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FREE RADICAL ADDITION REACTIONS—IV[1]

THE REACTION OF METHANESULPHONYL AND METHANEDISULPHONYL CHLORIDES WITH ALKENES

H. GOLDWHITE
Chemistry Department, California State College at Los Angeles,
Los Angeles, California, U.S.A.

and

M. S. GIBSON and C. HARRIS[2]
Chemistry Department, Faculty of Technology, University of Manchester, England

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Abstract—Methanesulphonyl chloride reacts with hept-1-ene under the influence of short wave radiation to give β-chloroheptyl methyl sulphone. Methanedisulphonyl chloride, for which an improved preparation is described, and hept-1-ene react in the presence of benzoyl peroxide to give γ-chlorooctanesulphonyl chloride and 1,3-dichlorooctane, together with lesser amounts of methanesulphonyl chloride and a high boiling sulphone.

The feeble nucleophilicity of alkanesulphonate anion is exemplified.

THE free radical addition reactions of mono-, di- and tri-chloromethanesulphonyl chlorides and of chlorocarbonylmethanesulphonyl chloride with olefines have been described in parts I,[3] II[4] and III of this series. These reactions lead to 1:1-adducts formed by specific addition of the substituted alkyl radical (from decomposition of the alkanesulphonyl radical) to the double bond, followed by chain transfer, according to the general equation:

$$RCH{=}CH_2 + R'SO_2Cl \rightarrow RCHCl{-}CH_2R' + SO_2$$
$$(R' = CCl_3,\ CHCl_2,\ CH_2Cl,\ CH_2COCl)$$

Yields are excellent for the three chlorinated methanesulphonyl chlorides;[5] with chlorocarbonylmethanesulphonyl chloride, yields are reduced, apparently by the formation of telomeric products. Our investigations have now been extended to include the free radical addition reactions of methanesulphonyl chloride and methanedisulphonyl (methionyl) chloride with olefines.

Under the conditions normally used for these reactions (*viz*, olefine in small excess; benzoyl peroxide as initiator), simple alkanesulphonyl chlorides do not react

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[1] Part III, H. Goldwhite, M. S. Gibson and C. Harris, *Tetrahedron* **20**, 1657 (1964).

[2] Present address: C. Harris, Chemical Research Laboratories, Division of Organic Chemistry, C.S.I.R.O., Melbourne, Victoria, Australia.

[3] H. Goldwhite, M. S. Gibson and C. Harris, *Tetrahedron* **20**, 1613 (1964).

[4] H. Goldwhite, M. S. Gibson and C. Harris, *Tetrahedron* **20**, 1649 (1964).

[5] Similar adducts, where $R' = CCl_3$ and $CHCl_2$, are now also readily available from free radical addition of CCl_4 and $CHCl_3$ to terminal olefines under redox transfer conditions; cf. M. Asscher and D. Vofsi, *J. Chem. Soc.* 1887, 3921 (1963).

appreciably with olefines.[3,6] In the present study, we have found that the addition of methanesulphonyl chloride to hept-1-ene is readily accomplished under the influence of short wave radiation to give β-chloroheptyl methyl sulphone in good yield (cf. Ref.[3] footnote[16]):

$$C_5H_{11}CH{=}CH_2 + CH_3SO_2Cl \rightarrow C_5H_{11}CHCl{-}CH_2SO_2CH_3$$

Asscher and Vofsi have recently reported similar additions of methanesulphonyl and of some arenesulphonyl chlorides under redox transfer conditions.[7] The formulation of the sulphone as $CH_3(CH_2)_4CHClCH_2SO_2CH_3$ is supported by its ^1H NMR spectrum and is consonant with the observations of Asscher and Vofsi.[7] The main features of the spectrum, recorded at 60 Mc/s in carbon tetrachloride solution, are: (i) a broad region of absorption covering the range $\tau \sim 9{\cdot}2$ to $8{\cdot}0$, due to the $CH_3(CH_2)_4$- portion of the molecule; (ii) a sharp singlet at $\tau = 7{\cdot}0$, due to the CH_3SO_2 group; (iii) a multiplet, of at least four peaks, centred at $\tau = 6{\cdot}62$, due to the α-CH_2- group adjacent to the SO_2 group; (iv) a multiplet, centred at $\tau = 5{\cdot}65$, due to the -CHCl- group, the chemical shift of which is in good agreement with that observed for other groups of this kind.[3]

