220. *Mechanism of Polymerisation. Part V. Dimerisation of Unconjugated Pentadiene.*

By Ali Ahmad and Ernest Harold Farmer.

$\Delta^{\alpha\delta}$-Pentadiene, the unconjugated unsaturation of which resembles that of the acids of many di- and poly-ene drying oils, polymerises like these oils when it is heated above 200°. The product is a mixture of low-molecular polymerides in which the dimeride and trimeride predominate.

The dimeride, although not homogeneous, consists mainly of 1-methyl-2-allyl-*cyclo*hexene; the remainder of the yield is composed of less-unsaturated material, which is probably a bicyclic isomeride of the main product. The 1 : 2-position of the *cyclo*hexenic substituents points to a dimerisation mechanism which is dependent on the isomerisation of one of the pentadiene molecules prior to its participation in the dimerising addition reaction; or alternatively, to an additive mechanism which is dependent on the appearance of free-radical forms of the monomerides. The nature of the trimeric and higher forms has not been determined.

The unconjugated pentadiene system $\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot$ is one that occurs in linoleic and linolenic acids derived from vegetable oils, and in most of the polyene acids which are present as glycerides in fish oils (cf. Farmer and Van den Heuvel, *J. Soc. Chem. Ind.*, 1938, **57**, 24; J., 1938, 427). Since all of these acids and the oils in which they occur show strong tendencies to " thicken " or " body " when they are heated,[*] there is every reason to believe that the unconjugated pentadiene, octatriene, etc., systems present in the carbon chains of the acids are responsible for the main features of the thermal polymerisation processes here involved. It is of some interest, therefore, to examine the course of polymerisation in the simplest compound containing the unconjugated type-system, *i.e.*, $\Delta^{\alpha\delta}$-pentadiene, $CH_2{:}CH\cdot CH_2\cdot CH{:}CH_2$.

The most likely type of polymerisation both for the simple unconjugated hydrocarbon and for the long-chain unconjugated acids seemed to be one involving *cyclo*hexenic or *cyclo*pentenic ring formation at the dimeric stage, bicyclisation at the trimeric stage, and so on. A point of great importance, however, was whether the unconjugated system would polymerise as the result of independent reactions taking place at the individual double bonds of each molecule or whether the double bonds of one or more reacting molecules would have to become conjugated by isomerisation as a preliminary to union taking place by a reaction of Diels–Alder type.

Actually, thermal treatment of the hydrocarbon at 270° leads to the production of a series of low-molecular polymerides of which the dimeric and trimeric members are the most abundant. The dimeric hydrocarbon absorbs 1·5 mols. of hydrogen per mol., the first half rapidly and the second half slowly, and so gives rise to a product saturated towards bromine. The loss of unsaturation during dimerisation is therefore 2·5 double bonds and hence the dimeride cannot be homogeneous; indeed, it seems likely that it is composed of about equal proportions of mono- and bi-cyclic material.

On oxidation with permanganate the mixed dimeride yields formic acid together with

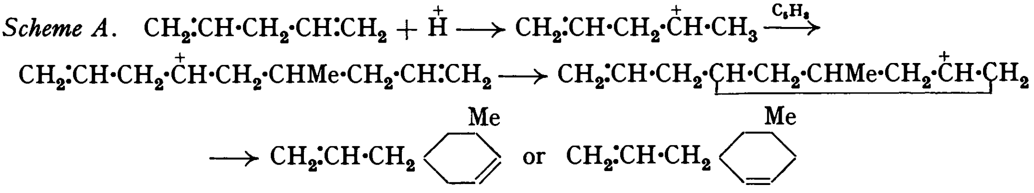
---

[1] Consideration is here restricted to thermal changes which occur in the absence of oxygen.

a non-homogeneous, liquid acid of high boiling point. On dehydrogenation it gives a product composed partly of an aromatic hydrocarbon and partly of a fully saturated non-aromatic hydrocarbon. The amount of hydrogen evolved during the dehydrogenation is rather less than 0·7 mol. and the average composition of the hydrocarbon mixture is $C_{10}H_{15}$. The aromatic component is with little doubt *o*-methylpropylbenzene, $C_{10}H_{14}$, since it gives *o*-phthalic acid on vigorous oxidation with boiling permanganate; the nature of the saturated hydrocarbon—whether composed entirely of *o*-methylpropyl*cyclo*hexane formed by disproportionation of the monocyclic dimeride, or partly of a substituted *bicyclo*hexane—has not been determined. It is clear, however, that the dimeride consists largely of a *cyclo*hexenic substance, *viz.*, 1-methyl-2-allyl*cyclo*hexene.

