Intramolecular Nitrene Insertions into Aromatic and Heteroaromatic Systems. Part II.[1] Insertions into Thiophen Rings

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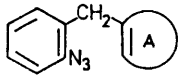
Thermal decomposition of 2-(2-azidobenzyl)thiophen (5) and of 2-(2-azidobenzyl)-5-methylthiophen (9) gives thieno[3,2-*b*]quinoline (14) and the 2-methyl derivative (19), respectively; in the former case a second major product was 1,2-dihydropyrrolo[1,2-*a*]indole-3-thione (17), obtained with a small amount of the corresponding 2-oxo-compound (18). Decomposition of 3-(2-azidobenzyl)-2,5-dimethylthiophen (13) gave 2,4-dimethylthieno[3,2-*c*]quinoline (22), with smaller amounts of 3-(2-aminobenzyl)-2,5-dimethylthiophen (12) and 2-methyl-3-propylquinoline (20). Mechanisms for these nitrene insertions are suggested; the thienoquinolines (14) and (22) have been synthesised by standard procedures.

We have reported examples of intramolecular nitrene insertions during thermal decomposition of 2-(2-azidobenzyl)-substituted aromatic systems of type (1) where ring A is benzenoid [1-3] or naphthalenic.[1] As a further step in a study of the effect on the type of insertion of varying degrees of electron availability in ring A, we now



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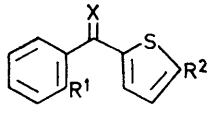
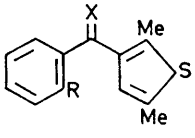




(10) R = NO_2, X = O
(11) R = NH_2, X = O
(12) R = NH_2, X = H_2
(13) R = N_3, X = H_2

(2) R^1 = NO_2, R^2 = H, X = O
(3) R^1 = NH_2, R^2 = H, X = O
(4) R^1 = NH_2, R^2 = H, X = H_2
(5) R^1 = N_3, R^2 = H, X = H_2
(6) R^1 = NO_2, R^2 = Me, X = O
(7) R^1 = NH_2, R^2 = Me, X = O
(8) R^1 = NH_2, R^2 = Me, X = H_2
(9) R^1 = N_3, R^2 = Me, X = H_2

report the reactions observed in the decomposition of three 2-azidobenzylthiophens.

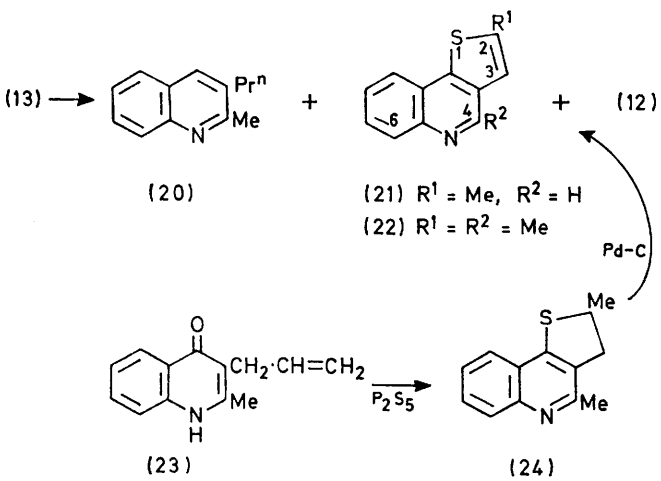
The three azides (5), (9), and (13) were prepared by similar sequences from the appropriate thiophens by Friedel–Crafts aroylation with 2-nitrobenzoyl chloride, sequential catalytic and Huang-Minlon reduction, and final treatment of the diazotised 2-aminobenzyl derivatives with azide ion. They were decomposed in trichlorobenzene solution at 180—190°, and the products were worked up by column and preparative layer chromatography.

