2*H*-Naphtho[1,8-*bc*]thiophen and 2-Methyl-2*H*-naphtho[1,8-*bc*]thiophen 1-Oxides: Synthesis, Configurational Assignments, and Stereoselective Interconversions

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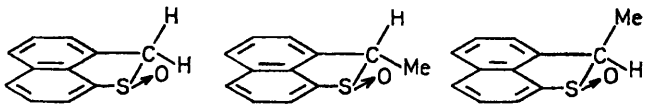
The carbonyl function of a thiolactone was reduced to obtain the 2*H*-naphtho[1,8-*bc*]thiophen, from which the 1-oxide (1) and the diastereoisomeric 2-methyl 1-oxides (2) and (3) were derived. The resonances of the diastereotopic methylene protons of (1) and the configurations of (2) and (3) were assigned through a study of solvent- and $Eu(dpm)_3$-induced shifts in their ^1H n.m.r. spectra. The interconversion of the sulphoxides (2) and (3) through the corresponding alkoxysulphonium salts was stereospecific when a weak base was used, but not in aqueous sodium hydroxide. In the latter case, the base was found to isomerize the initially formed sulphoxides (2) and (3) *via* an α-sulphinyl carbanion, and always to yield a final mixture containing >95% *cis*-sulphoxide (3). The composition of this equilibrium mixture was shown to be controlled by solubility factors and not by the relative thermodynamic stabilities of the two isomers.

FOR a study [1] of the mechanism and stereochemistry of H–D exchange α to the sulphinyl group in compounds for which the orientations of the α-protons were defined, the sulphoxides (1)—(3) were considered to be useful

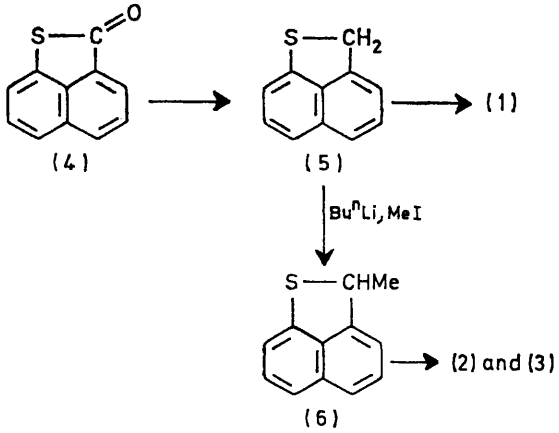


(1) (2) (3)

model systems. We report here their synthesis, the assignments of the α-proton signals in the ^1H n.m.r. spectrum of (1), and the configurational assignments for the diastereoisomeric sulphoxides (2) and (3) by the use of solvent- and lanthanide-induced shifts. The inversion of configuration at the sulphur atom in (2) and (3) through basic hydrolysis of the corresponding ethoxysulphonium salts demonstrated a peculiar stereoselectivity in the interconversion of the two stereoisomers, which is strongly dependent on the strength of the base employed. This behaviour was analysed and applied in a simple synthetic method whereby either isomer is obtained in almost diastereoisomerically pure form from a mixture of the two.

RESULTS AND DISCUSSION

The sulphoxides (1)—(3) were all derived from 8-mercapto-1-naphthoic acid thiolactone [2] (4). This was converted in one step into the cyclic sulphide (5) through an extension of a procedure by which lactones are reduced to cyclic ethers with borohydride in a large excess of boron trifluoride–diethyl ether.[3] The sulphide (5) readily gave the corresponding α-carbanion when



(4) (5) (1) (6)

treated with n-butyl-lithium. Subsequent quenching with methyl iodide yielded the 2-methyl derivative (6). Peroxy-acid oxidation of the sulphide (5) gave the sulphoxide (1).

The ^1H n.m.r. spectrum of (1) (0·27M in $CDCl_3$) shows a complex multiplet for the six naphthalene ring protons

[1] U. Folli, D. Iarossi, and F. Taddei, submitted for publication to *J.C.S. Perkin II*.

[2] P. Friedlander and N. Woroshzow, *Annalen*, 1912, **388**, 1.

[3] G. R. Pettit, U. R. Ghatak, B. Green, T. R. Kasturi, and D. M. Piatak, *J. Org. Chem.*, 1961, **26**, 1685.

