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FREE RADICAL ADDITION REACTIONS—III[1]

A ROUTE TO γ-CHLORO- AND γ-HYDROXY-CARBOXYLIC ACID DERIVATIVES

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Abstract—Chlorocarbonylmethanesulphonyl chloride reacts with hept-1-ene in the presence of benzoyl peroxide to give γ-chlorononanoyl chloride in 30–40% yield. The homogeneity and structure of this product follow from conversion to (a) a single amide, and (b) the known γ-nonanolactone and derived hydrazide respectively.

A MIXTURE of methanesulphonyl chloride with a slight excess of hept-1-ene shows little tendency to react in the presence of benzoyl peroxide at reflux temperature. When, however, one or more of the hydrogen atoms in the sulphonyl chloride is replaced by chlorine, the chlorinated methanesulphonyl radicals, produced in an initiated reaction, decompose to sulphur dioxide and chlorinated methyl radicals, and the latter add to hept-1-ene. The addition has been shown to be specific and leads to the more stable secondary alkyl radical. Chain transfer then occurs giving a single 1:1-adduct,[3] e.g. 1,3-dichlorooctane from chloromethanesulphonyl chloride:

$$\text{(i)} \quad XCH_2SO_2Cl \xrightarrow{(PhCOO)_2} XCH_2SO_2\cdot$$

$$\text{(ii)} \quad XCH_2SO_2\cdot \rightleftharpoons XCH_2\cdot + SO_2$$

$$\text{(iii)} \quad XCH_2\cdot + R{-}CH{=}CH_2 \rightarrow R{-}CH\cdot{-}CH_2CH_2X$$

$$\text{(iv)} \quad R{-}CH\cdot{-}CH_2CH_2X + XCH_2SO_2Cl \rightarrow R{-}CHCl{-}CH_2CH_2X + XCH_2SO_2\cdot$$

where $X = Cl$.

In the reaction with terminal olefines, the substitution of a hydrogen atom in methanesulphonyl chloride by suitable electron-attracting functional groups capable of subsequent transformations should lead to synthetically useful 1:1-adducts. Such a group would be the chlorocarbonyl group; the resulting 1:1-adducts would provide

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[1] Part II, preceding paper.

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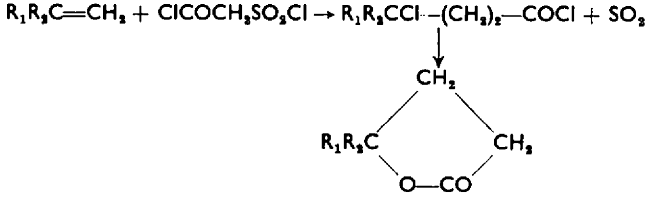
[3] Part I, this series; H. Goldwhite, M. S. Gibson and C. Harris, *Tetrahedron* **20**, 1613 (1964).

a convenient source of derivatives of γ-chloro- and γ-hydroxycarboxylic acids, including γ-lactones.



$$R_1R_2C{=}CH_2 + ClCOCH_2SO_2Cl \rightarrow R_1R_2CCl{-}(CH_2)_2{-}COCl + SO_2$$

This possibility has been realised in the initiated reaction of chlorocarbonylmethanesulphonyl chloride with hept-1-ene in the temperature range 70–100°, which gives a 1:1-adduct together with a higher boiling product; at temperatures above 100°, the yield of the latter increases at the expense of the 1:1-adduct.

The 1:1-adduct was shown to be homogeneous by conversion to a single amide in 87% yield; it was identified as γ-chlorononanoyl chloride by hydrolysis and lactonization to the perfumery intermediate γ-nonanolactone (γ-nonalactone), further characterized by hydrazinolysis to γ-hydroxynonanohydrazide.

The reactions leading to γ-chlorononanoyl chloride conform to the pattern (i)–(iv) above, with X = ClCO and the radical addition in step (iii) again specific.

As freshly distilled, the high boiling product apparently contains a carboxylic chloride (ν_{max} 1790 cm^{-1}), which is possibly telomeric, and a carboxylic acid (ν_{max} 1710 cm^{-1}); identification was not attempted as the product deposited a dark resin on standing.

