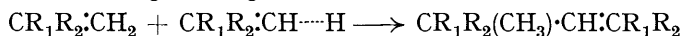


320. The Mechanism of Polymerisation Reactions. Part IV.\*  
*α*-Phenylbutadiene.

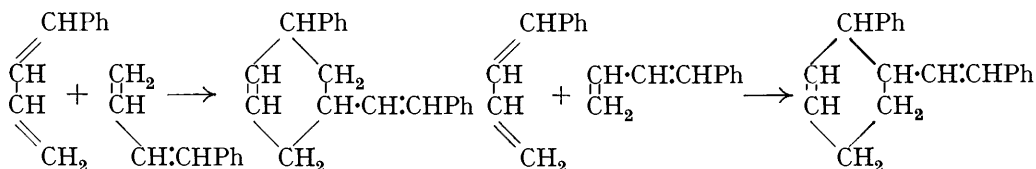
By E. BERGMANN.

THE catalytic dimerisation of simple unsaturated compounds has been shown by various authors to proceed according to the general scheme :

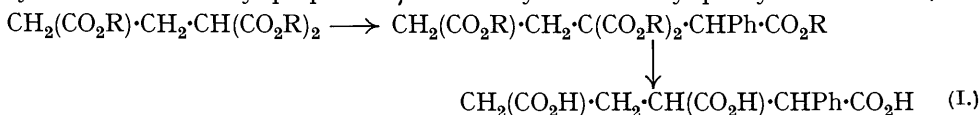


There is an obvious tendency to form a methyl group by displacement of an activated hydrogen atom (see Whitmore, *Ind. Eng. Chem.*, 1934, **26**, 94), and it may be expected that the same scheme is valid also for diene compounds. Actually, the results of Wagner-Jauregg (*Annalen*, 1931, **488**, 176; 1932, **496**, 52) and of Midgley and Henne (*J. Amer. Chem. Soc.*, 1929, **51**, 1294) support the view that the first step in the catalytic polymerisation of isoprene consists in an open-chain dimerisation. Formally, however, the dimerisation of dienes appears to occur so that the 1 : 4-system of one molecule reacts with the 1 : 2-double bond of the other. For asymmetrically substituted dienes the question arises as to which of the ethylene linkages of the second molecule participates in the condensation. With isoprene, both possibilities occur, *m*- or *p*-menthadiene being produced according as the double bond concerned is that remote from or adjacent to the methyl group (see, e.g., Wagner-Jauregg, *loc. cit.*).

From *α*-phenylbutadiene, only one dimeric product is formed, but its structure had not been determined. Lebedev (*Chem. Zentr.*, 1914, i, 1407; 1923, i, 1539) found that on oxidation it yields benzoic acid and a tricarboxylic acid, C<sub>13</sub>H<sub>14</sub>O<sub>6</sub>. If dimerisation occurs as in the case of isoprene, the formation of benzoic acid indicates that the CHPh:CH bond of the second reacting molecule does not participate in the ring formation. The two possible schemes are therefore :

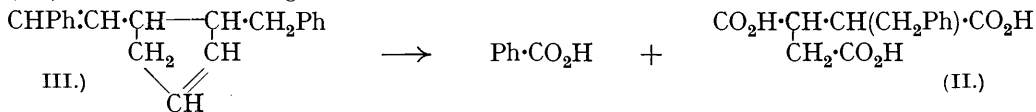


On oxidation the two cyclic compounds should give benzoic acid and either *δ*-phenyl-*n*-butane-*αβδ*- or -*αγδ*-tricarboxylic acid, respectively. The second *acid* (I) was therefore synthesised from ethyl propane-*ααγ*-tricarboxylate and ethyl phenylbromoacetate,



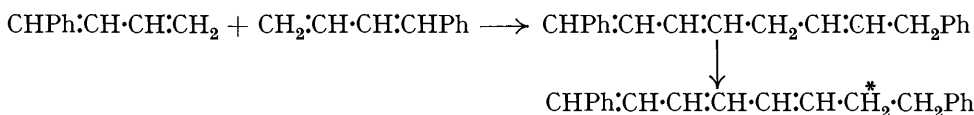
but was different from the acid obtained by oxidation. The first acid was synthesised by Duff and Ingold (*J.*, 1934, 87), but this also was not identical with the acid in question.

It was then found that the acid is the *αβγ*-tricarboxylic acid (II) synthesised by Duff and Ingold (*loc. cit.*; compare Rydon, this vol., p. 421; Ingold and Rydon, *ibid.*, p. 857). It therefore follows that the dimeric hydrocarbon is 2-benzyl-1-styryl-*Δ*<sup>3</sup>-cyclopentene (III), oxidation occurring as follows :



\* Part III: Bergmann and Taubadel, *Ber.*, 1932, **65**, 463.

