76. *The Preparation of Acenaphthylene Glycol and Some Condensation Reactions of Naphthalene-1 : 8-dialdehyde.*

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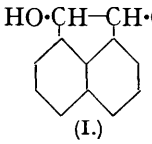
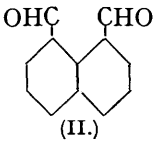
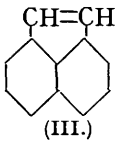
Criegee, Kraft, and Rank (*Annalen*, 1933, **507**, 159) have shown that acenaphthylene glycol (I) is oxidised by lead tetra-acetate to naphthalene-1 : 8-dialdehyde (II). The usefulness of this reaction depends on the availability of the glycol, hitherto obtainable only from the difficultly accessible acenaphthylene (III). A more promising source appeared to be acenaphthenequinone (IV). The first product of its reduction would undoubtedly be a benzoin, and in the experience of one of us further reduction would only take place satisfactorily in absence of oxygen (*J. pr. Chem.*, 1930, **127**, 260), since in alkaline solution benzoins autoxidise very rapidly (J., 1935, 226).


(I.)


(II.)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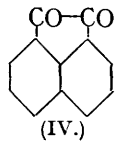
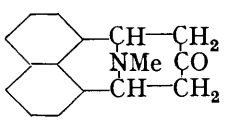
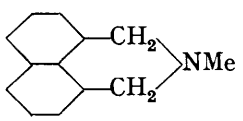

(IV.)

We have accordingly reduced acenaphthenequinone by means of sodium amalgam and alcohol in an atmosphere of nitrogen, and have isolated *cis*-acenaphthylene glycol in some 35% yield. The reduction of phenanthraquinone, carried out in the same way, proceeds only as far as 9 : 10-dihydroxyphenanthrene. The reason for this difference is evidently that 9 : 10-dihydroxyphenanthrene is a true aromatic *o*-dihydroxy-compound, whereas the corresponding reduction product of acenaphthenequinone (the enolic form of the α-ketol) is not.

Oxidation of *cis*-acenaphthylene glycol proceeds as described by Criegee *et al.*, giving naphthalene-1 : 8-dialdehyde. Neither this aldehyde nor 1 : 8-diacetylnaphthalene condenses with *o*-diamines or 1 : 8-diaminonaphthalene to give substances of the quinoxaline type.

Positive results were, however, obtained in the tropinone condensation. Using Robinson's conditions (J., 1932, 1429), we finally obtained 1-methyl-2 : 6(1′ : 8′)-naphthapiperid-4-one (V) isolated as the *picrate*, together with the *picrate* of a base $C_{13}H_{13}N$. The latter compound presumably originates from the condensation of the aldehyde and methylamine, with simultaneous reduction, and is probably (VI). When the condensation was carried out in buffered solution at p_H 6·5 (cf. Schöpf and Lehmann, *Annalen*, 1935, **518**, 1), the tropinone alone was formed.

(V.) 


(VI.)

Experimental.

cis-*Acenaphthylene Glycol* (I).—The reduction was carried out in a round-bottomed flask provided with an efficient mercury-sealed stirrer, a tap funnel, and a source of oxygen-free nitrogen. A liquid seal was provided for the escape of the gas. Acenaphthenequinone (5·5 g.) and 3% sodium amalgam (250 g.) were placed in the flask, and the air completely replaced by

nitrogen. Absolute alcohol (200 c.c.) was added through the tap funnel, the flask placed in a water-bath at 50°, and the mixture stirred. The solution soon became dark blue, and much blue solid separated. This gradually dissolved, and none remained after 24 hours' stirring; the colour of the solution was still blue, though less intense. Glacial acetic acid (20 c.c.) and water (50 c.c.) were then added through the tap funnel, causing the solution to become orange. (In the remaining stages of the preparation access of air is not prejudicial.) The mercury was separated, and the alcoholic solution clarified from a trace of amorphous material by filtering through charcoal. From the filtrate, four fractions (all melting above 160°) were obtained by addition of water and evaporation of alcohol. They were recrystallised from benzene (charcoal) and finally from aqueous alcohol, giving 1·5—2 g. of pure *cis*-acenaphthylene glycol. The mother-liquors gave a lower-melting mixture of both isomerides.

1-*Methyl*-2 : 6(1′ : 8′)-*naphthapiperid*-4-*one* (V).—The crude aldehyde prepared by the oxidation of acenaphthylene glycol (360 mg.) was condensed with acetonedicarboxylic acid (1 g.), chalk (1·4 g.), and 33% aqueous methylamine (4 c.c.) in methyl alcohol-water (1 : 1; 25 c.c.). After 24 hours the solution was acidified and boiled, the calcium precipitated as oxalate, and the bases extracted with ether. The brown oily mixture of bases was converted by means of picric acid in acetone into the picrates (378 mg.). These were separated by repeated crystallisation from acetone into a less soluble component [thin yellow plates, m. p. 197° (decomp.)] and a more soluble component (large, compact, garnet-red crystals, m. p. 165—166°). The yellow substance, m. p. 197°, was 1-*methyl*-2 : 6(1′ : 8′)-*naphthapiperid*-4-*one picrate* (Found : C, 56·3, 57·0; H, 4·1, 4·1; N, 12·2. $C_{22}H_{18}O_8N_4$ requires C, 56·7; H, 3·9; N, 12·0%). The free base could not be crystallised, and failed to give a characteristic dipiperonylidene derivative (cf. Blount, J., 1933, 553). The red substance, m. p. 165—166°, gave the analytical figures required for the *picrate* of a base $C_{13}H_{13}N$ (Found : C, 55·5; H, 3·9; N, 13·8. $C_{19}H_{16}O_7N_4$ requires C, 55·3; H, 3·9; N, 13·6%).

When the aldehyde (M/1000), acetonedicarboxylic acid (M/500), and methylamine (M/500) in 50% alcohol (50 c.c.), buffered with phosphate to p_H 6·5, were allowed to react for 5 days at 22°, the tropinone was formed exclusively, but the yield (15 mg. of the picrate) was not good.

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