

Synthesis of Potentially Basic Hydrocarbons by Sulphur Extrusion and/or Bis-Wittig Reactions. Two Syntheses of Benz[5,6]indeno[2,1-*a*]-phenalene and a New Synthesis of Dibenzo[*de,mn*]naphthacene (Zethrene)

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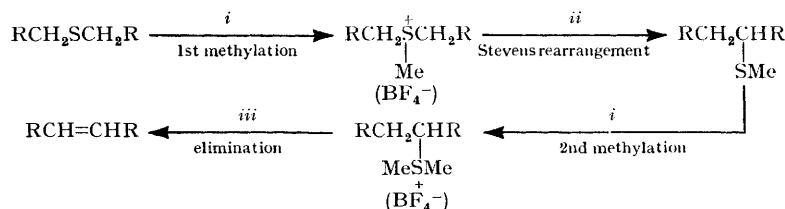
Macrocyclic bis-sulphides have been prepared from 1,2-, 2,3-, and 1,8-bis(bromomethyl)naphthalenes. Methylation of the bis-sulphides, followed by the Stevens rearrangement, gave the corresponding carbocycles with extra-annular sulphide groups; removal of these sulphide groups by Hofmann elimination led to spontaneous trans-annular condensation. Using this general method, two hydrocarbons were synthesized: benz[5,6]indeno[2,1-*a*]-phenalene and dibenzo[*de,mn*]naphthacene (or zethrene). An alternative synthetic route led to the synthesis of benz[5,6]indeno[2,1-*a*]phenalene, using the Wittig reaction between naphthalene-2,3-carbaldehyde and 1,8-bis(triphenylphosphoniomethyl)naphthalene dibromide.

CARBON-carbon bond formation by sulphur extrusion has been used extensively and successfully by Mitchell and Boekelheide¹ in their studies on pyrene-based molecules. In particular they have synthesized 15,16-dimethyldihydropyrene (4; R = Me) in 60–70% overall yield from the *anti*-2,11-dithia-9,18-dimethyl-[3,3]metacyclophane (1; R = Me, with aromatic rings on opposite sides of the sulphur centres) following the reactions of Scheme 1. The method has also been used by Mitchell and Carruthers,² Haenel and Staab,³ and Davy and Reiss.⁴

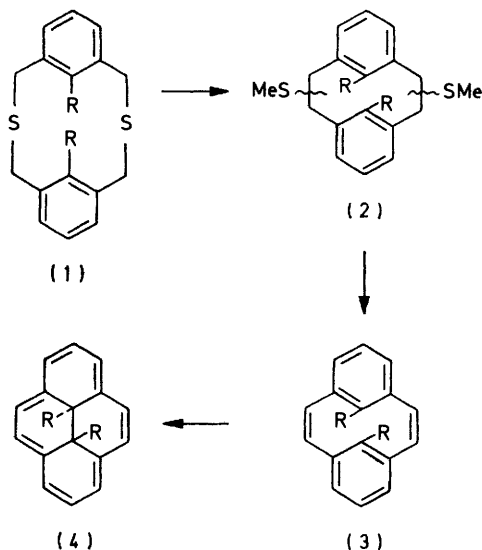
We were interested in the extension of this reaction to

syntheses of potentially basic polynuclear hydrocarbons in the naphthalene series, in particular application of the reaction to the three bis-sulphides (5)–(7); we now report the synthesis of these sulphides and the successful transformation of (5) into dibenzo[*de,mn*]naphthacene (zethrene) (8), and of (6) into benz[5,6]indeno[2,1-*a*]phenalene (18).

Treatment of 1,8-naphthalic anhydride (9) with lithium aluminium hydride yields 1,8-bis(hydroxymethyl)naphthalene⁵ (10; R = OH) which on treatment with phosphorus tribromide⁶ yields 1,8-bis(bromomethyl)naphthalene (10; R = Br). 1,8-Bis-

