

Free-radical Addition of Alkanethiols to Some Acyclic Olefins

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Butane-1-thiol and 1,1-dimethylethane-1-thiol added to some non-conjugated [(I)—(VIII)] and conjugated [(IX)—(XI)] olefins under free radical conditions to yield sulphides. The reactivity order was: conjugated diene > vinyl (anti-Markownikoff addition) > internal double bonds. The conjugated dienes yielded mainly 1,2- and 1,4-adducts.

ALKENYL ALKYL SULPHIDES were required as additives to ethylene-propylene co-polymerisations.¹ We report here the free-radical addition of butane-1-thiol and, in some cases, 1,1-dimethylethane-1-thiol to some acyclic dienes and trienes; the distribution of isomers in the

¹ D. N. Mattmews, F. G. Loveless, and R. J. Kelly, Ger. Offen. 1,903,100 (*Chem. Abs.*, 1969, **71**, 125,174g); P. Mornet, J. Teitgen, and G. Marie, Fr.P., 1,546,596 (*Post P.*, 1969, **6**, 71); W. P. Long, U.S.P. 3,203,940 (*Chem. Abs.*, 1965, **63**, 13,543e); Belg. Pat. 670,762 (*Chem. Abs.*, 1966, **65**, 10,688b).

products supplements the information on the relative reactivities of olefins towards thiyl radicals.²

The olefin and thiol (usually in the molar ratio 2 : 1) were heated at 90° for 3—5 h without solvent; benzoyl peroxide was added to catalyse the free-radical process. The products were separated by distillation and/or g.l.c.

² J. I. Cunneen, *J. Chem. Soc.*, 1947, 36; K. Griesbaum, *Angew. Chem. Internat. Edn.*, 1970, **9**, 273; R. M. Kellog, *Methods Free-Radical Chem.*, 1969, **2**, 1.

Addition of butane-1-thiol or 1,1-dimethylethanethiol to olefins

Olefin	Main products * (% of total sulphides)		Total yield of sulphides (%)	
Hept-1-ene (I)	Bu ^a S·[CH ₂] ₅ ·CH ₃ ^a	(XII)	(93)	68
Hept-1-ene (I)	Bu ^a S·[CH ₂] ₆ ·CH ₃	(XIII)	(93)	20
Hexa-1, <i>cis</i> -4-diene ^b (II)†	Bu ^a S·[CH ₂] ₃ ·CH=CH·CH ₃	(XIV)	(91)	50
Hexa-1, <i>trans</i> -4-diene ^c (III)	Bu ^a S·[CH ₂] ₃ ·CH=CH·CH ₃	(XV)	(96)	29
2-Methylhexa-1,5-diene (IV)	{ CH ₂ =C(CH ₃)·[CH ₂] ₄ ·SBu ^a Bu ^a S·CH ₂ CH(CH ₃)·[CH ₂] ₂ ·CH=CH ₂	(XVI) (XVII)	(66) (28)	70
3-Methylhexa-1, <i>trans</i> -4-diene ^c (V)	Bu ^a S·[CH ₂] ₂ ·CH(CH ₃)·CH=CH·CH ₃	(XVIII)	(98)	24
Octa-1, <i>trans</i> -6-diene ^d (VI)‡	Bu ^a S·[CH ₂] ₅ ·CH=CH·CH ₃	(XIX)	(95)	55
Deca-1, <i>trans</i> -5,9-triene ^e (VII)	Bu ^a S·[CH ₂] ₄ ·CH=CH·CH ₂ CH ₂ CH=CH ₂	(XX)	(92)	62
Deca-1, <i>trans</i> -5,9-triene (VII)	Bu ^a S·[CH ₂] ₄ ·CH=CH ₂ CH ₂ CH=CH ₂	(XXI)	(95)	40
Deca-1, <i>trans</i> -4,9-triene ^f (VIII)	{ Bu ^a S·[CH ₂] ₃ ·CH=CH·[CH ₂] ₃ ·CH=CH ₂ § CH ₂ =CH·CH ₂ CH=CH·[CH ₂] ₅ ·SBu ^a §	(XXII) (XXIII)	(45) (45)	55
Deca-1, <i>trans</i> -4,9-triene (VIII)	{ Bu ^a S·[CH ₂] ₃ ·CH=CH·[CH ₂] ₃ ·CH=CH ₂ § CH ₂ =CH·CH ₂ CH=CH·[CH ₂] ₅ ·SBu ^a §	(XXIV) (XXV)	(45) (45)	6
Octa-1, <i>trans</i> -3,7-triene ^g (IX)	{ Bu ^a S·CH ₂ CH=CH·[CH ₂] ₃ ·CH=CH ₂ § Bu ^a S·[CH ₂] ₂ ·CH=CH·[CH ₂] ₂ ·CH=CH ₂ § CH ₃ ·CH=CH·CH(SBu ^a)·[CH ₂] ₂ ·CH=CH ₂	(XXVI) (XXVII) (XXVIII)	(55) (25) (13)	33
3-Methylhepta-1, <i>trans</i> -4,6-triene ^h (X)	{ Bu ^a S·CH ₂ CH=CH·CH ₂ ·CH(CH ₃)·CH=CH ₂ § Bu ^a S·[CH ₂] ₂ ·CH=CH·CH·(CH ₃)·CH=CH ₂ §	(XXIX) (XXX)	(67) (29)	30
Octa-1, <i>trans</i> -3, <i>cis</i> -6-triene ^{h(ii),i} (XI)	{ Bu ^a S·CH ₂ ·CH=CH·[CH ₂] ₂ ·CH=CH·CH ₃ § Bu ^a S·[CH ₂] ₂ ·CH=CH·CH ₂ CH=CH·CH ₃ § CH ₃ ·CH=CH·CH(SBu ^a)·CH ₂ CH=CH·CH ₃	(XXXI) (XXXII) (XXXIII)	(49) (35) (12)	28

