Ring Contraction of Some 1-Benzothiepin Derivatives to 1-Benzothiophens [1]

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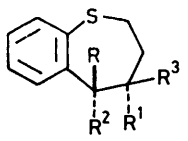
Transformations of some 1-benzothiepin derivatives (1) into a 1-benzothiophen derivative (2a) through ring contraction are reported. Similar ring contraction of *trans*-1,2-dibromo-1,2,3,4-tetrahydronaphtho[2,1-*b*]thiepin (8) affords the thiophen derivative (9a). Treatment of the bromo-compounds (2a) and (9a) with base in the presence of catalysts provides in excellent yields the dienes (2d) and (9b) respectively.

SULPHUR-4 anchimeric assistance [2] is not important in the hydrolysis of acyclic alkyl chlorides. This type of participation is, however, well known [3] in cyclic systems if proximity effects are favourable.

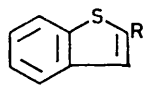
We report here a transannular S-participation involving a 5,4-fused-ring system in the novel ring contraction of some 1-benzothiepin derivatives to 1-benzothiophens in nearly quantitative yield. The current interest [4] in the 1-benzothiophens prompted us to undertake this investigation.

We first studied the thermal ring contraction of the *cis*-bromohydrin (1a),[5] this being prepared in respectable yield by sodium borohydride reduction of 4-bromo-2,3-dihydro-1-benzothiepin-5(4*H*)-one [6] under controlled conditions. (When conducted under the conditions



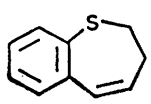
(1)

a; R = OH, R^3 = Br, R^1 = R^2 = H
b; R = OH, R^1 = Br, R^2 = R^3 = H
c; R = R^1 = Br, R^2 = R^3 = H



(2)

a; R = $[CH_2]_2Br$
b; R = $[CH_2]_2CN$
c; R = $[CH_2]_2CO_2H$
d; R = CH=CH_2



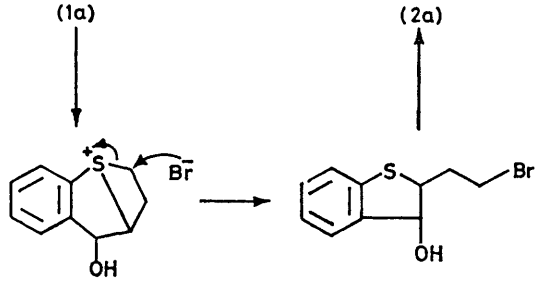
(3)

reported [5] this afforded an oily mixture.) Refluxing a solution of the *cis*-bromohydrin (1a) in anhydrous dioxan for 15 h afforded the 1-benzothiophen (2a) in nearly quantitative yield. Dehydration of (1a) with potassium hydrogen sulphate *in vacuo* also provided (2a) in comparable yield.

We next turned our attention to investigate the ring contraction of the isomeric *trans*-bromohydrin (1b) which was available by the addition of hypobromous acid to the known styrene (3) [7] following essentially the procedure of Dalton *et al.*[8] It is interesting to note that the *trans*-isomer (1b) in contrast to its *cis*-isomer (1a), was unchanged after refluxing in dioxan as before. An intimate mixture of the *trans*-isomer (1b) and potassium hydrogen sulphate on heating and subsequent distillation *in vacuo*, however, provided, amongst other unidentified products, the ring-contracted product (2a) in moderate yield. To study the behaviour of the related compound during the course of ring contraction, the *trans*-dibromide (1c) [9] was prepared by addition of bromine to the styrene (3). This dibromide (1c) was transformed to (2a) in excellent yield when heated under reflux in dioxan or acetone.

The structure of the thiophen derivative (2a) was unambiguously established through its conversion into the known 3-(1-benzothiophen-2-yl)propionic acid (2c).[10] Treatment of (2a) with potassium cyanide in wet dimethylformamide (DMF) afforded in excellent yield the crystalline nitrile (2b), which on alkaline hydrolysis furnished the acid (2c) reported above.

