The Synthesis of Potential Insecticides. Part I. 2,2-Dichlorovinyl Carbamates and Carbonates

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In contrast to the zinc-dust reduction of 1-alkylthio-2,2,2-trichloroethyl carbamates, which gives mainly 2,2-dichlorovinyl alkyl sulphides by an elimination–fragmentation reaction, zinc-dust reduction of 1-alkylsulphonyl-2,2,2-trichloroethyl carbamates affords good yields of the novel 2,2-dichlorovinyl carbamates. A similar reaction sequence has been applied to the preparation of 2,2-dichlorovinyl carbonates. 1-Alkylsulphonyl-2,2,2-trichloroethyl dimethylcarbamates also gave the corresponding 1-alkylsulphonyl-2,2-dichlorovinyl dimethylcarbamates by their reaction with triethylamine. The 2,2-dichlorovinyl carbamates did not inhibit crude enzyme preparations of acetylcholinesterase.

ALTHOUGH 2,2-dichlorovinyl phosphates [1] [*e.g.* (I), 'Dichlorovos'] are well known to possess insecticidal activity by inhibiting acetylcholinesterase, the corresponding 2,2-dichlorovinyl carbamates (II) have not, as far as we are aware, been described previously. We now report a general method for the preparation of mono- and di- *N*-substituted 2,2-dichlorovinyl carbamates (II), and also for the corresponding carbonates (III).

$(MeO)_2P(O)\cdot CH{=}CCl_2$ (I)

$R^1R^2N\cdot CO\cdot O\cdot CH{=}CCl_2$ (II)

$RO\cdot CO\cdot O\cdot CH{=}CCl_2$ (III)

$R^1R^2N\cdot CO\cdot O\cdot CH(SR^3)\cdot CCl_3$ (IV)

$R^1O\cdot CO\cdot O\cdot CH(SR^3)\cdot CCl_3$ (V)

$R^3S\cdot CH{=}CCl_2$ (VI)

$R^1R^2N\cdot CO\cdot O\cdot CH(SO_2R^3)\cdot CCl_3$ (VII)

$RO\cdot CO\cdot O\cdot CH(SO_2R^3)\cdot CCl_3$ (VIII)

$Me_2N\cdot CO\cdot OC(SO_2R^3){=}CCl_2$ (IX)

Although 2,2-dichlorovinyl acetate is readily obtained [2] by the treatment of the diacetate of chloral hydrate with zinc dust in acetic acid, attempts to prepare the bis-*N*-methylcarbamate of chloral hydrate in order to use a similar route to 2,2-dichlorovinyl methylcarbamate, were unsuccessful. Thus, the addition of methyl isocyanate to chloral hydrate caused the evolution of large quantities of carbon dioxide, and this route was not investigated further. On the other hand, the monothioacetals formed from the reaction of chloral with alkanethiols, but not isolated, were found to be converted into their mono-substituted carbamic esters (IV; $R^1 = H$) by their reaction with an alkyl or aryl isocyanate, or to their dimethylcarbamic esters (IV; $R^1 = R^2 = Me$), by their reaction with dimethylcarbamoyl chloride in the presence of pyridine. A similar reaction, but one employing chloroformic esters, gave the corresponding carbonates (V). Reduction with zinc dust and acetic acid both of the carbamic esters (IV) and the carbonates (V), caused an exothermic reaction with the loss of carbon dioxide and the formation of the alkyl 2,2-dichlorovinyl sulphides (VI) in good yields.

In the zinc-dust reduction of the carbonate (V; $R^1 = Ph$), phenol was also identified as being formed together with 2,2-dichlorovinyl ethyl sulphide, and these elimination–fragmentation reactions therefore parallel recent findings [3] where the zinc-dust reduction of 2,2,2-trichloroethyl carbonates to 1,1-dichloroethylene, the alcohol, and carbon dioxide provides a method of protecting hydroxy-groups. With the carbamic esters, very small quantities of the required 2,2-dichlorovinyl carbamates (II) accompanied the formation of the sulphides (VI), and were detected by the i.r. examination of the crude products from these reactions. Despite attempts to vary the conditions of the reaction, this method did not appear to offer a useful route to 2,2-dichlorovinyl carbamates.

