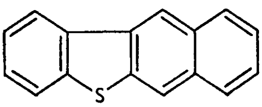
665. *Polynuclear Heterocyclic Systems. Part X.* The Elbs Reaction with Heterocyclic Ketones.*

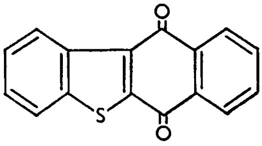
By G. M. BADGER and B. J. CHRISTIE.

Pyrolysis of 3-*o*-toluoylthionaphthen gives 9-thia-1 : 2-benzofluorene (X) and not the expected 9-thia-2 : 3-benzofluorene (I). A mechanism for this rearrangement has been suggested.

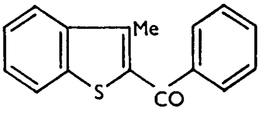
9-THIA-2 : 3-BENZOFLUORENE (I) was obtained by Mayer [1] by reduction of the quinone (II), prepared from phthalic anhydride and thionaphthen. The same quinone was obtained from thioisatin and ω-bromoacetophenone in sodium hydroxide solution. Werner [2] also prepared 9-thia-2 : 3-benzofluorene, albeit in only 5—8% yield, by pyrolysis of 2-benzoyl-3-methylthionaphthen (III), and its isolation was cited as a proof that the Friedel–Crafts acylation of 3-methylthionaphthen involves the 2-position. Other polynuclear heterocyclic compounds have also been prepared by the Elbs reaction; but synthesis involving cyclisation into a five-membered hetero-ring has been achieved only very rarely, and in poor yield.[3,4] 9-Thia-2 : 3-benzofluorene was required by us for spectroscopic examination and it was thought of interest to attempt to prepare it by pyrolysis of 3-*o*-toluoylthionaphthen (IV).



(I)



(II)



(III)

This ketone was prepared in good yield from thionaphthen and *o*-toluoyl chloride with stannic chloride, and was pyrolysed at 340—360°. Chromatography of the crude product gave a small quantity of the *p*-quinone (II), presumably the result of oxidation on the surface of the alumina; but the major product was unexpectedly 9-thia-1 : 2-benzofluorene (X), as proved by its m. p. and absorption spectrum,[5] and by oxidation with chromic acid to a red *o*-quinone (XI), which formed a quinoxaline derivative with *o*-phenylenediamine.

Although the evidence is still incomplete, a reasonable mechanism has been proposed for the Elbs reaction,[3,6] and the formation of the intermediate (V) seems very probable. In a " normal " Elbs reaction, this would be expected to undergo prototropic rearrangement to the alcohol (VI) and then dehydration to 9-thia-2 : 3-benzofluorene (I). A little of the corresponding *p*-quinone (II) has certainly been isolated following chromatography of the product, but this may have been formed directly by oxidation (on the alumina) of

---

* Part IX, *J.*, 1956, 122.

[1] Mayer, *Annalen*, 1931, **488**, 259.

[2] Werner, *Rec. Trav. chim.*, 1949, **68**, 520.

