406. *Properties and Reactions of Free Alkyl Radicals in Solution. Part II.* Reactions with Iodine, Bromine, and Sulphuryl Chloride.*

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The study (see Part I *) of free radicals generated by the thermal decomposition of aliphatic azo-compounds in solution has been extended. The radicals resemble triphenylmethyl in combining immediately with iodine and bromine. They attack sulphuryl chloride and thereby initiate radical-chain chlorinations just as do the radicals formed by thermal decomposition of benzoyl peroxide.

IN previous work (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 312, 1490; *J.*, 1950, 1764) it has been shown that aliphatic azo-compounds (I; R, R′ = Alkyl) decompose smoothly in solution at 80—120° to give free radicals (II) which exhibit only moderate chemical reactivity. These tertiary aliphatic radicals do not attack solvents such as benzene, toluene, or carbon tetrachloride, but react with each other by combination or disproportionation unless an active radical acceptor is present in the solution.

In our search for characteristic reactants for these free radicals we have now studied their

$$\begin{array}{ccc} \mathrm{RR'C(X){\cdot}N{:}N{\cdot}C(X)RR'} & \mathrm{RR'C(X){\bullet}} & \mathrm{RR'C(X){\cdot}Hal} \\ \text{(I.)} & \text{(II.)} & \text{(III.)} \end{array}$$

$$(\mathrm{X = CN\ or\ CO_2Me.})$$

actions upon iodine, bromine, and sulphuryl chloride, and have found that, like triphenylmethyl, the radicals (II) are in all cases effective halogen acceptors in non-ionising solvents.

Solutions of iodine in hot benzene or toluene are rapidly decolorised when added to decomposing solutions of the azo-compounds (I) in the same solvent, and iodo-compounds (III; Hal = I) result. Yields of about 75% of the latter can easily be obtained by adopting the reverse procedure of adding the azo-compounds (I) to hot solutions of iodine, so as to minimise the chance of mutual interaction of the radicals (II). Their normal radical dimerisation and disproportionation products constitute, however, the remainders of the reaction products. In this way we have prepared methyl α-iodo*iso*butyrate, α-iodo*iso*butyronitrile, (±)-α-iodo-α-

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* Part I, *J.*, 1950, 1764.

methylbutyronitrile and α-ethyl-α-iodobutyronitrile, which do not appear to have been described previously. They are all liquids which can be distilled under reduced pressure, but tend to decompose with separation of free iodine when heated at atmospheric pressure, or exposed to light. Their molecular refractions are consistently high by about one unit in comparison with values calculated from standard figures of atomic refractivities, perhaps owing to the juxtaposition of the iodine atom and the cyanide or ester groups.

Representative azo-compounds (I) react in a similar way with bromine and give the corresponding bromo-compounds III; Hal = Br), but since a little bromine substitution also occurs the yields of direct combination products are somewhat smaller (25—40%). For instance, in the reaction of dimethyl αα'-azo*iso*butyrate (I; R = R' = Me; X = CO_2Me) with bromine in boiling carbon tetrachloride solution an appreciable evolution of hydrogen bromide was noticed and the resulting methyl α-bromo*iso*butyrate was accompanied by methyl αβ-dibromo*iso*butyrate, a pure sample of which was prepared for comparison from bromine and methyl methacrylate. The molecular refractions of these α-bromo-compounds were also slightly higher than computed values. The liquid bromo- and iodo-nitriles were all characterised by acid hydrolysis to the corresponding amides which crystallised excellently from light petroleum.

The direct reaction of dimethyl αα'-azo*iso*butyrate with sulphuryl chloride in boiling carbon tetrachloride led to extensive chlorination of the ester, for both hydrogen chloride and sulphur dioxide were evolved in quantity. The main reaction product appeared to be methyl αβ-dichloro*iso*butyrate, though this could not be isolated in a pure state. When the reaction was carried out in boiling benzene then some *addition* of chlorine to benzene occurred, for the reaction product, on concentration, yielded the characteristically smelling mixture of isomeric hexachloro*cyclo*hexanes. Evidently the free radicals (II) react with sulphuryl chloride to produce chlorine atoms (equations 1, 2, below) which then may add on to the benzene nucleus, as in the photochemical addition process, and may also chlorinate the esters by hydrogen abstraction from the methyl groups.