Decomposition of 2-(2-azidobenzyl)thiophen (5) gave a dark-coloured mixture of which less than 20% was isolated as pure materials. Of the three major products the simplest was 2-(2-aminobenzyl)thiophen (4) (5%). A second product, $C_{11}H_7NS$, gave a typical polycyclic u.v. spectrum, and an n.m.r. spectrum in which all signals were below δ 7·0. The presence of a broad doublet (J 7 Hz) at δ 8·2 and of a singlet at δ 8·85 suggested a thienoquinoline structure. Addition of shift reagent caused a downfield shift in two signals, the aforementioned broad doublet and a second doublet which its coupling constant (3 Hz) indicated must be due to a proton on the thiophen ring; hence the product was thieno[3,2-*b*]quinoline (14) (5%). An acid-catalysed Friedländer synthesis using 4,5-dihydrothiophen-3-one [4] gave a mixture (2 : 1) of the dihydrothieno[3,2-*b*]quinoline (15) and the dihydro[3,4-*b*]-quinoline (16); dehydrogenation of the mixture, or of the

[1] Part I, R. N. Carde and G. Jones, preceding paper.
[2] E. W. Collington, G. Jones, and G. R. Cliff, *J. Chem. Soc.* (*C*), 1970, 1490.
[3] G. R. Cliff and G. Jones, *J. Chem. Soc.* (*C*), 1971, 3418.
[4] M. Gianturco, P. Friedel, and A. S. Giammarino, *Tetrahedron*, 1964, **20**, 1763.

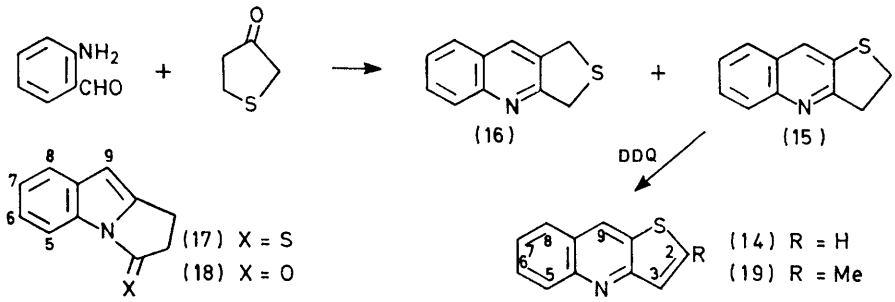
pure thienoquinoline (15), with dichlorodicyanobenzoquinone (DDQ), gave thieno[3,2-*b*]quinoline (14), identical with the insertion product.

The third major product, $C_{11}H_9NS$ [(6%) from the azide (5)], showed an indole chromophore ($\lambda_{max.}$ 273 and 310 nm) and a base peak in the mass spectrum at 187 (M^+) with major losses of 33 (*m/e* 154) and 33 + 28 (*m/e* 136) mass units. The n.m.r. spectrum showed an indole β-proton signal at δ 6·15, a high-field broadened doublet (1H) at δ 8·8, and two methylene triplets at δ 2·7—3·0 and 3·2—3·5. These data were in keeping with the 1,2-dihydropyrrolo[1,2-*a*]indol-3-thione structure (17); notable are the deshielding of H-5 shown by similar systems [3,5] and the similarity of the alicyclic section of the n.m.r. spectrum to that of indan-1-one. The residues left after removal of the three major products contained a small amount of 1,2-dihydropyrrolo[1,2-*a*]indol-3-one (18), identical with a specimen supplied by Professor Franck.[6] The similarity in spectral properties between compounds (17) and (18) supports the thione formula for compound (17). Decomposition of the homologous azide (9) gave as major product an unstable red compound which has not been characterised; some amine (8) and some 2-methylthieno[3,2-*b*]quinoline (19) were also identified.



Decomposition of the β-substituted thiophen (13) gave a much cleaner reaction mixture from which five compounds were isolated. The most easily identified were the amine (12) (15%) and 2-methyl-3-propylquinoline (20) (3%), which was identical with a synthetic specimen.

