.*:



Hickinbottom and his collaborators⁵ have shown that chromic acid oxidation of olefins takes place by preliminary oxidation of the C=C bond to give an epoxide, and epoxides readily rearrange in acid. It is interesting that terephthalic acid was the sole product isolated on reaction with chromium trioxide; chromium trioxide seems invariably to oxidise by hydrogen abstraction or oxygen-donation rather than by electron-transfer. It is also interesting that Buchner, using acid permanganate, isolated phthalic acid; this could have been formed by an analogous attack on the 2 : 3-bond. *iso*Phthalic acid, on the other hand, has never been obtained by oxidation of the acid (I), in accord with formulation of the acid as a *cycloheptatriene* derivative rather than a norcaradiene derivative (when the double bonds would be in the 3 : 4- and the 5 : 6-positions).

Of the two remaining oxidation products given in the Table, phenylacetic acid was obtained only in small amounts and was probably present as an impurity in the *cyclohepta-2 : 4 : 6-trienecarboxylic acid*, arising by substitution of ethyl diazoacetate into benzene; the other, α -*cycloheptatrienecarboxylic acid*, was obtained only with alkaline hydrogen peroxide, and alkali is known to isomerise the acid (I) to the α -isomer. Buchner also isolated *trans-cyclopropane-1 : 2 : 3-tricarboxylic acid* in very small amounts from the products given by acidic permanganate. We have not isolated this product and it is probable that it was present as an impurity, arising by self-addition of the decomposition products of ethyl diazoacetate. It is significant that the *cyclohepta-2 : 4 : 6-trienecarboxylic acid* described by Buchner melted below 0°, while the pure acid melts at 25°.

EXPERIMENTAL

cyclohepta-2 : 4 : 6-trienecarboxylic Acid.—Ethyl *cyclohepta-2 : 4 : 6-trienecarboxylate*, was prepared¹ from ethyl diazoacetate and benzene, was distilled and then fractionated through a column packed with Dixon gauzes and surrounded by a heating jacket, giving pure ester, b. p. 51–53°/0.1 mm., $n_D^{22.5}$ 1.5008 (impurities decrease n).

The ester was hydrolysed¹ in acetone–sulphuric acid and the product fractionated through a column packed with glass helices to give pure *cyclohepta-2 : 4 : 6-trienecarboxylic acid*, b. p. 103–105°/0.4 mm., n_D^{18} 1.5400 (impurities increase n), solidifying to needles, m. p. 24°, λ_{min} 2235 (log ϵ 2.98), λ_{max} 2580 Å (log ϵ 3.54).

Oxidation with Potassium Permanganate.—(a) To the trienecarboxylic acid (15.0 g., 0.11 mole), acetone (70 ml.), and 4*N*-sulphuric acid (20 ml.), stirred at 0°, was added potassium permanganate (18 g., 0.11 mole) in 2*N*-sulphuric acid (300 ml.) in a continuous stream (10 min.); the temperature rose to 35° and stirring was continued until the mixture became clear. The mixture was cooled and extracted with ether (4 × 100 ml.). The combined extracts were washed with water, alkali (twice), and water, and dried (Na₂SO₄). Removal of the solvent gave oily neutral products (0.32 g.). The combined alkali-washings were acidified and extracted with ether (4 × 100 ml.). The last ether extracts were washed with water and dried (Na₂SO₄). Removal of the solvent gave the acidic products (1.58 g.). The original reaction mixture was made alkaline with sodium hydroxide and extracted with ether (4 × 200 ml.). These ether extracts were washed with water and dried (Na₂SO₄). Removal of the solvent gave ditropyl ether (4.10 g., 38%).

⁵ Hickinbottom, Peters, and Wood, *J.*, 1955, 1360.

The mixture of neutral products gave an impure 2 : 4-dinitrophenylhydrazone which was chromatographed with benzene on alumina. Evaporation of the eluant gave benzaldehyde 2 : 4-dinitrophenylhydrazone (0.15 g., $\frac{1}{2}\%$), orange needles (from ethyl acetate), m. p. 235–236°, mixed m. p. 236–237°.

Trituration of the acid products with ether gave an unidentified *solid* which was filtered off (0.02 g.) and purified by vacuum sublimation (m. p. 229–229.5°) (Found: C, 67.3; H, 5.6. $C_{10}H_{10}O_3$ requires C, 67.4; H, 5.7%). The ethereal filtrate was evaporated and the residue extracted several times with warm light petroleum (b. p. 40–60°); partial evaporation of the petroleum extract gave phenylacetic acid (0.25 g., $1\frac{1}{2}\%$) which, recrystallised from light petroleum, had m. p. 75–77°, mixed m. p. 76–77°. The petroleum filtrate was evaporated to leave *cyclohepta-2 : 4 : 6-trienecarboxylic acid* (0.30 g., 2%).

The ditropylium ether was purified by vacuum-distillation, then having b. p. 98–100°/0.6 mm., n_D^{17} 1.5778. The distillate was initially colourless but in a few minutes became pale yellow. Ditropylium ether (0.500 g.) was treated in dry ether (30 ml.) with a saturated solution of hydrogen bromide in dry ether. The precipitate of tropylium bromide was filtered off (0.842 g., 98%), washed with dry ether, and crystallised from absolute ethanol [m. p. 199° (decomp.)]. With aqueous picric acid solution, tropylium picrate was formed, having m. p. 97–99° (decomp.); several recrystallisations from water containing picric acid did not change this m. p. (Found: C, 40.3; H, 2.7; N, 15.0. Calc. for $C_{19}H_{14}O_{15}N_6$: C, 40.3; H, 2.5; N, 14.9%).