When toluene is used as the solvent, its chlorination in the side chain occurs to a so much greater extent, by the chain reaction (1—4) which Kharasch and Brown (*J. Amer. Chem. Soc.*, 1939, **61**, 2142) first effected by using benzoyl peroxide as the radical-producing catalyst, that catalytic amounts of azo-compound suffice.

$$RR'\dot{C}(X) + SO_2Cl_2 \longrightarrow RR'C(X){\cdot}Cl + {\cdot}SO_2Cl \quad . \; . \; . \; . \; . \; . \quad (1)$$

$${\cdot}SO_2Cl \longrightarrow SO_2 + {\cdot}Cl \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$Cl{\cdot} + CH_3{\cdot}C_6H_5 \longrightarrow HCl + {\cdot}CH_2{\cdot}C_6H_5 \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

$$C_6H_5{\cdot}CH_2{\cdot} + SO_2Cl_2 \longrightarrow C_6H_5{\cdot}CH_2Cl + {\cdot}SO_2Cl \quad . \; . \; . \; . \; . \; . \quad (4)$$

By using only 0·3—0·5 mole % of αα'-azo*iso*butyronitrile and dimethyl αα'-azo*iso*butyrate as catalysts we have been able to effect the chlorinations of toluene to benzyl chloride, triphenylmethane to triphenylmethyl chloride, and *cyclo*hexane to *cyclo*hexyl chloride in yields of 50—80%. Propionic acid has been chlorinated too, but in contrast to Kharasch and Brown (*J. Amer. Chem. Soc.*, 1940, **62**, 927) we succeeded in isolating, in very low yield, only the α-chloropropionic acid.

The aliphatic azo-compounds (I) may have some advantages over benzoyl peroxide as catalysts for this chlorination process since they produce nitrogen themselves and thus there appears to be less necessity to remove traces of oxygen from the reacting systems. Similar advantages have been noted in their applications as polymerisation catalysts (U.S.P. 2,471,959/1949). As would be expected, iodine is a very effective inhibitor of this chlorination process. Chloranil is a decidedly less effective inhibitor though it combines readily with the free radicals (II) (Bickel and Waters, *J.*, *loc. cit.*; Ziegler, Deparade, and Meye, *Annalen*, 1950, **567**, 141).

EXPERIMENTAL.

*Reaction of Dimethyl αα'-Azo*iso*butyrate with Iodine.*—To a gently refluxing solution of iodine (6·33 g., 0·05 g.-atom) in dry benzene (AnalaR; 25 ml.) was added during 45 minutes one of dimethyl αα'-azo*iso*butyrate (16·1 g., 0·07 mole) in the same solvent (25 ml.). After a further 45 minutes' refluxing the colour of the solution had changed to light yellow. The solvent, together with traces of methyl *iso*butyrate, was distilled through a column under reduced pressure and the residual liquid was fractionated. Two fractions were collected: (i) b. p. 63—70°/12 mm. and (ii) 96—126°/10 mm. The first fraction was *methyl α-iodo*iso*butyrate* (8·45 g., 74% calc. on iodine), a pale yellow, pleasant-smelling liquid which rapidly darkened on exposure to light. For analysis it was kept over mercury for several days and then was distilled through a short column; it had b. p. 61°/10 mm., d_4^{20} 1·666, $n_D^{15.5}$ 1·5069 (Found: I, 55·2%; $[R]_D$ 40·7. $C_5H_9O_2I$ requires I, 55·7%; $[R]_D$ 39·7).

Treatment of this ester with a large excess of cold aqueous ammonia (*d* 0·88) during 15 hours gave *a-iodo*iso*butyramide*; this substance is dimorphous, crystallising from alcohol in small needles which on storage in contact with the mother-liquor were slowly transformed into glistening platelets, m. p. 183—184° (decomp.) with progressive darkening above 160° (Found: I, 59·8. C_4H_8ONI requires I, 59·6%).

Fraction (ii) (4·05 g., 44% calc. on the excess azo-ester) was shown to be dimethyl tetramethylsuccinate by hydrolysis to tetramethylsuccinic acid (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 317) of m. p. and mixed m. p. 191—192°. The residue amounted to 6·25 g.

