425. *Resin Acids. Part II. Synthesis of 1-Methyl-7-*isopropyl*phenanthrene (Retene).*

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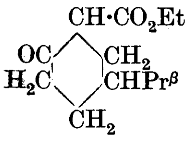
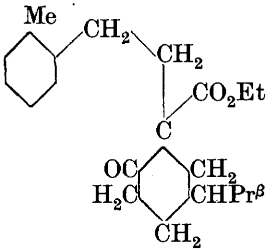
Ethyl γ-iso*propylpimelate* on treatment with " molecular " sodium yielded *ethyl* 4-iso*propyl*cyclo*hexan*-1-*one*-2-*carboxylate* (I), the potassio-derivative of which condensed with β-*o*-tolylethyl bromide with the production of *ethyl* 4-iso*propyl*-2-(β-o-*tolylethyl*)cyclo*hexan*-1-*one*-2-*carboxylate* (II). This on reduction with sodium amalgam furnished the expected *hydroxy-ester* (III), which was successively treated with phosphoric oxide and selenium exactly as described in Part I (this vol., p. 2521). 1-Methyl-7-*iso*propylphenanthrene thus produced was indistinguishable from retene obtained from abietic acid.

This synthesis and the earlier one by Haworth, Letsky, and Mavin (*ibid.*, p. 1791) establish beyond doubt that in abietic acid the methyl and the *iso*propyl group are in positions 1 and 7 respectively.

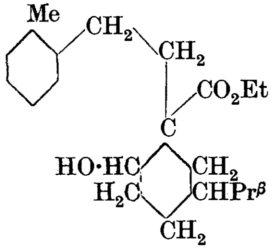
The position of the carboxyl group in abietic acid remains to be determined. Since Haworth and his collaborators have shown that 1 : 4-dimethyl-7-*iso*propylphenanthrene is not identical with methylretene (*loc. cit.*, p. 1787), the carboxyl group is not in position 4. Vocke has advanced (*Annalen*, 1932, **497**, 255) a new formula for abietic acid in which the carboxyl group occupies position 1, along with the methyl group. In view of the well-known difficulty of esterifying abietic acid and the very slow rate of hydrolysis of its ester (unfinished work by us), Vocke's formula must be preferred to the modified formula of Ruzicka (*Helv. Chim. Acta*, 1931, **14**, 545) in which the carboxyl group is in position 2. It seems to us that the synthesis of methylretene will not have any direct bearing on the question of the position of the carboxyl group in abietic acid. We are therefore trying to synthesise the acids $C_{12}H_{18}O_6$ and $C_{11}H_{16}O_6$, the two most important degradation products of abietic acid (Ruzicka and collaborators, *Helv. Chim. Acta*, 1925, **8**, 637 ; Levy, *Ber.*, 1929, **62**, 2501 ; Vocke, *loc. cit.*, p. 258), in order to throw further light on the analytical experiments of Vocke.



(I.)



(II.)



(III.)

EXPERIMENTAL.

Ethyl γ-iso*Propylpimelate*.—Ethyl γ-*iso*propylidenepimelate (Perkin and Simonsen, J., 1907, **91**, 1743) (25 g.) was dissolved in 95% EtOH (50 c.c.) and shaken with platinum oxide (Adams and Shriner, *J. Amer. Chem. Soc.*, 1923, **45**, 2171) (0·2 g.) in H. Much heat was evolved and hydrogenation was complete in a few hr.; it was necessary to revive the catalyst once by treatment with O. *Ethyl* γ-iso*propylpimelate* was obtained as a colourless liquid with an ethereal odour, b. p. 170°/27 mm. (Found : C, 64·9; H, 10·1. $C_{14}H_{26}O_4$ requires C, 65·1 ; H, 10·1%). It did not absorb Br in $CHCl_3$.

Ethyl 4-iso*Propyl*cyclo*hexan*-1-*one*-2-*carboxylate* (I).—Finely divided Na (3·5 g.) under dry C_6H_6 was treated with ethyl γ-*iso*propylpimelate (19 g.) diluted with 2 vols. of C_6H_6. Heat was applied to start the reaction and again later to complete the dissolution of the Na. The product was decomposed by ice and dil. HCl, and the oily layer washed (Na_2CO_3 aq.), dried, and distilled; b. p. 130—132°/10 mm. (yield, 50%) (Found : C, 67·5; H, 9·6. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·4%). *Ethyl* 4-iso*propyl*cyclo*hexan*-1-*one*-2-*carboxylate* has a pleasant odour, gives a deep violet colour with alc. $FeCl_3$, and yields on hydrolysis 4-*iso*propyl*cyclo*hexan-1-one (semicarbazone, m. p. 190—191° ; Cahn, Penfold, and Simonsen, J., 1931, 1369, give m. p. 188—189°).

Ethyl 4-iso*Propyl*-2-(β-o-*tolylethyl*)cyclo*hexan*-1-*one*-2-*carboxylate* (II).—The potassio-derivative (K 2 g., keto-ester 10·5 g., dry C_6H_6 50 c.c.) and *β*-*o*-tolylethyl bromide (10 g.) were refluxed for 28 hr. The *ester* (II) was a colourless viscous liquid (7 g.), b. p. 195—197°/2 mm. (Found: C, 76·3; H, 9·3. $C_{21}H_{30}O_3$ requires C, 76·4; H, 9·1%).

Ethyl 4-iso*Propyl*-2-(*β*-o-*tolylethyl*)cyclo*hexan*-1-*ol*-2-*carboxylate* (III).—The foregoing keto-ester was twice reduced with a large excess of Na–Hg, and the *hydroxy-ester* obtained as a very viscous liquid, b. p. 200—205°/2 mm. (Found: C, 75·3; H, 9·2. $C_{21}H_{32}O_3$ requires C, 75·9; H, 9·6%).

1-*Methyl*-7-iso*propylphenanthrene*.—The hydroxy-ester (4 g.) was heated with P_2O_5 (10 g.), and the product (2 g.) dehydrogenated with Se (5 g.) at 300—340° for 24 hr. The brown oil obtained was converted into the picrate, and the hydrocarbon regenerated with NH_3 aq. and twice crystallised from EtOH (charcoal), forming colourless plates, m. p. and mixed m. p. (with retene) 98—99° (Found: C, 92·4; H, 7·7. Calc.: C, 92·3; H, 7·7%). The picrate prepared from the pure hydrocarbon crystallised from EtOH in orange-yellow needles, m. p. and mixed m. p. (with retene picrate) 123—124°.

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