

IX.—*The Action of Sulphuryl Chloride on Organic Substances. Part I. Simple Monosubstituted Benzenes.*

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SULPHURYL chloride reacts readily with a large number of organic substances, generally functioning either as a chlorinating or as a dehydrating agent. Its action as a chlorinating agent is frequently, but not always, similar to that of chlorine, and sometimes to that of phosphorus pentachloride, whilst in its dehydrating action it resembles sulphur trioxide. Thus, in the absence of a catalyst, it

chlorinates benzene, toluene, phenol, anisole, phenetole, or aniline, and with salts of acids, such as sodium benzoate or acetate, it yields the corresponding acid anhydride and acid chloride (compare Dubois, *Bull. Acad. roy. Belg.*, 1876, **42**, 126; Wöhl, D.R.-P. 139552; Wenghöffer, *Ber.*, 1877, **10**, 441; Peratoner, *Gazzetta*, 1894, **24**, i, 236).

Although a large amount of work has already been done in this connexion, there is a lamentable lack of information regarding the action of sulphuryl chloride on the organic substances in common use. This investigation is designed to contribute a small addition to our existing knowledge in this direction.

The conditions of experiment have been those obtaining when the organic substance is boiled under atmospheric pressure for several hours with a large excess of sulphuryl chloride; consequently the products isolated represent the final products to be obtained in such circumstances, the isolation of any intermediate product not having been aimed at. The table shows briefly the results obtained :

Organic Substance.	Product.
Benzaldehyde	Benzoyl chloride.
Phenylacetoneitrile	Phenyldichloroacetoneitrile.
Acetophenone	<i>ωω</i> -Dichloroacetophenone.
Benzophenone	No action.
Nitrobenzene	" "
Sodium benzenesulphonate	" "
Sodium phenoxide (aqueous)	<i>p</i> -Chlorophenol.
" " (anhydrous)	2 : 3 : 4 : 6-Tetrachlorophenol.
Triphenyl phosphate	No action.
" " in presence of iron	Tri- <i>p</i> -chlorophenyl phosphate.
Sodium phenylacetate	Phenylacetic anhydride and phenyl-acetyl chloride.
Benzamide	Traces of benzonitrile only.

Phenylethyl alcohol yields an unstable product, probably a mixture of phenylethyl sulphate and phenylethyl chloride, the reaction being similar to that with benzyl alcohol (Behrend, *J. pr. Chem.*, 1877, [ii], **15**, 23).

EXPERIMENTAL.

Benzaldehyde.—Sulphuryl chloride (5 mols.) was distilled on to benzaldehyde (1 mol.); no sensible reaction took place. The mixture was slowly distilled until the excess of sulphuryl chloride was removed, the residue being distilled under reduced pressure. After repeated distillation, a fraction, b. p. 195—200°/760 mm., was obtained (benzoyl chloride boils at 198°), the only other substance present in any appreciable quantity being benzaldehyde; a small amount of tarry matter was formed (Found : Cl = 24.69. Calc., Cl = 25.27 per cent.).

The substance was identified with benzoyl chloride by conversion into benzoic acid and ethyl benzoate. The action of sulphuryl chloride on benzaldehyde is therefore similar to that of chlorine, but differs in that the simultaneous formation of traces of benzyl chloride does not appear to take place.

Phenylacetoneitrile.—This substance (1 mol.) was treated with sulphuryl chloride (5 mols.) as in the foregoing experiment; the residual liquid distilled at $115^{\circ}/20$ mm.

The fraction was highly lachrymatory, but otherwise almost devoid of odour. It would not solidify when cooled to -15° (Found : Cl = 38.52. $C_6H_5 \cdot CCl_2 \cdot CN$ requires Cl = 38.18 per cent.).

The substance, when boiled with alcoholic sodium hydroxide solution, immediately deposited sodium chloride and evolved first a slight odour of hydrocyanic acid and then one of ammonia. On pouring the mixture into water and acidifying, benzoic acid was deposited; this, twice crystallised from water, melted at 120.5° . The acid was further identified by means of a mixed-melting point determination and of its ethyl ester, b. p. 213° .