However, in contrast to these discoveries, it was found that the 1-alkylsulphonyl-2,2,2-trichloroethyl carbamates (VII), formed in good yields from the corresponding sulphides by peroxide oxidation, underwent a different reaction upon reduction with zinc dust in acetic acid when cleavage of the CS bond occurred to give the required 2,2-dichlorovinyl carbamates (II), as stable,

[1] W. Perkow, K. Ullerich, and F. R. Meyer, *Naturwiss.*, 1952, **39**, 353.

[2] G. W. Deodhar, *J. Indian Chem. Soc.*, 1934, **11**, 83.

[3] T. W. Windholz and D. B. R. Johnston, *Tetrahedron Letters*, 1967, **27**, 2555.

crystalline solids or distillable oils, in good yields. Similarly, the reduction of the sulphone carbonates (VIII) afforded the 2,2-dichlorovinyl carbonates (III).

In another series of experiments, it was found that the dimethylcarbamates (VII; $R^1 = R^2 = Me$) smoothly eliminated hydrogen chloride in the presence of an excess of triethylamine in ether at room temperature to give another novel series of 1-alkyl-sulphonyl-2,2-dichlorovinyl dimethylcarbamic esters (IX), as stable, crystalline solids. However, the corresponding methylcarbamic esters (VII; $R^1 = Me$, $R^2 = H$) as well as the carbonates (VIII), did not afford identifiable products with triethylamine, and it is concluded that the products of these reactions were unstable under the basic conditions used for the elimination reaction.

In vitro determinations using crude acetylcholinesterase preparations obtained from house-fly heads, showed that the 2,2-dichlorovinyl carbamates, in contrast to the corresponding phosphate esters, were poor inhibitors of the enzyme. It is possible that the carbonyl group of these carbamic esters is insufficiently electrophilic to permit the rapid transfer of the carbamoyl group to the active site of the enzyme.

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 80—120° unless otherwise stated. Zinc dust was purified just prior to use by washing with dilute hydrochloric acid, water, and acetone. N.m.r. spectra were determined for deuteriochloroform solutions using tetramethylsilane as an internal reference.

The following experiment illustrates the general method used to obtain the 1-alkylthio-2,2,2-trichloroethyl monosubstituted carbamates.

1-*Isopropylthio*-2,2,2-*trichloroethyl Methylcarbamate* (IV; $R^1 = Me$, $R^2 = H$, $R^3 = Pr^i$).—To a solution of chloral (40 g., 0·27 mole) in anhydrous benzene (400 ml.) containing triethylamine (1 ml.) was added propane-2-thiol (20·6 g., 0·27 mole). The solution was allowed to cool to room temperature (*ca.* 30 min.), and then methyl isocyanate (20 g., 0·35 mole) was added all at once, followed by triethylamine (2 ml.). The solution was kept at room temperature for 3 hr. and the solvent then removed under reduced pressure. The residue crystallised from light petroleum as needles (61 g., 81%), m.p. 95·5—96·5° (Found: C, 30·2; H, 4·4; Cl, 38·3; N, 5·05; S, 11·5. $C_7H_{12}Cl_3NO_2S$ requires C, 29·95; H, 4·3; Cl, 37·9; N, 5·0; S, 11·4%), $\nu_{max.}$ (Nujol) 3205s, 1740s, 1720s, 1560m, and 1270s cm.$^{-1}$. The n.m.r. spectrum contained bands at τ 3·62 (s, 1H), 4·75br, (s, 1H), 6·55 (m, 1H), 7·1 (d, J 6 c./sec., 3H), 8·58 (d, J 8 c./sec., 3H) and 8·63 (d, J 8 c./sec., 3H). The two methyl groups of the isopropyl group are non-equivalent because of their proximity to the asymmetric carbon atom.