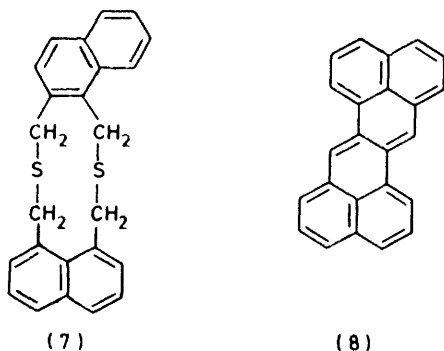
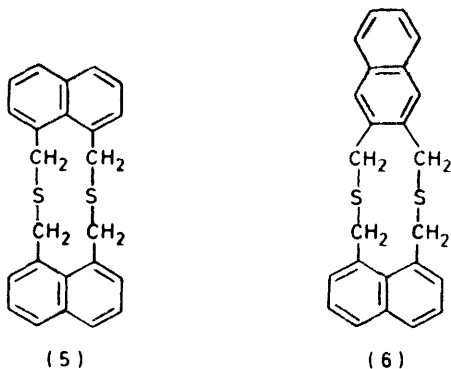


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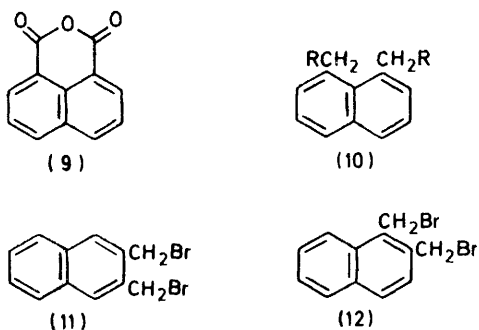


SCHEME 1 Reagents: *i*, (MeO)₂CH⁺BF₄⁻; *ii*, NaH-THF; *iii*, Bu^tOK

(mercaptomethyl)naphthalene (10; R = SH) can be obtained from this bromide by either of two variations of the isothiuronium salt method. Using Pan and Fletcher's variation,⁷ the thiuronium salt is prepared in



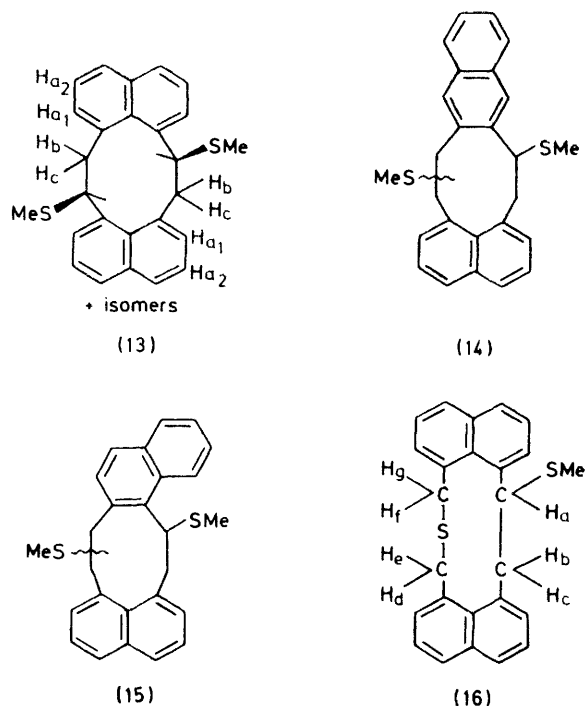
dimethyl sulphoxide and is not isolated but immediately hydrolysed. In the second variation the bromide is refluxed with thiourea in ethanol; the intermediate salt is isolated and subsequently hydrolysed. Treatment of this bismercaptan respectively with 1,8-bis(bromomethyl)naphthalene (10; R = Br), 2,3-bis(bromomethyl)naphthalene (11), and 1,2-bis(bromomethyl)naphthalene (12), yields the three bis-sulphides (5), (6), and (7).



The methylation of each of the sulphides occurs in essentially quantitative yield using dimethoxycarbonium tetrafluoroborate.⁸ The Stevens rearrangement is easily carried out using either sodium hydride in dry tetrahydrofuran or by sodium ethoxide-ethanol in dry tetrahydrofuran, the latter being the more rapid method. The products formed are mixtures of isomers represented by (13), (14), and (15) respectively.

The mixtures represented by (14) and (15) were very complex mixtures of approximately eight isomers each. There are no major components in either mixture and it was not found possible to isolate individual compounds. The n.m.r. spectra of the mixtures were also complicated, but indicated that the above structures were present. The mixture represented by (13) on the other hand, comprised only three components, one of which was preponderant; this was separated by chromatography.