(δ 7·4—8·3) and an AB quartet (δ_A 4·39, δ_B 4·95, J_{AB} −16·5 Hz) owing to the expected non-equivalence of the diastereotopic methylene protons α to the sulphinyl group. We set out to establish which part of the AB quartet was to be assigned to which methylene proton (*cis* or *trans* to the sulphinyl oxygen atom). We first examined the benzene- and trifluoroacetic-acid- (TFA) induced shifts of these resonances ($CDCl_3$ was used as reference solvent; the more inert CCl_4 could not be used because of solubility problems). The results are collected in Table 1, together with our assignments.

TABLE 1

Chemical shifts (δ values) and geminal coupling constants (J_{AB}/Hz) for methylene protons of (1) in various solvents (0·27M); Δ refers to chemical shift differences (p.p.m.) on changing solvent; *cis* and *trans* define proton assignments and are stereochemically referred to the sulphinyl oxygen atom

	δ_{CDCl_3}	δ_{TFA}	$\delta_{C_6H_6}$	$\Delta_{TFA-CDCl_3}$	$\Delta_{C_6H_6-CDCl_3}$
cis-H	4·39	4·87	3·90	0·48	−0·49
trans-H	4·95	5·16	3·90	0·21	−1·05
J_{AB}	−16·5	−17·6			

Solvent-induced shifts have recently been proved [4] to be reliable tools for proton and configuration assignments in cyclic sulphoxides, particularly in the presence of severe conformational restrictions. Since structure (1) is almost ideal in this respect, the expected trends in the solvent-induced shifts should allow reliable proton assignments. In going from a weakly interacting solvent ($CDCl_3$) to TFA, a greater deshielding is expected for the α-proton closest to the sulphinyl oxygen atom (H-bond or protonation may be expected); thus the upfield doublet (δ 4·39 in $CDCl_3$) is assigned to the *cis* α-proton of (1). Conversely, in going from $CDCl_3$ to benzene, a greater shielding is expected for the more remote proton; [4] hence the downfield doublet (δ 4·95 in $CDCl_3$) is assigned to the *trans* α-proton.

These assignments were confirmed by a comparison of the downfield shifts of the methylene signals of (1) in the presence of increasing amounts of tris(dipivaloylmethanato)europium [Eu(dpm)$_3$], which is known [4-6] to co-ordinate at the sulphinyl oxygen atom and to induce shifts essentially through a pseudocontact mechanism, so that the magnitude of downfield shifts may be expected to decrease with the distance from the co-ordination centre (when certain angular term differences can be neglected). The results are plotted in Figure 1. On increasing the Eu(dpm)$_3$ concentration, the chemical shift difference between the two diastereotopic protons should steadily increase if the *cis*-proton resonance, for which the major downfield shift is expected, is initially ($CDCl_3$ solution, without shift reagent) the downfield doublet of the AB quartet. On the other hand, if the *cis*-proton resonance is initially the upfield doublet, as the previous findings suggest, then when the Eu(dpm)$_3$ concentration is increased the chemical shift differences should diminish, reach zero, and then steadily increase. The experimental findings confirm the latter alternative: the two protons have the same chemical shift and give rise to a singlet at a molar ratio [Eu(dpm)$_3$ to (1)] of *ca.* 0·075 : 1; for lower or higher molar ratios respectively the *cis*-proton doublet appears as the upfield or downfield part of the AB quartet.

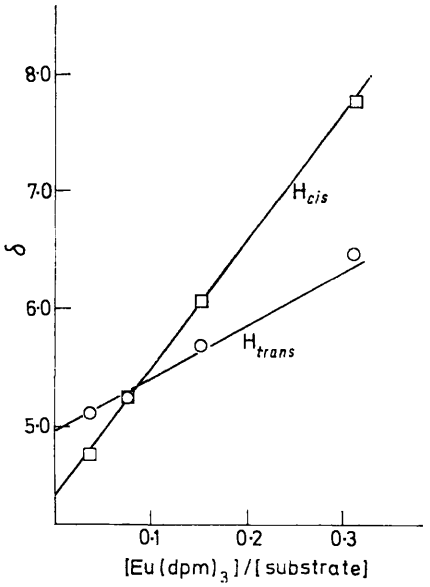


FIGURE 1 Chemical shifts of diastereotopic methylene protons of (1) in $CDCl_3$ (0·27M), as a function of concentration of Eu(dpm)$_3$; *cis* and *trans* define proton assignments and are stereochemically referred to the sulphinyl oxygen atom