1-*Ethylthio*-2,2,2-*trichloroethyl Methylcarbamate* (IV; $R^1 = Me$, $R^2 = H$, $R^3 = Et$).—The compound crystallised (76%) from light petroleum and had m.p. 79—80° (Found: C, 27·3; H, 4·1; Cl, 39·7; N, 5·4; S, 12·3. $C_6H_{10}Cl_3NO_2S$ requires C, 27·05; H, 3·8; Cl, 40·0; N, 5·25; S, 12·0%).

1-*Ethylthio*-2,2,2-*trichloroethyl Ethylcarbamate* (IV; $R^1 = Et$, $R^2 = H$, $R^3 = Et$).—The compound crystallised (83%) from light petroleum, and had m.p. 68—69° (Found: C, 30·0; H, 4·55; Cl, 38·1; N, 4·85; S, 11·0. $C_7H_{12}Cl_3NO_2S$ requires C, 29·95; H, 4·3; Cl, 37·9; N, 5·0; S, 11·4%).

1-*Isopropylthio*-2,2,2-*trichloroethyl Phenylcarbamate* (IV; $R^1 = Ph$, $R^2 = H$, $R^3 = Pr^i$).—The compound crystallised (84%) from light petroleum and had m.p. 83—84° (Found: C, 41·9; H, 4·25; Cl, 30·5; N, 4·0; S, 9·0. $C_{12}H_{14}Cl_3NO_2S$ requires C, 42·05; H, 4·1; Cl, 31·05; N, 4·1; S, 9·35%).

1-*Ethylthio*-2,2,2-*trichloroethyl* 3-*Chlorophenylcarbamate* (IV; $R^1 = 3\text{-}ClC_6H_4$, $R^2 = H$, $R^3 = Et$).—This compound failed to crystallise, but the i.r. spectrum, containing peaks at 3300m, 1760s, 1605s, and 1535s cm.$^{-1}$, indicated its presence. The sulphone formed from this compound by oxidation (see below) was fully characterised.

1-*Isopropylthio*-2,2,2-*trichloroethyl Dimethylcarbamate* (IV; $R^1 = R^2 = Me$, $R^3 = Pr^i$).—To a solution of chloral (20 g., 0·135 mole) in anhydrous benzene (100 ml.) containing triethylamine (1 ml.) was added propane-2-thiol (10·25 g.; 0·135 mol.). The solution was allowed to cool and then the benzene was removed under reduced pressure. The residue was dissolved in anhydrous pyridine (20 ml.), dimethylcarbamoyl chloride (14·5 g.; 0·135 mol.) was added, and the mixture was heated on a steam-bath for 3 hr. The dark solution was allowed to cool, and was then poured into water (400 ml.) and extracted with chloroform (3 × 75 ml.). The combined chloroform extracts were washed with water (2 × 100 ml.), dried ($MgSO_4$), and evaporated under reduced pressure; the residual oil was distilled. The *product* (21 g., 53%) had b.p. 110—112°/0·5 mm. n_D^{27} 1·5010 (Found: C, 32·6; H, 4·45; Cl, 36·0; N, 4·45; S, 10·8. $C_8H_{14}Cl_3NO_2S$ requires C, 32·6; H, 4·8; Cl, 36·1; N, 4·75; S, 10·9%), $\nu_{max.}$ 1730s, 1390s, 1160s, 1050m, 870m, and 751m cm.$^{-1}$.

1-*Ethylthio*-2,2,2-*trichloroethyl Dimethylcarbamate* (IV; $R^1 = R^2 = Me$, $R^3 = Et$).—This was obtained (59%) as above by use of ethanethiol; the *product* had b.p. 98—100°/0·15 mm., n_D^{25} 1·5072 (Found: C, 29·6; H, 4·15; Cl, 38·4; N, 4·6; S, 11·7. $C_7H_{12}Cl_3NO_2S$ requires C, 29·95; H, 4·3; Cl, 37·9; N, 5·0; S, 11·4%).