On the evidence of coupling constants (see Experimental section) we infer that the two naphthalene residues in (13) have the *syn* configuration with respect to the two disubstituted ethane bridges; two vicinal couplings are involved in each bridge, between the methine proton and, successively, each proton of the methylene group. In molecular models of the *syn* isomers, dihedral angles of approximately 10 and 140° arise between the coupling protons, and predicted coupling constants (Karplus equations) are 8 and 6 Hz



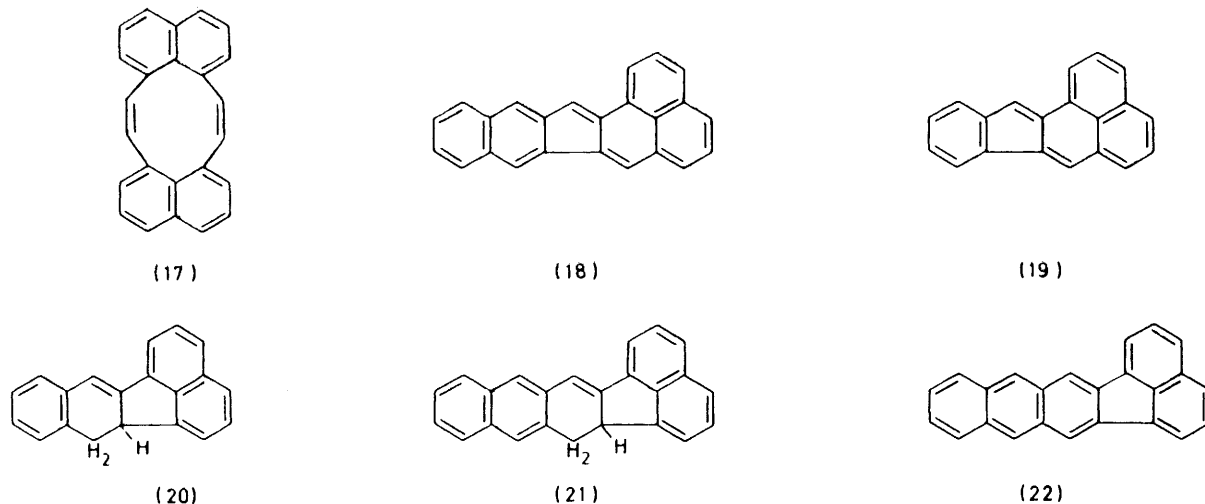
respectively: the observed coupling constants are 10 and 8 Hz. Models of all *anti* isomers show dihedral angles of 60 and 180°, which would lead to predicted coupling constants of 2 and 10 Hz respectively.

Since both methyl groups in (13) have the same chemical shift value (δ 2.1), and since one hydrogen in each naphthalene residue is strongly deshielded (at δ 7.8) it seems likely that (13) has the SMe groups disposed as shown in formula (13), bringing the SMe and naphthalene rings into closest proximity. [In one run of the reaction sequence (5)→(13) there was also isolated a bis-sulphide which has been assigned the structure (16), in which the naphthalene residues have *syn* configuration with respect to the ethane bridge, on the basis of chemical shifts and

coupling constants as above. It is obviously formed by the Stevens rearrangement of the mono-methylated derivative of (5).

The methylation of the mixture represented by (13) proved surprising in that zethrene itself was isolated in

contrast, adding a solution of the phosphonium salt and naphthalene-2,3-dicarbaldehyde to a stirred solution of sodium ethoxide in ethanol under nitrogen yielded benz[5,6]indeno[2,1-*a*]phenalene (18) as the major component.



low yield from the reaction mixture along with the expected mixture of sulphonium salts. It is likely that this arises by spontaneous elimination of molecules of dimethyl sulphide, but no zethrene is obtained when the mixture of sulphonium salts is simply refluxed in benzene. Treatment of this mixture of sulphonium salts with sodium ethoxide and ethanol in THF rapidly gives zethrene, which is isolated by chromatography. The formation of zethrene must involve initial formation of the unstable hydrocarbon (17) as intermediate. This compound has been prepared⁹ and is known to cyclize to zethrene in the presence of oxygen.

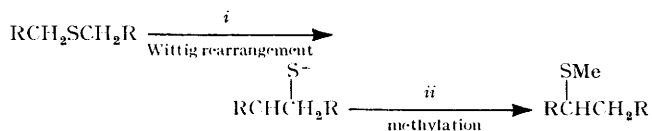
Methylation of the mixtures of sulphides represented by (14) and (15) proceeded in poor yield; treatment of the crude methylated products with sodium hydride or sodium ethoxide and ethanol in THF gave but trace amounts of hydrocarbon material.

