48. *The Action of Selenium on Compounds containing Quaternary Carbon Atoms.*

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As a corollary to the work on the dehydrogenation of compounds containing angular methyl groups (J., 1935, 735) it was of particular interest to examine the action of selenium at high temperatures (280—360°) on compounds containing quaternary carbon atoms.

The best-authenticated apparent exception to the useful head-to-tail isoprene polymerisation rule up to and including the diterpenes is abietic acid. Even in this case there is dispute as to whether this acid itself is ever a primary product, being ordinarily obtained from lævopimaric and *pro*abietic acids by treatment with acetic acid. If instead of the *iso*propyl substituent postulated from selenium degradation and other evidence at position 7 in abietic acid (I), the primary acids have either *gem**-methylethyl or -methylvinyl substituents attached, the rule holds as far as the diterpenes. It may be argued that, as the primary acids and also abietic acid condense with maleic anhydride, they have conjugated double bonds in ring (III) the possibility of a vinyl group at position 7 thus being ruled out, but such a condensation is not final proof of conjugation (compare Ruzicka, *Helv. Chim. Acta*, 1935, **18**, 219).

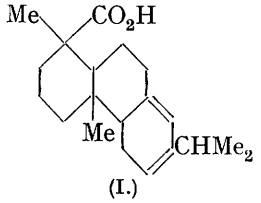
According to Kraft (*Annalen*, 1936, **524**, 1) the action of ozone on lævopimaric acid gives no formaldehyde, and although Ruzicka (*Helv. Chim. Acta*, 1925, **8**, 637) examined the action of ozone on abietic acid and its methyl ester, no mention is made of the production of formaldehyde. Under the conditions used by Clemo and Macdonald (J., 1935, 1294) abietic acid gives formaldehyde, but in amount insufficient to make certain of the presence of the $:CH_2$ group; and no lævopimaric acid is available for trial.

In the tetralin series, 1 : 1 : 6-trimethyltetralin (II) has been dehydrogenated by Ruzicka and Rudolph (*Helv. Chim. Acta*, 1927, **10**, 915), using sulphur, and by ourselves (*loc. cit.*), using selenium. In each case it was smoothly converted into 1 : 6-dimethylnaphthalene.

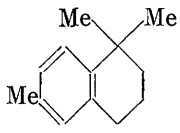
It was therefore decided to study in the first instance the dehydrogenation of 2 : 2-dialkyltetralins to test whether a *gem*-methylethyl group lost one of these groups or was

* The term *gem* is strictly applicable only to two like groups attached to the same atom, but its use here is extended to include two unlike groups.

converted into an *iso*propyl group during the process of selenium dehydrogenation. An αα-dialkylsuccinic anhydride was condensed with benzene in the presence of aluminium chloride, and the resulting β-*benzoyl-αα-dialkylpropionic acid* (III) reduced to the corresponding *benzylpropionic acid* (IV). Ring closure and reduction gave the dialkyltetralin (V).



(I.)



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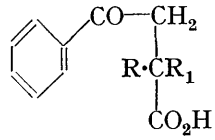
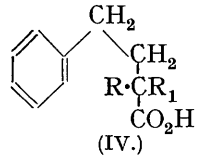
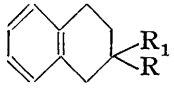


(III.)

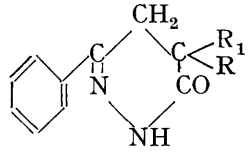
In this manner 2 : 2-*dimethyl-* and 2-*methyl*-2-*ethyl-tetralins* were synthesised. By analogy with the condensation of α-methylsuccinic anhydride and benzene (Oppenheim, *Ber.*, 1901, **34**, 4227; Meyer and Stamm, *ibid.*, 1923, **56**, 1424) the condensations would be expected to yield the αα-dialkyl acids (III) in preference to the ββ-dialkyl compounds. This is supported by the fact that, though the keto-acids (III) condense readily with hydrazine to give 6-*keto*-3-*phenyl*-5 : 5-*dialkyltetrahydropyridazines* (VI), the *tetralones* produced by ring closure of the acids (IV) would not react with hydrazine, hydroxylamine or semicarbazide, owing presumably to the blocking of the keto-group by the two adjacent alkyl groups.



(IV.)



(V.)



(VI.)

The dimethyl- and the methylethyl-tetralin (V; R = Me, R_1 = Me or Et) were obtained as colourless stable oils, but attempts to dehydrogenate them failed, prolonged treatment with selenium at 280—360° being without effect. This result is, at present, unexplained. That it is not due solely to the volatility of the hydrocarbon is clear, as both these compounds and 1 : 1 : 6-trimethyltetralin (II) have boiling points of the same order (*ca.* 130°/30 mm.). The above results give another instance of anomalous behaviour in selenium dehydrogenation and further investigation on these lines may serve to shed light on the mechanism of the reaction.

Experimental.

2 : 2-*Dimethyltetralin* (V; R and R_1 = Me).—β-*Benzoyl-αα-dimethylpropionic acid* (III; R and R_1 = Me). αα-Dimethylsuccinic anhydride (6·2 g.) (Higson and Thorpe, J., 1906, **89**, 1465) was added slowly to powdered aluminium chloride (13 g.) in dry benzene (30 c.c.), the reaction being controlled by cooling and, after 1 hour, completed on the water-bath (1—2 hours). The mixture was poured into ice-cold 5% hydrochloric acid, the excess of benzene removed on the water-bath under reduced pressure, and, when cold, the solid product filtered off. The *keto-acid* obtained was practically pure and crystallised from hot alcohol in prisms, m. p. 173° (Found : C, 69·9; H, 6·95. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·8%).