The outcome is unexpected and appears to prove that the dimerisation follows a course similar to that of simple ethylenes (see above), involving the formation of an open-chain hydrocarbon by displacement of one hydrogen atom of the methylene group (1 : 4-addition). Migration of one of the double bonds leads to the formation of a conjugated system in which the one of the hydrogen atoms marked with an asterisk is activated by the conjugated system and may migrate with the formation of the five-membered ring. The formation of dipentene from isoprene probably follows the same sequence : acyclic dimerisation by displacement of one hydrogen atom (1 : 4-addition), allylic rearrangement, and cyclisation.



The above formulation of the phenylbutadiene dimerisation may appear anomalous in view of the fact that the migrating hydrogen atom does not form a methyl group, as is usual in the dimerisation of simple ethylenes (see above); but possibly the phenylated carbon atom exerts an attraction on the displaced hydrogen, for phenylated ethylenes combine readily with sodium (see Schlenk and Bergmann, *Annalen*, 1930, **479**, 42).

#### EXPERIMENTAL.

The dimeric phenylbutadiene was prepared according to Klages and Riiber (*Ber.*, 1904, **37**, 2274); b. p. 210—212°/12 mm.

*δ-Phenyl-n-butane-αγδ-tricarboxylic Acid.*—The propanetricarboxylic ester was prepared by the usual method, the following quantities being boiled under reflux for 3 hrs. : ethyl malonate (98 g.), sodium (15 g.), alcohol (250 c.c.), ethyl β-chloropropionate (90 g.); it had b. p. 160—162°/13 mm. (Found : C, 55.4; H, 7.5. Calc. for C<sub>12</sub>H<sub>20</sub>O<sub>6</sub> : C, 55.4; H, 7.7%). (It is not necessary to start with the bromo- or iodo-propionate, as described in the literature.) This ester (66 g.) was added to a suspension of sodium powder (5.8 g.) in benzene (200 c.c.); after solution of the metal, ethyl phenylbromoacetate (45 g.) was introduced, the mixture refluxed for 3 hours, treated with water, and concentrated, and the residue distilled; b. p. 230—234°/16 mm. The slightly yellow oil crystallised after some time; m. p. 42° (Found : C, 62.5; H, 7.1. Calc. for C<sub>22</sub>H<sub>30</sub>O<sub>8</sub> : C, 62.6; H, 7.1%). The ester (10 g.) was heated with 18% methyl-alcoholic potassium hydroxide solution (300 c.c.) for 3 hours, the methyl alcohol distilled off, the residue dissolved in water and twice extracted with ether, and the solution acidified. The crude acid isolated by extraction with ether and evaporation was a mixture (1 : 2) of the tri- and the original tetracarboxylic acid. Decarboxylation was accomplished by 1 hr.'s heating at 130°; the product crystallised on trituration with benzene and was recrystallised from a large quantity of water; m. p. 163—165° (slight decomp.) (Found : C, 58.5; H, 5.8. C<sub>13</sub>H<sub>14</sub>O<sub>6</sub> requires C, 58.6; H, 5.3%).

*δ-Phenyl-n-butane-αβγ-tricarboxylic Acid.*—The condensation of ethyl sodiobenzylmalonate with ethyl fumarate (Duff and Ingold, *loc. cit.*) gives poor results; it is better to combine ethyl sodiomalonate (42 g. of malonate) with ethyl fumarate (45 g.) and then to benzylate 66 g. of the resulting tetracarboxylic ester by means of 5 g. of sodium and 25 g. of benzyl chloride in 100 c.c. of toluene. One of the four carbethoxy-groups is split off, and the oily product has the composition of *ethyl δ-phenyl-n-butane-αβγ-tricarboxylate*. Both methods lead to a mixture of two diastereoisomeric esters of different b. p. (220—230°/19 mm.; 230—240°/9 mm.) (Found : C, 64.6; H, 7.3, and C, 65.8; H, 7.7, respectively. C<sub>19</sub>H<sub>26</sub>O<sub>6</sub> requires C, 65.2; H, 7.4%). Hydrolysis of the higher-boiling fraction gave the acid, m. p. 168° (Ingold and Duff give m. p. 165°); whereas hydrolysis of the lower-boiling fraction afforded a small quantity of the stereoisomeric acid (see Duff and Ingold), which was identical (m. p. and mixed m. p.) with the acid, C<sub>13</sub>H<sub>14</sub>O<sub>6</sub>, prepared from dimeric phenylbutadiene according to Lebedev's procedure (*loc. cit.*).

The foregoing experiments were partly carried out together with Dr. Hans Taubadel in the laboratory of the Friedrich Wilhelm University, Berlin.