This failure of the sulphides (6) and (7) to lend themselves to hydrocarbon synthesis induced us to attempt the synthesis of the benzindenophenalene (18) using a Wittig reaction. It is known^{10,11} that *o*-phthalaldehyde reacts with the bisphosphonium salt (10; R = P⁺Ph₃Br⁻) to yield indenophenalene (19) together with the dihydrobenzo[*k*]fluoranthene (20). We have treated the same phosphonium salt with naphthalene-2,3-dicarbaldehyde to yield the corresponding compounds, reaction conditions being optimised for each compound.

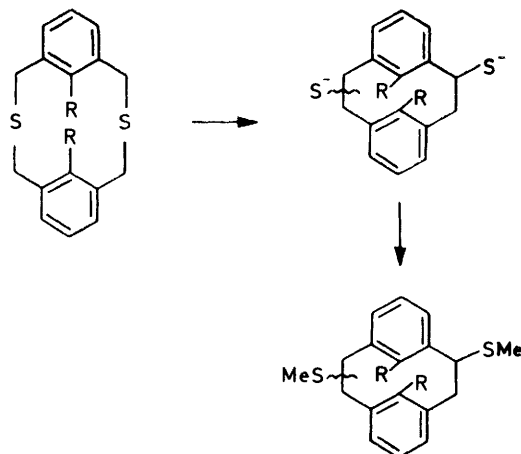
The phosphonium salt (10; R = P⁺Ph₃Br⁻) was first treated with sodium hydride in dry tetrahydrofuran (THF) to yield the phosphonium ylide, which was then treated with naphthalene-2,3-dicarbaldehyde to yield 7,8-dihydronaphtho[2,3-*k*]fluoranthene (21) as the major component. The structure was confirmed by dehydrogenation [with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)] to naphtho[2,3-*k*]fluoranthene (22). In

An adaptation of the original sulphur extrusion reaction has been used successfully.^{12,13} The reaction is outlined in Scheme 2.

As an alternative synthesis, therefore, of the indenophenalene (18), the bis-sulphide (6) was treated with *n*-butyl-lithium. Methylation with methyl iodide gave a mixture of isomers represented by (14). Further methylation with dimethoxycarbonium tetrafluoroborate and elimination using sodium ethoxide in ethanol yielded a red hydrocarbon confirmed to be benz[5,6]indeno[2,1-*a*]-



For example:



(Then as for Scheme 1, *i.e.* methylation followed by elimination.)

SCHEME 2 (for alternative route) Reagents: *i*, LiNPr₂; *ii*, MeI

phenalene by comparison with a sample obtained by the above Wittig reaction.

This hydrocarbon was expected to be basic, and this was indeed confirmed. The basicity of hydrocarbons is commonly defined¹⁴ as that concentration of a given volume of aqueous sulphuric acid which will extract 50% of the hydrocarbon from an equal volume of a solution of the hydrocarbon in cyclohexane, benzene, or toluene.

Using this scale (for solutions in benzene) we have measured the basicity of (18) to be 67.5% (H_0 5.45). This compares with 64% for indenophenale¹⁵ and 51% for azulene.¹⁶ The similarity in basicity for the two phenalenes (18) and (19) suggests that protonation of cyclopentaphenalenenes leads to an ion in which the charge is delocalised solely over the phenalenyl part of the molecule (rather than over the molecule as a whole) since, had the latter been true, the extended conjugation in benzindenophenale¹⁵ would be expected to stabilize the ion more than in the indenophenale¹⁵ system, leading to an increase in basicity beyond that which we observed.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer model 157G spectrophotometer. N.m.r. spectra were recorded on either a Perkin-Elmer model R12 spectrometer (60 MHz) or JEOL MH100 spectrometer (100 MHz); unless otherwise stated, $CDCl_3$ was used as solvent with tetramethylsilane as internal standard. Mass spectra were recorded on an AEI MS30 instrument.

