XCVII.—*The Reaction between Acid Chlorides and Nitrosylsulphuric Acid.*

By William James Deverall and Harry William Webb.

Acid chlorides react with nitrosylsulphuric acid in one or both of the following ways:

(1) $OH{\cdot}SO_2{\cdot}O{\cdot}NO + R{\cdot}COCl = OH{\cdot}SO_2{\cdot}O{\cdot}COR + NOCl$,

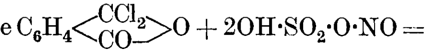
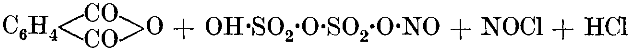
(2) $OH{\cdot}SO_2{\cdot}O{\cdot}NO + 2R{\cdot}COCl = R{\cdot}CO{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}COR + NOCl + HCl$,

and the end products undergo intramolecular rearrangement, especially on heating. The results obtained with acetyl and benzoyl chlorides have already been published (Elliott, Kleist, Wilkins, and Webb, J., 1926, 1219), but confirmation of the general nature of (1) and (2) has been obtained by examination of the reactions with the three nitrobenzoyl chlorides and with phthalyl chloride. *o*- and *p*-Nitrobenzoyl chlorides react readily with nitrosylsulphuric acid, but more slowly than benzoyl chloride itself, yielding *products*, $(NO_2\cdot C_6H_4\cdot CO\cdot O)_2SO_2$, which are completely decomposed by water into sulphuric and nitrobenzoic acids. When these products are heated under an inert liquid, the sulphuric acid obtainable by hydrolysis decreases, the total sulphur content remaining approximately constant; at 160° they are completely converted into a mixture of a sulphonic acid and a sulphone, with some evolution of sulphur dioxide.

m-Nitrobenzoyl chloride does not react with nitrosylsulphuric acid, even at 65° in absence of a diluent. This may be due to the general inhibiting effect of the nitro-group on the activity of other substituents (Shoesmith, Hetherington, and Slater, J., 1924, **125**, 1312), or to the setting up by this group of alternate chain polarity, but this assumption leads to the anomaly that chlorine of positive polarity is attacked while that of negative polarity is not.

All the methods of determining the relative orienting effects of various substituents in the benzene nucleus (Rule, *ibid.*, p. 1121) show that the groups containing semipolar double bonds have the least effect, and the results now obtained indicate that this is true also of the effect of such groups on the activity of other substituents in the nucleus. None of the three chloronitrobenzenes, for example, reacted with nitrosylsulphuric acid even at relatively high temperatures. On the other hand, the three chlorophenols reacted rapidly with the formation of products, $OH\cdot C_6H_4\cdot O\cdot SO_2\cdot OH$, which could not be purified satisfactorily. The relative velocity of the reaction shown by measurement of the rate of evolution of nitrosyl chloride was found to be *m*- : *p*- : *o*- = 6·5 : 4 : 3.

Evidence already published (*loc. cit.*) seemed to show that the reaction of nitrosylsulphuric acid with carbonyl chlorides was preceded by the formation of an addition compound to the carbonyl group of the acid chloride. Since the oxygen in a semipolar double bond (such as $>S\longrightarrow O$) occupies only one position, addition to such a bond would not be expected to take place, and hence experimental evidence bearing on the necessity for the preliminary formation of an addition product in the reaction between nitrosyl chloride and acid chlorides was obtained by an examination of certain sulphonyl chlorides and related substances. Benzene-and toluene-sulphonyl chlorides and sulphuryl and thionyl chlorides were all found to be unattacked by the reagent. The three nitrobenzenesulphonyl chlorides were also inert unless heated to 130°, whereupon the *o*- and *p*-derivatives reacted with explosive violence, whilst the *m*-compound was inert. Since complete decomposition ensued, no conclusion can be drawn concerning possible addition. The fact that chloropicrin, which behaves in many respects as a typical acid chloride, was unattacked, also supports the hypothesis of preliminary addition, and similar evidence was obtained from the inertness of chlorides of the type RCl (R = alkyl or aryl group not containing oxygen).

Both forms of phthalyl chloride appear to yield the same end-products. This was to be expected in view of the rapidity with which the unsymmetrical high-melting form changes into the stable low-melting modification. The main reaction with both forms appears to take the course  $\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{CCl_2}{CO}{>}O + 2OH{\cdot}SO_2{\cdot}O{\cdot}NO =}$  $\mathrm{C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O + OH{\cdot}SO_2{\cdot}O{\cdot}SO_2{\cdot}O{\cdot}NO + NOCl + HCl}$ and from the symmetrical form we isolated a small quantity of a *substance* $\mathrm{C_6H_4(CO)_2O,H_2S_2O_7}$. The condensation products obtained in the course of this investigation have not yet been examined in detail. They were all very hygroscopic and unstable, and owing to their insolubility neither conductivities nor molecular weights could be determined.

No satisfactory explanation can be offered of the fact that groups accepted as semipolar on the basis of the octet theory are relatively inert so far as their effect on the other substituents in the molecule is concerned, but the fact that the experimental results with co-ordination compounds indicate that the linkage in the case of oxygen is more stable than a non-polar double linkage in which oxygen is involved, probably has a bearing on the matter.

