## **240.** *The Action of Selenium at High Temperatures on* gem-*Methylethyl Groups.*

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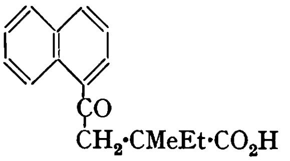
It has been shown that in the selenium dehydrogenation of hydroaromatic compounds containing *gem*-methylethyl groups, the ethyl group is eliminated.

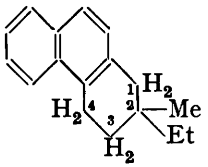
IN a previous communication (J., 1937, 255) it was pointed out that, if the group occupying the 7-position in abietic acid were a *gem*-methylethyl group instead of the postulated *iso*-propyl group, this acid would follow the isoprene " head to tail " rule instead of being a notable exception. If this were so, then such a group must be converted into an *iso*propyl group by the action of selenium at high temperatures, since retene is obtained in this way from abietic acid. The literature appears to contain no record of selenium dehydrogenation of compounds containing such groups and therefore it was decided to investigate this problem in order to determine whether the necessary rearrangement occurs or whether one of the groups is eliminated, leading to either an ethyl- or a methyl-substituted hydrocarbon.

β-1-*Naphthoyl-α-methyl-α-ethylpropionic acid* (I), obtained by the condensation of naphthalene and α-methyl-α-ethylsuccinic acid, was reduced by the Clemmensen method to γ-1-*naphthyl-α-methyl-α-ethylbutyric acid*, which on ring closure gave 1-*keto*-2-*methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.

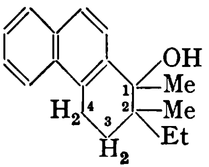
2-*Methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene* (II) and 1-hydroxy-1 : 2-dimethyl-2-ethyl-1 : 2 : 3 : 4-tetrahydrophenanthrene (III) were obtained from this cyclic ketone by Clemmensen reduction and condensation with methylmagnesium iodide, respectively.



(I.)



(II.)



(III.)

Both these compounds on selenium dehydrogenation eliminated the ethyl group, (II) giving 2-methylphenanthrene and (III) 1 : 2-dimethylphenanthrene. Thus it is apparent that there cannot be a *gem*-methylethyl group occupying the 7-position of abietic acid, especially as in both the above compounds the group under investigation occupies the same position as it would, if present, occupy in abietic acid.

From the condensation of naphthalene and α-methyl-α-ethylsuccinic acid, only one compound has been isolated so far and not two as expected (J., 1932, 1125). That condensation occurs in the 1- and not in the 2-position and gives (I) instead of one of the three other possibilities is proved by the result of the selenium dehydrogenation of (II) and (III). Attempts to prove the 1-naphthoyl structure by fusion with potassium hydroxide were fruitless, fission occurring between the keto-group and the naphthalene nucleus.

## EXPERIMENTAL.

*α-Methyl-α-ethylsuccinic Anhydride* (J., 1906, **89**, 1467).—Methyl ethyl ketone cyanohydrin was condensed with ethyl cyanoacetate in alcoholic sodium ethoxide solution, giving ethyl αβ-dicyano-β-methyl-β-ethylpropionate in 40% yield. This was hydrolysed quantitatively to α-methyl-α-ethylsuccinic acid (m. p. 104°), which was converted in 80% yield into its anhydride, a liquid, b. p. 130°/12 mm., by treatment with acetyl chloride.

β-1-*Naphthoyl-α-methyl-α-ethylpropionic Acid* (I).—Naphthalene (15 g.) and α-methyl-α-ethylsuccinic anhydride (7·5 g.) were added gradually with shaking to a cold solution of aluminium chloride (18 g.) in nitrobenzene (38 c.c.). After 12 hours, dilute hydrochloric acid was added and the excess of naphthalene and the nitrobenzene were removed by steam-distillation. The residue was cooled, washed with water, dissolved in sodium carbonate solution, filtered, and acidified (hydrochloric acid). The hard cake of crude acid was washed with water and crystallised from glacial acetic acid, giving small prisms (6·8 g.), m. p. 132—133°. From the mother-liquor a further 3·5 g. of impure acid, m. p. 115—130°, were obtained. The combined samples gave the pure *acid* in small prisms (7 g.), m. p. 135—136°, from methyl alcohol (Found: C, 75·5; H, 6·8. $C_{17}H_{18}O_3$ requires C, 75·6; H, 6·7%).