1-*n-Butylthio*-2,2,2-*trichloroethyl Dimethylcarbamate* (IV; $R^1 = R^2 = Me$, $R^3 = Bu^n$).—This was obtained (60%) as above by use of n-butanethiol; the *product* had b.p. 108—110°/0·15 mm., n_D^{24} 1·5001 (Found: C, 35·3; H, 5·25; Cl, 34·9; N, 4·4; S, 10·7. $C_9H_{16}Cl_3NO_2S$ requires C, 35·0; H, 5·2; Cl, 34·45; N, 4·55; S, 10·4%).

1-*Ethylthio*-2,2,2-*trichloroethyl Methylcarbonate* (V; $R^1 = Me$, $R^3 = Et$).—To a solution of anhydrous chloral (7·4 g., 0·05 mole) in chloroform (25 ml.) was added ethanethiol (3·1 g., 0·05 mole). The solution was allowed to cool to room temperature (*ca.* 30 min.) and then anhydrous pyridine (8·4 g., 0·05 mol.) was added. The solution was then stirred for 30 min.; methyl chloroformate (4·7 g., 0·05 mole) was added dropwise during *ca.* 10 min. with continued stirring at room temperature, and the mixture was heated under reflux for 1 hr. After the mixture had cooled to room temperature, it was washed with water (2 × 50 ml.) and the aqueous layer was extracted with chloroform (25 ml.); the combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was distilled to give a mobile liquid (11·0 g., 86%), b.p. 86—88°/0·05 mm. (Found: C, 27·2; H, 3·1; Cl, 39·6; S, 11·8. $C_6H_9Cl_3O_3S$ requires C, 26·9; H, 3·3; Cl, 40·1; S, 11·9%), $\nu_{max.}$ 1770s, 1450m, 1270s, 1320m, 825m, 780m, 750m, and 710m cm.$^{-1}$.

1-*Ethylthio*-2,2,2-*trichloroethyl Ethylcarbonate* (V; $R^1 = R^3 = Et$).—This was obtained (79%) as above, by using

ethyl chloroformate; the product had b.p. 92—94°/0·06 mm. (Found: C, 29·5; H, 3·6; Cl, 37·4; S, 11·0. $C_7H_{11}Cl_3O_3S$ requires C, 29·8; H, 3·9; Cl, 37·7; S, 11·3%).

1-*Ethylthio*-2,2,2-*trichloroethyl Phenylcarbonate* (V; R^1 = Ph, R^3 = Et).—This was obtained (80%) as above by using phenyl chloroformate; the product had b.p. 66—68°/0·01 mm., n_D^{20} 1·5394 (Found: C, 39·8; H, 3·1; Cl, 32·0. $C_{11}H_{11}Cl_3O_3S$ requires C, 40·05; H, 3·35; Cl, 32·3%).

1-*Ethylthio*-2,2,2-*trichloroethyl Benzylcarbonate* (V; R^1 = $PhCH_2$, R^3 = Et).—This was obtained (67%) as above, by using benzyl chloroformate; the product had b.p. 114—116°/0·01 mm. (Found: C, 42·2; H, 4·0; Cl, 31·2; S, 9·6. $C_{12}H_{13}Cl_3O_3S$ requires C, 41·9; H, 3·8; Cl, 30·95; S, 9·3%).

1-*Isopropylsulphonyl*-2,2,2-*trichloroethyl Dimethylcarbamate* (VIII, R^1 = R^2 = Me, R^3 = Pr^i).—A mixture of 1-isopropylthio-2,2,2-trichloroethyl dimethylcarbamate (8·8 g.; 0·03 mole) and hydrogen peroxide (100 vol.; 7·4 ml., 0·066 mole) in glacial acetic acid (25 ml.) was heated on a steam-bath for 1 hr. The solution was then cooled and poured into water (250 ml.) and the product was separated and washed with water; it crystallised from ethanol–light petroleum as needles (7·1 g., 72%), m.p. 91—92° (Found: C, 29·2; H, 4·4; Cl, 32·9; N, 4·15; S, 9·8. $C_8H_{14}Cl_3NO_4S$ requires C, 29·4; H, 4·3; Cl, 32·55; N, 4·3; S, 9·8%), $\nu_{max.}$ (Nujol), 1735s, 1370s, 1170m, and 1148s $cm.^{-1}$.