Peroxy-acid oxidation of the sulphide (6) yielded a mixture of the two diastereoisomeric sulphoxides (2) and (3) in a ratio of *ca.* 70 : 30 (^{1}H n.m.r. spectrum in benzene, from integrated areas of methyl resonances). T.l.c. of this mixture (Al_2O_3 or SiO_2) showed a smaller R_F value for the predominant stereoisomer, which was taken as an indication [7] of its configuration, *i.e.* the predominant isomer should be the *trans*-sulphoxide (2), in which the sulphinyl oxygen is likely to be less sterically crowded and therefore more accessible for association with a chromatographic support.

The same conclusion is reached by consideration of the mechanism of oxidation.[8,9] The electrophilic attack of the peroxy-acid should be preferentially directed towards the less-crowded diastereotopic lone-pair on the sulphur atom, preferentially producing the *trans*-sulphoxide (2) (not necessarily the more stable isomer [1]).

Through laborious fractional crystallization, the predominant diastereoisomer was isolated from the oxidation mixture * (low melting isomer, m.p. 107—

* Separation of the two diastereoisomers from this mixture by crystallization techniques is difficult, since the more abundant (low-melting) isomer is the one that is more soluble in the usual solvents.

[4] R. R. Fraser, T. Durst, M. R. McClory, R. Vian, and Y. Y. Wigfield, *Internat. J. Sulfur Chem.* (*A*), 1971, **1**, 133.

[5] M. Kishi and T. Komeno, *Internat. J. Sulfur Chem.* (*A*), 1972, **2**, 1.

[6] I. K. Nielsen and A. Kjaer, *Acta Chem. Scand.*, 1972, **26**, 853, and references quoted therein concerning sulphoxides.

[7] W. O. Siegel and C. R. Johnson, *J. Org. Chem.*, 1970, **35**, 3657.

[8] F. Montanari, M. Cinquini, and U. Folli, *Mech. Reaction Sulfur Compounds*, 1968, **3**, 121.

[9] R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, 1970, **35**, 740.

108°). The less abundant (m.p. 155—156°) isomer was obtained through basic hydrolysis of alkoxysulphonium tetrafluoroborate salts or, more simply, through isomerization in aqueous sodium hydroxide of a mixture of the isomeric sulphoxides.

The assignments of the *trans*-configuration to the low-melting isomer (2) and of *cis*-configuration to the high-melting one (3) were confirmed through a ^1H n.m.r. study of the benzene- and TFA-induced shifts on the resonances of both methyl and methine protons (respectively a doublet and a quartet of an AX_3 spin system), again with $CDCl_3$ as reference solvent. The data are shown in Table 2, together with the assignments.

TABLE 2

Chemical shifts (δ values) of methyl and methine proton resonances in the sulphoxides (2) and (3) in various solvents (0·27M); Δ refers to chemical shift differences (p.p.m.) on changing solvent; *cis* and *trans* define proton and configurational assignments

	δ_{CDCl_3}	δ_{TFA}	$\delta_{C_6H_6}$	$\Delta_{TFA-CDCl}$	$\Delta_{C_6H_6-CDCl_3}$
		Low-melting isomer (2)			
cis-H	4·61	5·21	4·32	0·60	−0·29
trans-CH_3	1·79	1·76	1·26	−0·03	−0·53
		High-melting isomer (3)			
trans-H	4·72	5·16	3·96	0·24	−0·32
cis-CH_3	1·81	2·06	1·50	0·44	−0·76

The interpretation of these solvent shifts follows the reasoning outlined before. Thus, for the methine proton resonances, since the TFA-induced shift is greater for the low-melting isomer, this must have a *cis*-H relative to the sulphinyl oxygen, *i.e.* its configuration must be that corresponding to structure (2); conversely, since the benzene-induced shift is greater for the high-melting isomer, this must have a *trans*-H, corresponding to structure (3). The same conclusion is reached by observing the methyl resonances.