The facile ring contraction of the *cis*-bromohydrin (1a) may be rationalised through S-participation in the ionisation step as shown in Scheme 1. Similar ring con-

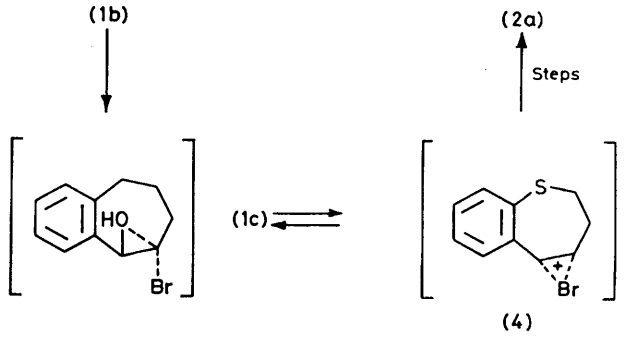


SCHEME 1

tractions of thiachroman derivatives have been reported [11] earlier to give 1-benzothiophen.

It is reasonable to assume that in the case of the *trans*-bromohydrin (1b) under similar conditions, participation by the S atom is not favourable since the back side of the carbon–bromine bond is protected by the oxygen atom of the appropriately situated hydroxy-group (Scheme 2). The smooth transformation of the *trans*-dibromide (1c) may be visualised through S-participation in the bromonium-ion intermediate (4) as shown in Scheme 2.

In an attempt to prepare the diene (2d), the bromo-compound (2a) was heated with 50% aqueous sodium hydroxide. The only product isolated was the unchanged starting material (2a). Similar treatment of (2a)



SCHEME 2

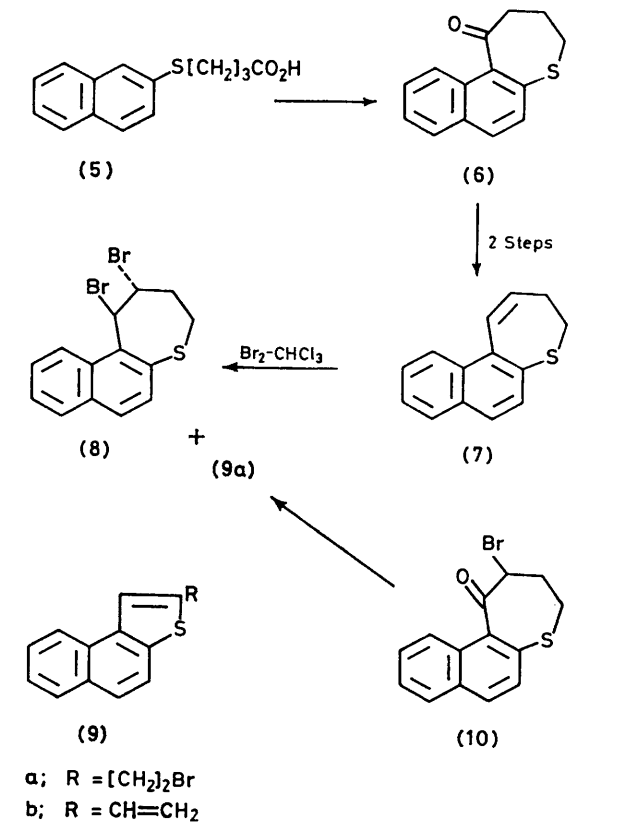
with methanolic sodium hydroxide afforded in moderate yield a crystalline product identified as the diene (2d) on the basis of its elemental analysis and characteristic n.m.r. spectrum.

Phase-transfer catalysts [12] have played a dramatic role in preparative organic chemistry. To improve the yield of the diene (2d) for its use in Diels–Alder reactions, the bromo-derivative (2a) was treated with 50% aqueous sodium hydroxide in the presence of tetra-n-butylammonium bromide and tetraethylammonium chloride. An excellent yield of the diene (2d) was realised when the latter quaternary salt was used as the catalyst (see Experimental section).

