THE BASE-CATALYSED SKELETAL REARRANGEMENT OF A THIANAPHTHOFLUORENE DERIVATIVE

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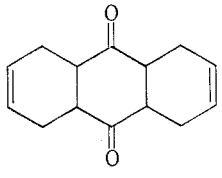
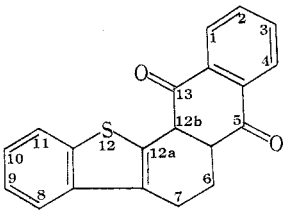
Summary

The Diels–Alder adduct of 3-vinylbenzo[*b*]thiophen and 1,4-naphthaquinone has been shown to undergo a novel base-catalysed rearrangement, in which its partly hydrogenated 12-thianaphtho[2,3-*a*]fluorene structure is replaced by a 5-thianaphtho[2,3-*b*]fluorene structure.

A simple method of aromatization of adducts from 1,4-quinones and dienes consists of aeration of an alkaline solution of the compound. Thus the octahydroanthraquinone (I), the adduct from 1,4-benzoquinone and butadiene, is readily converted in this way into anthraquinone.[1] The adduct (A) from 1,4-naphthaquinone and 3-vinylbenzo[*b*]thiophen, hitherto formulated as 5,5a,6,7,12b,13-hexahydro-5,13-dioxo-12-thianaphtho[2,3-*a*]fluorene (II),[2] has already been dehydrogenated to 12-thianaphtho[2,3-*a*]fluorene-5,13-quinone (III) using the conventional oxidant chloranil,[2] and it was decided to see if the aerial oxidation described would bring about the same result.



(I)



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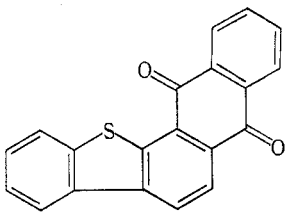

(III)

In fact, when the adduct (A) was treated with sodium hydroxide in ethanol a compound different from the quinone (III) was isolated. The infrared spectrum of this compound showed that it was a quinone, and analysis showed that it was

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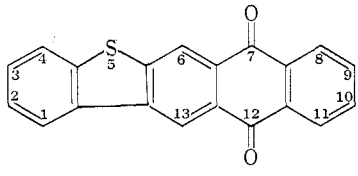
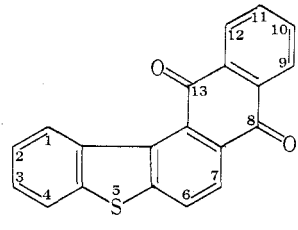
[1] Alder, K., and Stein, G., *Liebigs Ann.*, 1933, **501**, 247.

[2] Davies, W., and Porter, Q. N., *J. chem. Soc.*, 1957, 4961.

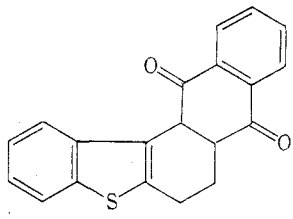
isomeric with compound (III). This suggested that rearrangement had accompanied the treatment with alkali, and since any drastic bond rearrangement seemed unlikely under the mild conditions used, a likely possibility for this unexpected product was either 5-thianaphtho[2,3-*b*]fluorene-7,12-quinone (IV) or 5-thianaphtho[2,3-*c*]-fluorene-8,13-quinone (V).



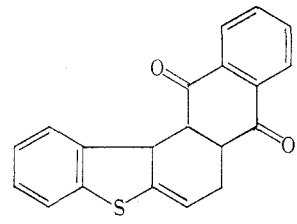
(IV)



(V)



(VI)



(VIa)

Quinone (V) has been prepared by Ennis[3] by chloranil dehydrogenation of the adduct (B) of 2-vinylbenzo[*b*]thiophen and 1,4-naphthaquinone, formulated as 6,7,7a,8,13,13a-hexahydro-8,13-dioxo-5-thianaphtho[2,3-*c*]fluorene (VI);* and this quinone was not identical with the rearrangement product. Quinone (IV) has been reported by Gilman and Jacoby[4] as resulting from the cyclization of 2-(2-carboxybenzoyl)dibenzothiophen (VII), and in fact the literature melting point was close to that of the rearrangement product. Although the position of reaction of dibenzothiophen with phthalic anhydride and the direction of the subsequent cyclization of the keto acid (VII) seem likely by analogies with other reactions of dibenzothiophen, neither was proven unambiguously, and it was decided to look for a completely conclusive structural proof.

