112. *Rearrangements of Some* cyclo*Octatetraene Derivatives.*

By C. R. Ganellin and R. Pettit.

A mechanism which involves intermediate formation of *cyclo*hepta-2 : 4 : 6-trienealdehyde is postulated for the acid-catalysed rearrangement of 7 : 8-epoxy*cyclo*octa-1 : 3 : 5-triene to phenylacetaldehyde. The epoxide gives tropylium salts in poor yield when oxidised by acid permanganate; with 2 : 4-dinitrophenylhydrazine in acidic alcohol below 0° it gives mainly the hydrazone of *cyclo*hepta-2 : 4 : 6-trienealdehyde, but at 70° gives the hydrazone of phenylacetaldehyde. Rearrangement in acids of those *cyclo*heptatriene derivatives capable of giving rise to ions of the type (VIII), to benzene derivatives, appears to be a general reaction.

A similar mechanism accounts for other rearrangements of *cyclo*octatetraene derivatives. The dichloride of *cyclo*octatetraene with methanol gives phenylacetaldehyde dimethyl acetal, and not phenylglycol dimethyl ether as reported earlier.

*cyclo*OCTATETRAENE [1] and its derivatives undergo a variety of rearrangements, but so far there is little to indicate their mechanisms. In this paper we suggest a route for some of them, in particular the acid-catalysed rearrangement of 7 : 8-epoxy*cyclo*octa-1 : 3 : 5-triene (*cyclo*octatetraene oxide) to phenylacetaldehyde and the solvolytic reactions of *cyclo*octatetraene dichloride.

We recently reported [2] that the tropylium cation (V) was one of the products formed when *cyclo*octatetraene (I) was oxidised with acid potassium permanganate. We suggested initial formation of the hydroxy-cation (II), which gave the protonated *cyclo*hepta-2 : 4 : 6-trienealdehyde * (III) by a pinacol–pinacone rearrangement. Compound (III) was then supposed to be oxidised to *cyclo*hepta-2 : 4 : 6-trienecarboxylic acid (IV) which gives the tropylium cation on reaction [3] with oxidising agents.

Known reactions of epoxides with acids suggested that the cation (II) could be formed

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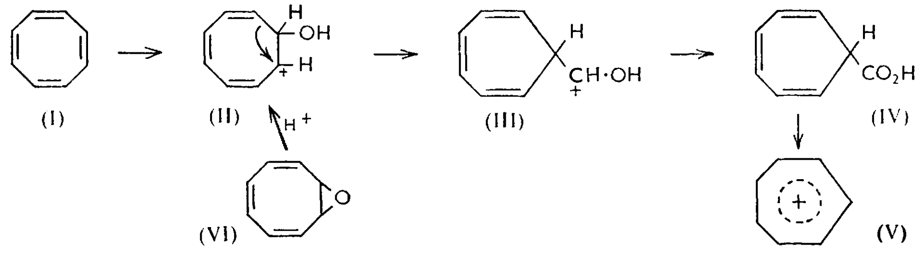
* By analogy with the corresponding acid [3] the 2 : 4 : 6-*cyclo*heptatriene formulation is preferred to a norcaradiene structure for this aldehyde, and is used also for other such compounds in this paper.

[1] Reppe, Schlichting, Klager, and Toepel, *Annalen*, 1948, **560**, 1.

[2] Ganellin and Pettit, *J. Amer. Chem. Soc.*, 1957, **79**, 1767.

[3] Dewar, Ganellin, and Pettit, *J.*, 1957, 55.

by treating 7 : 8-epoxy*cyclo*octa-1 : 3 : 5-triene (VI) with acids:[4] thus oxidation with acid permanganate should yield the tropylium cation. We have obtained a 7% yield of tropylium picrate from this reaction. The low yield is not surprising, since the tropylium cation itself is readily destroyed by permanganate,[5] and is of the same order as that obtained by oxidation of *cyclo*octatetraene with acid permanganate.