A similar ring contraction of a naphthalene analogue, (8), was next investigated. 4-(2-Naphthylthio)butanoic acid (5) [13] was most conveniently prepared by the reaction [14] of naphthalene-2-thiol with γ-butyrolactone in the presence of base. The acid (5), obtained in high yield, was then cyclised to 3,4-dihydronaphtho[2,1-*b*]thiepin-1(2*H*)-one (6) following the reported [13] procedure. The ketone (6) [13] was reduced with sodium borohydride, and the resulting crude alcohol was dehydrated by heating with dimethyl sulphoxide to provide the crystalline styrene (7) in good yield. Addition of bromine to the above styrene (7) under mild conditions afforded a separable mixture of the thiophen derivative (9a), and the expected dibromo-compound (8) in a ratio of *ca.* 2 : 1, respectively. This smooth formation of the ring-contracted product (9a) in the above reaction suggests S-participation in the bromonium ion [like (4)], an intermediate for the *trans*-addition of bromine to styrene (7). The above dibromide (8), simply by heating above its melting point, or by refluxing with dioxan or acetone, was smoothly transformed to the thiophen derivative (9a) mentioned above.

The α-bromo-ketone (10) prepared from (6), on reduction with sodium borohydride afforded an oily material which did not crystallise. This material, on heating with fused potassium hydrogensulphate furnished in moderate yield the ring-contracted product (9a).

The above bromo-compound (9a) in the presence of aqueous sodium hydroxide, using tetraethylammonium chloride as the catalyst as previously, furnished the expected diene (9b) in excellent yield.



EXPERIMENTAL

M.p.s were determined on a sulphuric acid bath. U.v. spectra were measured for solutions in ethanol with a Unicam SP 500 spectrophotometer, i.r. spectra for solutions in $CHCl_3$ with a Perkin-Elmer 337 instrument, and n.m.r. spectra for solutions in $CDCl_3$ (until otherwise stated) with a Varian T-60 spectrometer (tetramethylsilane as internal standard). Extracts were dried over Na_2SO_4, and light petroleum refers to the fraction of b.p. 60—80 °C.

cis-4-*Bromo*-5-*hydroxy*-2,3,4,5-*tetrahydro*-1-*benzothiepin* (1a).—To a stirred solution of 4-bromo-2,3-dihydro-1-benzothiepin-5(4*H*)-one [6] in MeOH (70 ml) was added in small portions $NaBH_4$ (1.56 g) at room temperature. After complete addition, the reaction mixture was stirred for 2—3 h and left at room temperature for 16 h. The reaction mixture was then poured over crushed ice (700 g) and acidified with acetic acid. The separated solid was filtered off to give the *cis*-bromohydrin (1a) (3.95 g), and this on recrystallisation provided the pure product (2.34 g, 60%), m.p. 92—93 °C (from ether–light petroleum) (lit.,[5] m.p. 93—94 °C).

trans-4-*Bromo*-5-*hydroxy*-2,3,4,5-*tetrahydro*-1-*benzothiepin* (1b).—To a stirred and cooled solution (10—15 °C) of the styrene [7] (3) (2.3 g) in dry dimethyl sulphoxide (DMSO) containing water (0.5 ml) was added, under nitrogen, *N*-bromosuccinimide (NBS) (5.06 g) at such a rate that the temperature of the reaction mixture did not rise above 20 °C.