γ-1-*Naphthyl-α-methyl-α-ethylbutyric Acid*.—β-1-Naphthoyl-α-methyl-α-ethylpropionic acid (I) (1 g.) was boiled with amalgamated zinc (5 g.) and concentrated hydrochloric acid (5 c.c.) for 24 hours. The product was diluted with water, ether-extracted, dried, and distilled. The *acid* was obtained as a colourless viscous liquid (0·7 g.), b. p. 190°/1 mm., which did not solidify (Found: C, 79·4; H, 7·8. $C_{17}H_{20}O_2$ requires C, 79·7; H, 7·8%).

1-*Keto*-2-*methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—A mixture of the preceding acid (1 g.) with water (2 c.c.) and concentrated sulphuric acid (6 c.c.) was warmed on the water-bath for 1 hour with continuous stirring. The mixture was then cooled and, after dilution with water, ether-extracted. The extracts were washed with water to remove sulphonated products and dried over anhydrous potassium carbonate. Distillation gave the *ketone* as a colourless oil (0·6 g.), b. p. 170°/1 mm., which did not solidify (Found : C, 85·5; H, 7·4. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%).

The *picrate* crystallised from methyl alcohol in light yellow needles, m. p. 85—86° (Found : C, 59·3; H, 4·4. $C_{17}H_{18}O,C_6H_3O_7N_3$ requires C, 59·1; H, 4·5%).

2-*Methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The cyclic ketone (1 g.), boiled for 24 hours with amalgamated zinc (5 g.) and concentrated hydrochloric acid (5 c.c.), gave the required *hydrocarbon*, which was ether-extracted, dried, and distilled. It was a colourless oil, b. p. 160°/1 mm., which was much less viscous than the original ketone (Found : C, 90·5; H, 9·0. $C_{17}H_{20}$ requires C, 91·0; H, 9·0%).

The *picrate* was obtained from methyl alcohol in yellow needles, m. p. 100—101° (Found : C, 60·9; H, 5·5. $C_{17}H_{20},C_6H_3O_7N_3$ requires C, 60·9; H, 5·1%).

*Selenium Dehydrogenation of* 2-*Methyl*-2-*ethyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*.—The tetrahydrophenanthrene (0·3 g.) was heated with selenium (0·5 g.) at 280—300° for 24 hours and then at 320° for a further 24 hours. The product was extracted while hot with chloroform, the solution filtered and evaporated, and the residue dissolved in ether and filtered. Distillation of the product over sodium gave a solid, which crystallised from methyl alcohol in colourless needles, m. p. 55—56° (the recorded m. p. of 2-methylphenanthrene is 55—56°; J., 1932, 1132) (Found : C, 93·7; H, 6·7. Calc. for $C_{15}H_{12}$ : C, 93·7; H, 6·3%).

The picrate crystallised from methyl alcohol in yellow needles, m. p. 115—116° (Haworth, J., 1932, 1133, gives 118°).

*Condensation of* 1-*Keto*-2-*methyl*-2-*ethyl*-1 : 2 : 3 :4-*tetrahydrophenanthrene with Methylmagnesium Iodide, and Selenium Dehydrogenation of the Product*.—A solution of the cyclic ketone (1 g.) in ether (10 c.c.) was added slowly to an ice-cold ethereal solution of methylmagnesium iodide prepared from magnesium (0·2 g.). The mixture was kept at room temperature for 12 hours, refluxed for an hour, and decomposed with ice and dilute sulphuric acid. The ethereal layer was separated, dried, and distilled, giving a colourless oil (0·9 g.), b. p. 150—160°/1 mm. As some dehydration occurred on distillation, no satisfactory analyses were obtained. An unstable picrate, m. p. 83—84°, was obtained in yellow needles, but this decomposed on drying.

The oil (0·2 g.) on selenium dehydrogenation as before gave 1 : 2-dimethylphenanthrene (0·1 g.), which crystallised in colourless plates, m. p. 139—140°, from methyl alcohol. Buten andt, Weidlich, and Thompson (*Ber.*, 1933, **66**, 601) reported the m. p. as 140° (Found : C, 93·6; H, 6·6. Calc. for $C_{16}H_{14}$ : C, 93·3; H, 6·7%).

The picrate was obtained in orange needles, m. p. 148°, from methyl alcohol (Butenandt, Weidlich, and Thompson reported orange needles, m. p. 148°).

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