Chlorination by Sulfuryl Chloride. V.[1] Reaction with Benzyl Alcohols

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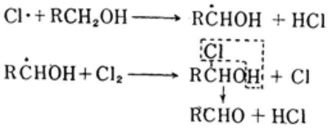
McBee et al.[2] reported that the reaction of fluorine-containing alcohols with elemental chlorine in an inert solvent yielded the corresponding aldehydes or ketones as follows:

$$CF_3CF_2CF_2CH_2OH \xrightarrow[h\nu]{Cl_2} CF_3CF_2CF_2CHO + 2HCl$$

These reactions have been considered to be a radical-chain reaction involving the following steps:



$$\begin{aligned} &Cl\cdot + RCH_2OH \longrightarrow R\dot{C}HOH + HCl \\ &R\dot{C}HOH + Cl_2 \longrightarrow R\overset{Cl}{\dot{C}}HOH + Cl \\ &\qquad\qquad\qquad\qquad\quad \downarrow \\ &\qquad\qquad\qquad\qquad RCHO + HCl \end{aligned}$$

Lecomte and Defour succeeded in obtaining aldehydes and ketones from primary and secondary aromatic alcohols with the hydroxy group in the α-position of the aromatic nucleus, by means of the reaction with *N*-bromoacetoamide in the presence of pyridine.[3]

Similarly it may be expected that the reaction with sulfuryl chloride in the presence of a radical initiator will result in the formation of the corresponding aldehydes or ketones. On the other hand, it is known that sulfuryl chloride reacts with the hydroxyl group of aliphatic alcohols as a chlorosulfonating agent, the products being alkyl chlorosulfonate,[4a] dialkyl sulfate, alkylsulfuric acid and alkyl chloride.[4b] The present paper will study whether or not the reaction of benzyl alcohols with sulfuryl chloride in the presence of benzoyl peroxide yields the corresponding aldehyde.

The reaction of benzyl alcohol with an equivalent amount of sulfuryl chloride in benzene results in the formation of benzaldehyde

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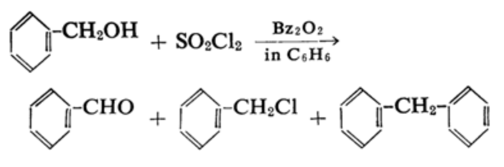
[1] Part IV: M. Arai, This Bulletin, **38**, 252 (1965).

[2] E. T. McBee, O. R. Pierce and W. F. Marzluff, *J. Am. Chem. Soc.*, **75**, 1609 (1953).

[3] J. Lecomte and C. Defour, *Compt. rend.*, **234**, 1887 (1952).

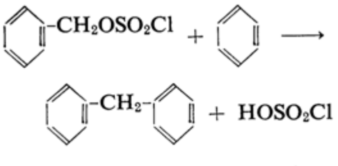
[4] a) P. Behrend, *Ber.*, **9**, 1334 (1876); W. W. Binkley and E. F. Degering, *J. Am. Chem. Soc.*, **60**, 2810 (1938); **61** 3250 (1939). b) R. Levaillent and L. Simon, *Compt. rend.*, **169**, 854 (1919).



(10%), diphenylmethane (23%) and benzyl chloride (15%).

However, the reaction in carbon tetrachloride gives only a chlorine-containing viscous substance. The reaction which is carried out without a solvent gives benzaldehyde and benzyl chloride.

The formation of diphenylmethane can be explained as resulting from the reaction of benzyl chlorosulfonate with benzene on the basis of the fact that it takes place only in benzene, and that the reaction between benzyl benzene sulfonate and benzene gives diphenylmethane in a good yield.[5]



These results suggest that sulfuryl chloride probably reacts as a homolytic chlorinating agent as well as a chlorosulfonating agent for benzyl alcohol, under these reaction conditions.

A similar reaction of anisalcohol in benzene gives anisaldehyde (60%) and a small amount of 3-chloroanisaldehyde. The total yield of aldehydes is 70%. Moreover, it might be noted that no product such as *p*-methoxybenzyl chloride was isolated from the reaction with the hydroxyl group. This striking effect of the substituent is interesting and makes this reaction suitable for the oxidation of various benzyl alcohols to the corresponding aldehydes.

Similar reactions with α-phenylethyl alcohol, α-phenylpropyl alcohol and benzhydrol give acetophenone, propiophenone and benzophenone in yields of 30%, 30% and 40% respectively.

Experimental

Materials and Reagents.—Benzyl alcohol (reagent grade), anisalcohol (reagent grade), α-phenylethyl alcohol (first grade) and α-phenylpropyl alcohol (first grade) were purifide by vacuum distillation under a nitrogen atomosphere before use. Benzhydrol (reagent grade) was used after recrystallization.

Sulfuryl chloride (first grade) was distilled, stored in a bottle wrapped with aluminum foil, and kept in a desiccator.