* Spectroscopic data for the products are available as Supplementary Publication No. SUP 20754 (7 pp.) For details of Supplementary Publications see Notice to Authors No. 7 [J. Chem. Soc. (A), 1970, Issue No. 20]. † Recovered olefin contained 3.6% *trans*-isomer; cf. starting material ca. 100% *cis*. ‡ Recovered olefin contained 15.7% *cis*-isomer; cf. starting material 97.1% *trans*, 2.9% *cis*. § Isomers not separated; proportions estimated by g.l.c. and n.m.r.

^a F. K. Signaigo, U.S.P. 2,406,410; E. W. Abel, D. A. Armitage, and R. P. Bush, *J. Chem. Soc.*, 1964, 2455. ^b M. Iwamoto and S. Yuguchi, *J. Org. Chem.*, 1966, **31**, 4290; *Bull. Chem. Soc. Japan*, 1968, **41**, 150; G. Hata and A. Miyake, *Bull. Chem. Soc. Japan*, 1968, **41**, 2762. ^c T. Alderson, E. L. Jenner, and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1965, **87**, 5638. ^d S. Gardner and D. Wright, *Tetrahedron Letters*, 1972, 163. ^e F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.*, 1962, **84**, 3520. ^f Fr.P. 424,314 (*Chem. Abs.*, 1966, **65**, 8758b); Neth.P. 6,613,603 (*Chem. Abs.*, 1968, **68**, 2569v). ^g S. Takahashi, T. Shibano, and N. Hagihara, *Tetrahedron Letters*, 1967, 2451; E. J. Smutny, *J. Amer. Chem. Soc.*, 1967, **89**, 6793; E. J. Smutny and H. Chung, Preprints, Division of Petroleum Chemistry, Amer. Chem. Soc., 1969, vol. 14, No. 2, B112. ^h (i) S. Otsuka, T. Kikuchi, and T. Taketomi, *J. Amer. Chem. Soc.*, 1963, **85**, 3709; *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1963, **66**, 1094; T. Saito, T. Ohno, Y. Uchida, and A. Misono, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, 1963, **66**, 1099; (ii) H. Takahashi, T. Kimata, and M. Yamaguchi, *Tetrahedron Letters*, 1964, 3173; S. Tanaka, K. Mabuchi, and N. Shimazaki, *J. Org. Chem.*, 1964, **29**, 1626. ⁱ H. Takahashi, S. Tai, and M. Yamaguchi, *J. Org. Chem.*, 1965, **30**, 1661.

and examined by u.v.,³ i.r.,⁴ and n.m.r. spectroscopy. The sulphides obtained from the olefins (I)—(XI) are given in the Table. Only the main products were examined in detail. Two to five minor products were detected in each case: these could arise from Markowni-

koff addition,^{5,6} *cis-trans*-isomerisation,^{7,8} or double-bond migration⁶ resulting from the reversibility^{7,9} of the addition step. In the three cases where the bulky dimethylethanethiol was used [(I), (VII), and (VIII)] the yields (6—40%) were lower than with butanethiol, but the products were analogous [(XIII), (XXI), (XXIV),

³ (a) H. P. Koch, *J. Chem. Soc.*, 1949, 387; (b) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1949, **71**, 84; (c) A. Mangini, *Gazzetta*, 1958, **88**, 1063; (d) A. Balasubramanian, *Indian J. Chem.*, 1963, **1**, 415; (e) C. W. N. Cumper, J. F. Read, and A. I. Vogel, *J. Chem. Soc. (A)*, 1966, 239; (f) P. Laur, H. Hauser, J. E. Gurst, and K. Mislow, *J. Org. Chem.*, 1967, **32**, 498; (g) S. D. Thompson, D. G. Carrol, F. Watson, M. O'Donnell, and S. P. McGlynn, *J. Chem. Phys.*, 1966, **45**, 1367; (h) D. R. Williams, D. L. Coffen, P. E. Garrett, and R. N. Schwartz, *J. Chem. Soc. (B)*, 1968, 1132; (i) P. Salvadori, *Chem. Comm.*, 1968, 1203; (j) J. S. Rosenfield and A. Moscowitz, *J. Amer. Chem. Soc.*, 1972, **94**, 4797.