After stirring for a further 1 h at 15—20 °C, the bright yellow solution was poured over ice–water (700 ml). The solid (1.95 g) which separated was filtered off, and the aqueous solution was extracted with ethyl acetate (3 × 50 ml). The extract was washed with water, dried, and evaporated to give a further amount of bromohydrin (0.6 g). Recrystallisation of the total material (2.55 g) finally afforded the pure *bromohydrin* (1b) (2.36 g, 71%), m.p. 160—162 °C (decomp.) (from acetone–light petroleum) (Found: C, 46.25; H, 4.35. $C_{10}H_{11}BrOS$ requires C, 46.33; H, 4.25%).

trans-4,5-*Dibromo*-2,3,4,5-*tetrahydro*-1-*benzothiepin* (1c).—To an ice-cooled (0—10 °C) and stirred solution of the styrene (3) (0.5 g) in dry $CHCl_3$ (10 ml) was added dropwise during 40 min a solution of bromine (0.53 g) in dry $CHCl_3$ (10 ml). Each drop of bromine solution was added after decolourisation of the preceding drop. The resulting reaction mixture was stirred for 2 h at 0—10 °C, and then left in the refrigerator for 16 h. Evaporation under reduced pressure afforded a solid which on recrystallisation gave the pure dibromo-compound (1c) (0.64 g, 64%), m.p. 106—108 °C (lit.,[9] 107—108 °C).

Ring Contraction of 1-*Benzothiepin Derivatives; Formation of* 2-(2-*bromoethyl*)-1-*benzothiophen* (2a).—(*a*) A solution of the *cis*-bromohydrin (1a) (2 g) in dry dioxan (25 ml) was heated under reflux for 15 h to give a brown mixture. Dioxan was removed under reduced pressure, and the resulting oil was evaporated to furnish a residual oil (1.78 g, 95%), b.p. 120 °C (bath) at 0.4—0.3 mmHg, which on cooling solidified to give the bromo-compound (2a), m.p. 45—47 °C [from ether–light petroleum (b.p. 40—60 °C)]; $\lambda_{max.}$ 226 (ε 28 840), 260 (9 772), 288 (2 138), and 298 nm (2 399); τ 2.2—2.85 (4 H, m), 2.97 (1 H, s), and 6.2—6.78 (4 H, m) (Found: C, 49.75; H, 3.45. $C_{10}H_9BrS$ requires C, 49.74; H, 3.75%).

(*b*) An intimate mixture of the *cis*-bromohydrin (1a) (0.3 g) and freshly fused $KHSO_4$ (0.19 g) was heated under vacuum to furnish the bromo-compound (2a) (0.26 g, 93%), b.p. 115—120 °C (bath) at 0.4 mmHg, m.p. 41—44 °C.

(*c*) The *trans*-dibromide (1c) (0.5 g) on refluxing in anhydrous dioxan as before afforded (2a) (0.36 g, 92%), m.p. 43 °C.

(*d*) A solution of the *trans*-dibromide (1c) (0.5 g) in a mixture of acetone (3 ml) and water (1.2 ml) was refluxed on a steam-bath for 10 h. The reaction mixture was then diluted with water, and the product was extracted with ether (3 × 50 ml). The combined extract was washed with water, dried, and evaporated. The resulting residue was distilled to furnish (2a) (0.35 g, 93%), b.p. 120 °C (bath) at 0.4 mmHg, m.p. 43 °C.

(*e*) The *trans*-bromohydrin (1b) (0.6 g) in refluxing dioxan as above afforded only recovered starting material (1b) (0.55 g), m.p. 160—161 °C.

(*f*) An intimate mixture of the *trans*-bromohydrin (1b) (0.5 g) and freshly fused $KHSO_4$ (0.32 g) was heated in an oil-bath at 160—165 °C for 5 min, and the resulting bluish mass was heated under vacuum as before to give (2a) (0.17 g, 37%).

2-(2-*Cyanoethyl*)-1-*benzothiophen* (2b).—A mixture of the bromo-derivative (2a) (0.5 g), KCN (4.72 g) in ordinary DMF (15.5 ml) was heated on a steam-bath for 10 h with continuous stirring. The resulting reddish-brown solution was poured into cold water saturated with NH_4Cl. The product was then extracted with ether (4 × 50 ml). The combined extract was washed with water, dried, and evaporated to furnish a reddish-brown oil which was distilled under vacuum to give the *cyano-compound* (2b) (0.3 g, 81%), b.p. 135—145 °C (bath) at 0.4 mmHg, m.p. 58—59 °C (from ether–light petroleum); $\lambda_{max.}$ 228 (ε 28 840), 258 (8 913), 290 (2 042), and 299 nm (2 344); $\nu_{max.}$ 2 260w cm^{-1} (Found: C, 70.55; H, 5.2. $C_{11}H_9NS$ requires C, 70.55; H, 4.83%).