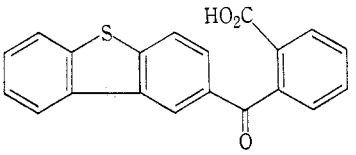
Naphthalene-2,3-dicarboxylic anhydride was allowed to react with 3-benzo[*b*]-thienylmagnesium bromide and the resulting 3-(3-carboxy-2-naphthoyl)benzo[*b*]-

* This structure may, like structure (II) postulated for adduct (A), require revision (to (VIa)) if the acid-catalysed allylic rearrangement implied by structure (VI) has not accompanied the original Diels–Alder reaction of 2-vinylbenzo[*b*]thiophen and 1,4-naphthaquinone. However, the position of the double bond in the adduct does not affect the structure of the quinone (V) obtained from it by chloranil dehydrogenation.

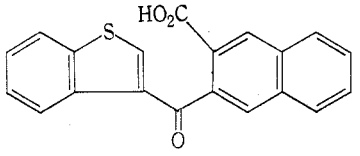
[3] Ennis, B. C., Ph.D. Thesis, University of Melbourne, p. 72 (1961).

[4] Gilman, H., and Jacoby, A. L., *J. org. Chem.*, 1938, **3**, 108.

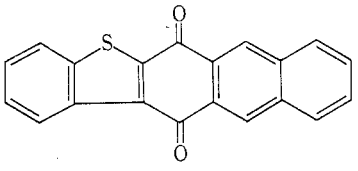
thiophen(VIII) was cyclized with concentrated sulphuric acid to 5-thianaphtho-[2,3-*b*]fluorene-6,13-quinone (IX). This was reduced with diborane[5] to 5-thianaphtho-[2,3-*b*]fluorene (X).*



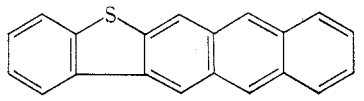
(VII)



(VIII)



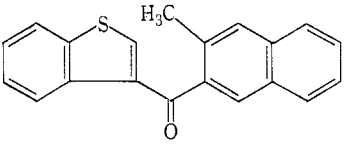
(IX)



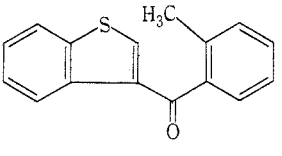
(X)

The same thiahydrocarbon was obtained by diborane reduction of the rearrangement product, showing that it has the basic 5-thianaphtho[2,3-*b*]fluorene ring system. It was now necessary to confirm that the quinone oxygen functions were at positions 7 and 13 in this skeleton. The presumed 2-(2-carboxybenzoyl)dibenzothiophen described by Gilman and Jacoby was prepared and cyclized by their method. Careful chromatography of the product showed that it was a mixture of a quinone identical with the rearrangement product together with a smaller amount of an isomer identical with quinone (V), already described. The isolation of these two compounds is of course consistent only with initial acylation of the dibenzothiophen in the 2-position as suggested by Gilman and Jacoby, and completely confirms the structure (IV) postulated both for the rearrangement product of the adduct of 3-vinylbenzo[*b*]thiophen and 1,4-naphthaquinone, and for the cyclization of 2-(2-carboxybenzoyl)dibenzothiophen.

* A compound of structure (X) has been claimed in the patent literature[6] to result from the Elbs pyrolysis of the methyl ketone (i). The melting point given is considerably below that obtained for (X) in this work. Badger and Christie[7] have shown that the ketone (ii) gives the "angular" thiafluorene derivative (iii) on pyrolysis rather than the expected "linear" compound, and it may well be that at least some rearrangement has also accompanied pyrolysis of (i).