The major product (34%) was shown by analysis and molecular weight to be a dimethylthienoquinoline, but



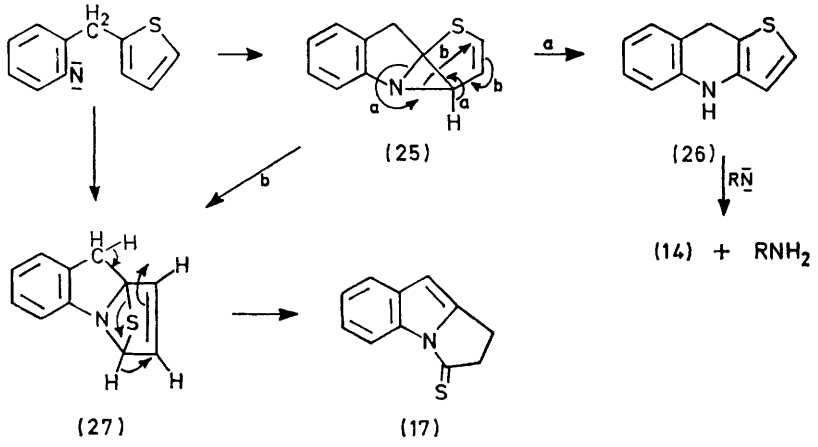
the u.v. spectrum was appreciably different from that of thieno[3,2-*b*]quinoline (14) and similar to that reported [7] for the isomeric thieno[3,2-*c*]quinoline (21). The n.m.r. spectrum showed signals at δ 2·6 (3H, d, *J* 1·2 Hz) and 2·74 (3H, s) (methyl groups), 6·99 (1H, q, *J* 1·2 Hz), and 7·35—8·1 (3H, m). All these observations accord well with the 2,4-dimethylthieno[3,2-*c*]quinoline structure (22); addition of the shift reagent Eu(fod)$_3$ produced large downfield shifts in a broadened n.m.r. doublet (aromatic region, H-6) and in the singlet methyl signal (4-Me). The reaction between 3-allyl-2-methyl-4-quinolone [8] (23) and phosphorus pentasulphide gave 2,3-dihydro-2,4-dimethylthieno[3,2-*c*]quinoline (24), which was dehydrogenated by palladium–charcoal to give 2,4-dimethylthieno[3,2-*c*]quinoline (22), identical with the insertion product. The other two minor products isolated were isomers, $C_{13}H_{13}NS$, but were not dihydro-derivatives of compound (22); their structures have not been elucidated.

The results of our insertion experiments can be explained as shown in Schemes 1 and 2. Intramolecular insertion of the nitrene appears to occur into the 2,3-bond whether the thiophen is α- or β-substituted, giving aziridine intermediates (25) and (28), respectively, as postulated previously.[9] Opening of the three-membered ring in intermediate (25) (Scheme 1) would give a dihydrothieno[3,2-*b*]quinoline (26). As no oxygen is present during the decomposition, and since the amine (hydrogen abstraction product) is a rarity in nitrene decompositions performed in trichlorobenzene, it seems probable that the nitrene abstracts hydrogen from the dihydro-intermediate (26), giving the observed products. More interesting in the case of the α-substituted thiophen is the formation of the thione (17), in which the thiophen ring has been ruptured. An intermediate which undergoes thiophen ring cleavage is possible,[10] but we now prefer an

[5] C. Kaneko, S. Yamoda, and M. Ishikawa, *Chem. and Pharm. Bull* (*Japan*), 1969, **17**, 1294.
[6] R. W. Franck and J. Auerbach, *J. Org. Chem.*, 1971, **36**, 31.
[7] G. Kobayashi, Y. Kuwayama, and S. Okamura, *Yakugaku Zasshi*, 1963, **83**, 234.
[8] Y. Makisumi, *Chem. and Pharm. Bull.* (*Japan*), 1964, **12**, 789.
[9] K. Hafner and W. Kaiser, *Tetrahedron Letters*, 1964, 2185.
[10] G. R. Cliff, G. Jones, and J. M. Woollard, *Tetrahedron Letters*, 1973, 2401.

