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# A SYNTHESIS OF *TRANS*-1-ALKYLTHIO-1-ALKENES*

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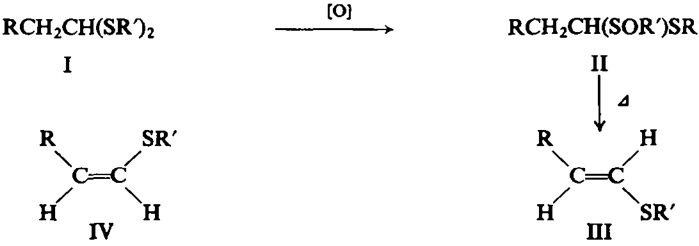
**Abstract**—A convenient synthesis of *trans*-1-alkylthio-1-alkenes (III) is reported using the reaction stages: aldehyde → mercaptal (I) → monosulphoxide (II). Thermal elimination of the alkylsulphinyl group from II afforded the corresponding *trans*-alkene (III) in high yields. *trans*-Structure of III is confirmed by chemical and spectroscopic methods. The steric course of the elimination reactions is discussed.

SINCE the first preparation of ethyl vinyl sulphide in 1900[2] several methods for the synthesis of 1-alkylthio-1-alkenes (*trans*: III; *cis*: IV) have been developed.[3] Except the stereospecific synthesis of *cis*-alkenes IV,[4] however, all the other hitherto described methods for the preparation of these compounds were non-stereospecific, and led to mixtures of the possible *cis* and *trans* isomers.

During our investigations concerning the synthesis of (±)-sulphoraphene we have found a convenient method for the preparation of 1-alkylthio-1-alkenes (III),[5] which consists in the oxidation of the appropriate mercaptal[6] (I) to its monosulphoxide II,



$$\underset{\text{I}}{RCH_2CH(SR')_2} \xrightarrow{[O]} \underset{\text{II}}{RCH_2CH(SOR')SR'} \xrightarrow{\Delta} \text{III}$$

I–IV:
a, R = Me; R′ = Ph
b, R = n-pentyl; R′ = Me
c, R = Ph; R′ = Me
d, R = $o$-$C_6H_4(CO)_2N$; R′ = Me
e, R = $o$-$C_6H_4(CO)_2NCH_2$; R′ = Me
f, R = $o$-$C_6H_4(CO)_2NCH_2CH_2$; R′ = Me

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* Dedicated to Sir Robert Robinson on his 80th birthday.

[1] Taken in part from A. Deljac's Ph. D. Dissertation, University of Zagreb (1965).

[2] D. Strömholm, *Ber. Dtsch. Chem. Ges.* **33**, 823 (1900).

[3] H. J. Boonstra, L. Brandsma, A. M. Wiegman and J. F. Arens, *Rec. Trav. Chim.* **78**, 252 (1959) and earlier work cited therein.

[4] W. E. Truce and J. A. Simms, *J. Amer. Chem. Soc.* **78**, 2756 (1956).

[5] Presented in part at the *International Symposium on the Organic Chemistry of Natural Products*, Brussels, June (1962); *Ind. Chim. Belge* **27**, 547 (1962).

[6] In our first approach to the synthesis of (±)-sulphoraphene we attempted to pyrolyse 1,1-di(methylthio)-4-phthalimidobutane (If) to the corresponding thioenol ether IIIf according to the method of Boonstra *et al.*[3] The results, however, were unsatisfactory because of the high temps required for the pyrolysis.

and in thermal elimination of alkylsulphenic acid from these 1-alkylsulphinyl-1-alkylthio derivatives (II) at comparatively low temperatures, which affords the *trans*-alkenes III in high yields.