2,3-Bis(bromomethyl)naphthalene (11) was prepared from 2,3-dimethylnaphthalene by bromination with *N*-bromosuccinimide, m.p. 144–145 °C (lit.,¹⁶ 145 °C), δ 7.8–8.3 (6 H, m) and 4.8 (4 H, s). 1,2-Bis(bromomethyl)naphthalene (12) was prepared similarly from 1,2-dimethylnaphthalene, m.p. 148–150 °C (lit.,¹⁶ 153 °C), δ 7.3–8.3 (6 H, m), 5.05 (2 H, s), and 4.77 (2 H, s). 1,8-Bis(hydroxymethyl)naphthalene (10; R = OH) was prepared by the method of Boekelheide and Vick,⁵ m.p. 156–158 °C (lit.,⁵ 157.8 °C), ν_{max} (KBr) 3 340 and 3 240 cm^{-1} . 1,8-Bis(bromomethyl)naphthalene (10; R = Br) was prepared by the method of Carpino,⁶ m.p. 126–128 °C (lit.,⁶ 130 °C), δ 7.2–7.9 (6 H, m) and 5.25 (4 H, s). 1,8-Bis(triphenylphosphoniummethyl)naphthalene dibromide (10; R = $P^+Ph_3Br^-$) was prepared by the method of Bestmann *et al.*¹⁷ Naphthalene-2,3-dicarbaldehyde was prepared by the method of Ried and Bodem.¹⁸

1,8-Bis(mercaptomethyl)naphthalene (10; R = SH).—(a) By the method of Pan and Fletcher.⁷ 1,8-Bis(bromomethyl)naphthalene (31.4 g, 0.1 mol) and thiourea (16.8 g, 0.22 mol) were stirred continuously in dimethyl sulphoxide (150 cm^3) for 15 h at 20 °C. To this was added a solution of sodium hydroxide (60 g) in water (600 cm^3) and the stirring continued for 30 min; the mixture was acidified slowly with 20% hydrochloric acid. The dithiol was filtered off, washed with water, and dried (average yield 70%).

(b) 1,8-Bis(bromomethyl)naphthalene (31.4 g, 0.1 mol) and thiourea (16.8 g, 0.22 mol) were refluxed in ethanol (200 cm^3) for 1 h; after cooling, the thiuronium salt was filtered off and subsequently refluxed with potassium hydroxide (100 g) in water (300 cm^3) for 5 h. The solution was cooled and acidified slowly with 5*M* sulphuric acid. The dithiol was extracted with methylene chloride and the organic layer washed with water and dried ($MgSO_4$).

Removal of solvent gave a solid (15 g, 70%) which was recrystallized from benzene–light petroleum (b.p. 40–60 °C) (1 : 1 v/v) to give the dithiol as white needles, m.p. 70–72 °C (Found: C, 65.6; H, 5.55. $C_{12}H_{12}S_2$ requires C, 65.45; H, 5.56%); ν_{max} (KBr) 2 540, 1 590, 1 435, 1 375, 1 230, 1 220, 1 170, 1 160, 1 110, 1 020, 965, 955, 825, 770, 690, and 640 cm^{-1} ; δ 7.3–7.9 (6 H, m, Ar), 4.45 [4 H, d, J 6 Hz (CH_2)₂], and 1.8 [2 H, t, J 6 Hz (SH)₂] (with D_2O the signal at δ 1.8 disappears and that at δ 4.45 collapses to a singlet); *m/e* 220 (51%; M^+), 186 (100), 185 (80), 171 (60), and 153 (90).

7H,9H,16H,18H,*Dinaphtho*[1,8-cd:1',8'-ij][1,7]*dithia-cyclododecin* (5).—The dithiol (10; R = SH) (10 g) was dissolved in a solution of sodium hydroxide (4 g) in ethanol (400 cm^3) and water (100 cm^3). 1,8-Bis(bromomethyl)naphthalene (14 g) was separately dissolved in benzene (250 cm^3) and ethanol (100 cm^3). These two solutions were added simultaneously to refluxing ethanol (1 litre) over 5 h and the final mixture was refluxed for 1 h; on cooling the bis-sulphide (5) was filtered off and dried (9.5 g, 56%). (This product was adequately pure for subsequent reactions.) Recrystallisation from chloroform gave *feathery needles*, m.p. 290–291 °C (decomp.) (Found: C, 77.4; H, 5.3; S, 17.45. $C_{24}H_{20}S_2$ requires C, 77.42; H, 5.37; S, 17.21%); ν_{max} (KBr) 3 060, 3 030, 2 920, 1 600, 1 510, 1 485, 1 385, 1 210, 1 170, 830, and 770 cm^{-1} ; δ 7.2–7.9 (12 H, m, Ar), and 4.65 [8 H, s, (CH_2)₄]; *m/e* 372 (20%, M^+), 186 (80), 185 (80), and 153 (100).