Acid-catalysed Rearrangement of 7 : 8-*Epoxy*cyclo*octa*-1 : 3 : 5-*triene to Phenylacetaldehyde.*—In the above mechanism for the oxidation of the epoxide, the first step is the acid-catalysed rearrangement to the cation (III), and the oxidant does not enter into the reaction until this has taken place. This suggests that acid-catalysed rearrangement of the oxide to phenylacetaldehyde[1] may involve intermediate formation of the aldehyde (VII) which subsequently rearranges to phenylacetaldehyde. We have so far been unable to synthesise this aldehyde, but from the following similar reactions there can be little doubt that it would isomerise to phenylacetaldehyde in mineral acid.

The acid-catalysed rearrangement of *cyclo*hepta-1 : 3 : 5-triene derivatives which are capable of giving rise to ions of the type (VIII) appears to be general, the products being ββ′-disubstituted styrene derivatives having the general formula (IX), the driving force arising from the larger resonance energy developed in the aromatic ring.

The rearrangement occurs when the cation (VIII) is produced by addition of a proton or by acid-catalysed removal of a hydroxyl group. Thus *cyclo*hepta-2 : 4 : 6-trienyl methyl ketone readily rearranges to benzyl methyl ketone in warm dilute alcoholic hydrochloric acid. This involves, first, the addition of a proton with formation of the cation (VIII; R′ = Me, R″ = OH), then rearrangement to (IX; R′ = Me, R″ = OH) which is the enolic form of benzyl methyl ketone. Similarly, 2-(*cyclo*hepta-2 : 4 : 6-trienyl)propan-2-ol (VIII; R′ = Me, R″ = Me) readily rearranges in dilute alcoholic hydrochloric acid to 2′-methylpropenylbenzene, and Doering[6] has found that *cyclo*hepta-2 : 4 : 6-trienylmethanol undergoes acid-catalysed rearrangement to styrene. It is interesting that the addition of phenylmagnesium bromide to 7-cyano*cyclo*hepta-1 : 3 : 5-triene, followed by hydrolysis with acid, gives deoxybenzoin and not *cyclo*heptatrienyl phenyl ketone:[7] this could occur by intermediate formation of the cation (VIII; R′ = Ph, R″ = OH).

Cope, Nelson, and Smith[8] prepared *cyclo*hepta-2 : 4 : 6-trienealdehyde dimethyl acetal from the dichloride of *cyclo*octatetraene and found that it yields phenylacetaldehyde on hydrolysis in aqueous acid. It is possible that the acetal is first hydrolysed to the aldehyde (VII) which then rearranges, *via* the ion (VIII; R′ = H, R″ = OH), to the enolic form of phenylacetaldehyde. Alternatively, rearrangement of the acetal can take place through the ion (VIII; R′ = H, R″ = OMe), to give β-methoxystyrene which undergoes acid hydrolysis very readily to phenylacetaldehyde.

In anhydrous methanol acid-catalysed rearrangement of the acetal should proceed *via* the ion (VIII; R′ = H, R″ = OMe), to give β-methoxystyrene. However, the product

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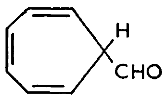
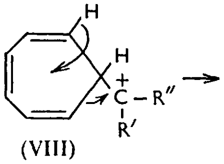
[4] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1953, p. 344.
[5] Dewar and Pettit, *J.*, 1956, 2026.
[6] Professor W. von E. Doering, personal communication.
[7] Doering and Knox, *J. Amer. Chem. Soc.*, 1957, **79**, 352.
[8] Cope, Nelson, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 1100.

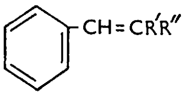
we obtained was phenylacetaldehyde dimethyl acetal. This is understandable in view of our finding that β-methoxystyrene readily adds the elements of methanol under the conditions used in the rearrangement.