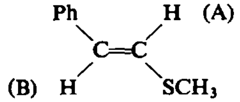
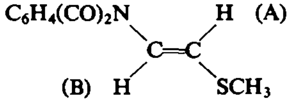
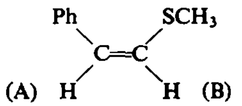
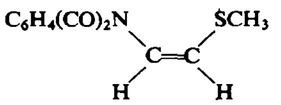
The mercaptals I a–f were carried through this new reaction. Phenylacetaldehyde dimethyl mercaptal (Ic), for instance, gave *trans*-methyl-ω-styryl sulphide (IIIc) in a 75% yield. To confirm its *trans* configuration the compound IIIc was converted by oxidation into the known *trans*-methyl-ω-styryl sulphone.[7] Preparation of the corresponding *cis*-sulphide (IVc) had been effected earlier by nucleophilic addition of methyl mercaptan to phenylacetylene.[4]

The pyrolysis of IId and IIf afforded, besides high yields of the corresponding *trans* thioenol ethers IIId and IIIf, the *cis* isomers IVd and IVf in small amounts. Thus, phthalimido acetaldehyde dimethyl mercaptal (Id) afforded via pyrolysis of IId two isomeric thio-alkenes showing characteristic differences for *cis* and *trans* isomers[8] in their UV spectra:

> orange-yellow needles in 60% yield ($CHCl_3$; 284 mμ, log ε 4·42) of *trans*-1-methylthio-2-phthalimidoethylene (IIId) and pale yellow crystals in 10% yield ($CHCl_3$; 270 mμ, log ε 4·02) of *cis*-isomer IVd.

The assignment of *trans* configuration in these and other cases is also justified by the results of the evaluation of IR and NMR spectra. IR spectra of the compounds IIIa–f (Table 5) show one by one strong absorption band between 929 and 944 $cm^{-1}$,

TABLE 1. CHEMICAL SHIFTS ASSIGNMENT (IN $CDCl_3$ SOLN) FOR THE TWO OLEFINIC PROTONS IN 1-ALKYLTHIO-1-ALKENES[a]

| Compound | | $\tau_{(A)}$ | $\tau_{(B)}$ | $J_{c/s}$ |
|---|---|---|---|---|
| IIIc |  | 3·26 | 3·78 | 15·5 |
| IIId |  | 2·66 | 3·42 | 14·5 |
| IVc[b] |  | 3·62 | 3·98 | 10·5 |
| IVd |  | 3·67 | 3·69 | 8·0[c] |

[a] Cf. C. Pascual, J. Meier and W. Simon, *Helv. Chim. Acta* 49, 164 (1966); F. Bohlmann, C. Arndt and J. Starnick, *Tetrahedron Letters* 1605 (1963).

[b] Prepared according to Ref. 4.

[c] Resolution achieved by running the spectrum on Varian A-100 spectrometer.

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[7] W. E. Truce, J. A. Simms and H. E. Hill, *J. Amer. Chem. Soc.* 75, 5411 (1953).

[8] Cf. e.g. C. N. R. Rao, *UV and Visible Spectroscopy* p. 69. Butterworths, London (1961).

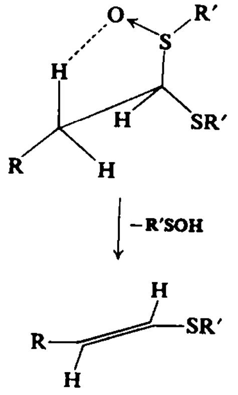
characteristic for the *trans* hydrogens in 1,2-disubstituted ethylenes.[9] The coupling constant values of the two proton nuclei on the double bond in the NMR spectra of IIIc–d (Table 1) are within the standard interval attributed to protons of *trans* ethylenic double bonds.[10]

Heating of geometrical isomers may result in a thermodynamically controlled composition of the products obtained, and in relation to the discussion on the stereochemical course of this elimination reaction the problem arises of *cis–trans* isomerization[11] during the pyrolysis. Moreover, the unexpectedly facile *cis–trans* isomerization of 4-methylthio-3-butenyl isothiocyanate during vapour phase chromatography has recently been observed.[12]

We, therefore, subjected pure *trans* and *cis* compounds (IIId and IVd) to the pyrolysis conditions. *cis*-1-Methylthio-2-phthalimidoethylene (IVd), heated at 160° for 2 hr gave only 5 % *trans* compound IIId, and, moreover, pure IIId remained entirely unchanged under similar treatment.