9,16-*Dihydro*-7H,18H-*dinaphtho*[1,8-hi:2',3'-c][1,6]*dithia-cycloundecin* (6).—Prepared as for (5) above, substituting 2,3-bis(bromomethyl)naphthalene for the 1,8-isomer, the bis-sulphide was isolated as *needles*, m.p. 255–257 °C (decomp.) (Found: C, 77.35; H, 5.4; S, 16.95%); ν_{max} (KBr) 3 040, 2 920, 1 590, 1 496, 1 460, 1 450, 1 370, 1 220, 1 200, 875, 820, 770, 745, and 740 cm^{-1} ; δ 7.2–7.9 (12 H, m, Ar), 4.5 [4 H, s, (CH_2)₂], and 4.25 [4 H, s, (CH_2)₂]; *m/e* 372 (20%, M^+), 186 (90), 185 (100), and 153 (50).

9,16-*Dihydro*-7H,18H-*dinaphtho*[1,2-c:1',8'-hi][1,6]-*dithiacycloundecin* (7).—This was prepared as for (5) above, substituting 1,2-bis(bromomethyl)naphthalene for the 1,8-isomer, as *needles*, m.p. 246–248 °C (decomp.) (Found: C, 77.1; H, 5.45; S, 17.3%); ν_{max} (KBr) 3 050, 3 020, 2 920, 1 590, 1 500, 1 440, 1 420, 1 375, 1 220, 1 210, 1 170, 860, 845, 820, 810, 770, 750, and 740 cm^{-1} ; δ 7.2–7.8 (12 H, m, Ar), and 4.2, 4.4, 4.5, and 4.53 (4 × 2 H, 4 × s, 4 × CH_2); *m/e* 372 (4%, M^+), 186 (100), 185 (95), and 153 (60).

Methylation of the Bis-sulphides (5), (6), and (7).—The respective bis-sulphide (10 g) was suspended in methylene chloride (100 cm^3) and added to a suspension of dimethoxy-carbonium fluoroborate (10 g, excess) in methylene chloride (100 cm^3) at –30 °C. When the addition was complete the temperature was allowed to rise to room temperature and the mixture was stirred for a further 4 h; ethyl acetate (100 cm^3) was added and stirring continued for 30 min, whereupon the precipitated sulphonium fluoroborate was filtered off, washed with ethyl acetate and dried. Yields were virtually quantitative. Thus 7H,9H,16H,18H-*dinaphtho*[1,8-cd:1',8'-ij][1,7]*dithioniacyclododecin bistetrafluoroborate*, a white powder, had m.p. 170–172 °C (Found: C, 54.25; H, 4.7. $C_{26}H_{26}S_2B_2F_8$ requires C, 54.16; H, 4.51%); δ ($[^2H_6]$ DMSO) 7.4–8.2 (12 H, m, Ar), 4.8 and 4.9 [4 H and 4 H, d, J_{gem} 15 Hz, (CH_2)₄], and 2.4 (6 H, s, 2 Me); 9,16-*dihydro*-7H,18H-*dinaphtho*[1,8-hi:2',3'-c][1,6]*dithioniacycloundecin bistetrafluoroborate*, a white powder, had m.p. 170–172 °C (Found: C, 53.9; H, 4.7%; δ ($[^2H_6]$ DMSO) 7.0–8.0 (12 H, m, Ar), 4.9–5.5 [8 H, distorted doublets, *gem*

coupling, $(\text{CH}_2)_4$, 2.9 (3 H, s, Me), and 1.8 (3 H, s, Me); and 9,16-dihydro-7H,18H-dinaphtho[1,2-c:1',8'-hi][1,6]dithionia-cycloundecim bistetrafluoroborate, a white powder, had m.p. 170—174 °C (Found: C, 53.75; H, 4.85%); δ ($^2\text{H}_6$)-DMSO) 7.2—8.2 (12 H, m, Ar), 4.8—5.6 [8 H, distorted doublets, *gem* coupling, $(\text{CH}_2)_4$], 3.5 (3 H, s, Me), and 3.5 (3 H, s, Me).