The Reaction of Benzyl Alcohol and Sulfuryl Chloride. — *1) Reaction in Benzene.* — 10.8 g. (0.1 mol.) of benzyl alcohol was dissolved in 20 ml. of benzene. After the air in the system had been replaced by dry nitrogen, 50 mg. of benzoyl peroxide was added to the solution. Then the system was heated at 70°C, and an equivalent amount of sulfuryl chloride (8.2 ml.) was dropped through the dropping funnel while the solution was being stirred. After the reaction mixture had stood about 4 hr., when the evolution of gas had ceased, it was cooled and washed with water. The benzene layer, dried with anhydrous sodium sulfate, was then distilled under reduced pressure, yielding 2.80 g. of liquid A (b. p. 45°C/5 mmHg), 3.80 g. of substance B (b. p. 103—105°C/5 mmHg) and a viscous substance which could not be distilled.

The treatment of A with 2, 4-dinitrophenylhydrazine sulfate gave a reddish-orange crystalline substance m. p. 237°C, which was identified as benzaldehyde 2, 4-dinitrophenylhydrazone by a mixed-melting point test. The yield of benzaldehyde as 2, 4-dinitrophenylhydrazone was 10%. The residue of A, from which benzaldehyde had been removed, gave benzyl chloride (yield, 15%); it was identified by the following experiments: benzoic acid formed by oxidation with potassium permanganate, and the reaction with β-naphtol in the presence of sodium hydroxide in ethanol, yielded a crystalline substance which was further converted into a yellow crystalline when treated with picric acid. The yellow crystalline substance, m. p. 123°C, was identified as the picrate of β-naphthol benzyl ether by a mixed-melting point test. As for B, it was crystallized out on cooling, its melting point being 26°C. The ultraviolet absorption spectrum and the infrared absorption spectrum indicate that B is diphenyl methane.

Found: C, 92.36 ; H, 7.25. Calcd. for $C_{13}H_{12}$: C, 92.81 ; H, 7.19%.

2) Reaction without the Solvent.—The same reaction was carried out in the absence of the solvent, using 10.8 g. of benzyl alcohol and 8.2 ml. of sulfuryl chloride. By distillation under reduced pressure, 3.60 g. of a liquid (b. p. 45°C/5 mmHg) was isolated from the remaining viscous substance. This liquid was identified as a mixture of benzaldehyde and benzyl chloride by the same procedure as that performed in 1). The yields were 10% and 20% respectively.

3) Reaction in Carbon Tetrachloride. — The same reaction was also carried out in carbon tetrachloride (20 ml.). All attempts to isolate the reaction mixture under reduced pressure failed. Only a dark colored substance was obtained in this procedure, a substance which could not be further purified.

Reaction with Anisalcohol.—In an atmosphere of nitrogen, 6.9 g. (0.05 mol.) of anisalcohol, dissolved in 10 ml. of benzene, was treated with 30 mg. of benzoyl peroxide and 4.1 ml. (0.05 mol.) of sulfuryl chloride at 70°C. After the termination of the reaction, the reaction mixture was distilled under reduced pressure, 4.10 g. of substance A (b. p. 86—88°C/3 mmHg) and 0.95 g. of B (b. p. 101—104°C/3 mmHg) being thus obtained. A was identified as anisaldehyde-2, 4-dinitrophenylhydrazone.

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[5] Z. Foeldi, *Ber.*, **61**, 1609 (1928).

Found: N, 17.90. Calcd. for $C_{14}H_{12}O_5N_4$: N, 17.72%.

B was crystallized out on cooling; recrystallization from ligroin gave needles, m. p. 52°C. The infrared spectrum shows a strong absorption at 1690 cm^{-1} ($\nu_{C=O}$), and moderate intensity bands at 815, 885 cm^{-1} (δ_{CH}), and at 640 cm^{-1} attributable to the C-Cl bond, suggesting 3-chloroanisaldehyde. It was also identified as 2,4-dinitrophenylhydrazone.

Found: N, 16.21. Calcd. for $C_{14}H_{11}O_4N_4Cl$: 15.98%.

Reaction with α-Phenylethyl Alcohol.—2.44 g. of α-phenylethyl alcohol in 15 ml. of benzene was submitted to the reaction described above with an equivalent amount of sulfuryl chloride. After the evaporation of the solvent, treatment with 2,4-dinitrophenylhydrazine sulfate gave 1.72 g. of the 2,4-dinitrophenylhydrazone, m. p. 251—253°C.

Reaction with α-Phenylpropyl Alcohol. — In a way similar to that used with α-phenylethyl alcohol, 1.79 g. of the 2,4-dinitrophenylhydrazone, m. p. 190—191°C, was yielded by 2.72 g. of α-phenylpropyl alcohol.

Reaction with Benzhydrol.—In a way also similar to that used with α-phenylethyl alcohol, 2.45 g. of the 2,4-dinitrophenylhydrazone, m. p. 239—240°C, was yielded by 2.72 g. of benzhydrol.

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