

ZIERONE.

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Some years ago one of us (Penfold, *J. Proc. Roy. Soc. N.S.W.*, 1926, 60, 104) separated from the essential oil of *Zieria macrophylla* (Bonpland) a cyclic ketone, zierone. Analysis of the ketone (and of the semicarbazone) appeared to show that it was isomeric with irone and that it had the formula $C_{13}H_{20}O$. A reconsideration of its physical constants suggested to us that this formula was incorrect, and we have therefore made a further study of the ketone. Although the analytical figures (see p. 202) for a new specimen of a ketone, which had been regenerated from its semicarbazone by hydrolysis with oxalic acid and distillation in steam, gave figures in fair accord with those previously recorded, the analysis of the semicarbazone and of the 2:4-dinitrophenylhydrazone have shown conclusively that zierone cannot have the formula previously assigned to it, but that it must be a sesquiterpene ketone, $C_{15}H_{22}O$, isomeric with eremophilone (*J.C.S.*, 1932, 2744; *J. Proc. Roy. Soc. N.S.W.*, 1932, 66, 420). It may be noted that

satisfactory analytical figures could not be obtained for this ketone and seems to us probable that slight oxidation or hydration occurs during the prolonged steam distillation involved in the regeneration of these ketones from their semicarbazones and the impurity so introduced cannot later be eliminated.

Partly owing to the difficulty in obtaining the ketone in sufficient quantity, we have not succeeded in determining its constitution, but we consider it to be tricyclic with one ethylenic linkage for the following reasons: (i) titration with benzoylhydroperoxide shows the presence of only one double bond; (ii) reduction with sodium and alcohol results in the formation of an alcohol, *zierol*, $C_{15}H_{24}O$, from which zierone can be regenerated by oxidation with chromic acid; (iii) on catalytic hydrogenation approximately two molecules of hydrogen are absorbed, but the product is a mixture containing hydrocarbon, so that addition does not occur only at the ethylenic linkage.

Zierone has a $-CH_2$ group adjacent to the carbonyl group as it yields a liquid hydroxymethylene derivative, characterised by the preparation of a crystalline 2:4-*dinitrophenylhydrazone*, m.p. $155-157^\circ$. The ethylenic linkage is not in the $\alpha\beta$ - position to the carbonyl group since it is not reduced by sodium in ethyl alcoholic solution, and in agreement with this is the fact that the ketone is not oxidised by hydrogen peroxide in the presence of alkali. The ethylenic linkage is almost certainly present as a part of a ring system as on ozonolysis only traces of formaldehyde and no acetone are formed. Unfortunately, the decomposition products of the ozonide did not lend themselves to purification. Zierone is remarkably resistant to oxidation with O—July 5, 1933.

potassium permanganate, and this agrees well with the suggestion that it is tricyclic.

The dehydrogenation with selenium of the hydrocarbon obtained by the dehydration of zierol yields an "azulene" resembling in its properties the Se-guaiazulene prepared by Ruzicka and Haagen-Smith (*Helv. Chim. Acta*, 1931, 14, 1104) from the hydrocarbon guaiene. The determination of the structure of this azulene would probably throw light on that of zierone. The molecular refraction of the ketone, $[R_L]_D = 66.93$, is high, and suggests conjugation of a cyclopropane ring both with the ethylenic linkage and the carbonyl group.

EXPERIMENTAL.

The ketone was purified through its semicarbazone (see below) from which it was regenerated by hydrolysis with oxalic acid and distillation in steam. The freshly distilled ketone, b.p. 147–149°/18 mm., was a somewhat viscid, colourless oil, which became yellow on keeping. Analysis showed it to be impure.

3.56 mgm. gave 10.54 mgm. CO_2 and 2.98 mgm. H_2O .

C = 80.8, H = 9.3.

3.67 mgm. gave 10.90 mgm. CO_2 and 3.12 mgm. H_2O .

C = 80.9, H = 9.4.

$\text{C}_{15}\text{H}_{22}\text{O}$ requires C = 82.6, H = 10.1%.

Zierone is not attacked by hydrogen peroxide in alkaline solution, whilst in acetone solution it was stable to potassium permanganate even on boiling. When treated with benzoylhydroperoxide in chloroform solution 0.66 atom of oxygen was taken up in one day at 2; after two days 0.91 atom and after seven days 0.95 atom had been taken up. Zierone did not react with maleic anhydride, whilst with hydrogen bromide it gave an extremely unstable hydrobromide.

The semicarbazone crystallised from methyl alcohol in prisms, m.p. 182°.

4.085 mgm. gave 10.42 mgm. CO₂ and 3.485 mgm. H₂O.