⁴ H. J. Boonstra and L. C. Rinzema, *Rec. Trav. chim.*, 1960, **79**, 962; M. Horak, J. Pitrova, R. Rericha, and V. Horak, *Coll. Czech. Chem. Comm.*, 1970, **35**, 3223.

⁵ A. A. Oswald and W. Naegele, *J. Org. Chem.*, 1966, **31**, 830.

⁶ J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. (B)*, 1966, 1191.

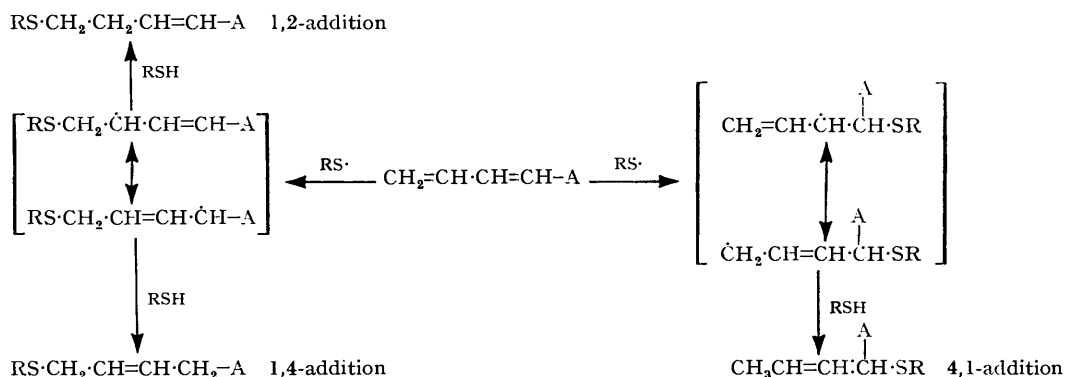
⁷ C. Walling and W. Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.

⁸ E. W. Duck and J. M. Locke, *Chem. and Ind.*, 1965, 507.

⁹ (a) R. H. Pallen and C. Sivertz, *Canad. J. Chem.*, 1957, **35**, 723; (b) E. S. Huyser and R. M. Kellog, *J. Org. Chem.*, 1965, **30**, 2867; (c) L. H. Gale, *J. Org. Chem.*, 1969, **34**, 81; (d) D. M. Graham and J. F. Soltys, *Canad. J. Chem.*, 1970, **48**, 2173; (e) N. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1960, **82**, 5354; (f) M.-P. Crozet, J.-M. Surzur, and C. Dupuy, *Tetrahedron Letters*, 1971, 2031.

and (XXV)]. The yields of the butanethiol adducts of the conjugated olefins (IX), (X), and (XI) were lower ^{9a} (ca. 30%) than with most of the non-conjugated olefins (50—70%).

The formation of the sulphides (XIV), (XV), and (XVIII)—(XXV) from the olefins (II), (III), and (V)—(VIII), which contain isolated double bonds, illustrates the preference for anti-Markownikoff addition to an external (vinyl), rather than an internal double bond.^{2,6,7} Isomerisation of recovered olefin was observed with hexa-1,*cis*-4-diene (II) and octa-1,*trans*-6-diene (VI), where g.l.c. indicated the formation of 2% of the *trans*- and 12% of the *cis*-isomer, respectively. Steric factors^{6,10} explain the marked preference for addition to the vinyl double bond (XVI) of 2-methylhexa-1,5-diene (IV) compared with the isopropylene group (XVII), despite the increased stability of the tertiary radical which results from the latter addition.⁷



SCHEME

Mechanism of addition of thiyl radicals to conjugated olefins;¹² A = H, alkyl, or alkenyl