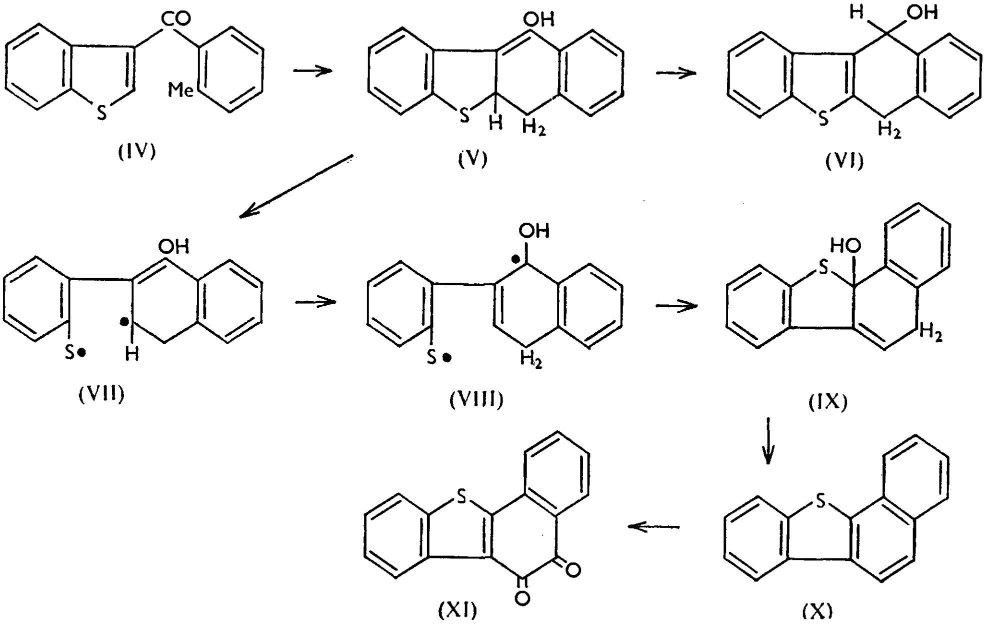
[3] Fieser, *Org. Reactions*, 1942, **1**, 129.

[4] de Clercq, *Ind. chim. belge*, 1955, **20**, 157.

[5] Kruber and Grigoleit, *Chem. Ber.*, 1954, **87**, 1895.

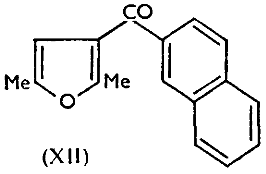
[6] Badger and Pettit, *J.*, 1953, 2774.

the intermediate (V). The present reaction appears, however, to be " abnormal " in that the major product is the angular compound (X); experiment has shown that it is not formed by heating 9-thia-2 : 3-benzofluorene (I) at 390° for 3 hours, and the rearrangement must therefore occur at an intermediate stage in the synthesis. It is suggested that the carbon–sulphur bond in the intermediate (V) may be ruptured at the temperature of the pyrolysis, the resulting radical (VII) rearranging to (VIII) and finally (IX), dehydration of which would lead to the observed product (X).

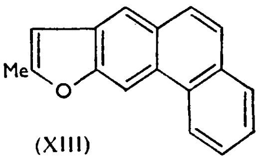


It must be concluded that the structure of the product of an Elbs reaction can be accepted only with caution.

An attempt has also been made to prepare the methylfuranophenanthrene (XIII) by pyrolysis of the ketone (XII). The ketone was prepared from 2 : 5-dimethylfuran,



(XII)



(XIII)

2-naphthoyl chloride, and stannic chloride, though the yield was low, and longer reaction times and higher temperatures led to resins. The pyrolysis was attempted under various conditions but, although water was evolved, no crystalline material could be obtained. The instability of the furan nucleus at high temperatures may preclude the use of the Elbs reaction with such compounds.

EXPERIMENTAL

3-o-*Toluoylthionaphthen*.—Stannic chloride (22 g.) in thiophen-free benzene (100 c.c.) was added during 30 min., at room temperature, to a stirred solution of thionaphthen (10 g.) and *o*-toluoyl chloride (11·5 g.) in thiophen-free benzene (150 c.c.). The mixture was refluxed for 4 hr., then poured on ice and hydrochloric acid. The benzene layer was washed with 10% hydrochloric acid, water, 10% sodium hydroxide solution, and water, then dried (Na_2SO_4) and evaporated. The resulting 3-o-*toluoylthionaphthen* (17 g., 90%) recrystallised from ethanol as colourless plates, m. p. 94° (Found: C, 76·6; H, 4·8; S, 12·85; O, 6·4. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7; O, 6·3%). The 2 : 4-*dinitrophenylhydrazone* crystallised from chloroform–ethanol as orange needles, m. p. 261° (Found: C, 61·1; H, 3·9; N, 12·7; S, 7·3. $C_{22}H_{16}O_4N_4S$ requires C, 61·1; H, 3·7; N, 13·0; S, 7·4%).