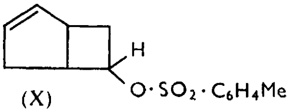
(VII)



(VIII)



(IX)



(X)

If, as postulated, *cyclo*hepta-2 : 4 : 6-trienealdehyde is an intermediate in the rearrangement of epoxy*cyclo*octatriene to phenylacetaldehyde it would be convincing evidence to isolate a derivative of (VII) from this reaction. Cope, Nelson, and Smith [8] were able to prepare its 2 : 4-dinitrophenylhydrazone by treatment of the corresponding dimethyl acetal with 2 : 4-dinitrophenylhydrazine in acidic aqueous ethanol at 0°. We have isolated this 2 : 4-dinitrophenylhydrazone as the major product of the reaction of the epoxide with 2 : 4-dinitrophenylhydrazine in aqueous acidic ethanol at —5°. A similar reaction at 70° gave as main product the corresponding derivative of phenylacetaldehyde. Rearrangement of the intermediate aldehyde (VII) must be sufficiently slow at lower temperatures to allow formation of the hydrazone.

These results provide good evidence that a seven-membered ring intermediate is involved in the acid-catalysed rearrangement of epoxy*cyclo*octatriene to phenylacetaldehyde. The gain in resonance energy [9] and a decrease in the steric strain involved in going from the *cyclo*octatriene to the *cyclo*heptatriene system would provide the driving force for the initial ring-contraction. The same arguments could account for the production of *cyclo*heptatriene in 50% yield on acetolysis of the toluene-*p*-sulphonate [10] (X).

Rearrangements of the Dichloride of cyclo*Octatetraene.*—The products obtained from solvolytic reactions of the dichloride (XII; R = R′ = Cl) vary remarkably with the medium and may have one of three different ring systems. Hydrolysis in water produces phenylacetaldehyde. Reppe *et al.*[1] found that treatment with acetic acid gave β-acetoxystyrene, whereas that with potassium acetate in acetic acid gave the diacetoxy-compound (XII; R = R′ = OAc). Cope, Nelson, and Smith [8] have shown that the dichloride with sodium methoxide in methyl alcohol gives *cyclo*hepta-2 : 4 : 6-trienealdehyde dimethyl acetal, and not compound (XI) as reported by Reppe *et al.*[1] All these products are readily accounted for by a scheme similar to that described above for the rearrangement of the epoxide.

Hydrolysis of the dichloride in water would proceed *via* the cation * (XIII; R = OH); a pinacol–pinacolone rearrangement would then give protonated *cyclo*heptatrienealdehyde (VIII; R = OH), which, under the acid conditions produced by the hydrolysis, would rearrange to phenylacetaldehyde as described earlier. Similarly, solvolysis of the dichloride in the absence of base would occur with the production (in the presence of the hydrochloric acid liberated) of the cation (VIII; R = OAc) which would rearrange to β-acetoxystyrene. Acetolysis of the dichloride in acetic acid containing potassium acetate involves no rearrangement. Possibly this reaction involves S_N2 substitution by the acetate ion; no intermediate cation of the type (XIII) would then be formed. Methanolysis in the presence of base could proceed by rearrangement of the cation (XIII; R = OMe) to the cation (VIII; R = OMe), which would yield the dimethyl acetal of the

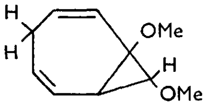
* There is good evidence that the dichloride has the bicyclic structure (XII), but in view of the ready conversion of the bicyclic system into the eight-membered ring shown by some compounds, *e.g.*, *cyclo*octatrienes, there can be no justification for preferring either the bicyclic or the monocyclic structure for the cations (XIII).

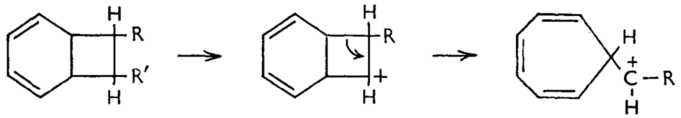
[9] Doering and Knox, *J. Amer. Chem. Soc.*, 1956, **78**, 5448.

[10] Dryden, *ibid.*, 1954, **76**, 2841.