The trienes (IX)—(XI) contain both conjugated and isolated double bonds. The sulphides obtained (XXVI)—(XXXIII) from their reaction with butanethiol show that the latter adds exclusively to the conjugated system.^{11,12c} Oswald *et al.*¹² have demonstrated that a thiol adds to the terminal carbon atoms of a conjugated diene to form allyl radicals, which then pick up hydrogen atoms on the least substituted carbon atoms of the allyl system (see Scheme). Thus, the olefins (IX)—(XI) give 1,4-adducts [(XXVI), (XXIX), and (XXXI)], 1,2-adducts [(XXVII), (XXX), and (XXXII)], and 4,1-adducts [(XXVIII) and (XXXIII)] in proportions approximately the same as was found in the reaction of alkanethiols with penta-1,3-diene¹² (A = Me). The lack of a 4,1-adduct with 3-methylhepta-1,*trans*-4,6-triene (X) can be attributed to the steric effect of the 3-methyl substituent. As with penta-1,3-diene,¹² 4,3-adducts did not constitute a major product with any of the conjugated olefins. The fact that the 1,4-addition to the conjugated olefins results in the formation of *trans*-double bonds [(XXVI),

(XXIX), and (XXXI)] implies that the olefins react in their *transoid* conformation.^{12c}

EXPERIMENTAL

G.l.c. of the sulphides was carried out with polyethylene glycol (Carbowax 1540), Apiezon L, and diethylene glycol succinate polyester (DEGS) columns for the analytical work and with a $\frac{3}{8}$ in \times 20 ft column of SE-30 Silicone on Chromosorb W for the preparative separations. The g.l.c. of the olefins was done with columns of *m*-bis(*m*-phenoxyphenoxy)benzene plus Apiezon L (MBMA). I.r. spectra^{4,13} were measured for films; the following bands were important for identification: ν_{max} 700ms—s, 1655—1660w, 3010—3030w (*cis*-CH=CH-), 895s, 1645ms, 3080m ($\text{>C}=\text{CH}_2$), 970—975s, 1655—1670vw, 3000vw,sh (*trans*-CH=CH-), 915—920s, 990—995m—s, 1640m—ms, 3070—3100w—m (—CH=CH₂), and 1160—1165s cm⁻¹ (Bu^tS⁻¹³). U.v. spectra³ were run in hexane: the *t*-butyl sulphides (XIII) and (XXI) and the mixture of (XXIV) and (XXV) had

¹⁰ E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, 1963, **28**, 1666.

¹¹ R. E. Benson and R. V. Lindsey, *J. Amer. Chem. Soc.*, 1959, **81**, 4253; J. A. Claisse and D. I. Davies, *J. Chem. Soc.*, 1965, 4894.

λ_{max} 212—213 nm (log ϵ 3.16—3.30), the *n*-butyl sulphides (XII) and (XX), the mixture of (XXII) and (XXIII), (XXVIII), the mixture of (XXIX) and (XXX), (XXXIII), and the mixture of (XXXI) and (XXXII) had λ_{max} 206—212 and 232—237sh nm (log ϵ 3.07—3.55 and 2.1—2.9). The u.v. spectra of compounds (XXVIII)—(XXXIII) exclude the possibility of conjugated double bonds. N.m.r. spectra were measured for solutions in carbon tetrachloride (60 MHz instruments), with tetramethylsilane as internal standard; typical values were as follows: τ 3.7—4.6, 4.7—5.3 (—CH=CH₂), 4.6 (—CH=CH—), 6.93 (—S—CH—C=), 6.93—7.00 (—S—CH₂—C=), 7.05—7.35 (=C—CH—C=, =C—CH₂—C=), 7.5—7.6 (—S—CH₂—), 7.9—8.0 (=C—CH₂—, =C—CH—), 8.3—8.4 (—C—CH₃), 8.1—8.9 (—CH₂—), 8.72 (—S—CMe₃), 8.95 (C—CH₃), and 9.06—9.11 (CH₃ of Buⁿ).

General Procedure.—The olefins were purified, where necessary, by washing with iron(II) sulphate, distillation, and drying over molecular sieve. A 2:1 molar ratio of

¹² (a) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, *J. Amer. Chem. Soc.*, 1962, **84**, 3897; (b) A. A. Oswald, K. Griesbaum, and B. E. Hudson, *J. Org. Chem.*, 1963, **28**, 1262; (c) W. A. Thaler, A. A. Oswald, and B. E. Hudson, *J. Amer. Chem. Soc.*, 1965, **87**, 311.

¹³ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 2nd edn., 1958; 'Advances in Infrared Group Frequencies,' Methuen, London, 1968.

olefin to thiol was used with the exception of octa-1,*trans*-3,*cis*-6-triene (XI) and one run with 3-methylhepta-1,*trans*-4,6-triene (X) where the ratio was 1 : 1. Benzoyl peroxide (0.05 mol % relative to thiol) was used as initiator. The reactions were done under nitrogen in a flask fitted with reflux condenser at a bath temperature of 90° for 3—5 h. The mixture was either distilled directly, or mixed with pentane, washed with 2N-sodium hydroxide, then saturated aqueous sodium chloride, and dried (Na₂SO₄) prior to distillation. The distillates were resolved and purified

by preparative g.l.c. Di-n-butyl disulphide,^{3e} higher boiling bis-adducts, and oligomers were observed in many cases.

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