Analogous heating of 1-methyl-sulphinyl-1-methylthio-2-phthalimidoethane (IId) afforded *trans* and *cis* compounds IIId and IVd as products of pyrolysis, in the ratio 6 : 1. Consequently it can be assumed that the *trans–cis* ratio of pyrolytic products is predominantly determined by the stereochemistry of the transition state of the elimination reaction.

The earlier described transformation of sulphoxide to olefin by low temperature pyrolysis[13,14] is predominantly stereospecific and at lower temperatures the classical cyclic *cis*-elimination mechanism was found to be probable.[13] It is evident from Fig. 1 that *cis*-elimination of the sulphoxide group connected with the most favourable conformation of other groups (R and R'S) in the molecule of compound II affords predominantly *trans* olefin:



II

III

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[9] Cf. L. J. Bellamy, *The IR Spectra of Complex Molecules* (2nd Edition) p. 45. Methuen, London (1959).

[10] L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry.* Pergamon, New York (1959).

[11] Cf. e.g. E. L. Eliel, *Stereochemistry of Carbon Compounds* p. 341. McGraw-Hill, New York (1962).

[12] Private communication from Professor A. Kjaer; P. Friis and A. Kjaer, *Acta Chem. Scand.* **20**, 698 (1966).

[13] C. A. Kingsbury and D. J. Cram, *J. Amer. Chem. Soc.* **82**, 1810 (1960).

[14] T. Colclough and J. I. Cunneen, *Chem. & Ind.* 626 (1960).

## EXPERIMENTAL

M.ps are uncorrected. NMR spectra: Varian A-60 instrument for $CDCl_3$ solns containing TMS as internal reference. All chemical shifts are quoted on the $\tau$-scale. UV spectra: Perkin-Elmer spectrophotometer Model 137 UV. The IR spectra: KBr, in chf soln, Perkin-Elmer Infracord 137. TLC: Silica Gel G (E. Merck, Darmstadt, Germany) in solvent system chf–MeOH (9:1). Spots were developed with 1% $KMnO_4$aq.[15] For loose layer-[16] and column chromatography alumina (neutral, E. Merck) was used. Light petroleum, b.p. 40–60°.

*Aldehydes* for the preparation of mercaptals Id–f were synthesized by the method of Radde.[17] Other aldehydes were commercial products.

*Mercaptals.* A mixture of the corresponding aldehyde, thiol and anhydrous $ZnCl_2$ was heated in a sealed tube for 3 hr at 80–90°.[3,15] Mercaptals were obtained in 60–85% yields. Details of the new compounds prepared under this heading are given in the Table 2.

TABLE 2. MERCAPTALS Ia–e

| Mercaptal | B.p. (mm) or M.p. | Formula | Found (%) C | Found (%) H | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|
| Ia | 150–155° (0·1) | $C_{15}H_{16}S_2$ | 68·78 | 6·59 | 69·18 | 6·19 |
| Ib | 125° (12) | $C_9H_{20}S_2$ | 56·62 | 10·58 | 56·19 | 10·48 |
| Ic | 95° (0·02) | $C_{10}H_{14}S_2$ | 60·86 | 6·95 | 60·59 | 7·12 |
| Id | 89–90° | $C_{12}H_{13}O_2NS_2$ | 54·01 | 4·99 | 53·90 | 4·90 |
| Ie | 104–105° | $C_{13}H_{15}O_2NS_2$ | 55·74 | 5·38 | 55·49 | 5·37 |

1-*Alkylsulphinyl*-1-*alkylthio derivatives* (II)

Equimolar amounts of mercaptal and perbenzoic acid (*method A*) or (+)-*cis*-percamphoric acid (method B) were used for the preparation of these compounds. A typical example for the oxidation with perbenzoic acid is the preparation of 1-methylsulphinyl-1-methylthio-4-phthalimidobutane (IIf) described previously.[15]

*Method B.* 1-Methylsulphinyl-1-methylthioheptane (IIb). To a soln of 1,1-di(methylthio)-heptane (4·22 g, 0·022 mole) in ether (200 ml) cooled to 0°, an ethereal soln of (+)-*cis*-percamphoric acid[18] (0·2 M, 120 ml, 0·022 mole) was added dropwise during 1 hr under stirring, the temp being kept at 0°. The ethereal mother liquor was evaporated to dryness (below 20°) and on addition of chf (20 ml) to the residue, camphoric acid separated. Distillation of remaining oil at 90° (0·025 mm) afforded IIb (4·05 g, 87%).