*Reaction of aa′-Azo*iso*butyronitrile with Iodine.*—To a gently refluxing solution of iodine (19·0 g., 0·15 g.-atom) in dry toluene (100 ml.) was added during 20 minutes one of aa′-azo*iso*butyronitrile (22 g., 0·134 mole) in the same solvent (150 ml.). A few seconds after the addition was complete the purple colour of the solution had changed to a light brown. Refluxing was continued for a further 30 minutes after which the solvent, together with traces of *iso*butyronitrile, was removed by distillation through a column (b. p. *ca.* 52°/65 mm.). The residual liquid was treated with light petroleum (50 ml.; b. p. 40—60°) and left overnight at 0°. The tetramethylsuccinonitrile which had precipitated was then collected (m. p. after recrystallisation from alcohol, 170°, mixed m. p. 169·5°), and the filtrate was distilled. Removal of the light petroleum gave a purple oil (22·8 g.) from which *a-iodo*iso*butyronitrile* (b. p. 62·5°/16 mm., d_4^{19} 1·717, n_D^{23} 1·5125) was obtained as a pale yellow liquid with a penetrating odour. It rapidly darkened if exposed to the light. Further small quantities resulted from refractionation of the toluene fraction, the total yield being 21·6 g. (74% calc. on iodine) (Found: C, 25·2; H, 3·30; I, 64·7%; $[R]_D$ 34·1. C_4H_6NI requires C, 24·6; H, 3·10; I, 65·1%; $[R]_D$ 33·2). A further small quantity of tetramethylsuccinonitrile (total yield, 5·9 g., 73% calc. on the excess of azonitrile taken) and traces of iodine were obtained by steam-distillation of the residue which remained after distillation of the iodo-nitrile. The steam-involatile residue constituted a dark oily mass (0·7 g.) which when triturated with alcohol slowly gave crystals of 2 : 3 : 5-tricyano-2 : 3 : 5-trimethylhexane, m. p. 83—85°, undepressed in admixture with an authentic specimen (Bickel and Waters, *Rec. Trav. chim.*, 1950, **69**, 1493).

By gentle warming of the iodo-nitrile with twice its volume of 90% sulphuric acid over a free flame (cf. Stevens, *J. Amer. Chem. Soc.*, 1948, **70**, 165; Stevens and Coffield, *ibid.*, 1951, **73**, 103) until decomposition was just about to set in and pouring of the resulting oil on ice, a-iodo*iso*butyramide was obtained (m. p. and mixed m. p. after recrystallisation from alcohol, 183—184°). The same compound (m. p. 184—185°, undepressed in admixture with an authentic specimen), and not the expected amidoxime (cf. Steinkopf and Bohrmann, *Ber.*, 1907, **40**, 1633), resulted, in small yield, when the iodo-nitrile was treated with cold alcoholic hydroxylamine (Found: C, 23·0; H, 4·0; I, 59·4. Calc. for C_4H_8ONI: C, 22·6; H, 3·8; I, 59·6%).

a-Iodo-a-methylbutyronitrile.—This was prepared from aa′-azo-(a-methylbutyronitrile) (Dox, *J. Amer. Chem. Soc.*, 1925, **47**, 1471) by a similar process. In this case the corresponding succinonitrile was appreciably soluble in light petroleum (b. p. 40—60°) and repeated fractionation of the filtrate from the light petroleum precipitation was necessary. Eventually (±)-*a-iodo-a-methylbutyronitrile* was obtained in 81% yield (calc. on iodine) as a pale yellow oil (b. p. 63·5°/6 mm.); for analysis this was set aside over mercury for several days before refractionation (d_4^{19} 1·619, n_D^{19} 1·5142) (Found: I, 60·2%; $[R]_D$ 38·9. C_5H_8NI requires I, 60·7%; $[R]_D$ 37·9). The total yield of *s*-diethyldimethylsuccinonitrile (m. p. 97—102°) was 73% calc. on the excess of azo-nitrile (Found: C, 73·4; H, 9·8; N, 16·8. Calc. for $C_{10}H_{16}N_2$: C, 73·1; H, 9·8; N, 17·1%). Overburger, O'Shaughnessy, and Shalit (*J. Amer. Chem. Soc.*, 1949, **71**, 2661) record m. p. 96—98°. It may be noted that this product may be a mixture of *meso-* and racemic forms.