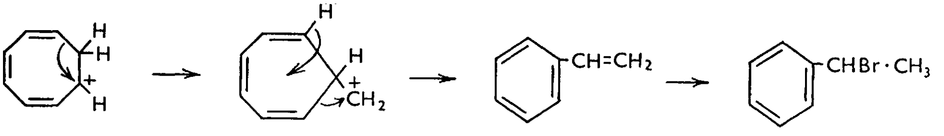
aldehyde (VII) by reaction with methoxide ion and, under the basic conditions prevailing, no further rearrangement would be expected.

We have re-investigated the products of methanolysis of the dichloride in methyl


(XI)


(XII) (XIII) (VIII)

alcohol in the absence of base. Reppe and his co-workers [1] report that phenylglycol dimethyl ether is produced. However, from the above mechanism we would expect β-methoxystyrene to be formed, *via* the ions (XIII and VIII; R = OMe), which would then be converted into phenylacetaldehyde dimethyl acetal. We found the product to be this


(XIV) (XV)

acetal which, though similar in some respects to phenylglycol dimethyl ether, has a different infrared absorption spectrum. The two compounds can readily be distinguished by the much faster hydrolysis of the acetal to phenylacetaldehyde.

Other Rearrangements.—Willstätter and Heidelberger [11] first treated *cyclo*octatetraene with hydrogen bromide, and Reppe and his co-workers [1] identified the product as 1′-bromoethylbenzene. This rearrangement presumably involves addition of a proton to give the cation (XIV), followed by Wagner–Meerwein rearrangement to the cation (XV). Further rearrangement would give styrene which adds hydrogen bromide.

Cope, Nelson, and Smith [8] have repeated the work of Reppe and his co-workers [1] on the reactions of mercuric salts with *cyclo*octatetraene in various solvents and in two instances found erroneous identification of the products by the earlier workers. The product formed from the tetraene by mercuric acetate in acetic acid is the diacetate (XII; R = R′ = OAc), in methanol the product is *cyclo*hepta-2 : 4 : 6-trienealdehyde dimethyl acetal, and in water it is phenylacetaldehyde. These products are identical with those obtained in the solvolytic reactions of the dichloride. Although the nature of organic intermediates involved in reactions of mercuric complexes is not completely understood, it seems likely that very similar intermediates occur in the two sets of rearrangements.

EXPERIMENTAL

Oxidation of 7 : 8-*Epoxy*cyclo*octa*-1 : 3 : 5-*triene.*—Potassium permanganate (1·5 g.) in N-sulphuric acid (68 ml.) was added quickly, with stirring, to a solution of the epoxide [1] (1·0 g.) in acetone (25 ml.) at 0°. The temperature rose to 30° and stirring was continued until the solution became clear. The mixture was then extracted several times with ether. These extracts contained an acid (40 mg.) and a neutral fraction (250 mg.), the latter consisting of some unchanged epoxide and an unidentified crystalline material. The aqueous residue was made alkaline with sodium hydroxide solution and extracted again with ether (4 × 150 ml.). These extracts were dried (Na_2SO_4) and evaporated. The residue of crude ditropyl ether was treated in dry ether with hydrogen bromide. The precipitated tropylium bromide was filtered off and dissolved in water (2 ml.), and a saturated aqueous picric acid solution added (5 ml.). Tropylium picrate was collected as yellow needles (170 mg., 7·2%), m. p. and mixed m. p. 98—99° (decomp.) after two crystallisations from water.

Similar experiments using hydrogen peroxide, lead tetra-acetate, or ceric ammonium nitrate gave mainly benzaldehyde and other unidentified products, but no tropylium salts.