The choice of the method A or B was not essential and depended only on the solubility of starting materials and reaction products. In both cases yields of pure compound were between 80–95%. Compounds IId–f crystallized immediately from the ethereal soln of the reaction mixture in almost quantitative yields. Oxidation to the monosulphoxide stage (II) has been conveniently carried out using TLC or loose layer chromatography under conditions described above. In the same manner the purification for analysis was controlled. This consisted in dissolving the compound in dichloromethane and precipitating with light petroleum.

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[15] Cf. K. Balenović, A. Deljac, I. Monković and Z. Štefanac, *Tetrahedron* **22**, 2139 (1966).

[16] V. Černý, J. Joska and L. Lábler, *Coll. Czech. Chem. Comm.* **26**, 1658 (1961).

[17] E. Radde, *Ber. Dtsch. Chem. Ges.* **55**, 3174 (1922); K. Balenović, I. Jambrešić and I. Furić, *J. Org. Chem.* **17**, 1459 (1952).

[18] N. A. Milas and A. McAlevy, *J. Amer. Chem. Soc.* **55**, 349 (1933).

TABLE 3. 1-ALKYLSULPHINYL-1-ALKYLTHIO-DERIVATIVES (IIa–e)

| Compound | B.p. (mm) or M.p. | Formula | Found (%) C | Found (%) H | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|
| IIa | *a* | $C_{15}H_{16}OS_2$ | 65·61 | 5·98 | 65·18 | 5·84 |
| IIb | 85° (0·02) | $C_9H_{20}OS_2$ | 52·27 | 9·76 | 51·87 | 9·68 |
| IIc | *a* | $C_{10}H_{14}OS_2$ | 55·68 | 6·29 | 56·03 | 6·58 |
| IId | 148–149° | $C_{12}H_{13}O_3NS_2$ | 51·02 | 4·61 | 50·86 | 4·62 |
| IIe | 136–137° | $C_{13}H_{15}O_3NS_2$ | 52·40 | 5·33 | 52·50 | 5·08 |

[a] Over 100° dec.

All 1-alkylsulphinyl-1-alkylthio-derivatives listed in Table 3 were prepared by method B; compounds IIc and IId by both methods.

trans-1-*Alkylthio*-1-*alkenes* (III). Compound II (0·5–1 g) on glass wool (Corning, No 800) was heated under red. press. in a micro distillation flask. After 2–3 hr heating pyrolysis was complete and the distillate consisted of the corresponding crude 1-alkylthio-1-alkene, which after crystallization from $CH_2Cl_2$–light petroleum gave the pure *trans* compound. Liquid IIIa and IIIc were oxidized[4] to solid *trans*-sulphones (*vide infra*). In Table 4 are given the pyrolysis conditions and yields of resulting 1-alkylthio-1-alkenes. Analytical results and constants for these compounds are presented in Table 5.

TABLE 4. PYROLYSIS OF 1-ALKYLSULPHINYL-1-ALKYLTHIO- DERIVATIVES (II); YIELDS OF RESULTING ALKENES (III AND IV)

| Starting compound | Pyrolysis Temp | Pyrolysis Press (mm) | Yield % III *trans* | | Yield % IV *cis* | |
|---|---|---|---|---|---|---|
| IIa | 140–150° | (14) | IIIa | 80 | | |
| IIb | 120–130° | (14) | IIIb | 68 | | |
| IIc | 125–130° | (15) | IIIc | 71 | | |
| IId | 160° | (*a*) | IIId | 61 | IVd | 10 |
| IIe | 140° | (0·01) | IIIe | 70 | | |
| IIf | 130° | (0·01) | IIIf | 60–64 | IVf | 14–16 |

[a] Pyrolysed at 14 mm, then distilled at 0·01 mm.