1,11-Bis(methylthio)[2,2](1,8)naphthalenophane (13).—In the case of (13), the mixture was chromatographed on silica gel (70—230 mesh, Kieselgel 60, Merck) using benzene-light petroleum (b.p. 40—60 °C; 1 : 1 v/v) as eluant and the major product was crystallized from benzene-light petroleum (b.p. 60—80 °C; 1 : 1 v/v) yielding fine white needles, m.p. 166—170 °C, δ 7.8 (2 H, dd, $J_{a1,a2}$ 6, $J_{a1,a3}$ 2 Hz, H_{a1}), 7.2—6.4 (10 H, m, Ar), 6.2 (2 H, dd, J_{bc} 8, J_{bd} 10 Hz, H_b), 4.5 (2 H, dd, J_{bc} 8, J_{cd} 15 Hz, H_c), 3.0 (2 H, dd, J_{bd} 10, J_{cd} 15 Hz, H_d), and 2.1 (6 H, s, SMe); *m/e* 400 (9%, M^+), 352 (15), 306 (40), 305 (70), 304 (30), 303 (25), 289 (25), 153 (100), and 152 (50).

Stevens Rearrangement.—To a stirred suspension of the respective methylsulphonium salt (5 g) in dry tetrahydrofuran was added a solution of sodium ethoxide in ethanol (10 cm³ of 10% solution). The mixture was stirred for 30 min and poured into an excess of 2M-hydrochloric acid. The whole was extracted with methylene chloride, which was then washed with water, dried (MgSO_4), and the solvent evaporated off. This method gave yields of approximately 60—70% of total product mixtures, *viz.* (13), (14), and (15).

13-Methylthio-2-thia[3,2](1,8)naphthalenophane (16).—In one run of the reaction sequence (5) \rightarrow (12) white crystals formed in the reaction vessel. The solution was reduced in volume by half and filtered. Crystallization from chloroform yielded colourless crystals, m.p. 223—225 °C; δ 7.9—7.0 (12 H, m, Ar), 5.7 (1 H, dd, J_{ac} 10, J_{ab} 2 Hz, H_a), 4.5 (1 H, d, J_{fg} 12 Hz, H_g), 4.3 (1 H, d, J_{de} 13 Hz, H_d or H_e), 4.0—3.7 (3 H, m, H_e or H_d , H_f , and H_h), 3.2 (1 H, dd, J_{ac} 10, J_{bc} 16 Hz, H_c), 1.8 (3 H, s, SMe); *m/e* 386 (4%, M^+), 388 (10), 303 (10), 201 (40), 185 (100), and 153 (30).

2nd Methylation.—The products from the Stevens rearrangements (5 g) were methylated with dimethoxycarbonium tetrafluoroborate (5 g, excess) using the same method as before. The mixtures (14) and (15) yielded small quantities of brown sticky solids. Mixture (13) yielded a pinkish solid (6 g).

Dibenzo[de,mn]naphthacene (8).—The mother-liquors from the methylation of (13) were concentrated and, after chromatography on alumina (Brockmann Grade I, BDH) using benzene-light petroleum (b.p. 40—60 °C; 1 : 2 v/v), yielded dibenzo[de,mn]naphthacene as violet needles (70 mg) m.p. 258—260 °C (lit.,¹⁹ 262 °C), λ_{max} (benzene) 550, 510, 473, 408, 385, and 307 nm (log ϵ 4.95, 4.81, 4.40, 3.44, 3.43, and 4.65). The hydrocarbon dissolved in concentrated sulphuric acid to give a blue colour which rapidly turned red.

Elimination.—The methylated sulphides were stirred in tetrahydrofuran (50 cm³) and sodium ethoxide (1 g) in absolute ethanol (10 cm³) was added. After stirring for 1 h, water (50 cm³) was added and the mixture extracted with benzene (100 cm³). The benzene layer was washed thoroughly with 10% aqueous sodium chloride. The benzene solution was dried (MgSO_4), concentrated, and chromatographed on alumina (Brockmann Grade I). Only the bis-sulphide mixture (13) yielded recognizable product, *viz.* dibenzo[de,mn]naphthacene (100 mg, 10%), similar in all details to the sample obtained above.

