LXXV.—n-*Butyl Chloroformate and its Derivatives.*

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n-*Butyl chloroformate*, $Cl\cdot CO_2\cdot C_4H_9$, is best prepared by passing carbonyl chloride into cooled *n*-butyl alcohol until the calculated increase in weight is reached, and fractionally distilling the product.

It is difficult to separate the chloroformate from the unchanged *n*-butyl alcohol, and the yield is not large, as in the repeated fractional distillations necessary a considerable amount reacts with the alcohol to form di-*n*-butyl carbonate. If the first fractionations are slow, a distillate is frequently obtained which contains only this and *n*-butyl chloride.

n-Butyl chloroformate is a colourless, mobile liquid of a sharp, but pleasant, odour; the vapour attacks the eyes. It boils at 137·8°/734·5 mm., and has D_4^{25} 1·074 and $n_D^{8\cdot4}$ 1·417.

It is only slowly hydrolysed when heated with water, in which it appears to be insoluble:

0·2587 gave 0·2725 AgCl. Cl = 26·05.

$C_5H_9O_2Cl$ requires Cl = 25·97 per cent.

Di-*n*-butyl carbonate, $(C_4H_9)_2CO_3$, was originally prepared by Lieben and Rossi (*Annalen*, 1873, **165**, 112) by heating *n*-butyl iodide with silver carbonate. The quantity obtained was very small, as much Δ^{α}-butylene and di-*n*-butyl ether are produced in the reaction.

It is always formed in small amount during the fractionation in the preparation of *n*-butyl chloroformate, and is easily obtained in quantity by passing carbonyl chloride into hot *n*-butyl alcohol or by boiling *n*-butyl chloroformate with about twice the equivalent amount of *n*-butyl alcohol, and fractionating to separate any unchanged alcohol and the *n*-butyl chloride formed. Di-*n*-butyl carbonate is a colourless, mobile liquid of a somewhat pleasant smell, which boils at 207°/745 mm.

When *n*-butyl chloroformate is heated with any alcohol, it gives the corresponding alkyl *n*-butyl carbonate. The isolation of these alkyl *n*-butyl carbonates in a pure state by fractional distillation is generally tedious, as both the dialkyl carbonate and di-*n*-butyl carbonate are formed as well as the mixed ester, otherwise their preparation offers no difficulty. To avoid so far as possible the actions by which these by-products are formed, it is best to add the equivalent amount of the alcohol to boiling *n*-butyl chloroformate.

Methyl n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot OMe$, is a colourless, mobile liquid having a sweet smell, somewhat recalling that of amyl acetate; it boils at 150·5°/745 mm.:

0·2154 gave 0·4301 CO_2 and 0·1769 H_2O. C=54·46; H=9·19.
$C_6H_{12}O_3$ requires C=54·50; H=9·15 per cent.

Ethyl n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot OEt$, is a colourless, mobile, sweet-smelling liquid, which boils at 168·5°/748 mm.:

0·1757 gave 0·3693 CO_2 and 0·1507 H_2O. C=57·32; H=9·60.
$C_7H_{14}O_3$ requires C=57·49; H=9·65 per cent.

n-*Propyl* n-*butyl carbonate*, $C_4H_9\cdot O\cdot CO\cdot O\cdot C_3H_7$, is a colourless, mobile liquid having a pleasant smell, and boils at 187·5°/755 mm.:

0·1688 gave 0·3703 CO_2 and 0·1517 H_2O. C=59·83; H=10·05.
$C_8H_{16}O_3$ requires C=59·95; H=10·07 per cent.

n-Butyl chloroformate reacts very readily and energetically with ammonia and with amines to form *n*-butyl carbamates. In the case of ammonia, it is sufficient to shake vigorously the chloroformate with concentrated aqueous ammonia. With the amines it is best to add an ethereal solution of the base mixed with an equivalent amount of pyridine to an ethereal solution of the equivalent quantity of *n*-butyl chloroformate. The *n*-butyl carbamates are, as a rule, colourless, well-crystallised compounds readily soluble in alcohol or other ordinary organic solvents.