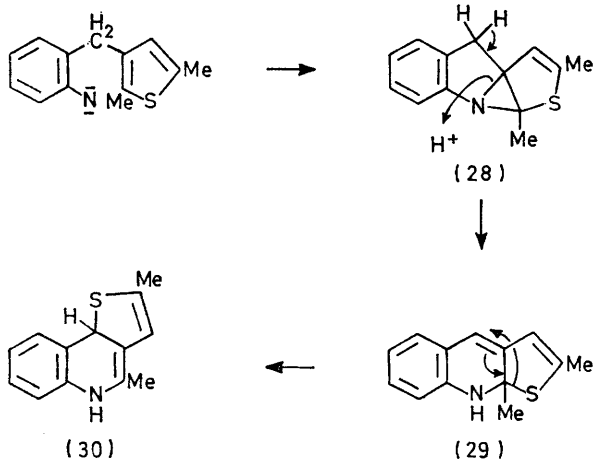
insertion procedure leading either *via* the aziridine (25) (see ref. 9) or possibly directly to the bicyclic intermediate (27). The possibility of a 1,4-insertion of a nitrene into a diene system has been discussed but no proved examples are available.

From the β-substituted thiophen (13), insertion into the 2,3-bond gives the aziridine (28). Proton transfer



SCHEME 1

gives the intermediate (29), which by a 1,3-sulphur shift can produce a dihydrothieno[3,2-*c*]quinoline (30). Dehydrogenation can again be envisaged by hydrogen



SCHEME 2

abstraction, accounting for the formation of the amine (12).

EXPERIMENTAL

U.v. spectra were recorded for solutions in 95% ethanol. Column chromatography was performed on Woelm alumina and preparative layer chromatography (p.l.c.) on 40 cm plates of Merck P_{254} silica gel.

2-(2-*Nitrobenzoyl*)*thiophen* (2).—A mixture of tin(IV) chloride (70 g) and 2-nitrobenzoyl chloride (70 g) was added dropwise to a stirred ice-cold solution of thiophen (46 ml; *ca.* 2-fold excess) in carbon disulphide (300 ml). The tarry mixture was allowed to come to room temperature, the supernatant carbon disulphide was poured onto ice–hydrochloric acid, and the organic layer was separated. The aqueous phase was extracted with ether and the combined organic layers were dried and evaporated, giving crude 2-(2-nitrobenzoyl)thiophen as an oil. More product was obtained by treating the remaining tarry mixture with cold dilute hydrochloric acid; the tar solidified and a brown oil was obtained by washing the solid with benzene and evaporation. Exhaustive extraction of the solid with hot methanol and evaporation of the extracts gave more crude 2-(2-nitrobenzoyl)thiophen. The three fractions were combined and crystallised several times from methanol, giving the benzoylthiophen (2), m.p. 97—98° (lit.[11] 97—98°) (50% yield).

2-*Methyl*-5-(2-*nitrobenzoyl*)*thiophen* (6).—Prepared as above, the *thiophen* (6) had m.p. 105—107° (from methanol) (Found: C, 58·4; H, 4·15; N, 5·4. $C_{12}H_9NO_3S$ requires C, 58·3; H, 3·65; N, 5·75%); $\nu_{max.}$ (Nujol) 1520 and 1640 cm^{-1}; δ 2·5 (3H, s), 6·75 (1H, d), 7·1 (1H, m), 7·5—7·9 (3H, m), and 8·15 (1H, m).

2,5-*Dimethyl*-3-(2-*nitrobenzoyl*)*thiophen* (10).—Prepared as above, the *thiophen* (10) was isolated mainly from the methanolic extracts, and, after chromatography (30% ether–chloroform), crystallised from methanol; m.p. 89—90° (Found: C, 60·0; H, 4·5; N, 5·4. $C_{13}H_{11}NO_3S$ requires C, 59·9; H, 4·2; N, 5·35%); $\nu_{max.}$ (Nujol) 1520 and 1665 cm^{-1}; δ ($CDCl_3$) 2·3 (3H, s), 2·6 (3H, s), 6·5 (1H, s), 7·4—7·9 (3H, m), and 8·3 (1H, m).