1-*Isopropylsulphonyl*-2,2,2-*trichloroethyl Methylcarbamate* (VII; R^1 = Me, R^2 = H, R^3 = Pr^i).—This was formed by the oxidation of 1-isopropylthio-2,2,2-trichloroethyl methylcarbamate as above; the product (62%) formed needles from aqueous ethanol and had m.p. 112—113° (Found: C, 26·6; H, 3·8; Cl, 34·4; N, 4·25; S, 10·7. $C_7H_{12}Cl_3NO_4S$ requires C, 26·9; H, 3·95; Cl, 34·0; N, 4·5; S, 10·25%), $\nu_{max.}$ (Nujol), 3370m, 1745s, 1530w, 1310m, 1140m, and 1115m $cm.^{-1}$.

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl Dimethylcarbamate* (VII; R^1 = R^2 = Me, R^3 = Et).—This compound, prepared in an analogous manner to the above examples, failed to crystallise, and its attempted distillation caused extensive decomposition. Its conversion into 2,2-dichlorovinyl-1-ethylsulphonyl dimethylcarbamate in the presence of triethylamine (see below) demonstrates its presence.

1-*n-Butylsulphonyl*-2,2,2-*trichloroethyl Dimethylcarbamate* (VII; R^1 = R^2 = Me, R^3 = Bu^n).—This was prepared in an analogous manner to the above; the *product* (83%) formed prisms, m.p. 62—63° [from light petroleum (b.p. 60—80°)] (Found: C, 32·2; H, 5·05; Cl, 31·0; N, 3·9; S, 9·8. $C_9H_{16}Cl_3NO_4S$ requires C, 31·7; H, 4·75; Cl, 31·2; N, 4·1; S, 9·4%).

1-*Isopropylsulphonyl*-2,2,2-*trichloroethyl Phenylcarbamate* (VII; R^1 = Ph, R^2 = H, R^3 = Pr^i).—This was prepared in an analogous manner to the above; the *product* (80%) formed small needles, m.p. 167—168° [from benzene–light petroleum (b.p. 60—80°)] (Found: C, 38·8; H, 3·95; Cl, 28·4; N, 3·95; S, 7·9. $C_{12}H_{14}Cl_3NO_4S$ requires C, 38·45; H, 3·75; Cl, 28·4; N, 3·75; S, 8·55%).

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl* 3-*Chlorophenylcarbamate* (VII; R^1 = 3-ClC_6H_4, R^2 = H, R^3 = Et).—This was prepared by oxidation of the crude 1-ethylthio-2,2,2-trichloroethyl 3-chlorophenylcarbamate (above); the product (53%) formed prismatic needles, m.p. 181—182° (decomp.) (from acetone–light petroleum) (Found: C, 33·6; H, 2·75; N, 3·45. $C_{11}H_{11}Cl_4NO_4S$ requires C, 33·45; H, 2·8; N, 3·55%).

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl Methyl Carbonate* (VIII; R = Me, R^3 = Et).—A mixture of 1-ethylthio-2,2,2-trichloroethyl methyl carbonate (20·0 g., 0·075 mole) and hydrogen peroxide (100 vol.; 18 ml., 0·158 mole) in glacial acetic acid (25 ml.) was heated on a steam-bath for 1 hr.; the solution was cooled and poured into water (150 ml.). The product was extracted with chloroform (3 × 24 ml.) and the organic layer was washed with saturated aqueous sodium hydrogen carbonate (2 × 100 ml.), dried ($MgSO_4$), and the solvent removed at reduced pressure to yield a viscous oil (18·5 g., 82%) (Found: C, 23·4; H, 3·19; Cl, 35·5. $C_6H_9Cl_3O_5S$ requires C, 24·0; H, 3·0; Cl, 35·5%), $\nu_{max.}$ 1780s, 1340s, 1160s, and 1125s $cm.^{-1}$. An attempt to distil the product under high vacuum caused considerable darkening of the distillant and the product was not further purified.