The iodo-nitrile was characterised by conversion, as above, into (±)-*a-iodo-a-methylbutyramide* which crystallised from light petroleum (b. p. 40—60°) in feathery prisms, m. p. 63—65° (slight decomp.) (Found: C, 26·9; H, 4·4; I, 55·9. $C_5H_{10}ONI$ requires C, 26·5; H, 4·4; I, 56·0%).

a-Ethyl-a-iodobutyronitrile.—This was prepared from aa′-azo-(a-ethylbutyronitrile) (Dox, *loc. cit.*); the by-product, tetraethylsuccinonitrile (m. p. and mixed m. p. 47° with an authentic specimen prepared by the decomposition of the azo-nitrile alone in toluene), was completely soluble in light petroleum. The *a-ethyl-a-iodobutyronitrile*, b. p. 81°/6 mm., was obtained in 90% yield (calc. on iodine) by repeated fractionation of the reaction product in the form of an amber oil, d_4^{20} 1·547, $n_D^{15·5}$ 1·5161 (Found: I, 56·3%; $[R]_D$ 43·5. $C_6H_{10}NI$ requires I, 56·9%; $[R]_D$ 42·6). If kept over mercury, slight decomposition occurred (Found: I, 55·0%). The compound was characterised by conversion into *a-ethyl-a-iodobutyramide* which crystallised from light petroleum in shining needles or massive prisms, m. p. 76—78·5°. These became yellow in a few hours if exposed to the light (Found: C, 30·3; H, 5·0; I, 52·9. $C_6H_{12}ONI$ requires C, 29·9; H, 5·0; I, 52·6%).

*Reaction of aa′-Azo*iso*butyronitrile with Bromine.*—The azo-compound (19·7 g., 0·12 mole) was added in small portions to a vigorously refluxing solution of bromine (9·6 ml., 0·18 mole) in dry carbon tetrachloride (35 ml.) during 45 minutes, and the mixture was then refluxed for a further 75 minutes. Hydrogen bromide was evolved extremely slowly. The solvent and excess of bromine were removed through a column, and light petroleum (40 ml.) was added to the residue. The mixture was left overnight at 0° and filtered. The filtrate gave crude a-bromo*iso*butyronitrile (b. p. 30—40°/10 mm.) which was fractionated first at atmospheric pressure (b. p. 137—139°; 9·15 g., 26% calc. on the azo-nitrile taken) and finally, after removal of traces of hydrogen bromide (dry K_2CO_3), at reduced pressure (b. p. 29°/10 mm., n_D^{16} 1·4474) (Found: Br, 53·9. Calc. for C_4H_6NBr: Br, 54·0%). Stevens (*loc. cit.*) records b. p. 137—139°, n_D^{25} 1·4460. a-Bromo*iso*butyramide, prepared by his method and recrystallised from chloroform, had m. p. 146—147°. The mixed m. p. with an authentic specimen (m. p. 147—148°) prepared from a-bromo*iso*butyryl bromide was 147—148°. No attempt was made to isolate higher brominated substances from the crude mixture (5·7 g.) of tetramethylsuccinonitrile and unchanged azo-nitrile which constituted the remainder of the reaction product.

Reaction of αα′-*Azo-*(α-*methylbutyronitrile*) *with Bromine.*—This azo-nitrile did not decompose at the temperature of boiling carbon tetrachloride, and the reaction was carried out in the absence of a solvent. Bromine (3·2 ml., 0·06 mole) was added to the just molten azo-nitrile (11·5 g., 0·06 mole), and the mixture was cautiously heated with a free flame. The violent reaction which rapidly set in was moderated by cooling of the mixture under the tap and after a few seconds the bromine had all disappeared. Very little hydrogen bromide was evolved. Carbon tetrachloride (7·5 ml.) was then added and the mixture was gently refluxed for 20 minutes to complete the decomposition of the azo-nitrile. The solvent was distilled and the residual red oil treated with light petroleum (15 ml.) and set aside overnight at 0°. The solution was then decanted from the resulting mixture of tar and *s*-diethyldimethylsuccinonitrile, shaken with N-sodium carbonate, then with water, and dried. Fractionation gave (±)-α-bromo-α-methylbutyronitrile (6·8 g., 35% calc. on the azo-nitrile) which was collected at 40°/8—9 mm. The residue deposited more of the succinonitrile (m. p. and mixed m. p. after crystallisation from alcohol, 97—102°). Refractionation of the liquid gave the bromo-nitrile as a colourless oil, b. p. 41°/8 mm., n_D^{17} 1·4555 (Found: N, 8·6. Calc. for C_5H_8NBr: N, 8·65%). Stevens (*loc. cit.*) records b. p. 66—67°/27 mm., n_D^{25} 1·4512. (±)-α-Bromo-α-methylbutyramide, prepared from the above nitrile, had m. p. 48—50° (Stevens records m. p. 46·5—48°) (Found: C, 33·2; H, 5·7; N, 7·8; Br, 44·7. Calc. for $C_5H_{10}ONBr$: C, 33·3; H, 5·6; N, 7·8; Br, 44·4%).

