368. *Acenaphthenone and Acenaphthenequinone.*

By H. Gordon Rule and Samuel B. Thompson.

The bromination of acenaphthenequinone is readily effected by boiling the quinone with excess of liquid bromine, 3-bromoacenaphthenequinone being formed in excellent yield. More vigorous bromination in the presence of iron yields a *tribromoacenaphthenequinone* of uncertain constitution.

An improved method for the preparation of acenaphthenone is the reduction of acenaphthenequinonephenylhydrazone by means of iron and acid. When treated with excess of bromine in carbon disulphide solution, acenaphthenone yields 7 : 7-dibromoacenaphthenone.

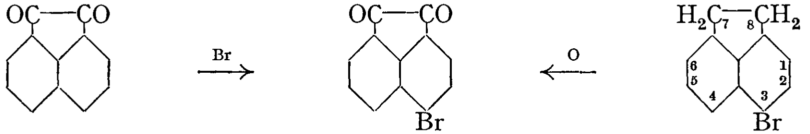
7 : 7-Dichloroacenaphthenone, when treated with hot aqueous sodium sulphide solution, is converted almost quantitatively into 7 : 7′-diacenaphthylidene-8 : 8′-dione. With sodium hyposulphite the latter undergoes further reduction to the colourless 7 : 7′-*diacenaphthenonyl*, the constitution of which has been confirmed by synthesis.

The characteristically wide range over which acenaphthenequinonemonoxime melts is shown to be due to molecular rearrangement into naphthalimide at the temperature of fusion.

Although acenaphthenequinone and acenaphthenone have been recognised as individuals for many years and have formed the subject of various important investigations, our knowledge of their chemistry is still far from complete. The constitutions of the dinitro-derivatives of the quinone have only recently been established with certainty (Rowe and Davies, J., 1920, **117**, 1349; Mayer and Kaufmann, *Ber.*, 1920, **53**, 296; Rule and Brown, J., 1934, 171) and up to the present the only bromoacenaphthenequinone described in the literature has been obtained indirectly by way of bromoacenaphthene. Further, no convenient method of preparing acenaphthenone has yet been recorded.

Bromoacenaphthenequinones.—Mayer and Kaufmann (*loc. cit.*, p. 289) stated that no uniform product could be isolated by the direct bromination of acenaphthenequinone, and Mayer and Schoenfelder (*Ber.*, 1922, **55**, 2972), using bromine in nitrobenzene solution at 200°, obtained only naphthalic anhydride.

Direct bromination has now been achieved by boiling a solution of acenaphthenequinone (6 g.) in bromine (10 c.c.) for 2 hours under reflux at 60—70°. The mixture was poured into water acidified with sulphuric acid, and the excess of bromine boiled off. Crystallisation of the resulting solid from acetic acid gave 3-bromoacenaphthenequinone, m. p. 231—233° (6·7 g.; 80% yield). Further recrystallisation gave the pure compound, m. p. 238°, unchanged on admixture with a specimen prepared by the oxidation of 3-bromoacenaphthene (Guha, J., 1931, 582, records m. p. 238°). Even under the most favourable conditions the oxidation process only led to a yield of about 10%.



3-Bromoacenaphthenequinone condensed with *o*-phenylenediamine to give the phenazine, m. p. 272° (Guha, *loc. cit.*, 272°; Dziewonski, Schoen, and Glazner, *Bull. Acad. Polonaise*, 1929, *A*, 636, find 261—263°). 3-*Bromoacenaphthenequinonemonoxime*, prepared from the quinone and hydroxylamine hydrochloride in aqueous alcohol, melted at 213—214·5° (Found: N, 5·0. $C_{12}H_6O_2NBr$ requires N, 5·1%).

No further bromination of 3-bromoacenaphthenequinone could be effected with bromine alone. A solution of the quinone (2 g.) in bromine (5 c.c.) was treated carefully with iron filings (1 g.) and the mixture, after being heated for 2 hours at 60—70°, was poured into water acidified with sulphuric acid and was boiled to expel the excess of bromine. Repeated crystallisation of the product from acetic acid afforded fine yellow needles of a *tribromoacenaphthenequinone* (1·2 g.), m. p. 253—256° (Found: Br, 57·7. $C_{12}H_3O_2Br_3$ requires Br, 57·3%); the somewhat wide range of fusion may be due to the presence of a trace of a tetrabromo-derivative. In all probability the tribromo-quinone contains the bromine atoms in the 2-, 3-, and 5-positions.