(i)



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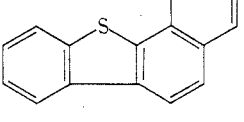
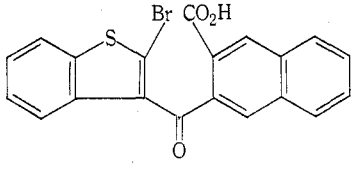


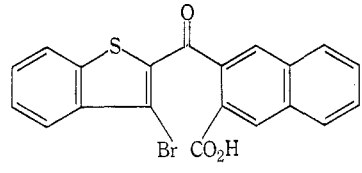
(iii)

[5] Bapat, D. S., Subba Rao, B. C., and Venkataraman, K., *Tetrahedron Lett.*, 1960, No. 5, 15.
[6] French Pat., 614,959 (1926); *Chem. ZentBl.*, 1929 (II), 797.
[7] Badger, G. M., and Christie, B. J., *J. chem. Soc.*, 1956, 3435.

It is pertinent to mention at this point a difficulty initially experienced in the preparation of the keto acid (VIII) from 3-benzo[*b*]thienylmagnesium bromide and naphthalene-2,3-dicarboxylic anhydride. The product first isolated had the formula $C_{20}H_{11}BrO_3S$ and is thus a bromine substitution product of the expected keto acid (VIII). It has now been shown that unless the conditions used in the bromination of benzo[*b*]thiophen are very carefully controlled the product is contaminated with varying amounts of 2,3-dibromobenzo[*b*]thiophen. This contamination leads to a wide boiling range when the 3-bromobenzo[*b*]thiophen is distilled and gives it a yellow colour. The dibromo compound apparently readily gives a mono-Grignard reagent, and thus the anomalous keto acid has structure (XI) or (XII). (It has not as yet been shown which bromine atom is displaced in the metallation reaction.)



(XI)



(XII)

It is of interest that the bromo keto acid also cyclizes readily to the quinone (IX) with expulsion of the bromine atom.

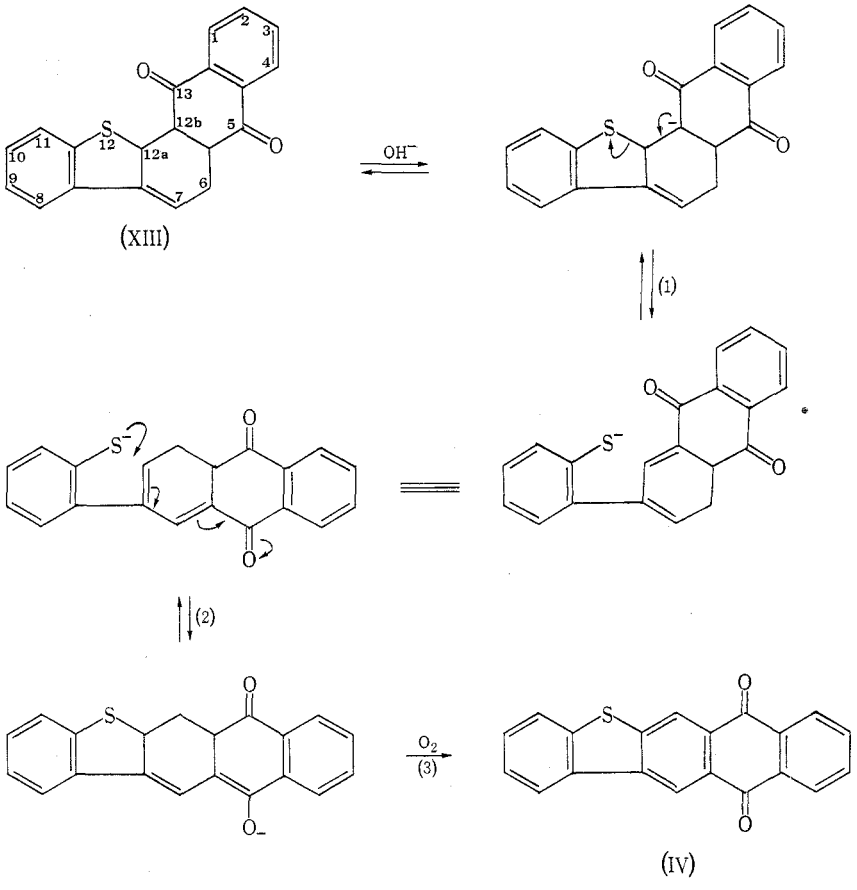
The mechanism of rearrangement of adduct (A) is of some interest but, before it is considered, it is necessary to decide between the structures (II) and (XIII) for (A). The isomerized structure (II) was originally suggested[2] because (A) was relatively stable to acidic reagents, and the prototropic rearrangement necessary to produce this structure was thought to occur before the product was isolated from the acetic acid solvent. However, the n.m.r. spectrum of the adduct (A)[8] now shows that this suggestion is incorrect, since there is an absorption at τ 3·94 (one proton) which can only be assigned to the olefinic proton at position 7 of structure (XIII). The adduct (A) thus has the structure (XIII), which is formally expected from the Diels–Alder addition of 1,4-naphthaquinone and 3-vinylbenzo[*b*]-thiophen.

