

Thiophen Derivatives. Part XXII.¹ Preparation of Naphtho[2',3':4,5]-thieno[3,2-*b*][1]benzothiophen and Some Methyl Homologues

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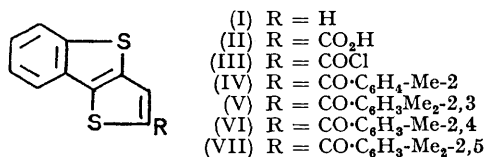
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The Friedel-Crafts condensation of thieno[3,2-*b*][1]benzothiophen with some mono- and di-methyl homologues of benzoyl chloride, and of thieno[3,2-*b*][1]benzothiophen-2-carbonyl chloride with *m*- and *p*-xylene, afforded a series of ketones which underwent Elbs pyrolysis to furnish naphtho[2',3':4,5]thieno[3,2-*b*][1]benzothiophen and three of its methyl homologues.

THIENO[3,2-*b*][1]BENZOTHIOPHEN (I) has previously been prepared from thiophen-3-thiol² and from benzo[*b*]thiophen-3-thiol.³ Recently, Ricci *et al.*⁴ recorded the preparation in 80% yield of thieno[3,2-*b*][benzothiophen-2-carboxylic acid (II) from 3-chlorobenzo[*b*]thiophen-2-carbaldehyde; the acid (II) undergoes easy decarboxylation to (I).

We have used compounds (I) and (II) to obtain a series of new ketones (IV)–(VII), by Friedel-Crafts reactions of (I) with mono- and di-methylbenzoyl chlorides, and of the acid chloride (III) with *m*- and *p*-xylene. We have compared the behaviour of thieno[3,2-*b*][1]benzothiophen with that of benzo[*b*]thiophen in the course of these Friedel-Crafts acylations, and also in the subsequent Elbs reactions which led to novel sulphur-containing isosteres of pentacyclic aromatic hydrocarbons.

The reactions of compound (I) with 2,5-dimethylbenzoyl chloride and of (III) with *p*-xylene both gave the ketone (VII), which suggests that where the electrophilic attack occurs on the thiophen ring, position 2 alone is



involved. This is in line with the observations of Chapman *et al.*⁵ (concerning acetylation) and Ricci *et al.*⁴ (concerning succinylation). Substitution of benzo[*b*]thiophen takes place preferentially in position 3 in the same type of reaction.⁶

Elbs pyrolysis of compounds (IV)–(VII) gave naphtho[2',3':4,5]thieno[3,2-*b*][1]benzothiophen (VIII) and its methyl homologues (IX)–(XI), in *ca.* 1–3% yields. Compounds (VIII)–(XI) are π -isoelectronic

¹ Part XXI, N. P. Buu-Hoï, M. Dufour, P. Jacquignon, and A. Martani, *J. Chem. Soc. (C)*, 1971, 2428.

² V. V. Ghaisas and B. D. Tilak, *Current Sci.*, 1953, **22**, 184; *Proc. Indian Acad. Sci.*, 1954, **39A**, 14.

³ N. B. Chapman, C. G. Hughes, and R. M. Scrowston, *J. Chem. Soc. (C)*, 1970, 2431.

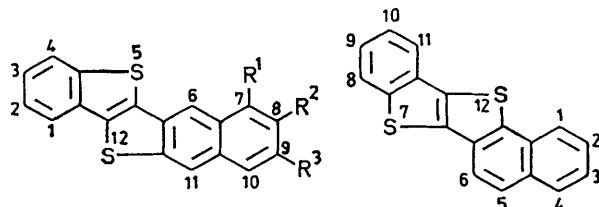
⁴ A. Ricci, D. Balucani, and M. Betteli, *Gazzetta*, 1971, **101**, 774.

⁵ N. B. Chapman, C. G. Hughes, and R. M. Scrowston, *J. Chem. Soc. (C)*, 1971, 463.

⁶ H. B. Hartough and S. L. Meisel, 'Compounds with Condensed Thiophene Rings', Interscience, New York, 1954, p. 5; B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **2**, 244.

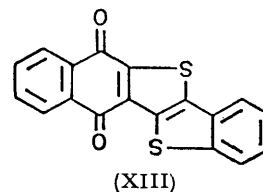
analogues of naphtho[2,1-*a*]anthracene and its corresponding methylated derivatives.

Earlier work⁷⁻⁹ has shown that the pyrolysis of aroylbenzothiophens results in the expected compounds with optimal yields when the temperature is maintained close to the b.p. of the ketone for 15–30 min. As we briefly reported recently,¹⁰ the present Elbs cyclisations conform to this rule.