The substance, heated on a steam-bath with an equal weight of 75 per cent. sulphuric acid for three hours, yielded, on cooling, a precipitate of benzoic acid. It is clearly phenyldichloroacetoneitrile and is identical with the substance obtained by Claisen (*Ber.*, 1879, 12, 626).

Acetophenone.—Sulphuryl chloride (3 mols.) was slowly distilled on to acetophenone (1 mol.), and a vigorous reaction ensued. When this had subsided, the excess of sulphuryl chloride was slowly distilled off; the residual liquid distilled at $124-140^{\circ}/12$ mm. By repeated fractional distillation a fraction boiling at $121-122^{\circ}/10$ mm. and at $245^{\circ}/760$ mm. was obtained, which could not be made to solidify even at -10° (Found : C = 50.12; H = 3.16; Cl = 38.45. $C_6H_5OCl_2$ requires C = 50.79; H = 3.17; Cl = 37.58 per cent.).

When the substance was boiled for several hours with *N*/10-aqueous-alcoholic silver nitrate, only a trace of silver chloride was formed, this probably arising from an impurity in the substance. The substance was not oxidised by chromic acid mixture, but yielded readily to alkaline permanganate solution, a faint odour of chloroform being evolved. This chloroform probably arose from a trace of the trichloride, $C_6H_5 \cdot CO \cdot CCl_3$, the presence of which would account for the slightly high chlorine content. From the mixture obtained by the alkaline permanganate oxidation, benzoic acid was isolated in good yield.

The chief substance resulting from the reaction between acetophenone and sulphuryl chloride is therefore *ωω*-dichloroaceto-

phenone and is identical with the ketone obtained by Gautier (*Ann. Chim. Phys.*, 1888, [vi], **14**, 348).

Sodium Phenoxide.—The action of sulphuryl chloride on the sodium salts of certain acids is to produce the acid anhydride and the acid chloride. It was thought possible that with sodium phenoxide diphenyl ether or phenyl sulphate might result. There was also the possibility that in aqueous solution a reaction similar to the Schotten-Baumann reaction might take place, whilst a fourth possibility was that its action would be similar to that with phenol, where *p*-chlorophenol is obtained. Two experiments were therefore conducted.

A large excess of sulphuryl chloride was slowly distilled on to carefully dried sodium phenoxide, a very vigorous reaction taking place. The excess of sulphuryl chloride was distilled off and the solid remaining extracted with benzene. After the removal of the benzene from the extract, a liquid remained which had an initial boiling point of about 150°/17 mm. A fraction, b. p. 190—210°/17 mm., was collected, and this solidified on cooling. The residue was black and evolved hydrogen chloride.

The solid was insoluble in sodium carbonate solution but readily soluble in sodium hydroxide solution, from which it was precipitated on acidifying. It did not contain sulphur and was therefore not phenyl sulphate. Crystallised three times from ether, it melted at 65—66°. Its benzoyl derivative had m. p. 116° (compare Zincke and Wallbaum, *Annalen*, 1891, **261**, 246) (Found : C = 31.2; H = 1.22; Cl = 61.4. $C_6H_2OCl_4$ requires C = 31.0; H = 0.86; Cl = 61.2 per cent.).

The fractions of lower boiling point obtained in small yield were redistilled and a small fraction, b. p. about 217°/760 mm., was obtained (*p*-chlorophenol boils at 217°). This, on cooling and seeding with a crystal of *p*-chlorophenol, solidified immediately, and after drying on a porous tile had m. p. 40°. The substance was identified with *p*-chlorophenol.

The substances produced by the action of sulphuryl chloride on anhydrous sodium phenoxide are therefore *p*-chlorophenol and a tetrachlorophenol, probably the 2 : 3 : 4 : 6-isomeride obtained by Zincke and Schaum (*Ber.*, 1894, **27**, 549).

The reaction in aqueous solution was conducted as follows : ninety-four grams of phenol were dissolved in a solution of 40 grams of sodium hydroxide in 200 grams of water, and the excess of phenol was removed by boiling under diminished pressure. Seventy grams of freshly-distilled sulphuryl chloride were then added to the cold solution, with shaking and cooling in iced water. An oil formed and was separated, dried, and distilled, the b. p.