The rearrangement of (A) may be imagined formally to result from fission of the 12b–13 carbon–carbon bond followed by recyclization at position 6, or from fission of the 12–12a carbon–sulphur bond followed by recyclization at position 7. On the basis of structure (XIII), a plausible mechanism for the rearrangement can be postulated and it is shown in Scheme 1.

This mechanism is undoubtedly an oversimplification and neglects other contributions to the equilibria, in particular dianionic species. However, the essential steps have ample precedent. Step (1) is essentially a retro-Michael reaction, the base-catalysed elimination of substituted thiophenoxide from a position β to a carbonyl group. An analogy is the base-catalysed elimination of thiophenoxide

[8] Cherry, W. H., and Porter, Q. N., unpublished data.

from the diphenyl dithioketal of ethyl acetoacetate.[9] Step (2) is a vinylogous Michael addition, similar to that occurring, for example, with methyl pentadienoate and diethyl malonate.[10]



(XIII) (IV)

Scheme 1

The nature of the final oxidation (step (3)) is at this stage uncertain, but may well involve a semiquinone anion.[11] Free radicals are certainly present during oxidation since a strong signal was observed when the reaction was allowed to proceed in an electron spin resonance spectrometer. This signal decayed as the reaction went to completion.

Work relating to the mechanism of the rearrangement and to the synthesis of the oxygen, nitrogen, and carbon analogues of the adduct (A) will be the subject of further communications.

[9] Escales, R., and Baumann, E., *Ber. dt. chem. Ges.*, 1886, **19**, 1787.
[10] Farmer, E. H., and Mehta, T. N., *J. chem. Soc.*, 1931, 1904.
[11] Michaelis, L., *Trans. electrochem. Soc.*, 1937, **71**, 107.

Experimental

Melting points were determined on a Kofler hot-stage and are uncorrected. Infrared spectra were determined on a Perkin–Elmer 137 Infracord and n.m.r. spectra with a Varian Associates HR60 spectrometer. Mass spectral molecular weights were obtained on an AEI MS9 instrument. Refractive indices were measured with a temperature-controlled precision Abbé refractometer (Bellingham & Stanley Ltd). Microanalyses were carried out by Dr K. W. Zimmermann and the staff of the Australian Microanalytical Service, Melbourne.

3-Bromobenzo[b]*thiophen*

The following method has been shown to give a product essentially free from 2,3-dibromobenzo[*b*]thiophen.