- (VIII) R¹ = R² = R³ = H
 (IX) R¹ = Me, R² = R³ = H
 (X) R² = Me, R¹ = R³ = H
 (XI) R³ = Me, R¹ = R² = H

(XII)



The possibility of an 'abnormal' cyclisation like the one described by Badger *et al.*¹¹ for an Elbs pyrolysis of 3-*o*-toluoylbenzo[*b*]thiophen leading to naphtho[2,1-*b*][1]benzothiophen instead of the expected naphtho[2,3-*b*][1]benzothiophen could not *a priori* be discarded. However, chromic acid oxidation of the product of the pyrolysis of compound (IV) led to a quinone which did not condense with *o*-phenylenediamine and which was therefore the *para*-aquinone (XIII). In support of structure (VIII) the n.m.r. spectrum shows resonances at τ 2.75–2.34 (2-, 3-, 8-, and 9-H, envelope) corresponding to the β -protons,¹² 2.37–1.92 (1-, 4-, 7-, and 10-H,

⁷ P. Faller, *Bull. Soc. chim. France*, 1966, 3618, 3667.

⁸ Cl. Marie, N. P. Buu-Hoï, and P. Jacquignon, *J. Chem. Soc. (C)*, 1971, 431.

⁹ A. Croisy and P. Jacquignon, Abstr. Papers of Vth Symposium on Organic Sulphur Chemistry, Lund, June 5–9, 1972, IV-A-18.

¹⁰ P. Jacquignon, A. Croisy, A. Ricci, and D. Balucani, ref. 9, p. IV-A-19.

¹¹ G. M. Badger and B. J. Christie, *J. Chem. Soc.*, 1956, 3435.

¹² For an explanation of the terms α -, β -, and γ -protons, see R. H. Martin, *Tetrahedron*, 1964, **20**, 897.

envelope) corresponding to the α -protons, and 1.75 (6- and 11-H, s) corresponding to the γ -protons. In the alternative structure (XII) the 5- and 6-protons would not be equivalent because of the *peri* effect of the 4-proton.

EXPERIMENTAL

N.m.r. spectra were measured for solutions in [^2H]-chloroform with a Varian A60 spectrometer (Me_4Si as internal reference). Mass spectra were determined with an A.E.I. MS9 apparatus at 70 eV. U.v. spectra were taken for solutions in cyclohexane with a Leres S66 instrument. M.p.s were taken on a Maquenne block. The purity of compounds was checked by g.l.c. on a Girdel instrument with flame ionisation detectors (1 m column packed with 5% SE 30 on Chromosorb W treated with hexamethyldisilazane at 250°; N_2 as carrier gas).

2-(2-Methylbenzoyl)thieno[3,2-b][1]benzothiophen (IV).—A solution of thieno[3,2-b][1]benzothiophen (I) (4 g, 0.02 mol) and *o*-toluoyl chloride (3.5 g, 0.022 mol) in benzene (75 ml) was treated with tin(IV) chloride (3 ml, 0.025 mol) in benzene (25 ml). The solution was gently boiled for 2 h, cooled, and decomposed with ice-hydrochloric acid. The organic layer was washed first with water, then with aqueous 5% sodium hydroxide, then again with water, dried (CaCl_2), and evaporated. The residue was distilled to give the *ketone* (IV), b.p. 305–307° at 22 mmHg, as yellow needles (4.7 g), m.p. 88° (from methanol) (Found: C, 70.2; H, 3.9. $\text{C}_{18}\text{H}_{12}\text{S}_2\text{O}$ requires C, 70.1; H, 3.9%), τ 7.6 (Me), 2.42 (3-H), 2.4–2.0 (5- and 8-H, m), and 2.85–2.4 (m).

Naphtho[2',3':4,5]thieno[3,2-b][1]benzothiophen (VIII).—The *ketone* (IV) (3 g) was heated in a metal bath at 420° for 15 min under a slow nitrogen stream; after cooling, the residue was taken up in chloroform and adsorbed on silica, then chromatographed on a Merck silica column with cyclohexane as eluant. *Compound* (VIII) formed pale yellow leaflets (0.05 g), m.p. 287° [from ethanol-cyclohexane (1:1)] (Found: C, 74.6; H, 3.4. $\text{C}_{18}\text{H}_{10}\text{S}_2$ requires C, 74.4; H, 3.5%), λ_{max} 208 (ϵ 4380), 236 (4680), 253 (4300), 273 (4649), 282 (4650), 293 (4820), 309 (4090), 320 (4250), 335 (4030), 353 (4140), and 375 nm (4180), *m/e* 290 (M^+) and *m/e* 145 (M^{2+}); other fragments (not quantitatively significant) *m/e* 258 ($M - \text{S}$), 245 ($M - \text{SCH}$), 213 ($M - \text{S} - \text{SCH}$), and 200 ($M - 2\text{SCH}$). Oxidation of product (VIII) with chromic acid in acetic acid furnished the 6,11-quinone (XIII) as yellow crystals, m.p. 408–410° (from benzene), ν_{max} 760s (four aromatic C-H), 1380w (this would be strong only in the case of an *o*-quinone), 1150s, 1265s, 1315s, and 1670s cm^{-1} .