If the two double bonds of $\Delta^{\alpha\delta}$-pentadiene remain unconjugated as dimerisation proceeds, a 1-methyl-3-allyl*cyclo*hexene might be expected to result. This would be the case whether the proton-addition mechanism of Whitmore (see Scheme A) or the hydrogen-separation mechanism were followed. If, on the other hand, one of the reacting molecules

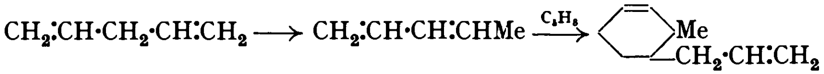
Scheme A.



$$CH_2{:}CH{\cdot}CH_2{\cdot}CH{:}CH_2 + \overset{+}{H} \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_3 \xrightarrow{C_5H_8}$$

$$CH_2{:}CH{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2 \longrightarrow CH_2{:}CH{\cdot}CH_2{\cdot}CH{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}\overset{+}{C}H{\cdot}CH_2$$

Scheme B.



becomes conjugated before it unites with a second molecule (Scheme B) then a 1-methyl-2-allyl*cyclo*hexane should be formed. In support of Scheme B it may be mentioned that Lebedev and Slobodin (*J. Gen. Chem. Russ.*, 1934, **4**, 123) have observed that diallyl (in which two methylene groups separate the double bonds) passes on heating with floridin at 205° into an equilibrium mixture of diallyl and its conjugated isomeride, αδ-dimethylbutadiene, and at the same time undergoes some polymerisation. It seems, however, not impossible that a free-radical mechanism could function during the thermal polymerisation, and in this case the dimeric free-radical form, $CH_2{:}CH{\cdot}CH_2{\cdot}\overset{|}{C}H.CH_2{\cdot}CH_2{\cdot}\overset{|}{C}H{\cdot}CH_2{\cdot}CH{:}CH_2$, would be a likely intermediate (see Burk, *Ind. Eng. Chem.*, 1938, **30**, 1054).

EXPERIMENTAL.

$\Delta^{\alpha\delta}$-*Pentadiene.*—This was prepared by the method of Shoemaker and Boord (*J. Amer. Chem. Soc.*, 1931, **53**, 1505; see also Kistiakowsky and Vaughan, *ibid.*, 1938, **56**, 147). The hydrocarbon was washed many times with ice water, dried with calcium chloride, and distilled several times over sodium (b. p. 27—28°).

Polymerisation.—(a) *With boron trifluoride.* When the hydrocarbon (10 g.) was mixed with a 15% solution (20 g.) of boron trifluoride in acetic acid and left for 24 hours, the products were unchanged pentadiene, a colourless oxygenated oil (b. p. 138°; yield, 65%) which was with little doubt iso*pentenyl acetate*, $CH_2{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}OAc$ (Found: C, 65·55; H, 9·4; *M*, cryoscopic, 129·6. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%; *M*, 128), and a residue which was probably the corresponding diacetate, βδ-diacetoxypentane. Increase in the concentration of the boron trifluoride gave an increased yield of acetate but no polymerisation product. When the hydrocarbon, in light petroleum solution, was treated at − 15° with boron trifluoride and then left for 16 hours at 0°, no polymerisation occurred; when, however, the trifluoride was passed into undiluted pentadiene at − 15°, and the mixture allowed to attain room temperature and then to stand overnight, a thick undistillable polymeric oil was formed. Attempts to produce distillable, low-molecular polymerides by modifying the conditions of reaction were unsuccessful.

(b) *By heating.* Preliminary experiments in sealed glass tubes showed that little polymerisation of pentadiene occurred below 225°. The hydrocarbon was accordingly placed in a well-cooled copper autoclave, the air in the free space displaced by nitrogen, and the closed vessel then electrically heated for 36 hours. At 250° polymerisation occurred to the extent of 15% (7—8% dimeride), at 270° to the extent of 30—35% (15—16% dimeride), and at 280—290° to the extent of 90% (polymerised portion: 25% dimeride, 10—15% trimeride, 60—65% higher polymerides). In order, therefore, to obtain the dimeric and trimeric products unmixed with unduly large proportions of higher polymerides the subsequent experiments were conducted at 270°. Distillation of the product gave a dimeric fraction (b. p. 176—179°), a trimeric fraction (b. p. 120—126°/1 mm.), and higher fractions of b. p. 126—140°/1 mm., 140—180°/1 mm., and 200—205°/1 mm., which appeared to correspond very roughly with tri-, tetra-, and penta-meric pentadiene respectively. There remained a residue which was undistillable without decomposition at 1 mm.