6-*Keto*-3-*phenyl*-5 : 5-*dimethyltetrahydropyridazine* (VI, R and R_1 = Me), prepared by heating the above keto-acid with half its weight of hydrazine hydrate on the water-bath for 1 hour, was washed with water and recrystallised from hot alcohol, forming felty colourless needles, m. p. 167—168° (Found : C, 71·6; H, 7·1. $C_{12}H_{14}ON_2$ requires C, 71·3; H, 6·9%).

β-*Benzyl-αα-dimethylpropionic acid* (IV, R and R_1 = Me). The above keto-acid (10 g.) was refluxed with amalgamated zinc (50 g.) and concentrated hydrochloric acid (10 c.c.) for 15 hours, the *product* extracted with ether, dried, and filtered from high-melting by-products, and the solvent removed. The residue was distilled; it solidified instantly in the receiver and on recrystallisation from light petroleum formed fine needles (6 g.), m. p. 97°, b. p. 140—150°/0·2 mm. (Found : C, 74·7; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

2 : 2-*Dimethyl*-1-*tetralone*.—The above acid (5 g.) was covered with 80% sulphuric acid, kept overnight, and then heated for ½ hour on the water-bath, care being taken that no evolution of

sulphur dioxide occurred. The red solution was diluted with water and extracted with ether, and the extract washed with bicarbonate solution until neutral. It was then dried and distilled, giving the pure *ketone* (1·9 g.), b. p. 137°/15 mm. (Found : C, 82·4; H, 8·2. $C_{12}H_{14}O$ requires C, 82·7; H, 8·0%).

The ketone (1·5 g.) was refluxed with amalgamated zinc (15 g.) and concentrated hydrochloric acid (7 c.c.) for 12 hours, more acid (3 c.c.) then added, and refluxing continued for 3–4 hours. The product was extracted with ether and dried, the solvent removed, and the residue distilled. The pure 2 : 2-*dimethyltetralin* was redistilled over sodium and obtained as a colourless fragrant oil (0·9 g.), b. p. 104°/12 mm. (Found : C, 89·8; H, 9·7. $C_{12}H_{16}$ requires C, 90·0; H, 10·0%).

Attempted Dehydrogenation of 2 : 2-*Dimethyltetralin.*—The hydrocarbon (0·9 g.) in a 3 c.c. flask with a sealed-on air-condenser was refluxed with selenium (2 g.) for 15 hours at 280°. The heating was then continued at 300—320° for 12 hours and at 340—360° for a further 10 hours. The product was extracted with chloroform and filtered, the solvent removed, and the residue taken up with light petroleum. It was again filtered from precipitated selenium (charcoal) and refluxed for 2 hours over sodium, the solvent removed, and the residue distilled. It consisted entirely of unchanged material, b. p. 104—106°/12 mm. (Found : C, 89·8; H, 10·0%).

2-*Methyl*-2-*ethyltetralin* (V; R = Me, R_1 = Et).—β-*Benzoyl*-α-*methyl*-α-*ethylpropionic acid* (III; R = Me, R_1 = Et), prepared from α-methyl-α-ethylsuccinic anhydride (Higson and Thorpe, J., 1906, **89**, 1455) (4·8 g.) and aluminium chloride (7·2 g.) in benzene (18 c.c.) as in the case of the dimethyl compound, crystallised from alcohol in prisms, m. p. 94—95° (Found : C, 70·75; H, 7·2. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·3%).

6-*Hydroxy*-3-*phenyl*-5-*methyl*-5-*ethyltetrahydropyridazine* (VI; R = Me, R_1 = Et), prepared in a similar manner to the dimethyl compound (above), crystallised from petroleum (b. p. 80—100°) in stout needles or from dilute alcohol in prisms, m. p. 108° (Found : C, 72·1; H, 7·6. $C_{13}H_{16}ON_2$ requires C, 72·2; H, 7·4%).

β-*Benzyl*-α-*methyl*-α-*ethylpropionic acid* (IV; R = Me, R_1 = Et), prepared from the above keto-acid by reduction in the same manner as the dimethyl keto-acid (above), was distilled and then recrystallised from light petroleum, forming needles, m. p. 63° (Found : C, 75·9; H, 8·6. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

2-*Methyl*-2-*ethyl*-1-*tetralone* was obtained in the same way as the dimethyl compound. It was isolated as a colourless oil, b. p. 140°/13 mm. (Found : C, 83·0; H, 8·5. $C_{13}H_{16}O$ requires C, 83·0; H, 8·5%), and on reduction gave 2-*methyl*-2-*ethyltetralin* (V; R = Me, R_1 = Et), which was obtained as a colourless oil, b. p. 118°/20 mm. (Found : C, 89·9; H, 10·2. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%).

Attempted Dehydrogenation of 2-*Methyl*-2-*ethyltetralin.*—The hydrocarbon (0·9 g.) was refluxed with selenium as before, for, in all, 48 hours at 280—360°. The product was extracted with light petroleum (b. p. 60—80°) and refluxed with sodium for ½ hour on the water-bath, and the solvent removed, yielding 0·62 g. of a colourless oil. It was distilled into three fractions : 78°/0·1 mm. (0·12 g.); 80—82°/0·1 mm. (0·36 g.); 82°/0·1 mm. (0·11 g.). None of these fractions yielded a picrate and the highest fraction gave the following analysis (Found : C, 90·3; H, 10·1. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%. $C_{13}H_{16}$ requires C, 90·7; H, 9·3%).

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