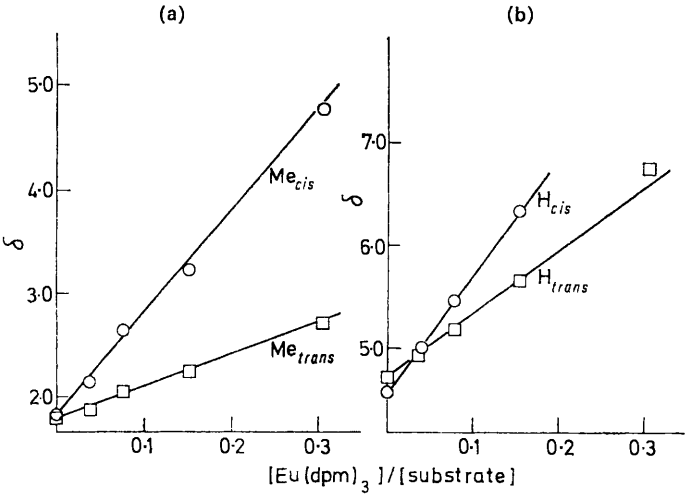


FIGURE 2 Chemical shifts of methyl (a) and methine (b) protons in the diastereomeric sulphoxides (2) and (3) in $CDCl_3$ solution (0·27M), as a function of concentration of Eu(dpm)$_3$

Lanthanide-induced shifts were then studied in $CDCl_3$ solution; the results are plotted in Figure 2. In the presence of equal amounts of Eu(dpm)$_3$, the signals due to the methyl protons in the low-melting isomer (2) are less shifted (*trans* relationship with the sulphinyl oxygen) and those due to the methine proton are more shifted (*cis* relationship) than the corresponding signals in the spectrum of the higher-melting isomer (3), thus confirming the assignments.

When interconversion of the diastereoisomeric sulphoxides (1) and (2) was attempted through basic hydrolysis of the corresponding ethoxysulphonium tetrafluoroborate salts, according to a known method for inverting the configuration at sulphinyl sulphur,[10] the expected stereospecific interconversion was observed only when hydrolysis was performed by leaving the salts in contact with aqueous sodium hydrogen carbonate overnight [both (1) and (2) as well as the corresponding ethoxy-tetrafluoroborates, were apparently insoluble in aqueous medium]. When the same hydrolysis was performed with aqueous sodium hydroxide (2·5 equiv.), interconversion was no longer stereospecific and always produced the *cis*-isomer (3) almost exclusively (>95%).

Since, in the presence of aqueous sodium hydroxide, an equilibration step was clearly involved before or after hydrolysis of the salts, we examined first the products obtained by treating the salts with H_2O–NaOH and D_2O–NaOD under standard conditions (substrate 0·2M in the medium; 2·5 mol. equiv. of base) for short and long periods, and then the behaviour of the sulphoxides (2) and (3) in the same media under comparable conditions.* The first set of experiments demonstrated that the hydrolysis of the salts was fast and stereospecific: at the very beginning the salt from the sulphoxide (2) produces compound (3) and *vice versa*, but the products, once formed, isomerize in the presence of an excess of NaOH or NaOD giving almost exclusively (>95%) the *cis*-isomer (3). This was confirmed by the second set of experiments in which the same isomerization process was directly observed starting from the sulphoxide (2) or (3) or from a mixture of the two.

The experiments in the deuteriated medium showed, moreover, that when the final mixture of isomers (equilibrium mixture) was attained from either of the two isomeric sulphoxides, only the product derived from the *trans*-isomer was completely H–D exchanged at the α-position. Thus, whereas after 14 h the *trans*-sulphoxide was recovered essentially as [α-$^2H_1$]-*cis*-isomer, the *cis*-sulphoxide was recovered without any appreciable change of its isomeric purity and only 40% H–D exchanged at the methine proton; in reactions for longer periods, H–D exchange increased but the isomeric composition of the product did not change.