2-(2-*Aminobenzoyl*)*thiophen* (3).—A solution of the nitrobenzoylthiophen (2) (57·3 g) and concentrated hydrochloric acid (12 ml) in ethanol (600 ml) and dimethoxyethane (300 ml) was hydrogenated at atmospheric temperature and pressure over 10% palladium–charcoal (10 g) until 3 equiv. had been absorbed. The mixture was filtered, and the filtrate evaporated. The residue was basified with 10% sodium hydroxide solution and extracted with ether (3 × 100 ml). The extracts were dried, and on evaporation left substantially pure 2-(2-*aminobenzoyl*)*thiophen* (3) (48 g, 96%), distilled for analysis; b.p. 151° at 0·25 mmHg (Found: C, 65·1; H, 4·75; N, 7·1. $C_{11}H_9NOS$ requires C, 65·0; H, 4·45; N, 6·9%); $\nu_{max.}$ (CCl_4) 3500, 3340, and 1625 cm^{-1}; δ

[11] W. Steinkopf and E. Gunther, *Annalen*, 1936, **522**, 33.

($CDCl_3$) 5·7 (2H, s, exch. D_2O) and 6·5—7·9 (7H, m); $\lambda_{max.}$ 239 (log ε 4·25) and 267 nm (4·02).

2-(2-*Aminobenzoyl*)-5-*methylthiophen* (7).—Prepared by reduction of compound (6), the aminobenzoylthiophen (7) had m.p. 50—54°; $\nu_{max.}$(film) 3460, 3350, and 1620 cm^{-1}; δ ($CDCl_3$) 2·5 (3H, s), 5·4—6·0br (exch. D_2O), and 6·5—7·9 (6H, m).

3-(2-*Aminobenzoyl*)-2,5-*dimethylthiophen* (11).—Prepared by reduction of the nitrobenzoylthiophen (10), in 97% yield, the 3-aminobenzoyl-2,5-dimethylthiophen (11) was an oil; $\nu_{max.}$ (film) 3460, 3340, and 1620 cm^{-1}; δ ($CDCl_3$) 2·40 (6H, s), 5·7 (2H, s, exch. D_2O), and 6·6—7·7 (5H, m).

2-(2-*Aminobenzyl*)*thiophen* (4).—A mixture of the aminobenzoylthiophen (3) (48 g), hydrazine hydrate (50 ml; 98%), and ethylene glycol (500 ml) was distilled till the temperature reached 180°. The solution was cooled, potassium hydroxide (40 g) added, and the mixture distilled to the b.p. of ethylene glycol, then maintained under reflux (3 h). The cooled mixture was poured onto crushed ice and extracted with ether (3 × 150 ml). The extracts were dried and evaporated, and the residue distilled to give the *aminobenzoylthiophen* (4), b.p. 120° at 0·25 mmHg (40 g, 90%) (Found: C, 69·6; H, 5·6; N, 7·5. $C_{11}H_{11}NS$ requires C, 69·8; H, 5·85; N, 7·4%); $\nu_{max.}$ (film) 3440 and 3360 cm^{-1}; $\lambda_{max.}$ 234 (log ε 4·18) and 286 nm (3·38); δ (CCl_4) 3·4 (2H, s, exch. D_2O), 3·95 (2H, s), and 6·5—7·2 (7H, m).