3-(1-*Benzothiophen*-2-*yl*)*propionic Acid* (2c).—The above nitrile (2b) (0.3 g) was hydrolysed by heating under reflux for 7 h with a solution of KOH (0.66 g) in MeOH (5.9 ml) and water (0.7 ml). Most of the MeOH was then removed, and the residue was dissolved in cold water. The resulting alkaline solution was extracted with ether (1 × 50 ml) to remove neutral material if any. The aqueous solution was then acidified with HCl, and the liberated acid was extracted with ether (3 × 50 ml). The combined solvent was washed with water, and the acid was purified by extraction with saturated aqueous $NaHCO_3$ (3 × 25 ml). The $NaHCO_3$ extract was then acidified, and extracted with ether (3 × 50 ml). Evaporation of the dried solvent finally afforded the desired acid (2c) (0.31 g, 94%), m.p. 134—135 °C (from ether–light petroleum), mixed m.p. with an authentic sample [10] 133—135 °C (Found: C, 64.1; H, 5.05. Calc. for $C_{11}H_{10}O_2S$: C, 64.08; H, 4.89%).

2-*Vinyl*-1-*benzothiophen* (2d).—(a) *Using aqueous alkaline* MeOH. The above bromo-compound (2a) (0.25 g) was heated on a steam-bath with stirring for 2 h with a solution of NaOH (0.1 g) in MeOH (6 ml) and water (0.5 ml). The MeOH was then removed, and the residue was diluted with ice–water. The alkaline mixture was extracted with ether (3 × 25 ml), and the combined extracts were washed with water, dried, and evaporated to furnish a light yellow oil (0.15 g) which soon solidified, m.p. 53—59 °C. This was distilled under vacuum to give the desired *diene* (2d) (80 mg, 48%), b.p. 55—65 °C (bath) at 0.5 mmHg, m.p. 63—65 °C; $\lambda_{max.}$ 232 (ε 18 200), 252 (10 230), 262 (10 720), 284 (23 440) and 293 nm (22 910). Two more sublimations of the above diene at 55 °C as before provided an analytical sample of (2d) as a white shining solid, m.p. 65—66 °C, $\nu_{max.}$ 1 620m cm^{-1}; τ 2.20—3.03 (5 H, m), 3.03—3.47 (1 H, 2 d overlapping, J_{cis} 11.0, J_{trans} 17.0 Hz), 4.40 (1 H, d, *J* 17.0 Hz), and 4.76 (1 H, d, *J* 11.0 Hz) (Found: C, 75.4; H, 5.15. $C_{10}H_8S$ requires C, 74.99; H, 5.03%).

The above diene (2d) has been reported [11] earlier, but was not properly characterised.

(b) *With* 50% *aqueous* NaOH *containing tetraethylammonium chloride as catalyst.* The bromo-compound (2a) (0.5 g) was added in portions to a stirred mixture of tetraethylammonium chloride pentahydrate (0.8 g) in aqueous NaOH (5 ml; 50%) maintained at 65—75 °C. After complete addition of (2a) (5 min), the reaction mixture was further stirred for 2 h at 65—75 °C. This was then diluted with ice-water, and the product was extracted with $CHCl_3$ (3 × 50 ml). The combined extract was washed with water, dried ($CaCl_2$), and evaporated to provide a red solid. Purification of this material by sublimation at 70 °C (bath) and 1 mmHg afforded the diene (2d) (0.32 g, 80%) as a solid, m.p. 63—65 °C.

(c) Use of tetra-n-butylammonium bromide as catalyst in the above dehydrohalogenation furnished the desired diene (2d) (55%).