EXPERIMENTAL.

p-*Nitrobenzoyl Chloride and Nitrosylsulphuric Acid*.—8 G. of *p*-nitrobenzoyl chloride were dissolved in 50 c.c. of dry carbon tetrachloride and warmed at 60° with 2 g. of nitrosylsulphuric acid for 4 hours. The clear liquid was decanted, and the residue washed repeatedly with carbon tetrachloride until free from the chloride, whereby a theoretical yield of *di*-p-*nitrobenzoylsulphuric acid* was obtained (Found : S, 7·75, 8·3, 8·0; N, 6·7. $\mathrm{C_{14}H_8O_{10}N_2S}$ requires S, 8·1; N, 7·1%). The analytical methods were similar to those used for the corresponding benzoyl derivative (*q.v.*), the substance being completely decomposed on boiling with dilute hydrochloric acid into sulphuric and *p*-nitrobenzoic acids; when the evolved gases were passed through silver nitrate solution, 97·6% of the theoretical amount of chlorine was obtained.

When the substance was boiled for 3 hours in carbon tetrachloride, the amount of sulphuric acid obtainable on hydrolysis was equivalent to 5·60, 5·51% of sulphur, and the total sulphur content of the product was 7·43%. After 15 hours' refluxing, the corresponding figures were 4·10 and 7·00%. After 12 hours' heating at the boiling point of pentachloroethane (161°), no sulphuric acid was obtainable by prolonged hydrolysis of the product, which appeared to contain a sulphonic acid and a sulphone but was not examined in further detail.

o-*Nitrobenzoyl Chloride and Nitrosylsulphuric Acid.*—Considerable difficulty was found in obtaining this isomeride free from *o*-nitrobenzoic acid and repeated treatment with phosphorus pentachloride was necessary. 6·2 G. of the acid chloride were dissolved in 12 c.c. of carbon tetrachloride and warmed at 60° for 1 hour with 2·1 g. of nitrosylsulphuric acid, the resulting *di-*o*-nitrobenzoylsulphuric acid* being treated as above (Found: S, 8·2, 8·3%). The velocity of reaction, as measured by the rate of evolution of nitrosyl chloride, was greater than in the case of the para-compound, and some tar was formed.

Reaction with Phthalyl Chlorides. (With LIONEL FREDERICK BARRON.)—Nitrosyl chloride was vigorously evolved by reaction in the cold from both forms of this chloride. 30 G. of nitrosylsulphuric acid were treated with 79 g. of *s*-phthalyl chloride out of contact with air. When the reaction had ceased, the product was heated at 50—55° for 30 minutes, and then extracted repeatedly with boiling carbon tetrachloride until no further phthalic anhydride could be extracted. The residual oil solidified on cooling to a light yellow *substance* (Found: S, 19·3, 19·8. $C_8H_4O_3,H_2S_2O_7$ requires S, 19·6%), which was completely decomposed on hydrolysis into sulphuric and phthalic acids. The procedure adopted in the case of *as*-phthalyl chloride was exactly similar, but no condensation product could be isolated; phthalic anhydride was recovered in high yield.

Reaction with o- *and* p-*Nitrobenzenesulphonyl Chlorides.* (With CHARLES KENNETH WILLIAMS.)—The chlorides were prepared by a modification of Limpricht's method (*Annalen*, 1875, **177**, 60). 200 G. of benzene were added slowly to 300 c.c. of fuming sulphuric acid with cooling below 80°; after 2 hours the uncombined benzene was separated, and nitric acid (*d* 1·5) slowly added with constant shaking until no further action was apparent. The product was poured into water and filtered. The filtrate was saturated with milk of lime, and the filtered solution evaporated and fractionally crystallised. (*a*) The first crop was boiled with potassium carbonate, and the evaporated filtrate yielded a potassium salt which was converted into the chloride by grinding with phosphorus pentachloride. The mass was washed well with water and extracted with ether; when the extract was dried with calcium chloride, and the ether partly evaporated, the *m*-nitrobenzenesulphonyl chloride crystallised. (*b*) The middle crop of crystals of the calcium salts from the mother-liquor yielded the *o*-compound by similar treatment, and the final crop yielded a mixture of the *o*- and *p*-compounds, from which the former crystallised on standing, leaving the latter as an oil.

All three isomerides were treated with nitrosylsulphuric acid under conditions precisely similar to those used for the corresponding nitrobenzoyl chlorides, but no evolution of nitrosyl chloride could be detected. When heated at higher temperatures (130°), the *o*- and *p*-compounds reacted with explosive violence, with rapid evolution of nitrosyl chloride; the *m*-compound was unattacked at 130°, and at temperatures sufficiently high to cause reaction it was so explosive that no product other than sulphur trioxide and *m*-nitrobenzenesulphonic acid could be isolated.

A number of aliphatic and aromatic chlorides (*e.g.*, carbon tetrachloride, pentachloroethane, chlorobenzene, and benzyl chloride) were also examined under conditions similar to those used for the nitrobenzoyl chlorides and also at the higher temperatures used for the sulphonyl chlorides. No evolution of nitrosyl chloride could be detected in any case.

Reaction with Chlorophenols.—5 G. of the chlorophenol were warmed to 50° with 4·5 g. of nitrosylsulphuric acid in the presence of 50 c.c. of carbon tetrachloride. A vigorous reaction with rapid evolution of nitrosyl chloride ensued. The solid was separated and washed with carbon tetrachloride as previously described. The production of tar was far greater than in any other condensation examined, and owing to the instability of the product purification was unsatisfactory.

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