6b,7-Dihydronaphtho[2,3-k]fluoranthene (21).—(a) 1,8-Bis(triphenylphosphoniomethyl)naphthalene dibromide (10; R = $\text{P}^+\text{PR}_3\text{Br}^-$) (4.2 g, 0.005 mol) was stirred overnight in tetrahydrofuran (100 cm³) with sodium hydride (2 g of a 50% suspension in oil) under nitrogen. Naphthalene-2,3-dicarbaldehyde (1 g, 0.005 mol) in tetrahydrofuran (50 cm³) was added and the mixture stirred for a further 1 h. Water was carefully added, the mixture was extracted with benzene, and the organic layer was washed with 10% sodium chloride solution and then dried (MgSO_4). Concentration of the solution was followed by chromatography on alumina (Brockmann Grade I) using a gradient elution of light petroleum (b.p. 40—60 °C) up to light petroleum-benzene (4 : 1 v/v) when 6b,7-dihydronaphtho[2,3-k]fluoranthene (21) was eluted (100 mg, 6%). The fine yellow needles had m.p. 278—280 °C (Found: C, 94.7; H, 5.3. $\text{C}_{24}\text{H}_{16}$ requires C, 94.73; H, 5.26%); δ 7.9—7.3 (13 H, m, Ar) and 4.5—3.0 (3 H, indistinct multiplet, $-\text{CH}_2-\text{CH}-$); *m/e* 304 (80%, M^+), 303 (90), 302 (100), 277 (80), and 152 (20); λ_{max} (EtOH) 437, 412, 377, 359, 333, 319, 300, 286.5, 265, 255.5, and 227 nm (log ϵ 3.44, 3.44, 4.09, 4.12, 4.51, 4.25, 4.02, 4.17, 4.29, 4.32, and 4.40). The hydrocarbon dissolved slowly in concentrated sulphuric acid to give a deep red solution with green fluorescence.

The structure of this hydrocarbon was confirmed by dehydrogenation with 2,3-dichloro-5,6-dicyanobenzo-1,4-quinone (DDQ) in boiling toluene to the known naphtho[2,3-k]fluoranthene, m.p. 300—302 °C (lit.,²⁰ 301—303 °C).

Benz[5,6]indeno[2,1-a]phenalene (18).—The dibromide (10; R = $\text{P}^+\text{Ph}_3\text{Br}^-$) (8.4 g, 0.01 mol) and naphthalene-2,3-dicarbaldehyde (2 g, 0.01 mol) in ethanol (75 cm³) were added dropwise to a stirred solution of sodium ethoxide in ethanol (0.5 g of sodium metal in 100 cm³ of ethanol) under nitrogen. The reaction mixture was stirred for a further 1 h, filtered, and the residue dissolved in a minimum of benzene and chromatographed on alumina (Brockmann Grade I) using a gradient elution of light petroleum (b.p. 40—60 °C) up to light petroleum-benzene (4 : 1 v/v), when a red hydrocarbon was eluted. The red coloured fractions were combined and the solvent evaporated. Crystallization from light petroleum-benzene (1 : 1 v/v) gave benz[5,6]indeno[2,1-a]phenalene (18) as red flakes with a coppery sheen, m.p. 284—285 °C (decomp.) (Found: C, 95.5; H, 4.6. $\text{C}_{24}\text{H}_{14}$ requires C, 95.36; H, 4.63%); δ (CCl_4) (^1H F.T. spectrum on Varian XL 100 instrument) 8.21—7.33 (m, Ar); *m/e* 302 (20%, M^+), 165 (30), 151 (74), and 132 (100); λ_{max} (benzene) 558, 518, 485, 450, 400, 381, 360, 336, 306, and 282.5 nm (log ϵ 3.90, 4.18, 4.18, 4.00, 4.05, 4.10, 3.96, 4.38, and 4.65). The hydrocarbon dissolved in concentrated sulphuric acid to give a green solution from which the original hydrocarbon could be regained by dilution with water.

(b) The bis-sulphide (6) (3.7 g, 0.01 mol) was stirred in dry tetrahydrofuran under nitrogen at 0 °C. *n*-Butyl-lithium in tetrahydrofuran [from 1-bromobutane (3 cm³) and lithium metal (0.5 g)] was added slowly to give a black solution. After stirring for 0.5 h, iodomethane (5 cm³, excess) was added followed by water (100 cm³). Extraction with dichloromethane followed by washing with water, drying (MgSO_4), and removal of solvent left a yellow oil as a mixture of isomers represented by (14) (3.5 g, 88%).

This oil was further methylated with dimethoxycarbonium tetrafluoroborate using the standard method. Treatment of the solid residue with sodium ethoxide in ethanol and tetrahydrofuran according to the method used for the other

sulphonium salts and similar work-up yielded a red hydrocarbon (10 mg, 0.3%) which was identical with the sample of benz[5,6]indeno[2,1-*a*]phenalene as prepared by the Wittig reaction.

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