Reaction of Dimethyl αα′-*Azo*iso*butyrate with Bromine.*—A solution of the azo-ester (12·5 g., 0·054 mole) in dry carbon tetrachloride (50 ml.) was added dropwise during 20 minutes to a boiling solution of bromine (3·2 ml., 0·06 mole) in the same solvent (15 ml.). When the addition was complete, the evolution of hydrogen bromide (which had been considerable) began to slacken; the mixture was then refluxed for a further 75 minutes, by which time the bromine had all reacted. The solvent was removed through a column, and the residual dark oil was fractionated to give pale yellow *methyl* α-*bromo*iso*butyrate*, b. p. 36·5—38°/7—8 mm. (5·7 g., 29% calc. on the azo-ester). Refractionation gave a colourless product having b. p. 38°/9 mm., n_D^{16} 1·4531 (Found: C, 33·1; H, 5·05; Br, 44·4. $C_5H_9O_2Br$ requires C, 33·2; H, 5·0; Br, 44·2%). Wheeler and Barnes (*Amer. Chem. J.*, 1900, **24**, 79) record b. p. 51—52°/19 mm., Kahovic and Kohlrausch (*Sitzungsber. Akad. Wiss. Wien*, 1942, **151**, IIb, 48) record b. p. 46—46·5°/13 mm., $n_D^{17.5}$ 1·4520, and Kharasch, Skell, and Fisher (*J. Amer. Chem. Soc.*, 1948, **70**, 1059) give b. p. 52·2°/21 mm., n_D^{20} 1·4509, but ultimate analyses have not been reported. Treatment of the bromo-ester with cold ammonia during 15 hours gave α-bromo*iso*butyramide, of m. p. and mixed m. p. 147—148°.

Methyl (±)-αβ-dibromo*iso*butyrate was present in higher-boiling fractions (1·3 g.; b. p. 79—82°/9 mm., n_D^{17} 1·4883) of the reaction product from the above, but it could not be isolated in a pure state. It was independently synthesised for comparison as follows: a solution of bromine (24 ml., 0·45 mole) in dry carbon tetrachloride (25 ml.) was added to methyl methacrylate (45 g., 0·45 mole), cooled in a freezing mixture, at such a rate that the temperature did not exceed 20°. There was a slight evolution of hydrogen bromide. The product was fractionally distilled, *methyl* (±)-αβ-*dibromo*iso*butyrate* passing over at 77—78°/7—8 mm. (103 g., 88%). This was shaken twice with sodium hydrogen carbonate solution and then with water, dried, and refractionated; it then had b. p. 79·5—80°/9 mm., d_D^{16} 1·814, n_D^{17} 1·5092 (Found: Br, 61·6%; $[R]_D$ 42·8. $C_5H_8O_2Br_2$ requires Br, 61·5%; $[R]_D$ 42·2).

Catalysed Chlorinations with Sulphuryl Chloride.—The sulphuryl chloride was freshly distilled over mercury. All reactions were carried out with the exclusion of moisture ($CaCl_2$ guard-tube), but no special precautions were taken to de-oxygenate the reacting mixtures.