Bromine (59·0 g, 0·369 mole) in carbon tetrachloride (70 ml) was added with stirring over 12 hr to a solution of benzo[*b*]thiophen (50·0 g, 0·373 mole) in carbon tetrachloride (200 ml) maintained at 15–20°. The solution was stirred for a further 36 hr at room temperature, the washed (sodium thiosulphate and water) solution was evaporated, and the 3-bromobenzo[*b*]-thiophen distilled as a very pale yellow liquid (73 g, 92%), b.p 70–72°/0·2 mm, n_D^{20} 1·6635, $n_D^{27\cdot5}$ 1·6600 (lit. b.p. 98°/0·3 mm,[12] 136°/13 mm,[13] n_D^{20} 1·6294,[13] $n_D^{27\cdot5}$ 1·6610[12]). The mass spectrum of the compound showed the presence of 0·06% of 2,3-dibromobenzo[*b*]thiophen (based on the intensity of the triplet at 290, 292, and 294) (Found: C, 45·4; H, 2·55. Calc. for C_8H_5BrS: C, 45·1; H, 2·35%). Bromination according to the method of Szmuszkovicz and Modest[14] (chloroform solvent and anhydrous sodium acetate at a low temperature) gave, in our hands, a product which was often heavily contaminated with 2,3-dibromobenzo[*b*]thiophen (particularly if bromination was carried out at less than 10°), even though no more than 1 mole of bromine was used. In some cases the dibromo compound crystallized from the reaction mixture, and was recrystallized from methanol to give needles, m.p. 59–59·5° (lit.[15] 55·3°) (Found: C, 33·1; H, 1·7; Br, 54·6. Calc. for $C_8H_4Br_2S$: C, 32·9; H, 1·4; Br, 54·8%).

It was found that this dibromide could readily be debrominated to 3-bromobenzo[*b*]-thiophen as follows: a mixture of 2,3-dibromobenzo[*b*]thiophen (52·0 g, 0·18 mole) and zinc dust (70 g of 75% pure material, 0·8 mole) in glacial acetic acid (32 ml) and water (100 ml) was shaken for 30 min (much heat liberated), then refluxed for 24 hr. The precipitated zinc bromide and zinc dust were removed by centrifugation and thoroughly washed with carbon tetrachloride; the aqueous layer was extracted with carbon tetrachloride (2 × 100 ml). The carbon tetrachloride extracts and washings were combined, washed with water (100 ml), and dried ($MgSO_4$); after evaporation of the solvent 3-bromobenzo[*b*]thiophen was distilled (28·5 g, 75%), b.p. 60–64°/0·1 mm, n_D^{20} 1·6637.

3-Vinylbenzo[b]*thiophen*

The following method is an improvement on that already published.[16] 3-Benzo[*b*]thienylmagnesium bromide was prepared in ether (120 ml) under a nitrogen atmosphere from 3-bromobenzo[*b*]thiophen (33·0 g, 0·155 mole) and magnesium turnings (5·5 g, 0·23 mole). The solution was cooled to 0° and acetaldehyde (10 g, 0·23 mole) in ether (100 ml) was added (35 min) with stirring. Stirring was continued for a further 90 min at 0°, then the solution was refluxed (25 min), cooled, and decomposed with saturated ammonium chloride solution (40 ml) to give, after evaporation of solvent, the crude 1-(3-benzo[*b*]thienyl)ethanol as an orange oil (28·3 g), n_D^{20} 1·628, ν_{max} (liquid film) 3400 (OH stretching) and 1075 cm^{-1} (OH deformation).