Dimeric and Trimeric Pentadiene.—Systematic fractionation of the crude dimeric fraction under a Widmer column fitted with a reflux head gave a colourless oily *dimeride* of characteristic odour, boiling fairly sharply at 176°. It had $n_D^{19°}$ 1·48143 $d_{4°}^{19°}$ 0·8985 (Found: C, 88·0; H, 11·6; *M*, cryoscopic, 134, 135·2. $C_{10}H_{16}$ requires C, 88·2; H, 11·8%; *M*, 136). The crude trimeric fraction on refractionation gave a colourless, oily *trimeride*, b. p. 120—122°/1 mm., $n_D^{19°}$ 1·4912; $d_{4°}^{19°}$ 0·9156; *M*, cryoscopic, 204·5, 203·6 (Found: C, 87·9; H, 11·55%).

Unsaturation of Dimeride.—When hydrogenated at room temperature and atmospheric pressure in presence of Adams's catalyst, the dimeride absorbed 1·46 mols. of hydrogen per mol. in alcohol and 1·51 mols. in acetic acid. The hydrogenated product was saturated towards bromine. In chloroform at 0° the dimeride absorbed 1·56 mols. of bromine.

Oxidation of Dimeride with Permanganate.—To the dimeride (2 g.), dissolved in acetone (60 c.c.) and cooled in ice, sufficient 4% aqueous permanganate was slowly added dropwise with stirring to yield 8 atoms of oxygen per mol. of hydrocarbon. The flask was removed from the ice and left for 2 hours before the product was worked up. The residual permanganate was decolourised with sulphurous acid, the solution then basified (if acid), filtered to remove manganese mud, and evaporated to small bulk. The concentrate, after acidification, was extracted with ether in a continuous extractor, and the extract dried and evaporated. The residue was a pale yellow, strongly acidic, syrup which gave on careful heating at reduced pressure a small distillate of formic acid, but contained no oxalic acid. The main product was a non-homogeneous oily acid which could not be solidified or adequately purified. Repetitions of the oxidation, with somewhat smaller proportions of permanganate, gave closely similar results.

Dehydrogenation of Dimeride.—The dimeride (1·4 g.) was dehydrogenated in the vapour phase at 178—181° in presence of 33% palladised charcoal (0·14 g.). After 6½ hours the process was complete and 0·6 mol. of hydrogen had been evolved. The product was a colourless oil, b. p. 185°, of aromatic odour, which was entirely saturated towards permanganate. This oil had an empirical composition (Found: C, 88·8; H, 11·2. Calc. for $C_{10}H_{15}$: C, 88·9; H, 11·1%) corresponding to the production of 82% of methylpropylbenzene with 18% of methylpropyl*cyclo*hexane or 75% of methylpropylbenzene with 25% of dimethyl*bicyclo*octane.

Oxidation of the Dehydrogenated Dimeride.—The dehydrogenated hydrocarbon (1 mol.) was heated on a steam-bath with 50 c.c. of water to which successive portions of 2·5 g. of powdered potassium permanganate were added from time to time as reduction occurred. Nearly 20 g. of permanganate were reduced before reaction ceased (8 hours), and when at the end of this procedure the manganese mud was dissolved with sulphurous acid, a thin layer of oil remained floating on the aqueous liquor. Retreatment of this oily layer separately for a further 6 hours with hot permanganate led to no further reaction.

The filtered oxidation liquor was cooled, acidified, and extracted with ether. The extract yielded a crystalline acid, m. p. 195°, which was identified as *o*-phthalic acid by comparison with an authentic specimen (Found: C, 57·6; H, 3·7. Calc. for $C_8H_6O_4$: C, 57·7; H, 3·6%).

We thank the Government Grant Committee of the Royal Society and the Chemical Society for grants (to E. H. F. and A. A. respectively).

IMPERIAL COLLEGE, LONDON, S.W. 7. [*Received, June 18th, 1940.*]