2-(2-*Aminobenzyl*)-5-*methylthiophen* (8).—Prepared by reduction of the aminobenzoylthiophen (7), in 83% yield, 2-*aminobenzyl*-5-*methylthiophen* had m.p. 27—30° (Found: C, 71·3; H, 6·65; N, 7·0. $C_{12}H_{13}NS$ requires C, 70·9; H, 6·4; N, 6·9%); $\nu_{max.}$ (film) 3430 and 3360 cm^{-1}; $\lambda_{max.}$ 236 and 287 nm; δ ($CDCl_3$) 2·37 (3H, s), 3·5br (2H, exch. D_2O), 3·85 (2H, s), and 6·55—7·25 (6H, m).

3-(2-*Aminobenzyl*)-2,5-*dimethylthiophen* (12).—Prepared by reduction of the ketone (11), in 73% yield, the *aminobenzyldimethylthiophen* (12) had m.p. 50—52° (Found: C, 71·4; H, 6·85; N, 6·5. $C_{13}H_{15}NS$ requires C, 71·8; H, 6·9; N, 6·45%); $\nu_{max.}$ (Nujol) 3365, 3290br, and 3180br cm^{-1}; δ (CCl_4) 2·27 (6H, s), 3·31br (2H, exch. D_2O), 3·52 (2H, s), 6·21br (1H, s), and 6·5—7·05 (5H, m).

2-(2-*Azidobenzyl*)*thiophen* (5).—The azide (5) was prepared in 96% yield by a previously described method [3] (method 1) from the amine (4); $\nu_{max.}$ (CCl_4) 2120 cm^{-1}; δ (CCl_4) 4·0 (2H, s) and 6·6—7·2 (7H, m); *m/e* 187 (100%) ($M^+ - N_2$).

2-(2-*Azidobenzyl*)-5-*methylthiophen* (9).—Prepared from the amine (8) as described [3] (method 1) in 93% yield, the *azide* (9) had m.p. 55—58° (Found: C, 63·2; H, 4·6; N, 17·9. $C_{12}H_{11}N_3S$ requires C, 62·8; H, 4·8; N, 18·3%); $\nu_{max.}$ (Nujol) 2120 cm^{-1}; $\lambda_{max.}$ 248, 278sh, and 287sh nm; δ ($CDCl_3$) 2·39 (3H, s), 4·0, (2H, s), 6·57 (2H, s, thiophen β-H), and 7·0—7·4 (4H, m).

3-(2-*Azidobenzyl*)-2,5-*dimethylthiophen* (13).—Prepared from the amine (12) in almost quantitative yield [3] (method 1), as an oil, the azide (13) had $\nu_{max.}$ (film) 2120 cm^{-1}; δ (CCl_4) 2·24 (6H, s), 3·62 (2H, s), 6·25br (1H, s), and 6·78—7·1 (4H, m).

Decomposition of 2-(2-*Azidobenzyl*)*thiophen* (5).—The azide was decomposed in 1,2,4-trichlorobenzene solution at 180° (2·5 h) as previously described.[3] Evaporation left a residue containing three main products (g.l.c. peaks A, B, and C; *M* 189, 185, and 187, respectively). The crude residue was chromatographed (Al_2O_3 activity II; 350 g); elution with petroleum (b.p. 60–80°)–chloroform (7 : 3) gave only one substantially pure material (peak C), crystallised from acetone (charcoal) to give 1,2-*dihydropyrrolo*[1,2-a]-*indole*-3-*thione* (17), m.p. 103° (Found: C, 70·2; H, 4·75; N, 7·4. $C_{11}H_9NS$ requires C, 70·55; H, 4·85; N, 7·5%); $\lambda_{max.}$ 233 (log ε 4·0), 273 (4·09), and 310 nm (4·0); δ (CCl_4) 2·7—3·0 (2H, m), 3·2—3·5 (2H, m), 6·15 (1H, s, H-9), 7·1—7·5 (3H, m, H-6, -7, -8), and 8·8 (1H, m, H-5). A partition of the crude residue (or of the unresolved fractions from the alumina column) between chloroform and 25% hydrochloric acid gave the acid-soluble fractions A and B. Basification of the acid layer and extraction with ether gave (after evaporation) a residue separable by crystallisation from petroleum (b.p. 60—80°). The petroleum-insoluble fraction was *thieno*[3,2-b]*quinoline* (14), m.p. 113° (Found: C, 71·1; H, 3·9; N, 7·65. $C_{11}H_7NS$ requires C, 71·3; H, 3·8; N, 7·55%); $\lambda_{max.}$ 253 (log ε 4·91) and 336 nm (3·92); δ (CC_4) 7·3—7·9 (5H, m, H-2, -3, -6, -7, -8, 8·2br (1H, d, *J* 8 Hz, H-5), and 8·55 (1H, s, H-9); *m/e* 185 (M^+, 100%), 141 (12), 140 (12), and 92·5 (20). The petroleum-soluble fraction was purified by p.l.c. [petroleum (b.p. 60—80°)–ether (2 : 3)]; the upper band was removed and yielded the amine (4), identical with a synthetic specimen.