Since the *trans*-sulphoxide was generally found to

* To obtain comparable conditions, only 1·5 mol. equiv. of base were used in the case of the sulphoxides as against 2·5 in the case of the salts, for in the latter case 1 mol. equiv. of base is consumed in the hydrolysis step. In each case the products were isolated by extraction and neutralization of the base and submitted to n.m.r. analysis in order to determine their composition [$CDCl_3$ solutions in the presence of Eu(dpm)$_3$].

[10] C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, 1965, **87**, 5404.

have a greater solubility than the *cis*-isomer, a reasonable explanation of these observations is that, even if the phase is apparently heterogeneous, isomer interconversion only takes place in solution, where an appreciable concentration of *trans*-sulphoxide and the base are present. Carbanion formation in solution from the *trans*-isomer, through α-proton abstraction, can lead [1] to the less soluble *cis*-isomer which, by precipitation, removes itself from the equilibria existing in solution, so that epimerization (and H–D exchange in deuteron-donating medium) can proceed rapidly and almost to completion. On the other hand, little epimerization is required to reach the equilibrium conditions when the less soluble *cis*-isomer is the starting material and, since minor amounts of *cis*-isomer can be dynamically transferred into solution, where carbanion formation is taking place, a slow deuterium exchange of the α-proton can be observed in deuteron-donating medium without further modification of the isomer composition.

This explanation seems reasonable also in view of the following behaviour: when the base-catalysed isomerization was performed in more dilute system, both (2) and (3) afforded a mixture with an appreciably greater content of *trans*-isomer (*trans*-isomer hardly detectable in a 0·2M-system; *ca.* 7% in a 0·025M-system); when it was performed in MeOH–H_2O mixed solvent, changing the water content from 0 to 100% (MeONa as catalyst), both (2) and (3) after 14 h yielded products having the compositions shown in Table 3. As long as isomerization occurs in a completely homogeneous phase (entries 1—4), the *cis–trans* ratio in the product remains

TABLE 3

Sodium methoxide-catalysed isomerization of the sulphoxides (2) and (3) in methanol–water mixtures [a]

Entry	Water (%) in medium	Product composition [b] (3) : (2)	Reaction phase † Initial	Final
1	0	69 : 31	Hom	Hom
2	20	67 : 33	Hom	Hom
3	40	67 : 33	Hom	Hom
4	60	68 : 31	Hom	Hom
5	80	82 : 18	*c*	Het
6	90	89 : 11	Het	Het
7	100	93 : 7	Het	Het

[a] Substrate 0·05M; base *ca.* 1 mol. equiv.; reaction time 14 h. [b] Determined by ^{1}H n.m.r. analysis of the isolated product in $CDCl_3$ solution (*ca.* 0·6M) in the presence of Eu(dpm)$_3$ [molar ratio Eu(dpm)$_3$: sulphoxide *ca.* 0·09 : 1]. [c] Homogeneous when starting with (2) and heterogeneous when starting with (3).

† Hom, homogeneous; Het, heterogeneous.

essentially unchanged (*cis*-isomer *ca.* 68 ± 1%); but when the water content becomes high, so that starting materials or products are apparently insoluble (entries 5—7), a sudden and progressive increase of the proportion of *cis*-isomer in the final product is attained. We therefore conclude that the observed stereoselectivity in the isomerization of the diastereoisomeric sulphoxides (2) and (3) by contact with aqueous sodium hydroxide is essentially determined by solubility factors.

By use of either the selective isomerization of these sulphoxides in aqueous sodium hydroxide or the stereospecific hydrolysis in sodium hydrogen carbonate of their alkoxysulphonium salts, it was possible to obtain either compound in almost diastereoisomerically pure form from a mixture of the two, such as the 70 : 30 mixture obtained from peroxy-acid oxidation of the sulphide (6) (see Experimental section).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a JEOL-C-60HL spectrometer.

