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# DESULFONYLATION OF AROMATIC SULFONYL CHLORIDES.
# A NEW SYNTHESIS OF ARYL CHLORIDES

by
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In a recent communication (1), a synthesis of aryl and benzyl chlorides has been described, based on the decarbonylation of the corresponding acyl halides with the aid of either equimolar or catalytic amounts of chlorotris (triphenylphosphine) rhodium $RhCl(PPh_3)_3$ (I). As sulfur dioxide behaves in a manner similar to carbon monoxide in insertion reactions (2) and can be extruded from metal sulfinates analogously to the decarbonylation of metal carbonyls (3), it seemed possible to desulfonylate sulfonyl chlorides with the above rhodium complex. Such a conversion of arylsulfonyl to aryl chlorides is indeed, feasible.

The method is illustrated by the following two examples:

A. A mixture of 17.6 g. of benzosulfonyl chloride (twice distilled in vacuo) and 0.07 g. of I was heated in a Claisen flask equipped with a 25 cm. long Vigreux column. The temperature at the top of the column was controlled by the rate of heating and was not allowed to exceed 132°. The evolution of sulfur dioxide decreased gradually and may be stimulated - though this is not essential - by adding a further 0.02 g. of I every 30 min. After 75 min. no more chlorobenzene distilled over, and in the distilling flask a polymer remained. The distillate was extracted with methylene chloride, washed with 10% aqueous sodium hydroxide and water and dried over magnesium sulfate. Redistillation at 131° gave 8.8 g. (79%) of pure chlorobenzene.

B. Freshly distilled 2-naphthalenesulfonyl chloride (6.0 g.) was heated with I (0.005 g.) in a Claisen flask connected to an oil pump. The temperature of the boiling sulfonyl chloride was kept between 255-275 with the aid of a pressure regulator. The reaction was completed after 20 min. The distillate was worked up as described above, affording 2.95 g. (69%) of 2-chloronaphthalene, b.p.250-262°, m.p. 58-60°.

The results of further experiments are listed in Table I.

## TABLE I

| Exp. | Sulfonyl Chloride used (g.) | | Product | Yield of pure product (%) a) |
|---|---|---|---|---|
| 1 | Benzene - | (17.6) | chlorobenzene | 79 |
| 2(b) | *p*-Toluene - | (15.0) | *p*-chlorotoluene | 72(c) |
| 3 | *p*-Fluorobenzene - | (15.5) | *p*-chlorofluorobenzene | 61(d) |
| 4 | *p*-Chlorobenzene - | (10.0) | *p*-dichlorobenzene | 85 |
| 5(b) | 2,5-Dichlorobenzene - | (10.0) | 1,2,4-trichlorobenzene | 65 |
| 6 | 2-Naphthalene - | ( 6.00) | 2-chloronaphthalene | 69 |
| 7(b) | 4-Fluoro-1-naphthalene- | (5.0) | 1-chloro-4-fluoronaphthalene | 70 |
| 8(b) | Benzene-1,3-di- | (10.0) | *m*-dichlorobenzene | 62 |

[Notes: (a) The crude products from experiments 2,5,7 and 8 were contaminated with small quantities (up to 4%) of dehalogenated compounds. For exp.3 see below.

(b) The internal temperature was kept at 260-280° during the distillation.

(c) Highly purified tosyl chloride was used. The BDH "98% Reagent" grade material polymerized violently after a quantity of 28% of *p*-chlorotoluene and 3% of toluene had distilled over.

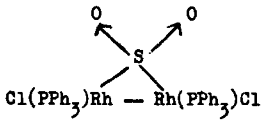
(d) in the best of four experiments.]

The main obstacle in the catalytic desulfonylation of the aromatic sulfonyl chlorides is their tendency to thermal polymerization; however, this side reaction can be minimized by using highly purified starting materials, keeping the internal temperature below 280° and shortening the reaction time.

The relatively low boiling p-fluorobenzenesulfonyl chloride (238°) loses sulfur dioxide very slowly. Thus special precautions had to be taken to prevent the polymerization of unreacted sulfonyl chloride during the prolonged heating. In the best of four trials, 15.5 g. of the sulfonyl chloride was heated with 0.1 g. of I as described in procedure A. After 4 hours, 8.2 g. of the starting material could be recovered by distillation, and 3.1 g. of p-chlorofluorobenzene (61% , calculated on the chloride entered into reaction) and 0.3g. of fluorobenzene had been formed. Longer heating caused progressive polymerisation. The slowness of the decomposition of p-fluorobenzenesulfonyl chloride is not due to the presence of the fluorine atom, as 4-fluoro-1-naphthalenesulfonyl chloride was desulfonylated normally.

The yields of aryl chlorides obtained by decarbonylation of aroyl chlorides are somewhat higher than those obtained in the desulfonylation reaction. However, the latter has the advantage of being much faster, at least in the benzene series. Thus, one may follow easily the stepwise decarbonylation of terephthaloyl chloride (4) , while benzene-1,3-disulfonyl chloride is so rapidly converted into m-dichlorobenzene, that no m-chlorobenzenesulfonyl chloride can be detected.

Both the catalytic decarbonylation and desulfonylation reactions with I have a threshold temperature, 190 and above 235°, respectively. These may well be the temperatures at which the primarily formed complexes, $RhCl(CO)(PPh_3)_2$ in the case of acyl and a corresponding sulfur compound in that of sulfonyl chlorides, are converted back into I or into some other active species. Such a primary complex has, indeed, been isolated: benzenesulfonyl chloride gave with I, when heated for 5 min. at 50°, in the same manner as benzoyl chloride, a yellow complex (dec.> 215°) which could be isolated by the addition of benzene or carbon tetrachloride to the mixture. The analysis corresponds to the formula $C_{36}H_{30}Cl_2O_2P_2Rh_2S$ [Calcd.: C,50.5; H,3.6; S,3.7. Found: C,50.1; H,3.7; S,3.4%], for which tentatively a formula such as II might be written. The infrared spectrum shows the $SO_2$ absorption at 1090 $cm^{-1}$. Although structures of this type are not well known, sulfur-bridged complexes are quite numerous (5,6).



II

We failed to decompose benzenesulfonyl chloride with palladium chloride or with palladium-charcoal under the conditions described for the decarbonylation of benzoyl chloride (7).

In conclusion, it is recalled that pyrolytic desulfonylation of aromatic sulfonyl chlorides has been known for some time (8), and also the formation of aryl chlorides from aromatic sulfonic acids and thionyl chloride at high temperature (9) may be rationalised as thermolysis of corresponding sulfonyl chlorides. The same may apply to the formation of polychloro-compounds during sulfonation reactions with chlorosulfonic acid (10).

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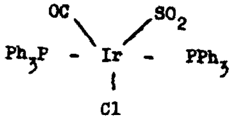

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