9-*Thia*-1 : 2-*benzofluorene*.—The above ketone (10 g.) was heated at 340—360° for 3 hr. The cooled product was chromatographed in benzene on alumina. Elution with benzene gave two fractions: (i) light brown crystals (3·5 g.) and (ii) brown-yellow needles (0·4 g.). Recrystallisation of the second fraction from benzene gave 9-thia-2 : 3-benzofluorene-1 : 4-quinone as bright yellow needles, m. p. 215°, not depressed by admixture with an authentic specimen prepared by Mayer's method.[1] Fraction (i), repeatedly crystallised from hexane (charcoal), gave 9-thia-1 : 2-benzofluorene as colourless plates, m. p. 185° (Found: C, 82·2; H, 4·6; S, 13·8. Calc. for $C_{16}H_{10}S$: C, 82·0; H, 4·3; S, 13·7%). Its m. p. and ultraviolet absorption spectrum were identical with those recorded by Kruber and Grigoleit.[5] The 2 : 4 : 7-*trinitrofluorenone complex* crystallised from benzene as orange needles, m. p. 234° (sealed capillary) (Found: C, 63·9; H, 2·95; N, 7·5. $C_{29}H_{15}O_7N_3S$ requires C, 63·4; H, 2·75; N, 7·65%).

9-*Thia*-1 : 2-*benzofluorene*-3 : 4-*quinone*.—A mixture of 9-thia-1 : 2-benzofluorene (0·5 g.), chromic acid (0·5 g.), acetic acid (15 c.c.), and water (10 c.c.) was refluxed for 15 min., then poured into water. After recrystallisation from benzene the *quinone* formed red needles, m. p. 217° (Found: S, 12·1; O, 11·8. $C_{16}H_8O_2S$ requires S, 12·1; O, 12·1%). The *quinoxaline derivative*, prepared by use of *o*-phenylenediamine in acetic acid–ethanol, recrystallised from benzene as yellow needles, m. p. 230° (sealed capillary) (Found: C, 78·95; H, 3·7. $C_{22}H_{12}N_2S$ requires C, 78·5; H, 3·6%).

Attempted Isomerisation of 9-*Thia*-2 : 3-*benzofluorene*.—An authentic specimen of 9-thia-2 : 3-benzofluorene (0·5 g.) was heated at 390° for 3 hours. A small amount of isomerisation would be difficult to detect; so, after cooling, the product was oxidised with chromic acid (0·5 g.) in acetic acid, and the resulting quinone chromatographed in benzene on alumina. No red *o*-quinone was observed, 9-thia-2 : 3-benzofluorene-1 : 4-quinone (0·3 g.) being isolated as yellow needles, m. p. 215°.

2 : 5-*Dimethyl*-3-2′-*naphthoylfuran*.—A solution of stannic chloride (30 g.) in thiophen-free benzene (50 c.c.) was added during 30 min. to a stirred ice-cold solution of 2 : 5-dimethylfuran (10·5 g.) and freshly distilled 2-naphthoyl chloride (21 g.) in anhydrous benzene (200 c.c.). Stirring was continued at room temperature for 30 min., after which the temperature was raised to 35° for 15 min. The cooled mixture was decomposed with dilute hydrochloric acid and extracted with chloroform, and the organic layer washed with 10% hydrochloric acid, water, 10% aqueous sodium hydroxide, and water, then dried (Na_2SO_4) and evaporated. After distillation (b. p. 137—140°/0·02 mm.) and recrystallisation from hexane, the *furan* (11 g., 40%) formed colourless needles, m. p. 76° (Found: C, 81·75; H, 5·8; O, 13·0. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6; O, 12·8%). The 2 : 4-*dinitrophenylhydrazone* crystallised from chloroform–hexane in orange needles, m. p. 211—212° (Found: C, 64·0; H, 4·3; O, 18·6. $C_{23}H_{18}O_5N_4$ requires C, 64·2; H, 4·2; O, 18·6%).

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA. [*Received, February 7th,* 1956.]