2H-*Naphtho*[1,8-bc]*thiophen* (5).—8-Mercapto-1-naphthoic acid thiolactone [2] (4) (11·8 g) was dissolved in freshly distilled boron trifluoride–diethyl ether (227 ml) contained in a dropping funnel with the aid of an external flow of warm air. This solution was added dropwise (1·5 h) to a stirred solution of sodium borohydride (4·5 g) in anhydrous tetrahydrofuran (40 ml) and bis-(2-methoxyethyl) ether (80 ml) and cooled at 0—5° in an ice–salt bath. Stirring was continued for 2 h at room temperature and then for 2 h at 70° (internal temperature) while volatile materials were allowed to escape. The mixture was cooled to room temperature and poured into concentrated hydrochloric acid (200 ml) and crushed ice. The precipitate was filtered off, washed with water, and dissolved in ether. The solution was dried ($MgSO_4$) and evaporated. The crude product was dissolved in a small volume of warm petroleum (b.p. 80—120°) and passed through an alumina column (*ca.* 45 cm) with petroleum as eluant. The colourless fractions first eluted (*ca.* 2 l) were combined and concentrated to *ca.* 80 ml; the *sulphide* (5) crystallized from this solution in the cold; yield 8 g (77·3%), m.p. 83—85° (Found: C, 76·7; H, 5·1; S, 18·5. $C_{11}H_8S$ requires C, 76·7; H, 4·7; S, 18·6%).

2H-*Naphtho*[1,8-bc]*thiophen* 1-*Oxide* (1).—To a stirred solution in dichloromethane (50 ml) of the sulphide (5) (5 g) at −5° was added dropwise a solution in dichloromethane of *m*-chloroperbenzoic acid (0·465N by iodometric titration; 125 ml). Oxidation was complete after a further 15 min (negative iodometric test). Precipitated *m*-chloroperbenzoic acid was filtered off and the filtrate was washed with aqueous sodium hydrogen carbonate (3 times) and with water, and then dried ($MgSO_4$) and evaporated. Crude (1), m.p. 113—115°, was obtained almost quantitatively. Washing with ether (to remove colour) and crystallization from ethyl acetate gave *material* (3·3 g) of m.p. 118—120° (Found: C, 70·2; H, 4·3; S, 17·05. $C_{11}H_8OS$ requires C, 69·7; H, 4·55; S, 17·3%).

2-*Methyl*-2H-*naphtho*[1,8-bc]*thiophen* (6).—A freshly prepared [11] solution of n-butyl-lithium in tetrahydrofuran, stored at −78° (0·799M by titration; [12] 90 ml), was added dropwise with a syringe through a rubber cap to a stirred solution of (5) (12·38 g) in anhydrous tetrahydrofuran (190 ml), cooled at −60° under nitrogen. The solution turned deep red. After 5 min a solution of methyl iodide (15·32 g) in anhydrous tetrahydrofuran (20 ml) was introduced at the same temperature (the colour faded slightly). The solution was allowed slowly to reach room temperature. The solvent was evaporated off and the residue dissolved in water and washed with ether. The ethereal solution was treated with $MgSO_4$ and decolourizing carbon and evaporated. The oily residue was distilled, yielding *compound* (6)

[11] H. Gilman and B. J. Gay, *J. Org. Chem.*, 1965, **22**, 1165.

[12] W. Voskuil and J. F. Arens, *Org. Synth.*, 1968, **48**, 47, note 5: R. A. Ellison, R. Griffin, and F. N. Kotsonis, *J. Organometallic Chem.*, 1972, **86**, 209.

as an oil (11·1 g, 83%), b.p. 97—100° at 0·03 mmHg (bath at 115—120°), $n_D^{20·5}$ 1·6730. When an equivalent amount of commercial n-butyl-lithium in n-heptane was used for the reaction, the yield was only slightly lower (Found: C, 77·15; H, 5·3; S, 16·95. $C_{12}H_{10}S$ requires C, 77·4; H, 5·4; S, 17·2%).

2-*Methyl*-2H-*naphtho*[1,8-bc]*thiophen* 1-*Oxides* (2) *and* (3).—The sulphide (6) (8 g) was oxidized in dichloromethane solution (70 ml) at −5° with a solution in dichloromethane of *m*-chloroperbenzoic acid (0·432N, 180 ml) as described for compound (1). Evaporation left a solid residue, m.p. 75—78°, in almost theoretical yield. Solidification was readily achieved by contact with a non-protic solvent such as diethyl or di-isopropyl ether. ^{1}H N.m.r. analysis (see Discussion section) showed that (2) and (3) were present in this crude product in the ratio 70 : 30 (minor impurities of sulphone and sulphide were also present). T.l.c. analysis (Al_2O_3 or SiO_2; petroleum–Et_2O–EtOAc, 50 : 30 : 20) showed two close spots for the isomeric sulphoxides, the largest one having the smaller R_F value. Preliminary purification was achieved by stirring the solid in ether and then filtering to give a white solid. Laborious fractional crystallization from carbon disulphide and ethyl acetate gave a small amount (1 g) of pure isomer (2), m.p. 107—108°. A better way of obtaining compounds (2) and (3) in pure form involves chemical transformation of the oxidation mixture as described later.