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl Ethyl Carbonate* (VIII; R = R^3 = Et).—This was formed by the oxidation of 1-ethylthio-2,2,2-trichloroethyl ethyl carbonate as above; the product (65%) was a viscous oil (Found: C, 27·9; H, 3·56; Cl, 34·6; S, 9·4. $C_7H_{11}Cl_3O_5S$ requires C, 26·8; H, 3·5; Cl, 33·9; S, 10·2%).

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl Phenyl Carbonate* (VIII; R = Ph, R^3 = Et).—This was formed by the oxidation of 1-ethylthio-2,2,2-trichloroethyl phenyl carbonate; the oily product (73%) was used for the zinc-dust reduction (see below).

1-*Ethylsulphonyl*-2,2,2-*trichloroethyl Benzyl Carbonate* (VIII; R = $PhCH_2$, R^3 = Et).—This was formed by the oxidation of 1-ethylthio-2,2,2-trichloroethyl benzyl carbonate; the oily product (48%) was used without purification.

1-n-*Butylsulphonyl*-2,2-*dichlorovinyl Dimethylcarbamate* (IX; R^3 = Bu^n).—To a solution of 1-n-butylsulphonyl-2,2,2-trichloroethyl dimethylcarbamate (23·5 g.) in anhydrous ether (200 ml.) was added triethylamine (20 ml.), which produced an almost immediate precipitation of triethylamine hydrochloride. The solution was set aside at room temperature for 1 hr., after which time water (100 ml.) was added and the ethereal layer was separated, dried ($MgSO_4$), and evaporated to leave an oil which solidified upon trituration with light petroleum. Crystallisation from light petroleum at 0° gave the *product* as plates (19·7 g., 93%), m.p. 44—44·5° (Found: C, 35·6; H, 5·15; Cl, 23·1; N, 4·6; S, 10·5. $C_9H_{15}Cl_2NO_4S$ requires C, 35·55; H, 4·95; Cl, 23·3; N, 4·6; S, 10·5%), $\nu_{max.}$ (Nujol), 1752s, 1605w, 1338s, 1180s, and 1125s $cm.^{-1}$.

2,2-*Dichloro*-1-*isopropylsulphonylvinyl Dimethylcarbamate* (IX; R^3 = Pr^i).—This was prepared in an analogous manner to the above; the *product* (84%) had b.p. 122—124°/0·01 mm. and m.p. 45—47° (Found: C, 32·7; H, 4·75; Cl, 24·8; N, 4·55; S, 11·05. $C_8H_{13}Cl_2NO_4S$ requires C, 33·1; H, 4·5; Cl, 24·45; N, 4·85; S, 11·05%).

2,2-*Dichloro*-1-*ethylsulphonylvinyl Dimethylcarbamate* (IX; R^3 = Et).—This was prepared in an analogous manner to the above by using the crude 1-ethylsulphonyl-2,2,2-trichloroethyl dimethylcarbamate; the product (85%) crystallised from light petroleum as needles, m.p. 61·5—62·5° (Found: C, 30·2; H, 4·0; Cl, 25·3; N, 4·85; S, 11·1. $C_7H_{11}Cl_2NO_4S$ requires C, 30·45; H, 4·0; Cl, 25·65; N, 5·05; S, 11·6%).