The formation of a sulphone in this reaction provides further evidence of the relative stability of the methanesulphonyl radical,[3] previously indicated by bond dissociation energy data[8] and by the ability of sulphur dioxide to scavenge alkyl radicals in the liquid phase.[9] The behaviour of chloromethanesulphonyl chloride under redox transfer conditions is also pertinent.[7]

By contrast, the reaction of methanedisulphonyl chloride with terminal alkenes appeared to offer an attractive general route to γ-chloroalkanesulphonyl chlorides:

$$CH_2(SO_2Cl)_2 \xrightarrow{(PhCOO)_2} ClSO_2CH_2SO_2\cdot \qquad (1)$$

$$ClSO_2CH_2SO_2\cdot \rightleftharpoons ClSO_2CH_2\cdot + SO_2 \qquad (2)$$

$$ClSO_2CH_2\cdot + RCH{=}CH_2 \longrightarrow RCH\cdot{-}CH_2CH_2SO_2Cl \quad (I) \qquad (3)$$

$$(I) + CH_2(SO_2Cl)_2 \longrightarrow RCHClCH_2CH_2SO_2Cl + ClSO_2CH_2SO_2\cdot \qquad (4)$$

Methanedisulphonyl chloride has previously been prepared by reaction of hydrated methionic acid with phosphorus pentachloride; the conditions appear to be critical, and some variability of yield is reported.[10]

We prepared sodium methionate essentially by Lauer and Langkammerer's procedure,[11] *viz*,

$$CHI_3 \xrightarrow{Na_2SO_3aq} ICH_2SO_3Na \xrightarrow{Na_2SO_3aq} CH_2(SO_3Na)_2$$

and attempted to convert the salt directly to methanedisulphonyl chloride by reaction with phosphorus pentachloride and phosphorus oxychloride (cf. Ref.[3]); at the elevated

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[6] M. S. Kharasch and A. F. Zavist, *J. Amer. Chem. Soc.* **73**, 964 (1951).

[7] M. Asscher, *Chem. & Ind.* 32 (1964); M. Asscher and D. Vofsi, *J. Chem. Soc.* 4962 (1964).

[8] H. Mackle, *Tetrahedron* **19**, 1159 (1963).

[9] W. K. Busfield, K. J. Ivin, H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.* **57**, 1064 (1961).

[10] G. Schroeter, *Liebig's Ann.* **418**, 161 (1919); J. C. Bauer and G. L. Jenkins, *J. Amer. Pharm. Assoc.* **26**, 485 (1937); R. Shu, G. L. Jenkins and J. E. Christian, *J. Amer. Pharm. Assoc.* **40**, 86 (1951).

[11] W. M. Lauer and C. M. Langkammerer, *J. Amer. Chem. Soc.* **57**, 2360 (1935).

temperature required for reaction, chlorination and thermolysis occurred, and trichloromethanesulphonyl chloride was isolated in poor yield.[12] The sodium salt was therefore converted *via* the barium salt to hydrated methionic acid,[10] and alternative procedures for conversion to the disulphonyl chloride considered. At first, reaction with phosphorus oxychloride[13] seemed promising, but yields were capricious and the reaction was only suited to small scale work. On reaction of the hydrated acid with thionyl chloride-dimethylformamide,[14] anhydrous methionic acid separated as a solid phase, and formation of the acid chloride was not observed. Methionic acid proved quite tractable in the anhydrous condition, and could be converted to methanedisulphonyl chloride with reproducible yields of 70–80% by a modification of the Bauer-Jenkins procedure.[10]