(d) Use of simple aqueous NaOH (50%) in the above reaction (no catalyst being used) afforded only the unchanged bromo-compound (2a).

4-(2-*Naphthylthio*)*butanoic Acid* (5).—To a cold solution

of NaOEt, prepared from Na (1.56 g) and absolute EtOH (20 ml), was added naphthalene-2-thiol (10 g) in one portion. To the resulting mixture was then added γ-butyrolactone (10 ml) with shaking. The reaction mixture was then heated under reflux for 4 h in an oil-bath. The resulting solid was dissolved in water, and the mixture filtered. Acidification of the filtrate gave an acid, which was further purified by dissolving in saturated aqueous $NaHCO_3$. The resulting solution was once extracted with benzene (100 ml) to remove any neutral material. The alkaline solution was then acidified and the liberated acid was extracted with EtOAc (4 × 75 ml). The combined extract was washed with water, dried, and evaporated to afford the pure acid (5) (13.5 g, 87%), m.p. 86—88 °C (lit.,[13] 86—87 °C).

3,4-*Dihydronaphtho*[2,1-b]*thiepin*-1(2H)-*one* (6).—This ketone was prepared by cyclisation of the above acid (5) according to the reported [13] procedure and had m.p. 77—78 °C (lit. [13] 78—79 °C).

3,4-*Dihydronaphtho*[2,1-b]*thiepin* (7).—To a stirred cold (10—15 °C) mixture of $NaBH_4$ (0.1 g) and aqueous EtOH (8 ml, 25%) was added dropwise a solution of the ketone (6) (0.5 g) in EtOH (10 ml). The mixture was then heated under reflux for 30 min. The homogeneous solution so obtained was then cooled, and poured into ice–water containing concentrated HCl (1.5 ml). The product was extracted with ether (4 × 50 ml), and the combined extract was washed with water. Evaporation of the dried solvent gave an alcohol as an oil (0.5 g), $\nu_{max.}$ 3 450br cm^{-1}. Dehydration of this alcohol (3.1 g) by heating with DMSO for 24 h at 160 °C under nitrogen (*cf.* ref. 7) furnished a solid (2.7 g), which on recrystallisation afforded the crystalline *styrene* (7) (1.75 g, 60% based on consumed ketone), m.p. 93—94 °C (from ether–light petroleum), τ 1.85—2.95 (7 H, complex m), 3.57 (1 H, m), 6.74 (2 H, t, *J* 6 Hz), and 7.25—7.60 (2 H, m) (Found: C, 78.85; H, 5.95. $C_{14}H_{12}S$ requires C, 79.23; H, 5.70%).

Addition of Bromine to the Styrene (7); *Formation of* trans-1,2-*Dibromo*-1,2,3,4-*tetrahydronaphtho*[2,1-b]*thiepin* (8) *and* 2-(2-*Bromoethyl*)*naphtho*[2,1-b]*thiophen* (9a).—Addition of bromine to the styrene (7) (0.65 g) was carried out as before to furnish a mixture of solid products. Treatment of this mixture with ether afforded an ether-soluble fraction and a fraction insoluble in ether. Recrystallisations of the ether-soluble fraction afforded the *bromide* (9a) (0.6 g, 66%), m.p. 84—85 °C (from ether–light petroleum), $\lambda_{max.}$ 245 (ε 34 670), 255 (23 590), 298 (10 290), and 306 nm (9 111); τ 1.74—2.50 (7 H, complex m, 6 aromatic and 1 vinylic) and 6.30—6.45 (4 H, m), *m/e* 290 and 292 (M^+, doublet) and 197 ($M^+ - CH_2Br$, 100%) (Found: C, 57.95; H, 4.15. $C_{14}H_{11}BrS$ requires C, 57.76; H, 3.80%). The ether-insoluble portion was recrystallised to furnish the *dibromide* (8) (0.35 g, 30%), m.p. 110—111 °C [from CH_2Cl_2–light petroleum (b.p. 40—60 °C)] (Found: C, 44.9; H, 3.9. $C_{14}H_{12}Br_2S$ requires C, 45.18; H, 3.25%).