86°/22 mm. rising to 145°/16 mm. The distillate, which solidified on cooling, was dissolved in sodium carbonate solution and a small portion of insoluble oil (phenol) removed by extraction with ether; on acidifying, an oil was obtained which had b. p. 215—217° (*p*-chlorophenol boils at 217°) and m. p. 42°. The substance was identified with *p*-chlorophenol.

Triphenyl Phosphate.—Sulphuryl chloride is almost entirely without action on triphenyl phosphate when boiled with it under atmospheric pressure (compare Peratoner, *Gazzetta*, 1898, **28**, i, 197), but in the presence of quite small quantities of iron tri-*p*-chlorophenyl phosphate is readily formed.

No reaction having been found to take place between triphenyl phosphate and sulphuryl chloride under the usual conditions, an addition of 1 per cent. of 60-mesh iron filings was made and the mixture heated under reflux for ten hours. After the excess of sulphuryl chloride had been distilled off, the residue was poured into water, well washed, and neutralised. The solid, after crystallising three times from alcohol, melted at 113° (Found: C = 49.95; H = 3.00; Cl = 24.46. $C_{18}H_{12}O_4Cl_3P$ requires C = 50.29; H = 2.79; Cl = 25.08 per cent.).

The substance was hydrolysed with 2*N*-alcoholic sodium hydroxide, the product poured into water, acidified, extracted with benzene, and the extract distilled. The main fraction, after removal of the benzene, boiled at 210—220° and when seeded with *p*-chlorophenol solidified (m. p. 40°). Dried on porous tile and reprecipitated from sodium carbonate solution, the substance melted at 43° (Found: Cl = 27.22. Calc., Cl = 27.63 per cent.).

It follows, therefore, that the substance obtained by the action of sulphuryl chloride on triphenyl phosphate in the presence of iron is tri-*p*-chlorophenyl phosphate.

Benzamide.—Sulphuryl chloride (9 mols.) was distilled on to benzamide (1 mol.), no apparent reaction ensuing. The sulphuryl chloride was very slowly distilled off and the residue distilled under reduced pressure. A small early fraction was obtained and the contents of the distillation flask then solidified. The solid, crystallised twice from benzene, had m. p. 124—125° and b. p. 290° and was therefore unchanged benzamide (Found: C = 69.61; H = 5.67. Calc., C = 69.4; H = 5.79 per cent.).

The early fraction from the distillation had b. p. 80°/15 mm. and an odour similar to that of benzaldehyde. It dissolved in hot water and was redeposited on cooling. When it was boiled with sodium hydroxide solution, ammonia was slowly evolved and, on acidifying, benzoic acid was deposited (m. p. 120°). The substance is evidently benzonitrile (Found: N = 13.57. Calc., N = 13.59 per cent.).

formed by the dehydration of the benzamide. Sulphuryl chloride therefore does not attack benzamide except to a small extent to form benzonitrile.

Sodium Phenylacetate.—Freshly-distilled sulphuryl chloride (1.5 mols.) was slowly run on to anhydrous sodium phenylacetate (m. p. about 150°). The excess of sulphuryl chloride was removed in the cold under diminished pressure and the residue distilled as far as possible, a fraction boiling up to $100^{\circ}/12$ mm. being obtained. The solid remaining in the flask was extracted with benzene, and the extract distilled. After the removal of the benzene, a fraction, b. p. $130\text{--}168^{\circ}/12$ mm., was obtained which solidified. The solid, twice crystallised from benzene, had m. p. 75° . 1.235 Grams, boiled with *N*-aqueous-alcoholic sodium hydroxide, consumed 9.8 c.c., equivalent to 1.245 grams of phenylacetic anhydride. On acidifying a more concentrated similar solution, phenylacetic acid was deposited which, twice crystallised from water, had m. p. 76° .

The early fraction boiling up to $100^{\circ}/12$ mm. was redistilled, and a small fraction, b. p. $93\text{--}96^{\circ}/12$ mm., obtained, which fumed slightly in the air. This substance, on hydrolysis, yielded phenylacetic acid, m. p. 76° , and was evidently phenylacetyl chloride (Found: Cl = 23.06. Calc., Cl = 22.98 per cent.).

The products of the reaction between sulphuryl chloride and anhydrous sodium phenylacetate are phenylacetic anhydride and phenylacetyl chloride.

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