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A STUDY OF ALIPHATIC SULFONYL COMPOUNDS. III. SULFONYL CHLORIDE FORMATION FROM GRIGNARD REAGENTS[1]

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Probably the most generally applicable method for preparation of aliphatic sulfonyl chlorides is that of Cherbuliez (1), wherein organomagnesium chlorides are added to sulfuryl chloride. In spite of the general utility of this process it has not been widely used, perhaps because of the relatively low conversions, which are usually less than 35% based on the alkyl chloride from which the Grignard reagent is prepared.

In order to account for the formation of alkyl chlorides and other by-products in this process, Cherbuliez suggested a mechanism based on dissociation of an assumed intermediate complex between sulfuryl chloride and the Grignard reagent. His observation that the distribution of products is a function of temperature and that alkyl chloride formation is favored by low temperatures was cited as confirmation of the mechanism he proposed.

Our finding that the yield of octane-2-sulfonyl chloride is not significantly influenced by variations in temperature over the range −40° to 10° suggests that in this instance the mechanism proposed by Cherbuliez is not operative to an appreciable extent, and the results of subsequent experiments with other sulfonyl chlorides suggest that the following equations better account for production of sulfonyl chloride and alkyl chloride, principally, and of a small amount of sulfone (2).[3]

1.[4] $RMgCl + SO_2Cl_2 = RCl + MgCl_2 + SO_2$
2. $RMgCl + SO_2 = RSO_2MgCl$
3.[4] $RSO_2MgCl + SO_2Cl_2 = RSO_2Cl + MgCl_2 + SO_2$
4.[5] $RSO_2MgCl + RCl = RSO_2R + MgCl_2$

Formation of by-products according to equations 1 or 4 is probably responsible to a considerable extent for the low yields obtained with this process. Since

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[1] Partially from the dissertation presented by Robert B. Scott, Jr. at the University of Virginia (1949), partially from that presented by John B. Gayle at the University of Alabama (1954), and partially from material to be incorporated in the dissertation of Morgan S. Heller at the University of Alabama, in partial fulfillment for the Doctor of Philosophy degree at the respective universities.

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[3] In order to account for the sulfinic acids he obtained, Oddo (3) takes the opposite view, that the sulfonyl chloride is the primary reaction product which then reacts with the Grignard reagent to produce equivalent amounts of alkyl chloride and sulfinate.

[4] It is possible that chlorination follows dissociation of sulfuryl chloride.

[5] The possibility of $RMgCl + RSO_2Cl = RSO_2R + MgCl_2$ was rejected in view of the low yields of sulfone and of the failure of ethyl chlorosulfonate to react with Grignard reagents to yield esters of sulfonic acids (4).

these particular reactions are not essential to the formation of sulfonyl chlorides, it is evident that a modification of the Cherbuliez process consisting of successive operations in which Grignard reagents are reacted with anhydrous sulfur dioxide to give sulfinic acid salts which in turn are reacted with a suitable chlorinating agent, should result in increased yields of sulfonyl chlorides. In comparable experiments with α-toluene- and 2,3-dimethylbutane-1-sulfonyl chlorides, this modification gave yields nearly twice as great as those obtained with the single operation procedure, thereby suggesting that the modified procedure deserves consideration as a general method.

Besides giving increased yields, exceptionally pure products are obtained by the modified process. Also, the relatively slight heats of reaction, compared with those of the Cherbuliez process, make for greater ease in handling.

Another advantage lies in the flexibility of the process, which permits various chlorinating agents to be used as a matter of convenience. For instance, the use of gaseous chlorine, although slow, is of some advantage in that it does not appear to react with the ether under the conditions used, whereas sulfuryl chloride is apt to do so. Also, with chlorine, there is no excess to be decomposed or otherwise removed.

A further advantage is that it is a simple matter to free the sulfinic acid from halide ions derived from the original alkyl halide, thereby permitting preparation of sulfonyl chlorides from alkyl bromides, a possibility not realized with the Cherbuliez process.

Conversion of sulfinic acid salts to sulfonyl chlorides by treatment with sulfuryl chloride or chlorine is of interest in that it represents a variation of the well-known process for preparing sulfonyl chlorides by chlorinative oxidation of various sulfur bodies in aqueous medium (5). Use of an anhydrous medium with the sulfinate is feasible only because this sulfur body already possesses the requisite number of oxygen atoms and is therefore not dependent on the solvent or on the chlorinating agent as an oxygen donor.[6]

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[6] Of interest from a theoretical viewpoint is the seeming resemblance of the modified process to the reaction of halogens with silver salts of carboxylic acids wherein an intermediate product of the reaction has been shown to be the acyl hypohalite, RCO—O—X (6). Although admittedly speculative, an analogous sulfinyl hypohalite might have a real existence and may even be a common intermediate in some of the several methods for preparation of sulfonyl chlorides represented by the following equations:

$$\left.\begin{array}{l} \mathrm{RMgX} \xrightarrow{\mathrm{SO_2}} \mathrm{RSO{-}O{-}MgX} \xrightarrow{\mathrm{Cl_2}} [\mathrm{RSO{-}O{-}Cl}] \\ \mathrm{RSH} \xrightarrow{\mathrm{Cl_2,\ HOH}} \mathrm{RSO{-}O{-}H} \xrightarrow{\mathrm{Cl_2}} [\mathrm{RSO{-}O{-}Cl}] \\ \mathrm{RH} \xrightarrow{\mathrm{Cl}\cdot} \mathrm{R}\cdot \xrightarrow{\mathrm{SO_2}} \mathrm{RSO{-}O}\cdot \xrightarrow{\mathrm{Cl_2}} [\mathrm{RSO{-}O{-}Cl}] \\ \mathrm{RSO_2{-}O^-Na^+} \xrightarrow{\mathrm{PCl_5}} \mathrm{RSO_2{-}O{-}PCl_4} \xrightarrow{\mathrm{-POCl_3}} [\mathrm{RSO{-}O{-}Cl}] \end{array}\right\} \xrightarrow{\mathrm{S_N1}} \mathrm{RSO_2Cl}$$

While formation of a sulfinyl hypochlorite may be considered to be less probable in the last case, such a retrogressive step might be favored by the disposition of the atoms concerned in a pseudo five membered ring.