The crude alcohol (11·0 g) was slowly distilled (0·1 mm) from freshly powdered potassium hydrogen sulphate (2·2 g) to give the crude vinyl compound as a pale yellow liquid (6·8 g),

[12] Badger, G. M., Cheuychit, P., and Sasse, W. H. F., *Aust. J. Chem.*, 1964, **17**, 371.
[13] Komppa, G., *J. prakt. Chem.*, 1929, **122**, 319.
[14] Szmuszkovicz, J., and Modest, E. J., *J. Am. chem. Soc.*, 1950, **72**, 571.
[15] Komppa, G., *Acta Soc. Sci. fenn.*, 1897, **23**, 1 (*Chem. ZentBl.*, 1897 (II), 270).
[16] Davies, W., Porter, Q. N., and Wilmshurst, J. R., *J. chem. Soc.*, 1957, 3366.

b.p. 40–100°/0·1 mm. Redistillation gave 3-vinylbenzo[*b*]thiophen (5·0 g), b.p. 58–60°/0·1 mm (lit.[16] 133–134°/25 mm) (Found: C, 74·15; H, 5·2; S, 19·65. Calc. for $C_{10}H_8S$: C, 75·0; H, 5·05; S, 19·95%). n_D^{20} 1·6535; ν_{max} (cyclohexane solution) 1630 (C=C stretching), (liquid film) 980 (C–H out-of-plane deformation), and 910 cm^{-1} (CH_2 out-of-plane deformation). The mass spectrum confirmed the molecular weight (160) and showed the presence of 2% 3-bromobenzo[*b*]-thiophen, accounting for the analytical discrepancies.

5,5a,6,12a,12b,13-Hexahydro-5,13-dioxo-12-thianaphtho[2,3-a]fluorene (XIII)

This was prepared by the interaction of 3-vinylbenzo[*b*]thiophen and 1,4-naphthaquinone as previously described;[2] ν_{max} (KCl disk) 1710 and 1695 (C=O stretching) and 1655 cm^{-1} (C=C stretching); τ ($CDCl_3$ solution) 1·8–2·35 (4H), 2·5–3·15 (4H), 3·94 (1H), 5·19 (1H), 5·98 (1H), 6·39 (1H), and 7·35 (2H); all absorptions are multiplets.

Rearrangement of (XIII) to 5-Thianaphtho[2,3-b]fluorene-7,12-quinone (IV)

The adduct (XIII) (159 mg, 0·50 mmole) was suspended in gently refluxing ethanol (50 ml) in a 100-ml beaker and 2M aqueous sodium hydroxide (0·25 ml, 0·5 mmole) was added. The suspension immediately became very dark. After this colour had faded (10 min in the open beaker, up to 1 hr in a 100-ml Erlenmeyer flask) the mixture was cooled (18 hr) and filtered to give the quinone (IV) as yellow needles (0·148 g, 94%), m.p. 286–286·5° (lit.[4] 285–286°). Crystallization from acetic acid gave yellow needles, m.p. 286·5–287° (Found: C, 76·5; H, 3·3; S, 9·9. Calc. for $C_{20}H_{10}O_2S$: C, 76·4; H, 3·2; S, 10·2%). ν_{max} (KCl disk) 1670 cm^{-1} (C=O stretching).

Reduction of the Quinone (IV) to 5-Thianaphtho[2,3-b]fluorene (X)

The quinone (IV) (0·1 g) was suspended in diglyme (1·0 ml) and sodium borohydride (0·02 g) was added. To the dark red solution which resulted on warming was added freshly distilled boron trifluoride etherate (0·1 ml) in diglyme (1·0 ml). A yellow precipitate immediately formed, and after shaking for 1 hr the mixture was acidified (conc. hydrochloric acid) and the solvent removed (reduced pressure). The residue was extracted with hot toluene and the extract chromatographed on silica and eluted with light petroleum. *5-Thianaphtho[2,3-b]fluorene* (*X*) was obtained as highly fluorescent golden yellow plates (toluene), m.p. 285–288° unchanged by sublimation (20 mg) (Found: C, 84·2; H, 4·3. $C_{20}H_{12}S$ requires C, 84·5; H, 4·25%.)