Benzene. A solution of dimethyl αα′-azo*iso*butyrate (3·45 g., 0·015 mole) in sulphuryl chloride (15 ml.) was added dropwise to a gently refluxing solution of benzene (AnalaR; 17·6 ml., 0·2 mole) and sulphuryl chloride (33 ml.; total 0·60 mole). There was a mild evolution of hydrogen chloride and sulphur dioxide, and the solution became yellow. After refluxing for a further 45 minutes it had become colourless again. The excess of benzene and sulphuryl chloride was then distilled off and the residue, which had partly crystallised, was treated with light petroleum whereupon there was deposited a mixture of isomeric hexachloro*cyclo*hexanes (3·0 g., 5% calc. on benzene), m. p. 153—158°. From this the α-isomer, m. p. 157—158° (Slade, *Chem. and Ind.*, 1945, 314, gives m. p. 157·5—158°), was readily obtained by trituration with warm methyl alcohol followed by crystallisation from chloroform, as the main, and least soluble, component. In the absence of the azo-compound no reaction occurred between sulphuryl chloride and benzene, for the starting products could be recovered unchanged after being heated together.

Toluene. A mixture of dry toluene (84·8 ml., 0·8 mole) and sulphuryl chloride (32·4 ml., 0·4 mole) was heated on a water-bath under reflux and αα′-azo*iso*butyronitrile (0·2 g., 0·00125 mole) was added. After an induction period of a few seconds a vigorous reaction set in with evolution of hydrogen chloride and sulphur dioxide. Addition of a further quantity (0·2 g.) of the azo-compound did not appear to increase the rate of gassing, and after 15 minutes the reaction was complete. The product was fractionated twice; the excess of toluene was recovered and the yield of benzyl chloride (35·6 g.; b. p. 174—183°) was 70% calculated on the sulphuryl chloride. From it was prepared benzyl β-naphthyl ether of m. p. and mixed m. p. 99—100°. The residue (6 g.) in the flask was a black tar

Inhibition experiments were carried out as above with, in each case, 0·2 mole of toluene, 0·1 mole of sulphuryl chloride, and 0·0006 mole of the azo-nitrile, and refluxing for 20 minutes:

Inhibitor.	Yield of benzyl chloride, %.
Iodine, 0·0006 mole	0
Chloranil, 0·0006 mole	25
Chloranil, 0·0012 mole	12

Triphenylmethane. To a solution of triphenylmethane (8·4 g., 0·034 mole) in refluxing sulphuryl chloride (8·1 ml., 0·1 mole) was added methyl αα′-azo*iso*butyrate (0·11 g., 0·0005 mole); a vigorous reaction soon set in. After 30 minutes this was complete. The solid residue remaining after distillation of the sulphuryl chloride was crystallised from light petroleum (b. p. 80—100°), to give triphenylmethyl chloride, m. p. 105—108° (7·4 g., 77% calc. on triphenylmethane). Its identity was confirmed by hydrolysis with boiling water to triphenylcarbinol, m. p. 162°, undepressed by admixture with an authentic specimen.

cyclo*Hexane.* A mixture of *cyclo*hexane (64·7 ml., 0·6 mole), sulphuryl chloride (16·2 ml., 0·2 mole), and dimethyl *αα'*-azo*iso*butyrate (0·22 g., 0·000125 mole) was heated on the steam-bath under reflux; after an induction period the reaction set in, but this was not so vigorous as in the chlorination of toluene. After 20 minutes reaction was complete, and the product was then fractionated, giving 13·5 g. (57% calc. on sulphuryl chloride) of *cyclo*hexyl chloride, b. p. 141—143°, n_D^{16} 1·4642.

Propionic acid. A mixture of propionic acid (59·7 ml., 0·8 mole), sulphuryl chloride (32·4 ml., 0·4 mole), carbon tetrachloride (40 ml.), and dimethyl *αα'*-azo*iso*butyrate (0·45 g., 0·002 mole) was heated on the water-bath, light being excluded. After a short time hydrogen chloride and sulphur dioxide were slowly evolved. This ceased after 90 minutes. Excess of thionyl chloride (115 ml.) was then added, and the mixture was refluxed for 4 hours and then fractionated, *α*-chloropropionyl chloride (1·5 g., 3% calc. on sulphuryl chloride) passing over at 110°. This was characterised by conversion into *α*-chloropropionamide, m. p. 80° (Beckurts and Otto, *Ber.*, 1876, **9**, 1592, give 80°).

M. p.s and b. p.s are uncorrected; analyses and density determinations are by Drs. Weiler and Strauss.

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