Methanedisulphonyl chloride is immiscible with hept-1-ene, and a homogeneous reaction mixture was obtained by using benzene as solvent. Reaction occurred in the presence of benzoyl peroxide to yield the anticipated γ-chlorooctanesulphonyl chloride (37–50%) together with 1,3-dichlorooctane (ca. 26%), methanesulphonyl chloride (ca. 4%) and another high boiling compound. The formation of methanesulphonyl chloride and of 1,3-dichlorooctane are not unexpected, since the radical $ClSO_2CH_2\cdot$ may abstract hydrogen or chlorine, and since chloromethanesulphonyl chloride has been shown to react with hept-1-ene under these conditions;[3] however, the yield of 1,3-dichlorooctane is unusually high (cf. Ref.[3] for the corresponding yields of carbon tetrachloride in alkene-trichloromethanesulphonyl chloride reactions). It is possible that the intermediate $ClSO_2CH_2\cdot$ radical undergoes 1,2-halogen shift[15] to give the radical $ClCH_2SO_2\cdot$ or $ClCH_2\cdot$ and that 1,3-dichlorooctane is then formed by known processes.[3] A concerted fragmentation of radical (I) to sulphur dioxide and the $C_5H_{11}CHClCH_2CH_2\cdot$ radical, followed by chain transfer, appears less feasible under the conditions studied since there is evidence that radicals of this type rearrange to form the chloroalkanesulphonyl radical which then reacts with further alkene.[6] Rearrangement of (I) *via* a five-membered transition state and subsequent reaction with hept-1-ene should thus yield β-chloroheptyl γ-chlorooctyl sulphone, and the high boiling compound (see above), though not obtained in a pure condition, is provisionally regarded as this sulphone.

$$RCH\cdot{-}CH_2CH_2SO_2Cl \quad (I) \longrightarrow RCHClCH_2CH_2SO_2\cdot \quad (II)$$

$$RCH{=}CH_2 + (II) \longrightarrow RCH\cdot{-}CH_2SO_2CH_2CH_2CHClR$$

$$\big\downarrow CH_2(SO_2Cl)_2$$

$$RCHClCH_2SO_2CH_2CH_2CHClR + ClSO_2CH_2SO_2\cdot$$

$$(\text{where } R = C_5H_{11})$$

γ-Chlorooctanesulphonyl chloride was characterized by alkaline hydrolysis to γ-chlorooctanesulphonic acid and conversion to the S-benzylisothiuronium salt. It

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[12] Discordant opinions have been expressed about the reaction of potassium methionate with phosphorus pentachloride; cf C. M. Suter, *The Organic Chemistry of Sulphur* p. 157 *et seq.* J. Wiley, New York (1944).

[13] Cf. R. L. Hinman and L. Locatell, *J. Amer. Chem. Soc.* **81**, 5655 (1959).

[14] Cf. H. H. Bosshard, R. Mory, M. Schmid and H. Zollinger, *Helv. Chim. Acta* **42**, 1653 (1959).

[15] Cf. A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost and M. Ya. Khorlina, *Tetrahedron* **16**, 94 (1961); C. Walling, *Molecular Rearrangements* (Edited by P. de Mayo) Vol. I, p. 423 *et seq.* Interscience, New York (1963).

is interesting to note that no detectable displacement of the γ-chlorine atom takes place under conditions which allow the ready lactonization of γ-chlorononanoyl chloride.[1]

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin and Drs. F. and E. Pascher.

*The reaction of methanesulphonyl chloride with hept-*1*-ene*

Methanesulphonyl chloride (8·5 g, 0·074 mole, b.p. 52°/12 mm, n_D^{20} 1·4529) and hept-1-ene (6·5 g, 0·067 mole, n_D^{20} 1·4000) were placed in a 300 ml silica tube and degassed at 10^{-4} mm with cooling in liquid N_2. The tube was sealed and the contents irradiated for 15 hr, with shaking, by means of a Hanovia S 500 UV lamp at 3 inches distance (the reactants are initially immiscible but slowly form a homogeneous reaction mixture). After 15 hr the tube was opened. No SO_2 or HCl was evolved. Unreacted methanesulphonyl chloride was removed *in vacuo*. Distillation then gave a small forerun, b.p. 123–127°/0·4 mm, followed by *β-chloroheptyl methyl sulphone* (9·5 g), collected as fractions (i) b.p. 127–128°/0·4 mm and (ii) b.p. 128–130°/0·4 mm. At room temp, fraction (i) slowly crystallized as colourless irregular plates, m.p. 28–30° (Found: C, 45·3; H, 7·9; S, 15·5. $C_8H_{17}ClO_2S$ requires: C, 45·1; H, 8·0; S, 15·1%); fraction (ii) similarly crystallized as irregular plates, m.p. 24–26°. The IR spectrum of the sulphone (liquid film) showed strong bands[16] at 1282 and 1122 cm^{-1}.