TABLE 5. 1-ALKYLTHIO-1-ALKENES

| Compound | B.p. (mm) or M.p. | Formula | Found (%) C | Found (%) H | Required (%) C | Required (%) H | Cm⁻¹ (in KBr)[a] |
|---|---|---|---|---|---|---|---|
| IIIa | 110–115° (14)[b] | $C_9H_{10}S$ | 71·71 | 6·79 | 71·95 | 6·71 | 937 |
| IIIb | 75–80° (11) | $C_8H_{16}S$ | 66·90 | 11·31 | 66·60 | 11·18 | 940 |
| IIIc | 115–120° (16) | $C_9H_{10}S$ | 72·09 | 6·69 | 71·95 | 6·71 | 939 |
| IIId | 112–113° | $C_{11}H_9O_2NS$ | 60·27 | 4·26 | 60·25 | 4·14 | 929 |
| IIIe | 92–93° | $C_{12}H_{11}O_2NS$ | 61·96 | 5·02 | 61·78 | 4·75 | 942 |
| IIIf | 100–101° | $C_{13}H_{13}O_2NS$ | 63·43 | 5·41 | 63·13 | 5·30 | 944 |
| IVd | 113–114° | $C_{11}H_9O_2NS$ | 60·39 | 4·03 | 60·25 | 4·14 | |
| IVf | 70–71° | $C_{13}H_{13}O_2NS$ | 63·15 | 5·27 | 63·13 | 5·30 | |

[a] IR di-substituted ethylenes —HC═CH— *trans* absorption.

[b] A mixture of *trans* and *cis* propenyl phenyl sulphide (IIIa and IVa) was prepared earlier by isomerization of allyl phenyl sulphide;[19] cf. also Refs 20 and 21.

*Separation of* cis-*isomers.* After pyrolysis of IId, the distillate was crystallized from EtOH, and gave the pure *trans* IIId (m.p. 112–113°). The ethanolic filtrate, evaporated to dryness, was chromatographed on alumina (activity 1) with chf–benzene, 1:1. Elution gave first the *trans* IIId, a small quantity of the *cis–trans* mixture, then the pure *cis* IVd.

The distillate consisting of a mixture of *trans*- and *cis*-1-methylthio-4-phthalimido-1-butene (IIIf and IVf) was separated in the same way, after crystallization from $CH_2Cl_2$–ether and chromatography on alumina (activity 2) with solvent system chf–benzene–light petroleum, 1:1:1.

*Experiments on* cis-trans *isomerization.* The pure *cis* IVd (0·1 g) was heated for 2 hr at 160°, and then distilled at 130° (0·02 mm). Investigation by UV spectroscopy showed only 5% of *trans* IIId.

trans-*Sulphones derived from* IIIa *and* IIIc. A soln of IIIa (0·65 g) in glacial AcOH (4 ml) and $H_2O_2$ (25%; 1·2 ml) was refluxed for 1½ hr and then in turn diluted with $H_2O$, extracted with chf and dried. Chromatography on an $Al_2O_3$-column (activity 3) with chf gave *trans*-1-phenylsulphonyl-1-propene in a 71% yield (0·56 g). Colourless prisms from $CH_2Cl_2$–light petroleum, m.p. 70–71°; lit.[21] m.p. 68·5–69°.

After analogous oxidation of IIIc and dilution with $H_2O$, colourless prisms of *trans*-1-methylsulphonyl-2-phenyl-ethylene m.p. 76–77° separated in a 68% yield. Recrystallization from $CH_2Cl_2$–light petroleum gave m.p. 79–80°.[7]

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[19] D. S. Tarbell and M. A. McCall, *J. Amer. Chem. Soc.* **74**, 48 (1952).

[20] N. K. Kulbovskaya, E. P. Gracheva and M. F. Shostakovskii, *Zh. Obshch. Khim.* **30**, 81 (1960).

[21] E. N. Karaulova, D. Sh. Meilanova and G. D. Galpern, *Dokl. Akad. Nauk S.S.S.R.* **113**, 1280 (1957).