Zinc-dust Reductions

2,2-*Dichlorovinyl Isopropyl Sulphide* (VI; R^3 = Pr^i).—1-Isopropylthio-2,2,2-trichloroethyl methylcarbamate (15 g.) was added to a suspension of zinc dust (15 g.) in glacial acetic acid (70 ml.) which was stirred and cooled so that the temperature did not exceed 40°. After the addition was

complete, the solution was stirred for a further 1 hr.; the excess of zinc dust was filtered off and the filtrate was diluted with water (600 ml.). The oily products were extracted into ether and the extract was washed with water and dried ($MgSO_4$). Removal of the ether at 0°, and distillation of the residue afforded the *product* as a mobile liquid (6·1 g., 65%), b.p. 75—77°/25 mm. (Found: C, 35·5; H, 4·4; Cl, 41·9; S, 18·6. $C_5H_8Cl_2S$ requires C, 35·1; H, 4·7; Cl, 41·45; S, 18·75%), $\nu_{max.}$ 3010w, 1564w, 904s, and 820s cm.$^{-1}$. The n.m.r. spectrum showed the following resonances: τ 3·5 (s, 1H), 6·72 (m, 1H), and 8·65 (d, J 8 c./sec., 6H).

I.r. examination of the residue following the distillation, showed this to contain impure 2,2-dichlorovinyl methylcarbamate (see below).

2,2-*Dichlorovinyl Ethyl Sulphide* (VI; R^3 = Et).—Zinc dust (10 g.) was added to a stirred and cooled solution of 1-ethylthio-2,2,2-trichloroethyl phenyl carbonate (25 g.) in glacial acetic acid (50 ml.). After the initial vigorous reaction was over, the mixture was heated on a steam-bath for 30 min., cooled to room temperature, and then poured into water (200 ml.). The oil was extracted into methylene chloride (2 × 50 ml.) and the combined organic layers were extracted with 10% aqueous sodium hydroxide (3 × 50 ml.). The sodium hydroxide washings were acidified (HCl) and extracted with methylene chloride to give phenol (5·2 g.), the 4-nitrobenzoate derivative of which had m.p. 126°.

The combined methylene chloride extracts, following the removal of the phenol, were dried ($MgSO_4$) and the solvent was removed at 0°. Distillation of the residual oil afforded the *product* (6·4 g., 53%) as an oil, b.p. 70—71°/14 mm., n_D^{22} 1·5298 (Found: C, 30·8; H, 3·55; Cl 45·4; S, 20·2. $C_4H_6Cl_2S$ requires C, 30·55; H, 3·8; Cl, 45·25, S, 20·4%).

2,2-*Dichlorovinyl Methylcarbamate* (II; R^1 = Me, R^2 = H).—1-Isopropylsulphonyl-2,2,2-trichloroethyl methylcarbamate (12·5 g.) was added to a suspension of zinc dust (12·5 g.) in glacial acetic acid (50 ml.) which was stirred and cooled at such a rate that the temperature did not exceed 40°. After the addition was complete, stirring was continued for a further 90 min., the excess of zinc dust was filtered off, and the filtrate was diluted with water (300 ml.). The solution was extracted with ether (2 × 100 ml.) and the combined ether extracts were added with stirring to a saturated solution of sodium hydrogen carbonate in water (150 ml.). When effervescence ceased, the ether layer was separated, dried ($MgSO_4$), and evaporated. Trituration of the resultant oil with n-pentane caused the *product* (5·9 g., 87%) to solidify. Crystallisation from n-pentane gave waxy prisms, m.p. 48—49° (Found: C, 28·6; H, 2·95; Cl, 42·0; N, 8·05. $C_4H_5Cl_2NO_2$ requires C, 28·25; H, 2·95; Cl, 41·7; N, 8·25%), $\nu_{max.}$ ($CHCl_3$), 3340m, 3075w, 1745s, 1650w, 1530s, 1240s, and 1175s cm.$^{-1}$. The n.m.r. spectrum showed resonances at 2·38 (s, 1H), 4·5br (s, 1H), and 7·1 (d, J 6 c./sec., 3H).