Rearrangement of 2-(cyclo*Hepta*-2 : 4 : 6-*trienyl*)*propan*-2-*ol.*—Ethyl *cyclo*hepta-2 : 4 : 6-trienecarboxylate [5] (10·0 g.) in dry ether (20 ml.) was added at 5° with stirring to the Grignard reagent prepared from methyl iodide (20 g.) and magnesium (3·3 g.) in dry ether (200 ml.). The mixture

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[11] Willstätter and Heidelberger, *Ber.*, 1913, **46**, 517.

was then refluxed with continuous stirring for 1 hr., cooled, and poured into ice-cold, saturated ammonium chloride solution. Washing the organic layer with water and evaporating it left a pale yellow oil which solidified. The *alcohol* crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 59—60° (7·8 g., 85%) (Found: C, 79·7; H, 8·4. $C_{10}H_{14}O$ requires C, 80·0; H, 9·3%), $\lambda_{max.}$ 256 mμ (log ε 3·51), $\lambda_{min.}$ 222 mμ (log ε 2·85).

The above alcohol (2·0 g.) was stirred vigorously for 10 min. with 10% hydrochloric acid (40 c.c.). Extraction with ether, followed by drying (Na_2SO_4) and fractionation, gave an almost quantitative yield of 2′-methylpropenylbenzene, b. p. 68·5—69°/0·6 mm., n_D^{19} 1·5400 (Found: C, 90·7; H, 9·2. Calc. for $C_{10}H_{12}$: C, 90·9; H, 9·1%). The material rapidly decolorised bromine water and permanganate and showed the typical styrene ultraviolet absorption spectrum.

Rearrangement of cyclo*Hepta*-2 : 4 : 6-*trienyl Methyl Ketone.*—Anhydrous powdered cadmium chloride (10·3 g.) was added at 0° with stirring to methylmagnesium iodide (from 16·5 g. of methyl iodide and 2·75 g. of magnesium) in dry ether (250 ml.), and was followed by *cyclo*hepta-2 : 4 : 6-trienecarbonyl chloride [5] (9·2 g.) in ether (30 ml.). The mixture was stirred at room temperature for 1 hr., then excess of water was added. The ethereal solution was extracted with sodium carbonate solution and the organic layer fractionated. The *ketone* obtained (2·8 g., 30%) had b. p. 56—57°/0·6 mm., n_D^{18} 1·5207 (Found: C, 80·4; H, 7·6. $C_9H_{10}O$ requires C, 80·6; H, 7·5%). Its *semicarbazone* formed plates (from alcohol–water), m. p. 175—176° (mixed m. p. with benzyl methyl ketone semicarbazone, 155—156°) (Found: C, 62·4; H, 6·9; N, 22·1. $C_{10}H_{13}ON_3$ requires C, 62·8; H, 6·8; N, 22·0%). The ketone readily decolorised bromine water and permanganate.

The ketone (0·2 g.) in 10% alcoholic hydrochloric acid (10 ml.) was warmed at 50° for a few minutes and 2 : 4-dinitrophenylhydrazine (0·3 g.) in the same solvent (10 ml.) was then added. Cooling and dilution afforded benzyl methyl ketone dinitrophenylhydrazone (0·35 g.), yellow needles (from ethyl acetate), m. p. and mixed m. p. 154—155°.

A similar rearrangement in acidic alcohol, followed by neutralisation, extraction with ether, and treatment of the extracted ketone in the usual way afforded benzyl methyl ketone semicarbazone as needles (from alcohol–water), m. p. and mixed m. p. 191—193°.

Rearrangement of cyclo*Hepta*-2 : 4 : 6-*trienealdehyde Dimethyl Acetal.*—The acetal was prepared from the dichloride (XII) and sodium methoxide and after several fractionations still contained a trace of chlorinated impurity.[1] The acetal (4·0 g.) was dissolved in absolute methyl alcohol (20 ml.), and three drops of concentrated sulphuric acid were added. The mixture was refluxed for 2 min., then cooled, made alkaline with sodium hydroxide solution, and extracted with ether. The crude product, after removal of the ether, was hydrogenated with palladised charcoal at atmospheric pressure in methanol (50 ml.) containing potassium hydroxide (0·5 g.) (absorption, 90 ml.). Filtration, removal of the solvent, and fractionation afforded phenylacetaldehyde dimethyl acetal, b. p. 52°/0·5 mm., n_D^{20} 1·4930. The material showed an infrared spectrum identical with that of material prepared from phenylacetaldehyde and dimethyl sulphite.[12] If the hydrogenation step is omitted it is difficult to remove traces of chlorine-containing material from the product.