EXPERIMENTAL

Microanalyses were carried out by Mr. V. Manohin.

IR Spectra were measured for liquid films.

*The reaction of chlorocarbonylmethanesulphonyl chloride with hept-*1*-ene.* Chlorocarbonylmethanesulphonyl chloride[4] (36 g 0·2 mole, b.p. 61°/1·1 mm, n_D^{20} 1·4930) and hept-1-ene (30 g, 0·3 mole, n_D^{20} 1·4010) were placed in a flask fitted with reflux condenser, and the apparatus was flushed with N_2. The reactants were partly miscible at room temp, but on heating to 65° formed a homogeneous solution. At 70°, dry precipitated benzoyl peroxide[5] (0·4 g) was added, and the mixture heated to 93° over 1 hr and to 100° over a further 2 hr 40 min, during which time SO_2 was smoothly evolved. At the end of this period, excess hept-1-ene was removed *in vacuo* (12 mm). Distillation of the residual oil then gave (i) a small fore-run, b.p. < 90°/0·1 mm, (ii) *γ-chlorononanoyl chloride* (13·5 g), b.p. 90°/0·1 mm, (iii) several drops, b.p. 90–130°/0·1 mm, and (iv) an oil (9 g), b.p. 130–132°/0·1 mm, leaving a dark viscous residue.

γ-Chlorononanoyl chloride is relatively stable, and shows ν_{max} 2900(s), 2825, 1790(s), 1451, 1431, 1393, 1370, 1282, 1250, 1175, 1081, 1041, 985, 959, 906, 848, 730 and 697 cm^{-1}.

γ-Chlorononanoamide. γ-Chlorononanoyl chloride (0·9 g) was added dropwise to aqueous ammonia (10 ml, *d* 0·88) at 0°. The precipitate was collected, washed and dried giving *γ-chlorononanoamide* (0·71 g, 87%), m.p. 76°; crystallization from benzene–light petroleum (b.p. 60–80°) gave plates, m.p. 77° (Found: C, 56·5; H, 9·3; N, 7·4. $C_9H_{18}ClNO$ requires: C, 56·4; H, 9·4; N, 7·3%).

γ-Nonanolactone. 2N NaOH aq (44 ml) was added with shaking to a mixture of γ-chlorononanoyl chloride (9 g) and water (30 ml). A homogeneous solution slowly formed as the acid chloride was hydrolysed. After 24 hr, the solution was neutralized (litmus) with 18% HCl aq, and then extracted with ether (50 ml). The ether solution was washed with water, dried ($MgSO_4$) and evaporated.

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

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

[6] Y. Terai and T. Tanaka, *Bull. Chem. Soc., Japan* **29**, 822 (1956).

Distillation gave (i) a small fore-run, b.p. 147–148°/13 mm, followed by γ-nonanolactone (3·7 g), collected as fractions (ii) b.p. 148–149°/13 mm and (iii) b.p. 149–153°/13 mm (lit[6] b.p. 126–127°/8 mm).

The IR spectra of fractions (ii) and (iii) were identical with that of an authentic sample of γ-nonanolactone, and showed[7] ν_{max} 1776 cm^{-1}.

γ-Hydroxynonanohydrazide. A mixture of γ-nonanolactone (1 g, fraction (ii) above) and 64% w/w hydrazine hydrate (10 ml) was warmed gently with shaking. A homogeneous solution formed, but soon became pasty. After 1 hr, water (10 ml) was added, the solid collected and dried, giving γ-hydroxynonanohydrazide (0·9 g), m.p. 85–87°; the compound crystallized from ethyl acetate-light petroleum (b.p. 40–60°) as needles, m.p. and mixed m.p. 87° (lit[6] m.p. 84°). Found: C, 57·2; H, 10·7; N, 14·9. Calc. for $C_9H_{20}N_2O_2$: C, 57·4; H, 10·6; N, 14·9%).

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[7] Cf. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules* (2nd Edition) Chap. 11. Methuen, London (1958).