2,2-*Dichlorovinyl Dimethylcarbamate* (II; R^1 = R^2 = Me).—This was obtained by the zinc reduction of 1-isopropylsulphonyl-2,2,2-trichloroethyl dimethylcarbamate in a similar manner to the above; the *product* (79%) had b.p. 93—95°/12 mm., n_D^{25} 1·4813 (Found: C, 32·9; H, 4·05; Cl, 38·7; N, 7·6. $C_5H_7Cl_2NO_2$ requires C, 32·65; H, 3·85; Cl, 38·55; N, 7·45%), $\nu_{max.}$ 3090w, 1750s, 1650w, and 1180s cm.$^{-1}$. The n.m.r. spectrum showed resonances at τ 2·48 (s, 1H) and 7·05 (d, 6H).

2,2-*Dichlorovinyl Phenylcarbamate* (II, R^1 = Ph, R^2 = H).—This was obtained by the zinc reduction of 1-isopropylsulphonyl-2,2,2-trichloroethyl phenylcarbamate; the product (75%) crystallised from light petroleum, and had m.p. 74—75° (Found: C, 46·7; H, 2·95; Cl, 30·6; N, 6·1. $C_9H_7Cl_2NO_2$ requires C, 46·6; H, 3·05; Cl, 30·55; N, 6·05%).

2,2-*Dichlorovinyl 3-Chlorophenylcarbamate* (II, R^1 = 3-ClC_6H_4, R^2 = H).—This was obtained by the zinc reduction of 1-ethylsulphonyl-2,2,2-trichloroethyl 3-chlorophenylcarbamate; the product (82%) crystallised from light petroleum, and had m.p. 92—93° (Found: C, 40·8; H, 2·1; N, 5·0. $C_9H_6Cl_3NO_2$ requires C, 40·55; H, 2·25; N, 5·25%).

2,2-*Dichlorovinyl Methyl Carbonate* (III; R = Me).—This was obtained by the zinc-dust reduction of 1-ethylsulphonyl-2,2,2-trichloroethyl methyl carbonate in an analogous manner to the dichlorovinyl carbamic ester; the *product* (60%) had b.p. 62—64°/10 mm. (Found: C, 28·5; H, 2·35; Cl, 42·2. $C_4H_4Cl_2O_3$ requires C, 28·1; H, 2·35; Cl, 41·5%), $\nu_{max.}$ 3100m, 1780s, 1260s, 972s, and 778s cm.$^{-1}$. The n.m.r. spectrum showed two singlets at τ 2·6 (1H) and 6·1 (3H).

2,2-*Dichlorovinyl Ethyl Carbonate* (III; R = Et).—This was obtained as above by the zinc reduction of 1-ethylsulphonyl-2,2,2-trichloroethyl ethyl carbonate; the *product* (65%) had b.p. 82—84°/33 mm. (Found: C, 32·9; H, 3·25; Cl, 38·9. $C_5H_6Cl_2O_3$ requires C, 32·5; H, 3·3; Cl, 38·3%).

2,2-*Dichlorovinyl Phenyl Carbonate* (III; R = Ph).—This was obtained by the zinc reduction of 1-ethylsulphonyl-2,2,2-trichloroethyl phenyl carbonate; the product (58%) had b.p. 65—66°/0·1 mm. (Found: C, 46·6; H, 2·3; Cl, 30·7. $C_9H_6Cl_2O_3$ requires C, 46·35; H, 2·05; Cl, 30·4%).

2,2-*Dichlorovinyl Benzyl Carbonate* (III; R = $PhCH_2$).—This was obtained by the zinc reduction of 1-ethylsulphonyl-2,2,2-trichloroethyl benzyl carbonate; the product (50%) had b.p. 102—104°/0·1 mm. (Found: C, 48·3; H, 3·0; Cl, 28·5. $C_{10}H_8Cl_2O_3$ requires C, 48·6; H, 3·25; Cl, 28·7%).

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