Rearrangement of 7 : 8-*Epoxy*cyclo*octa*-1 : 3 : 5-*triene.*—The epoxide (0·8 g.) was added in alcohol (10 ml.) to a solution at −5° of 2 : 4-dinitrophenylhydrazine (1·4 g.) in alcohol (85 ml.) containing 30% hydrochloric acid (7 ml.). The mixture was kept at −5° for 5 hr., then the red precipitate of *cyclo*hepta-2 : 4 : 6-trienealdehyde 2 : 4-dinitrophenylhydrazone was filtered off and washed successively with cold alcohol, water, aqueous sodium carbonate, and water. The crude product (dried *in vacuo* at room temperature) (1·32 g.), had m. p. 132—133° (decomp.). Four crystallisations from alcohol–benzene gave pure material as an orange-red powder, m. p. 136° (decomp.) alone or mixed with a specimen prepared by the method of Cope *et al.*[8] (Found: C, 55·8; H, 4·2; N, 18·6. Calc. for $C_{14}H_{12}O_4N_4$: C, 56·0; H, 4·0; N, 18·7%), $\lambda_{max.}$ 260, 273, and 356 mμ (log ε 3·96, 4·11, 4·35 in chloroform).

A similar experiment at 70° for 15 min. gave mainly phenylacetaldehyde 2 : 4-dinitrophenylhydrazone.

Methanolysis of the Dichloride of cyclo*Octatetraene.*—Reaction of the dichloride with methanol was conducted as described by Reppe *et al.*[1] The final product was carefully fractionated and found to be principally one compound. The middle fraction had n_D^{20} 1·4931, the infrared spectrum of phenylacetaldehyde dimethyl acetal, and b. p. 49·5°/0·4 mm. (Found: C, 72·0; H, 8·5; OMe, 36·9. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4; OMe, 37·3%).

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[12] Voss, *Annalen*, 1931, **485**, 283.

Phenylacetaldehyde Dimethyl Acetal from β-*Methoxystyrene.*—β-Methoxystyrene was prepared from phenylacetylene and potassium methoxide as described by von Auwers,[13] but the yield was increased by continuous stirring. A solution of β-methoxystyrene (6·0 g.) in absolute methyl alcohol (60 ml.) containing 100% sulphuric acid (0·5 c.c.) was refluxed for 3 min. After cooling, the mixture was made alkaline. Extraction with ether and working up in the usual way gave phenylacetaldehyde dimethyl acetal (4·0 g.; n_D^{20} 1·4931). The middle fraction had an infrared spectrum identical with that of authentic material.

Phenylglycol Dimethyl Ether.—Phenylglycol (prepared from styrene dibromide [14]) was methylated in good yield with methyl sulphate as described for glucose.[15] The product had b. p. 55°/0·5 mm., n_D^{20} 1·4948 (Found: C, 72·4; H, 8·6; OMe, 35·8. Calc. for $C_{10}H_{14}O_2$: C, 72·3; H, 8·4; OMe, 37·3%). The material has a very similar odour to that of phenylacetaldehyde dimethyl acetal but does not give phenylacetaldehyde dinitrophenylhydrazone after hydrolysis with warm alcoholic acids. More vigorous hydrolysis of the dimethyl ether is reported to yield phenylacetaldehyde.

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QUEEN MARY COLLEGE, (UNIVERSITY OF LONDON),
MILE END ROAD, LONDON, E.1.
[Present address (R. P.): UNIVERSITY OF TEXAS, AUSTIN 12,
TEXAS, U.S.A.]

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[13] von Auwers, *Ber.*, 1911, **44**, 3519.
[14] Evans and Morgan, *J. Amer. Chem. Soc.*, 1913, **35**, 54.
[15] West and Holden, *Org. Synth.*, Coll. Vol. III, 1955, p. 800.