(b) When a similar ratio of permanganate to *cyclohepta-2 : 4 : 6-trienecarboxylic acid* was used under alkaline conditions at room temperature much starting material was recovered. The only product isolated was terephthalic acid (5%) [dimethyl ester, m. p. 137–139°, mixed m. p. 138–140° (Found: C, 61.8; H, 5.3. Calc. for $C_{10}H_{10}O_4$: C, 61.8; H, 5.2%)].

(c) When a larger proportion of permanganate to *cyclohepta-2 : 4 : 6-trienecarboxylic acid* was used, benzoic acid was also isolated (m. p. and mixed m. p. 120–121°).

Oxidation with Lead Tetra-acetate.—To a stirred solution of *cyclohepta-2 : 4 : 6-trienecarboxylic acid* (1.0 g., 0.0074 mole) in acetic acid (10 ml.) at 70° was added in 5 min. a suspension of lead tetra-acetate (4.0 g., 0.0091 mole) in acetic acid (10 ml.). The mixture was poured into water (100 ml.) containing 2*N*-nitric acid (10 ml.), and washed with ether (3 × 50 ml.), made alkaline with sodium hydroxide, and extracted again with ether (3 × 50 ml.). The last ether extracts were washed with water, dried (Na_2SO_4), and evaporated, and the residue dried in a vacuum, taken up in dry ether (20 ml.), and treated with hydrogen bromide. The resulting precipitate of tropylium bromide was collected (0.25 g., 20%). No other product was identified.

Oxidation with Ceric Ammonium Nitrate.—A solution of ceric ammonium nitrate (9.0 g., 0.016 mole) in 2*N*-nitric acid (60 ml.) was added with stirring to one of *cyclohepta-2 : 4 : 6-trienecarboxylic acid* (1.0 g., 0.0074 mole) in acetone (20 ml.) at room temperature. The mixture was washed with ether (3 × 50 ml.), made alkaline as above, and extracted again with ether (4 × 100 ml.). From the last ether extracts tropylium bromide (0.37 g., 30%) was obtained as described above. No other product was identified.

Oxidation with Persulphate.—To a stirred suspension of *cyclohepta-2 : 4 : 6-trienecarboxylic acid* (1.0 g., 0.0074 mole), in 4*N*-sulphuric acid (20 ml.) containing a catalytic amount of silver nitrate at 70°, was added in 10 min. an aqueous solution of sodium persulphate (1.8 g., 0.0076 mole). The mixture was extracted with ether (3 × 50 ml.) from which terephthalic acid (0.05 g., 4%) was isolated. The aqueous mixture was then made alkaline and extracted with ether (4 × 100 ml.), whence tropylium compounds were isolated as the picrate (0.17 g., 7.2%) by conversion into the bromide and addition of aqueous picric acid.

Oxidation with Periodic Acid.—An aqueous solution of periodic acid (1.4 g., 0.0073 mole) was added in 10 min. to a stirred suspension of *cyclohepta-2 : 4 : 6-trienecarboxylic acid* (1.0 g., 0.0074 mole) in 4*N*-sulphuric acid (25 ml.) at 80°. The mixture was cooled and extracted with ether (3 × 50 ml.). The combined ether extracts were washed twice with alkali and evaporated, benzaldehyde being then isolated as 2 : 4-dinitrophenylhydrazone (0.05 g., 2%). The combined alkali washings were acidified and extracted with ether (3 × 50 ml.). Evaporation of these ether extracts gave benzoic (0.03 g., 3%) and terephthalic acid (0.02 g., $1\frac{1}{2}\%$). The residual aqueous mixture was made alkaline and extracted with ether (3 × 50 ml.), whence tropylium picrate (0.03 g., $1\frac{1}{2}\%$) was obtained.

Oxidation with Nitric Acid.—*cyclohepta-2 : 4 : 6-trienecarboxylic acid* (2.0 g.) was added to nitric acid (25 ml.; *d* 1.42) at 3°. A deep green colour developed which was destroyed as the

mixture warmed to room temperature. The mixture was finally heated on a steam-bath until the evolution of nitrogen oxides was negligible. Terephthalic acid, which separated, was filtered off (0.15 g., 6%) and identified as the dimethyl ester. The filtrate was extracted with ether, from which benzoic acid (0.07 g., 4%) was isolated. No other oxidation product was identified.

When the oxidation was repeated without warming, no oxidation products could be isolated after 20 min.

Oxidation with Chromic Acid.—*cyclo*Hepta-2 : 4 : 6-trienecarboxylic acid (2.0 g., 0.015 mole) was added to a solution of chromic acid (4.5 g., 0.045 mole) in acetic acid (50 ml.) containing 4*N*-sulphuric acid (5 ml.) at room temperature. The oxidant was rapidly reduced and the temperature rose to 80°. Terephthalic acid (0.10 g., 4%), identified as the dimethyl ester, was the only product isolated.

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