n-*Butyl carbamate*, $C_4H_9\cdot O\cdot CO\cdot NH_2$, is very readily soluble in alcohol, and crystallises in long, colourless, flattened prisms, which melt at 54°:

0·1814 gave 0·3402 CO_2 and 0·1527 H_2O. C=51·14; H=9·42.
$C_5H_{11}O_2N$ requires C=51·24; H=9·47 per cent.

n-*Butyl phenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NHPh$, crystallises in long, colourless, flattened prisms which melt at 65·5°:

0·2543 gave 0·6381 CO_2 and 0·1740 H_2O. C=68·43; H=7·65.
$C_{11}H_{15}O_2N$ requires C=68·35; H=7·83 per cent.

n-*Butyl* o-*chlorophenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Cl$, is an oily liquid boiling at 235—240°/60 mm., which does not solidify on keeping or when cooled in a freezing mixture:

0·3513 gave 0·2160 AgCl. Cl=15·21.
$C_{11}H_{14}O_2NCl$ requires Cl=15·58 per cent.

n-*Butyl*-p-*chlorophenylcarbamate* crystallises in colourless, flattened, apparently rhombic, prisms, which melt at 72°:

0·2346 gave 0·1492 AgCl. Cl=15·73.
$C_{11}H_{14}O_2NCl$ requires Cl=15·58 per cent.

n-*Butyl* 2:4-*dichlorophenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_3Cl_2$, crystallises in colourless, very slender prisms, which melt at 48°:

0·2070 gave 0·2261 AgCl. Cl=27·02.
$C_{11}H_{13}O_2NCl_2$ requires Cl=27·06 per cent.

n-*Butyl* 2:4:6-*trichlorophenylcarbamate*,
$C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_2Cl_3$,
crystallises in slender, colourless prisms, which melt at 60°:

0·2236 gave 0·3252 AgCl. Cl=35·98.
$C_{11}H_{12}O_2NCl_3$ requires Cl=35·88 per cent.

n-*Butyl* m-*bromophenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Br$, crystallises in colourless, transparent, four-sided rhombic plates melting at 37·5°:

0·2425 gave 0·1669 AgBr. Br=29·29.
$C_{11}H_{14}O_2NBr$ requires Br=29·38 per cent.

n-*Butyl* p-*bromophenylcarbamate* crystallises in compact, colourless, rhombic prisms, which melt at 67°:

0·2424 gave 0·1670 AgBr. Br=29·32.
$C_{11}H_{14}O_2NBr$ requires Br=29·38 per cent.

n-*Butyl* 2:4-*dibromophenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_3Br_2$, crystallises in very slender, silky, hair-like prisms, which melt at 61·5°:

0·2130 gave 0·2278 AgBr. Br=45·51.
$C_{11}H_{13}O_2NBr_2$ requires Br=45·54 per cent.

n-*Butyl* 2-*chloro*-4-*bromophenylcarbamate*,
$C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_3BrCl$,
crystallises in very slender, hair-like prisms, which melt at 52°:

0·1913 gave 0·2061 AgCl+AgBr. Calc.: 0·2066 AgCl+AgBr.

n-*Butyl* p-*iodophenylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4I$, crystallises in long, colourless prisms, which melt at 72°:

0·3048 gave 0·2232 AgI. I = 39·58.
$C_{11}H_{14}O_2NI$ requires I = 39·78 per cent.

n-*Butyl* o-*tolylcarbamate*, $C_4H_9 \cdot O \cdot CO \cdot NH \cdot C_6H_4Me$, crystallises in colourless, slender prisms, which melt at 45·5°:

0·2173 gave 0·5534 CO_2 and 0·1596 H_2O. C = 69·45; H = 8·22.
$C_{12}H_{17}O_2N$ requires C = 69·51; H = 8·27 per cent.

n-*Butyl* p-*tolylcarbamate* crystallises in stout, colourless prisms, which melt at 63°:

0·2345 gave 0·5983 CO_2 and 0·1722 H_2O. C = 69·58; H = 8·21.
$C_{12}H_{17}O_2N_2$ requires C = 69·51; H = 8·27 per cent.

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