In a subsequent experiment the chromatography on alumina gave additionally a small quantity of 1,2-dihydropyrrolo[1,2-*a*]indol-3-one (18), m.p. 149° (from methanol) (lit.,[6] 150—154°; mixed m.p. showed no depression); $\nu_{max.}$ (Nujol) 1725, 1688, 1609, 1585, 1570, 1473, 1432, and 1412 cm^{-1}; δ ($CDCl_3$) 3·04 (4H, m), 6·25 (1H, s, H-9), 7·1—7·6 (3H, m), and 8·09br (d, H-5). Addition of Eu(fod)$_3$ caused the 4H multiplet to separate into two 2H multiplets, very similar to those for compound (17).

Decomposition of 2-(2-*Azidobenzyl*)-5-*methylthiophen* (9).—Decomposed in trichlorobenzene the azide (9) gave a mixture of which the main components were red. One fraction from column chromatography was 2-*methylthieno*[3,2-b]-*quinoline*, m.p. 111—114° (from toluene) (Found: C, 72·3; H, 4·65; N, 6·8. $C_{12}H_9NS$ requires C, 72·3; H, 4·55; N, 7·05%); $\lambda_{max.}$ 226sh (log ε 1·35), 255 (5·2), and 337 nm (0·81); δ ($CDCl_3$) 2·65 (3H, s), 7·2—8·0 (3H, m), 8·2 (1H, d, *J* 8 Hz, H-5), and 8·42 (1H, s, H-9).

Decomposition of 3-(2-*Azidobenzyl*)-2,5-*dimethylthiophen*-(13).—The azide was decomposed in trichlorobenzene at 180°; the crude residue left after evaporation of the solvent was chromatographed (Al_2O_3 activity II, 250 ml fractions). From fractions 5 and 6 was isolated 2,4-*dimethylthieno*-[3,2-c]*quinoline*, m.p. 71·5—73·5° (Found: C, 72·8; H, 5·1; N, 6·8. $C_{13}H_{11}NS$ requires C, 73·2; H, 5·25; N, 6·55%); $\lambda_{max.}$ 242 (log ε 3·23), 252sh, 260 (4·13), 280sh, 313 (0·21), 327 (0·34), and 342 nm (0·40); δ (CCl_4) 2·6 (3H, d, *J* 1·2 Hz, 2-Me), 2·74 (3H, s, 4-Me), 3·0 (1H, q, *J* 1·2 Hz, H-3), and 7·35—8·1 (4H, m) [signals at δ 2·74 and a broad doublet (*J* 8 Hz, H-5) moved downfield on addition of Eu(fod)$_3$]; *m/e* 213 (M^+, 100%), 212 (31), and 106·5 (11).

The other fractions from the column chromatography were subjected to p.l.c.; from faster-running fractions an oil was isolated, which slowly solidified and was identified as 2-methyl-3-propylquinoline (picrate, m.p. and mixed m.p. 224—227°); δ (CCl_4) 0·98 (3H, t, *J* 6 Hz, CH_3·CH_2), 1·3—2·0 (2H, m, CH_3·CH_2), 2·6 (2H, t, CH_2·CH_2·CH_3) underlying 3·6 (3H, s) [exposed by downfield shift of Me singlet on addition of Eu(fod)$_3$], 7·35—7·73 (4H, m), and 7·98 (1H, d, H-8). From later fractions the amine (12) was isolated.