Preparation of sodium methionate. Anhydrous Na_2SO_3 (231 g, 1·84 moles) was dissolved in water (1200 ml) and CHI_3 (236 g, 0·61 mole) was added, forming an upper solid layer. The mixture was then heated under reflux for 5 hr, by which time all the CHI_3 and intermediate CH_2I_2 has disappeared. The solution was evaporated to dryness *in vacuo*, and the residue extracted with hot 99% EtOH (500 ml), followed by hot 90% EtOH (2 × 500 ml). Crystallization at room temp gave sodium iodomethanesulphonate (71 g after drying at 100°).

Sodium iodomethanesulphonate (112 g), anhydrous Na_2SO_3 (170 g) and water (1200 ml) were refluxed for 130 hr. The solution was evaporated to dryness and the residue extracted with 50% aqueous EtOH (800 ml, then 500 ml). The extract crystallized at room temp giving sodium methionate (103 g after drying at 100–110°).

An attempt to prepare methanedisulphonyl chloride from the reaction of sodium methionate, PCl_5 and $POCl_3$ at 100–105° (5 hr) was unsuccessful, a small quantity of trichloromethanesulphonyl chloride (ca. 10%), m.p. and mixed m.p. 140–141° being recovered.

Preparation of anhydrous methionic acid. Sodium methionate (75 g) was dissolved in water (600 ml), and the solution heated to 60–70°. Conc HCl (4 ml) was added, followed, with stirring, by a solution of $BaCl_2$ (81 g) in water (200 ml). When cool, the crystalline deposit was collected, dried at 70–80° for 12 hr, and then at 100–105° for 2 hr giving barium methionate (101 g, dihydrate).

The barium salt (52 g, 0·15 mole) and a solution of 98% H_2SO_4 (15 g, 0·15 mole) in water (75 ml) were shaken intermittently for 15 hr. Barium sulphate was removed and the filtrate was evaporated on a steam bath for 3 hr, and finally in an oven at 150–160° for 2 hr. The residue was allowed to cool in a desiccator (P_2O_5), when crystallization occurred giving hydrated methionic acid (23 g). The free (hydrated) acid is very deliquescent and soon liquefies on exposure to the atmosphere.

A stirred mixture of hydrated methionic acid (20 g), freshly distilled $SOCl_2$ (60 ml) and dimethylformamide (5 drops) was gently refluxed for 1 hr, evolution of HCl beginning at 70° (bath temp). More $SOCl_2$ (20 ml) and dimethylformamide (5 drops) were added, and refluxing continued for 20 min. *Anhydrous* methionic acid gradually crystallized during the reaction and, after cooling, was collected and stored *in vacuo*. The acid (18 g) had m.p. 138–140° (Found: Equiv, 90·0. $CH_4O_6S_2$ requires: Equiv, 88·0), was hygroscopic (though less so than the hydrated acid) and readily soluble in water giving a strongly acid solution which contained no chloride ion.

Preparation of methanedisulphonyl chloride. PCl_5 (20 g) was added to anhydrous methionic acid (37 g, 0·21 mole) in a flask fitted with condenser and drying tube, and the mixture was shaken thoroughly. Evolution of HCl began immediately and the mixture gradually liquefied. After 1 hr, more PCl_5 (20 g) was added, followed by two further batches (each of 20 g) after 3 and 4 hr respectively, the temp being kept below 50°. After a further 4 hr, a final batch of PCl_5 (7 g) was added. After 15 hr at room temp, the almost colourless reaction mixture was filtered from a small amount

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[16] Cf. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (2nd Edition) Chap. 22. Methuen, London (1958).

of solid, and $POCl_3$ (61 g) then removed *in vacuo*. Distillation of the residual oil gave a small forerun, b.p. 83°/0·5 mm, followed by methanedisulphonyl chloride (34 g, 76%), collected as fractions (i) b.p. 83–86°/0·6 mm and (ii) b.p. 86–87°/0·6 mm (lit[10] 135–138°/15 mm).

Methanedisulphonyl chloride was characterized by conversion to the dianilide, which crystallized from EtOH as square tablets, m.p. 192–193° (lit[10] 192–193°).

A sample of methanedisulphonyl chloride (12 g, b.p. 128°/8 mm) was also prepared from the hydrated acid (21 g) and $POCl_3$ (40 ml) by heating gently till evolution of HCl slackened, and then raising the temp to 120–125° to complete the reaction (total time, 6 hr). This process is sensitive to small changes in reaction conditions and is often invalidated by the separation of an unidentified white solid.