cis-2-*Methyl*-2H-*naphtho*[1,8-bc]*thiophen* 1-*Oxide* (3).—(a) *Hydrolysis of ethoxysulphonium salts with aqueous alkali.* Freshly prepared [13] triethyloxonium tetrafluoroborate (2·91 g) and a mixture of (2) and (3) (70 : 30; 2·58 g) were dissolved in dichloromethane (30 ml) in a dry-box. The solution was stirred for 90 min at room temperature, then cooled to *ca.* 0°. Ether (100 ml) was added dropwise with stirring and the ethoxysulphonium tetrafluoroborate was filtered off, washed with ether, suspended in water, and stirred overnight (14 h) in the presence of 2·5 mol. equiv. of aqueous N-sodium hydroxide. The base was neutralized and the suspended solid was separated with dichloromethane. Drying ($MgSO_4$) and evaporation gave the product, m.p. 150—153° (2·59 g, 89%), shown by ^{1}H n.m.r. analysis to contain only traces (<5%) of the *trans*-isomer (2). After crystallization from benzene (or ethyl acetate), pure *sulphoxide* (3) had m.p. 155—156° (Found: C, 71·2; H, 4·5; S, 15·7. $C_{12}H_{10}OS$ requires C, 71·25; H, 4·5; S, 15·75%). This reaction sequence, when performed starting from pure (3) or pure (2), always produced (3) of high isomeric purity.

(b) *Isomerization with aqueous alkali.* Pure (3) or (2), or a mixture of the two, was suspended in water and aqueous N-sodium hydroxide (2·5 mol. equiv.) was added. The suspension was stirred overnight (14 h), neutralized with dilute sulphuric acid, and extracted with dichloromethane. Drying ($MgSO_4$) and evaporation gave a product of m.p. 150—153°, containing (3) in high isomeric purity (>95%), from which pure (3) was easily obtained by crystallization [see method (a)]. Isomerization in this way of the 70 : 30 mixture obtained by peroxy-acid oxidation of (6) is obviously the easiest way to obtain (3).

trans-2-*Methyl*-2H-*naphtho*[1,8-bc]*thiophen* 1-*Oxide* (2).—Pure (3) (4·36 g) was converted into the corresponding ethoxysulphonium salt as already described. This was suspended in water and aqueous N-sodium hydrogen carbonate (4 mol. equiv.) was added with stirring. Gas was evolved (CO_2) and the suspension became a viscous oil which slowly solidified. The suspension was stirred overnight, then extracted with dichloromethane; the extract was washed with water, dried ($MgSO_4$), and evaporated. The residue (m.p. 98—102°; 4·15 g, 97%) was identified through ^{1}H n.m.r. analysis as the *isomer* (2), which was further purified by crystallization from carbon disulphide, raising the m.p. to 107—108° (Found: C, 71·1; H, 5·05; S, 15·5. $C_{12}H_{10}OS$ requires C, 71·25; H, 5·0; S, 15·75%).

Lanthanide-induced Shift Measurements.—Commercial $Eu(dpm)_3$ was purified through sublimation at 160° and 0·01 mmHg and stored in a desiccator (P_2O_5). Commercial [^{2}H]chloroform was passed under nitrogen through a small column containing basic alumina previously heated at 200° overnight. Standard solutions of the sulphoxides (1)—(3) and of $Eu(dpm)_3$ were prepared (by weight) from which, by appropriate mixing and dilution, samples of the same sulphoxide concentration (0·27M) and different $Eu(dpm)_3$ concentrations were derived; these were subjected to ^{1}H n.m.r. analysis.

[3/2442 *Received, 28th November,* 1973]

[13] H. Meerwein, *Org. Synth.*, 1962, **46**, 113.