Treatment of the tribromo-quinone with *o*-phenylenediamine in boiling acetic acid afforded the *phenazine* of tribromoacenaphthenequinone, m. p. 303° (Found: N, 6·0. $C_{18}H_7N_2Br_3$ requires N, 5·7%).

Oxidation converted the quinone into a tribromonaphthalic anhydride, obtainable in better yield by direct bromination of naphthalic anhydride (see following paper).

Prolonged bromination in the presence of iron, followed by repeated crystallisation from acetic acid, gave a *tetrabromoacenaphthenequinone* (2 : 3 : 4 : 5-?) in fine needles, m. p. 300—305° (Found: Br, 64·7. $C_{12}H_2O_2Br_4$ requires Br, 64·3%), but owing to the small yield and the difficulty of purification this compound was not further investigated.

Acenaphthenone and its Derivatives.—The best method hitherto available for the preparation of acenaphthenone is that of Graebe and Jequier (*Annalen*, 1896, **290**, 195; Morgan and Stanley, *J. Soc. Chem. Ind.*, 1925, 493T) in which acenaphthenequinone is converted by treatment with phosphorus pentachloride into 7 : 7-dichloroacenaphthenone, and the latter then reduced with zinc and acetic acid ($CO{\cdot}CO \longrightarrow CO{\cdot}CCl_2 \longrightarrow CO{\cdot}CH_2$), the yield being about 30%.

A more convenient method (yield, 45%) is the following: Acenaphthenequinone (30 g.) in hot acetic acid (240 c.c.) was treated cautiously with phenylhydrazine (20 g.) in acetic acid (60 c.c.) and the red solution of the hydrazone was boiled for 5 minutes and treated with concentrated hydrochloric acid (100 c.c.); iron filings (40 g.) were then added in small portions to the boiling mixture.* After 1 hour at the b. p., the product was poured into water, and the acenaphthenone distilled in steam. Yield, 12·5 g.; m. p. 121°.

Another method, which has the merit of economy, is to convert acenaphthene (50 g.) into acenaphthenequinonemonoxime by treatment with amyl nitrite and hydrogen chloride (Reissert, *Ber.*, 1911, **44**, 1749) and to reduce the oxime as indicated above with iron in a mixture of acetic and hydrochloric acids. Yield, 14 g. (26%). The claim made by Reissert to have isolated an isomeric oxime, distinguished by a lower solubility in sodium carbonate solution than the one referred to above, could not be substantiated.

In this connexion the behaviour of acenaphthenequinonemonoxime in a melting point tube was examined. Fusion normally occurred over a range of 2—3° with apparent decomposition. The chemical change proceeded more rapidly at higher temperatures, and when the tube was immersed in a bath at 250° a crystalline sublimate of naphthalimide, m. p. and mixed m. p. 298°, deposited on the upper part of the tube. The molecular rearrangement thus represents a Beckmann transformation under the influence of heat alone.

Another method of preparing acenaphthenone is the reduction of the quinone monoanil: this was obtained by Sander (*Ber.*, 1925, **58**, 830) by the interaction of acenaphthenone and nitrosobenzene, but it is more readily prepared by heating acenaphthenequinone and aniline in the required proportion for a few minutes at 130°.

In agreement with the conclusions of earlier workers, the direct bromination of acenaphthenone was found to occur only in the side chain; the reaction, however, may proceed a stage further than the monobromo-compound obtained by Graebe and Jequier (*loc. cit.*). 7 : 7-Dibromoacenaphthenone was prepared by carefully treating a solution of acenaphthenone (2 g.) in carbon disulphide (15 c.c.) with a solution of bromine (2 c.c.) in the same solvent and after a short time boiling the mixture until no more hydrogen bromide was evolved. The dibromoacenaphthenone obtained on evaporation of the solvent formed colourless crystals,

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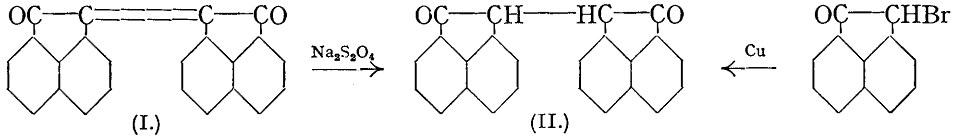
m. p. 161—162°, from ether (Behrend and Herms, *J. pr. Chem.*, 1899, **60**, 1, record m. p. 160—161° for the compound prepared indirectly by way of the hydrazide and the azide).