Friedländer Synthesis of Thieno[3,2-b]*quinoline* (14).—(*a*) A mixture of 4,5-dihydrothiophen-3(2*H*)-one [4] (2·9 g) and 2-aminobenzaldehyde (3·5 g) in acetic acid (50 ml) with concentrated sulphuric acid (0·3 ml) was boiled (2·5 h). Further 2-aminobenzaldehyde (2 g) was added, and boiling was

continued (6 h). The cooled mixture was poured into ammonia–ice mixture and extracted with chloroform, and the extracts were re-extracted with 5N-hydrochloric acid. The acidic extracts were basified and extracted with chloroform, and the chloroform solution was dried ($MgSO_4$) and evaporated. The crude mixture (2·8 g, 54%) was estimated by n.m.r. spectroscopy and g.l.c. to be a 2 : 1 mixture of compounds (15) and (16). Chromatography of a sample on 40 cm p.l.c. plates [toluene–ethyl acetate (1 : 1)] gave only two bands with appreciable amounts of material. The faster-running was 1,3-dihydrothieno[3,4-*b*]quinoline (16), physical properties identical with those reported.[13]

The slower-running band was extracted to give 2,3-*dihydrothieno*[3,2-b]*quinoline* (15), b.p. 150—155° at 0·1 mmHg (bulb tube), m.p. 73—74° (Found: C, 70·1; H, 5·1; N, 7·4. $C_{11}H_9NS$ requires C, 70·5; H, 4·8; N, 7·5%); δ ($CDCl_3$) 3·42br (4H, s) and 7·0—8·0 (5H, m).

(*b*) A solution of the dihydro-derivative (15) (187 mg) [or the crude mixture of dihydro-derivatives (15) and (16)] and dichlorodicyanobenzoquinone (220 mg) in benzene (20 ml) was boiled (2 h). A precipitate was filtered off; the benzene layer was washed with aqueous sodium hydroxide, dried, and evaporated giving no residue. The precipitate was shaken with aqueous sodium hydroxide and chloroform and the chloroform extracts were dried and evaporated; the residue, crystallised from petroleum, had m.p. 113° and was identical with the product (14) from the decomposition of the azide (5).

2-*Methyl*-3-*propylquinoline* (20) *and* 3,4-*Dimethylthieno*[3,2-c]*quinoline* (22).—(*a*) 3-Allyl-2-methyl-4-quinolone [8] was converted by treatment with phosphoryl chloride into 3-allyl-4-chloro-2-methylquinoline, which on hydrogenation gave 2-methyl-3-propylquinoline (20).[12]

(*b*) A solution of 3-allyl-2-methyl-4-quinolone (5·1 g) and phosphorus pentasulphide (5·5 g) in dioxan (100 ml) was boiled (12 h), cooled, and treated with aqueous sodium hydroxide and ether. The ethereal extracts were dried and evaporated to give almost pure 2,3-dihydro-2,4-dimethylthieno[3,2-*c*]quinoline (24), crystallising from petroleum (b.p. 60—80°) with m.p. 89—90°; δ ($CDCl_3$) 1·5 (3H, d, *J* 6 Hz, 2-Me), 2·6 (3H, s), 3·0—4·2 (3H, m), 7·0—7·8 (3H, m), and 8·0 (1H, d, H-6).

A mixture of the dihydrothienoquinoline (24) and palladium–charcoal (in excess by weight) was heated in a sealed tube at 310—320° (4 h). Extraction of the residue with chloroform gave, after evaporation, 2,4-dimethylthieno-[3,2-*c*]quinoline (22), identical with the product obtained by decomposition of the azide (13).

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