Naphthalene-2,3-dicarboxylic Anhydride

3-Hydroxy-2-naphthoic acid was converted into 3-amino-2-naphthoic acid as described by Dutta[17] in high yield (90%), provided the mixture was efficiently stirred and the bath temperature was maintained at 240–250°. The amino acid was converted into the nitrile by the method of Waldmann.[18] The crude acid was extracted with sodium carbonate solution, precipitated with mineral acid, and hydrolysed without further purification by boiling for 4 hr (efficient stirring) with a mixture of conc. sulphuric acid (2 parts), water (2 parts), and glacial acetic acid (1 part). The dicarboxylic acid was separated by filtration and sublimed at 250°/18 mm to give the anhydride, m.p. 246° (lit. 246°,[18] 254°[19]).

Preparation of the Keto Acid (VIII)

3-Benzo[*b*]thienylmagnesium bromide from 3-bromobenzo[*b*]thiophen (5 g) and magnesium (0·6 g) in ether (10 ml) was added to a warm suspension of naphthalene-2,3-dicarboxylic anhydride (5 g) in benzene (125 ml). The mixture was heated under reflux for 1 hr, 10% ammonium chloride (100 ml) was added, and the mixture was stirred for 1 hr. The organic layer and the solid at the interface were extracted with 2M sodium hydroxide solution (100 ml), and this

[17] Dutta, P. C., *Ber. dt. chem. Ges.*, 1934, **67**, 1319.
[18] Waldmann, H., *J. prakt. Chem.*, 1930, **128**, 150.
[19] Haworth, R. D., and Slinger, F. H., *J. chem. Soc.*, 1940, 1321.

solution on acidification (2M hydrochloric acid) gave the *keto acid* (VIII) (3 g), needles from acetic acid, m.p. 283–285° (Found: C, 72·4; H, 3·8. $C_{20}H_{12}O_3S$ requires C, 72·3; H, 3·65%).

Similar preparations using 3-bromobenzo[*b*]thiophen contaminated with the 2,3-dibromo compound gave the *bromo keto acid* (XI) or (XII), prisms from acetic acid, m.p. 255–256°, followed by solidification and remelting at 305–310° (Found: C, 58·8; H, 2·8; Br, 17·8; O, 13·1; S, 7·7; mol. wt., 410, 412. $C_{20}H_{11}BrO_3S$ requires C, 58·4; H, 2·7; Br, 19·5; O, 11·7; S, 7·8; mol. wt., 410, 412). The molecular weight was determined mass-spectrometrically and the two values correspond to molecules containing ^{79}Br and ^{81}Br.

Cyclization of the Keto Acid (VIII)

The acid (VIII) (1·0 g) was suspended in conc. sulphuric acid (10·0 ml) and warmed to 100°. The resulting dark solution was cooled and added to crushed ice (200 g). The product was crystallized from acetic acid to give yellow needles of 5-thianaphtho[2,3-*b*]fluorene-6,13-quinone (IX), m.p. 310–311° (lit.[20] 301°) (Found: C, 76·4; H, 3·4. Calc. for $C_{20}H_{10}O_2S$: C, 76·4; H, 3·2%).

The bromo keto acid (XI or XII) gave the same quinone when heated above its melting point or in refluxing acetic acid/acetic anhydride containing zinc chloride.

The quinone (IX) was reduced with diborane in exactly the same way as the quinone (IV) to give 5-thianaphtho[2,3-*b*]fluorene, m.p. and mixed m.p. 285–288°. The samples of the thiahydrocarbon from the two diborane reductions had superimposable infrared spectra.

Preparation of Quinones (IV) and (V) from Dibenzothiophen and Phthalic Anhydride

Dibenzothiophen and phthalic anhydride were condensed and the resulting keto acid cyclized as described by Gilman and Jacoby.[4] The cyclization product was chromatographed on silica gel in carbon tetrachloride. First eluted was the quinone (V), m.p. 278–279°. The compound had an infrared spectrum identical with that of a genuine sample,[3] and a mixed m.p. showed no depression. Next eluted was the quinone (IV), m.p. and mixed m.p. 286·5–287°. Identity was again confirmed by superimposable infrared spectra.

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[20] Mayer, F., *Liebigs Ann.*, 1931, **488**, 259.