2-*Bromo*-3,4-*dihydronaphtho*[2,1-b]*thiepin*-1(2H)-*one* (10).—To a solution of the ketone (6) (1.07 g) in dry $CHCl_3$ (6 ml) was added at room temperature a drop of a solution of bromine (0.8 g) in dry $CHCl_3$ (5 ml). After the bromine had decolourised, the reaction mixture was cooled to 20 °C, and the rest of the bromine solution was added dropwise during 20 min with stirring. After complete addition, the reaction mixture was stirred at room temperature (30 °C) for a further 1 h. The resulting dark brown solution was washed with cold water (1 × 50 ml), saturated aqueous $NaHCO_3$ (2 × 25 ml), and finally with water (2 × 25 ml). Evaporation of the dried solvent gave a solid, which on recrystallisation furnished the pure *bromo-ketone* (10) (1.2 g, 83%), m.p. 107 °C (from ether–light petroleum), $\nu_{max.}$ 1 696s cm^{-1} (Found: C, 54.5; H, 3.65. $C_{14}H_{11}BrOS$ requires C, 54.74; H, 3.54%).

2-(2-*Bromoethyl*)*naphtho*[2,1-b]*thiophen* (9a).—(a) *From the* trans-*dibromide* (8). (*i*) The pure dibromide (8) (0.2 g) was heated slowly to 120 °C in an oil-bath for 5 min. The compound decomposed at 110—111 °C. The resulting oil on crystallisation afforded the bromo-compound (9a) (0.1 g, 62%), m.p. 84—85 °C.

(*ii*) The dibromide (8) (0.2 g) in refluxing dioxan for 16 h as before provided (9a) (0.12 g, 77%), m.p. 84—85 °C.

(*iii*) A solution of the dibromide (8) (0.2 g) in acetone (10 ml) and water (1 ml) was heated under reflux for 12 h. Usual work-up of the reaction mixture as before furnished (9a) (0.11 g, 70%), m.p. 84—85 °C.

(b) *Directly from the* α-*bromo-ketone* (10). A solution of (10) (0.4 g) in MeOH (25 ml) and water (1 ml) was reduced with $NaBH_4$ (0.3 g) at room temperature as before to give an alcohol as an oil (0.4 g), $\nu_{max.}$ 3 425 br cm^{-1}. This oil (0.4 g) was mixed up with freshly fused $KHSO_4$ (0.5 g) and the mixture was heated under vacuum to furnish an oil (0.32 g), b.p. 140 °C (bath) at 0.1 mmHg, which on chromatography over silica gel (10 g) and elution with light petroleum afforded (9a) (0.15 g, 40%), m.p. 84—85 °C.

2-*Vinylnaphtho*[2,1-b]*thiophen* (9b).—To a stirred mixture of tetraethylammonium chloride pentahydrate (0.8 g) and aqueous NaOH (5 ml; 50%), maintained at 65—75 °C was added portionwise during 10 min the bromo-compound (9a) (0.7 g). The reaction mixture was stirred at that temperature for a further 2 h. It was then cooled and cold water (50 ml) was added. The separated solid was filtered off, and then dissolved in CH_2Cl_2 (50 ml). The solvent was washed with water, dried, and evaporated to furnish (9b) (0.4 g, 86%), m.p. 74—78 °C; τ 1.75—2.80 (7 H, m), 2.85—3.25 (1 H, 2 d overlapping, J_{cis} 11.0, J_{trans} 17.0 Hz), 4.33 (1 H, d, *J* 17 Hz), and 4.73 (1 H, d, *J* 11.0 Hz). Recrystallisation afforded the pure *diene* (9b), m.p. 81—82 °C [from ether–light petroleum (b.p. 40—60 °C)] (Found: C, 79.75; H, 4.9. $C_{14}H_{10}S$ requires C, 79.96; H, 4.79%).

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