C = 69.5, H = 9.5.

4.97 mgm. gave 12.73 mgm. CO₂ and 4.185 mgm. H₂O.

C = 69.8, H = 9.4.

C₁₆H₂₅ON₃ requires C = 69.8, H = 9.1%.

The 2:4-dinitrophenylhydrazone crystallised from alcohol in glistening terracotta needles, m.p. 95–97°.

3.50 mgm. gave 8.175 mgm. CO₂ and 2.07 mgm. H₂O.

C = 63.7, H = 6.6.

C₂₁H₂₆O₄N₄ requires C = 63.6, H = 6.6%.

Reduction of Zierone.

(i) *Catalytic.* The ketone (6.7 g.) in ethyl alcohol (20 c.c.) containing Pd-norite (1 g.; Pd 10%) was shaken with hydrogen when 1,400 c.c. (1.93 moles.) were absorbed. After filtration the alcohol was removed by distillation, the residual oil dissolved in ether, the ethereal solution dried and evaporated. The oil so obtained distilled irregularly from 110–145°/15 mm. and it only reacted partially with semicarbazide acetate yielding a gummy semicarbazone. The oxime was an oil. As mentioned on p. 204, the hydrogenation product contained some hydrocarbon, but we were not successful in separating a homogeneous product.

(ii) *With Sodium and Ethyl Alcohol.* *Zierol.* The ketone (12 g.) in ethyl alcohol (400 c.c.) was treated in boiling solution with sodium (40 g.). After solution of the sodium was complete the ethyl alcohol was removed in steam, the reduction product dissolved in ether, the ethereal solution dried over potassium carbonate and the solvent removed.

The residual oil distilled at 151–152°/17 mm., n_D^{20} 1.5094, $[\alpha]_{5461} + 37.4^\circ$ (in methyl alcohol, $c = 8.5$).

3.42 mgm. gave 10.25 mgm. CO_2 and 3.48 mgm. H_2O .

C = 81.7, H = 11.4.

3.39 mgm. gave 10.15 mgm. CO_2 and 3.37 mgm. H_2O .

C = 81.6, H = 11.1.

$\text{C}_{15}\text{H}_{24}\text{O}$ requires C = 81.8, H = 10.9%.

Zierol was a colourless viscid oil, which did not yield any crystalline derivatives. On oxidation with chromic acid in acetic acid solution *zierone* was regenerated (semicarbazone, m.p. 182°).

Hydroxymethylene-zierone.

To a well cooled solution of the ketone (5 g.) in ether (50 c.c.) containing finely divided sodium (0.58 g.) in suspension amyl formate (3 g.) was gradually added. The sodium slowly dissolved and after standing overnight ice was added to the yellow ethereal solution. The brown alkaline layer was separated, extracted twice with ether to remove neutral products and made just acid with acetic acid, when an oil separated. This was dissolved in ether, the ether separated, dried and evaporated when a viscid oil (3 g.) remained. It gave in alcoholic solution an intense purple coloration with ferric chloride. As hydroxymethylene-zierone did not crystallise, it was converted into the 2:4-dinitrophenylhydrazone, which separated from alcohol in brown plates, frequently twinned, m.p. 155–157°.

3.67 mgm. gave 8.38 mgm. CO_2 and 2.0 mgm. H_2O .

C = 62.3, H = 6.1.

3.959 mgm. gave 9.01 mgm. CO_2 and 2.05 mgm. H_2O .

C = 62.0, H = 5.8.

$\text{C}_{22}\text{H}_{26}\text{O}_5\text{N}_4$ requires C = 62.0, H = 6.1%.

Dehydrogenation of Zierol.

Zierol was dehydrated by digestion with formic acid, and the resulting hydrocarbon (7 g.) was heated with selenium (11 g.) at 250–280° for forty-four hours. Extraction with ether gave a violet coloured oil, b.p. 135–165°/15 mm. This was dissolved in three times its volume of ligroin (40–60°) and gently shaken with phosphoric acid (d. 1.7). The phosphoric acid layer acquired a reddish-brown colour, whilst the ligroin became brownish-yellow. The phosphoric acid solution was separated, treated with crushed ice and the violet oil which separated was dissolved in ether, the ethereal solution washed with sodium hydroxide solution, water, dried and the ether evaporated. The residual oil was dissolved in alcohol and mixed with a hot alcoholic solution of picric acid when, on standing, black needles of azulene picrate, m.p. 110–111°, were deposited (compare Ruzicka and Haagen-Smit, *loc. cit.*). The quantity of picrate obtained was insufficient for complete purification and identification. The ligroin solution (see above) gave on evaporation an oil which did not yield a crystalline picrate.

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