2-(2,3-Dimethylbenzoyl)thieno[3,2-b][1]benzothiophen (V).—Prepared as for *ketone* (IV) from 2,3-dimethylbenzoyl chloride, this *compound*, b.p. 298–300° at 14 mmHg, crystallised as pale yellow leaflets, m.p. 131° (from cyclohexane) (Found: C, 70.7; H, 4.4. $\text{C}_{19}\text{H}_{14}\text{S}_2\text{O}$ requires

C, 70.8; H, 4.4%). Pyrolysis of (V) (2.3 g) furnished 7-methylnaphtho[2',3':4,5]thieno[3,2-b][1]benzothiophen (IX), crystallising as yellow leaflets (0.035 g), m.p. 185–186° (from ethanol) (Found: C, 74.3; H, 3.4. $\text{C}_{19}\text{H}_{12}\text{S}_2$ requires C, 74.9; H, 4.0%), λ_{max} 208 (ϵ 4320), 237 (4580), 254 (4240), 276 (4590), 284 (4570), 296 (4690), 310 (3990), 322 (4140), 338 (3990), 354 (4060), and 378 nm (4140).

Pyrolysis of 2-(2,5-dimethylbenzoyl)thieno[3,2-b][1]benzothiophen (VII) [b.p. 295° at 14 mmHg; obtained like (IV) from 2,5-dimethylbenzoyl chloride (2.5 g) as needles (2.4 g), m.p. 97° (from cyclohexane) (Found: C, 71.0; H, 4.4%)] afforded 9-methylnaphtho[2',3':4,5]thieno[3,2-b][1]benzothiophen (XI), crystallising as pale yellow needles (0.04 g), m.p. 266–267° (from cyclohexane) (Found: C, 75.0; H, 4.1%), λ_{max} 208 (ϵ 4590), 236 (4790), 253 (4470), 273 (4720), 282 (4740), 293 (4900), 308 (4300), 320 (4380), 340 (4220), 354 (4300), and 372 nm (4310).

Thieno[2,3-b][1]benzothiophen-2-carbonyl Chloride (III).—A suspension of the acid (II) (23.5 g, 0.1 mol) in anhydrous ether (500 ml) was treated with thionyl chloride in excess and the mixture was boiled gently for 3 h. The ether and excess of thionyl chloride were evaporated off *in vacuo* and the residue was recrystallised to give yellow needles (24 g), m.p. 164° [from cyclohexane-benzene (1:1)] (Found: C, 52.2; H, 2.2; S, 25.0. $\text{C}_{11}\text{H}_5\text{ClOS}_2$ requires C, 52.2; H, 2.0; S, 25.3%).

2-(2,4-Dimethylbenzoyl)thieno[3,2-b][1]benzothiophen (VI).—To a solution of *m*-xylene (2.5 g, 0.024 mol) and aluminium chloride (3 g, 0.023 mol) in methylene chloride (50 ml), compound (III) (5 g, 0.02 mol) [previously dissolved in methylene chloride (125 ml)] was added dropwise. The mixture was stirred for 2 h at room temperature, and decomposed by ice-hydrochloric acid; the organic layer was treated in the usual way and evaporated. The residue was distilled under reduced pressure to give the *ketone* (VI), b.p. 310–315° at 20 mmHg, which crystallised as needles (4 g), m.p. 142–143° (from ethanol) (Found: C, 70.8; H, 4.5%). Pyrolysis of this *ketone* (1 g) afforded 8-methylnaphtho[2',3':4,5]thieno[3,2-b][1]benzothiophen (X), pale yellow needles (0.03 g), m.p. 269° (from cyclohexane) (Found: C, 74.7; H, 4.1%), λ_{max} 208 (ϵ 4470), 236 (4740), 255 (4380), 275 (4700), 284 (4660), 296 (4790), 310 (4120), 321 (4250), 334 (4120), 348 (4190), 358 (4080), and 378 nm (4120).

The same procedure as for (VI), but with *p*- in place of *m*-xylene, furnished, though in only 10% yield 2-(2,5-dimethylbenzoyl)thieno[3,2-b][1]benzothiophen (VII), obtained earlier from 2,5-dimethylbenzoyl chloride.

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