Dinuclear Condensation Products.—7 : 7′-Diacenaphthylidene-8 : 8′-dione (I) has been isolated in small yields by Graebe by several methods (*Annalen*, 1893, **276**, 1; 1896, **290**, 201); its preparation as a vat dye has also been claimed by the condensation of acenaphthenequinone with acenaphthenone (D.R.-P. 212, 858; *Cent.*, 1909, II, 775). It has now been obtained very readily and in almost quantitative yield as follows :

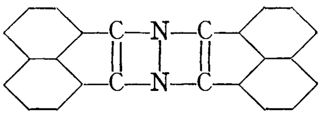
7 : 7-Dichloroacenaphthenone (10 g.) in alcohol (200 c.c.) was reduced with sodium sulphide (12 g. of $Na_2S,9H_2O$ in 50 c.c. of water). Rapid addition of the reagent led to a vigorous reaction and deposition of the flocculent red dione (yield, 6·5 g.; 93% of the theoretical). Purified from nitrobenzene, it melted at 300°.

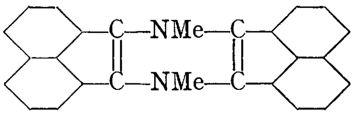


The orange diacenaphthylidenedione did not possess the properties of a vat dye. When the compound (2 g.) was heated at 100° with an alkaline solution of sodium hyposulphite, it was converted into a colourless reduction product which did not undergo reoxidation in air. After crystallisation from nitrobenzene the product (1·9 g.) melted at 258° (Found : C, 86·1; H, 4·1. $C_{24}H_{14}O_2$ requires C, 86·2; H, 4·2%). It could not be acetylated and is therefore concluded to be non-hydroxylic and is assigned the ketonic structure 7 : 7′-*diacenaphthenonyl* (II) to which the enolic compound first produced by reduction of the ketonic groups of the dione is assumed to isomerise. This constitution is supported by the formation of the same compound when 7-bromoacenaphthenone (1·2 g.) was boiled in xylene (10 c.c.) for 1 hour with copper bronze (0·6 g.). On filtration and cooling, fine colourless crystals (0·2 g.; 25% of the theoretical yield) were obtained, m. p. after crystallisation from acetic acid 258°, alone or mixed with the above product. Diacenaphthenonyl was also obtained by reduction of diacenaphthylidenedione with zinc dust (or iron filings) and acetic acid. While investigating the formation of the dione from acenaphthenequinone by heating with hydriodic acid and red phosphorus at 120°, Graebe records failure to obtain products other than the dione in this manner. When the temperature of the reaction is raised to 165°, however, the product is no longer Graebe's dione but the above diacenaphthenonyl (yield, 44%).

A red dinuclear condensation product of a different type was isolated by the action of ammonia upon 7 : 7-dichloroacenaphthenone. This proved to be identical with the compound obtained by Graebe by interaction of ammonia and acenaphthenequinone (*Annalen*, 1893, **276**, 9) and later formulated by Schönberg (*Ber.*, 1921, **54**, 238) as acenaphthazine (III). When the quinone (4·5 g.) was heated with aqueous methylamine (3 c.c. of 30% wt./vol.) in a sealed tube for 6 hours at 100°, a black mass was formed, which, on being washed with acetone and chloroform, left a brown amorphous residue. Crystallisation from nitrobenzene afforded large, dark brown crystals, presumably of *NN′*-dimethyldihydroacenaphthazine (IV), m. p. above 360°, not appreciably soluble in dilute hydrochloric acid. On sublimation it formed reddish-brown needles (Found : N, 8·0. $C_{26}H_{18}N_2$ requires N, 7·8%).

(III.)





(IV.)

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