EXPERIMENTAL

Effect of temperature on yield by the Cherbuliez method. Each of three preparations of the Grignard reagent from 2-octyl chloride was slowly added to a cold ethereal solution containing a 5% excess of sulfuryl chloride based on the octyl chloride used. The reactions were carried out at −40° to −30°, at 0° to 5°, and at 5° to 10°, respectively. The amounts of octane-2-sulfonyl chloride (2) obtained represent conversions based on 2-octyl chloride of 28%, 33%, and 31%, respectively, the differences being no greater than might be expected without varying the temperature.

α-Toluenesulfonyl chloride by the proposed modification. Over a period of 4 hrs. anhydrous sulfur dioxide was bubbled into a dilute ethereal solution of the Grignard reagent from 52 ml. (0.45 mole) of benzyl chloride. Chlorine then was bubbled into the resulting ethereal suspension of sulfinic acid salt over a period of six hours. After the suspension had been filtered to remove inorganic salts, the ether was evaporated, and 46 g. (0.24 mole) of relatively pure[7] α-toluenesulfonyl chloride (m.p. 83–88°) was obtained for a conversion of 53% based on benzyl chloride used. Cherbuliez obtained a 34% yield of this sulfonyl chloride by reacting the Grignard compound with sulfuryl chloride.

In a similar experiment the intermediate sulfinic acid salt was converted to the free sulfinic acid which then was treated in ether solution with sulfuryl chloride to obtain the sulfonyl chloride. While in this instance the yield was not determined it appeared to be at least as great as in the previously described experiment.

Direct comparison of the proposed modification and the Cherbuliez procedure. One mole (127 g.) of benzyl chloride was converted into the Grignard reagent which then was diluted with ether to approximately 400 ml. A 25-ml. aliquot (representing 0.063 mole of benzyl chloride) was added slowly with stirring to a cooled solution of 12 ml. (0.15 mole) of sulfuryl chloride in 25 ml. of ether. Upon working up in the usual manner, 3.72 g. (0.020 mole, 32% conversion based on benzyl chloride) of α-toluenesulfonyl chloride was obtained.

A second 25-ml. aliquot of the Grignard reagent was treated similarly except that only 6 ml. (0.07 mole) of sulfuryl chloride was used and the order of addition was reversed. The yield of sulfonyl chloride was 3.74 g. (0.020 mole, 32% conversion based on benzyl chloride).

A third 25-ml. aliquot was further diluted to 50 ml. with dry ether and a slow stream of anhydrous sulfur dioxide was directed at the surface of the solution. A solid film formed at the surface of the solution and was broken up by swirling. After about an hour the ether had evaporated, leaving a residue of solid sulfinic acid salt. The residue then was broken up, ether was added, and chlorine was bubbled into the suspension for about two hours. The yield of sulfonyl chloride isolated was 6.64 g. (0.035 mole, 57% conversion based on benzyl chloride). This is approximately 1.8 times as great as that obtained using sulfuryl chloride with the Grignard reagent (1.7 times that reported by Cherbuliez).

2,3-Dimethylbutane-1-sulfonyl chloride. Scott and Heller (7) converted 1-chloro-2,3-dimethylbutane into the Grignard reagent (yield 75% by titration) which then was reacted with sulfuryl chloride by the Cherbuliez method. To obtain pure 2,3-dimethylbutane-1-sulfonyl chloride it was necessary to distil the residue from evaporation of the water-washed ether solution of the resulting mixture of products. Conversion was 33% based on the original alkyl chloride, 44% based on the Grignard reagent.

The Grignard reagent (yield 90%) was prepared from one mole (121 g.) of 1-chloro-2,3-dimethylbutane, the final volume of solution being approximately 340 ml. Over a period of an hour anhydrous sulfur dioxide was bubbled slowly into three 25-ml. aliquots (65.8 mg.-moles of Grignard reagent by titration) each of which had been diluted further with 75 ml. of ether. The ether suspension of sulfinate from one aliquot was treated with chlorine as described in the case of α-toluenesulfonyl chloride. That from a second aliquot was treated instead with 30 g. (0.22 mole) of sulfuryl chloride. The ether was evaporated from the third aliquot, the residue was suspended in 100 ml. of water and chlorine was bubbled

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[7] A simple wash with 2,2,4-trimethylpentane occasions no noticeable loss and raises the melting point to 90–92° compared to an ultimate 92–94° by repeated crystallizations.

in as in the case of the ether suspension. On working up the products from these three experiments, yields of 2,3-dimethylbutane-1-sulfonyl chloride were obtained amounting, in the order described, to 84%, 78%, and 78%, based on the Grignard reagent, or to 76%, 70%, and 70%, based on alkyl chloride, which is about twice as great as that obtained by the Cherbuliez procedure. The undistilled product, although slightly discolored, had the same refractive index (n_D^{25} 1.4607) as previously determined for the distilled compound (7).

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SUMMARY

It is shown that sulfinic acid salts are probable intermediates during the reaction of Grignard reagents with sulfuryl chloride to form sulfonyl chlorides. A modified procedure for producing sulfonyl chlorides from Grignard reagents has been developed which gives increased yields and minimizes by-product formation.

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