Reaction of methanedisulphonyl chloride with hept-1-ene

The sulphonyl chloride and hept-1-ene are only partially miscible, even at 90°. Reaction was investigated under two sets of conditions.

(a) Methanedisulphonyl chloride (11 g, 0·052 mole, b.p. 83–86°/0·6 mm) and hept-1-ene (10 g, 0·102 mole, n_D^{20} 1·4000) were heated to reflux under N_2 (91°), and dry precipitated benzoyl peroxide[17] (0·1 g) was added. After 15 min, evolution of SO_2 was noticed. More benzoyl peroxide (0·1 g) was then added, followed by similar portions after 90 and 165 min respectively, during which time the temp was raised to 100–110°. After a further 45 min at 105–110°, the reaction was terminated, and hept-1-ene then removed *in vacuo*. Distillation then gave methanesulphonyl chloride (3·8 g, 66% based on sulphonyl chloride), b.p. 55–60°/15 mm, identified by comparison of the IR spectrum with that of an authentic sample. A black resin remained.

(b) Methanedisulphonyl chloride (20 g, 0·094 mole, b.p. 83–86°/0·6 mm), hept-1-ene (19 g, 0·194 mole, n_D^{20} 1·4000) and dry benzene (20 ml) were brought to reflux under N_2 (80°), and benzoyl peroxide (0·3 g) was then added. An exothermic reaction commenced with brisk evolution of SO_2. Two further portions of benzoyl peroxide (0·3 g) were added after 1 and 2·5 hr, and the reaction was concluded after 4 hr, the internal temp having risen to 95°. Benzene and hept-1-ene were then removed *in vacuo*; redistillation of this volatile mixture subsequently provided a small quantity (0·4 g, 3·7% based on sulphonyl chloride) of methanesulphonyl chloride. Distillation of the residual oil then gave (i) a few drops, b.p. 90–97°/12 mm, followed by 1,3-dichloro-octane (4·5 g, 26%), collected as fractions (ii) b.p. 97–99°/12 mm and (iii) b.p. 48–50°/0·4 mm, n_D^{20} 1·4535 (lit[8] b.p. 100°/14 mm, n_D^{20} 1·4554; the IR spectra of both fractions and of authentic 1,3-dichlorooctane were identical). Further distillation gave (iv) a few drops, b.p. 50–100°/0·4 mm, containing sublimed benzoic acid (m.p. and mixed m.p. 121°), (v) an oil (γ-chloro-octanesulphonyl chloride, 11·5 g, 50%), b.p. 103–109°/0·4 mm, (vi) several drops, b.p. 109–180°/0·4 mm, and (vii) an oil (3·5 g), b.p. 180°/0·4 mm; fraction (vii) showed ν_{max} (liquid film) 1295 and 1130 cm^{-1} (sulphone[18]), but was not further examined.

Fraction (v) was dissolved in ether, and traces of benzoic acid were removed by washing with $NaHCO_3$ aq. The ether solution was dried (Na_2SO_4), evaporated and distilled giving *γ-chloro-octanesulphonyl chloride* (8·5 g, 37%), b.p. 113°/0·6 mm, n_D^{20} 1·4765; the IR spectrum (liquid film) showed ν_{max} 1370 and 1170 cm^{-1} (sulphonyl chloride[18]).

S-*Benzylisothiuronium γ-chlorooctanesulphonate*. γ-Chloro-octanesulphonyl chloride (0·9 g, b.p. 113°/0·6 mm) was shaken with 2 N NaOH aq (7 ml) for 1 hr, the mixture remaining alkaline. One drop of phenolphthalein indicator was added and the colour just discharged by addition of 2 N HCl aq. The solution was filtered (to remove a trace of oily material) into a stirred solution of S-benzylisothiuronium chloride (2 g) in water (11 ml), and the precipitated solid (1·26 g, 88%) collected. S-*Benzylisothiuronium γ-chlorooctanesulphonate* crystallized from acetonitrile as colourless elongated plates, m.p. 99–100·5°. (Found: C, 48·6; H, 6·8; Cl, 9·1; N, 6·8; S, 16·1. $C_{16}H_{27}ClN_2O_3S_2$ requires: C, 48·7; H, 6·9; Cl, 9·0; N, 7·1; S, 16·2%.)

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[17] K. Nozaki and P. D. Bartlett, *J. Amer. Chem. Soc.* **68**, 1686 (1946).