# *Notes*

## Chlorination of Ketones with Selenium Oxychloride

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Selenium(IV) compounds are noteworthy for their specific ability to oxidize activated methylene groups in organic compounds. In recent years we have been concerned with the mechanism[1] and scope of these reactions and have found, for example, that oxidation of an α-halo ketone with selenium dioxide in an alcoholic solvent can provide an efficient route to α-keto esters.[2]

As a result of subsequent studies with related compounds we have found that selenium oxychloride (I) can be used as a reagent for the preparation of α-chloro ketones. When a ketone containing an α-methylene group is mixed with I in an inert solvent (benzene, ether) a rapid exothermic reaction takes place with the formation of a dichloroorganoselenium compound.[3-5] Decomposition of this intermediate by heating at its boiling point or by refluxing in benzene for several hours results in the precipitation of selenium and formation of the corresponding α-chloro ketone. Over-all yields are of the order of 50%.

$$2RCOCH_3 + SeOCl_2 \xrightarrow{-H_2O} [RCOCH_2]_2SeCl_2 \longrightarrow 2RCOCH_2Cl + Se$$

The following list summarizes some typical results.

acetophenone ⟶ α-chloroacetophenone (54%)
cyclohexanone ⟶ α-chlorocyclohexanone (41%)
pinacolone ⟶ α-chloropinacolone (46%)
*p*-bromoacetophenone ⟶ α-chloro-*p*-bromoacetophenone (58%)
propiophenone ⟶ α-chloropropiophenone (42%).

Yields are based on purified, distilled compounds and products were identified by physical constants, infrared spectrum, positive chlorine test, and, in most cases, a solid derivative.

For synthetic purposes it is unnecessary to isolate the organoselenium intermediate and we have found it convenient to prepare and decompose the adduct in the same flask, using benzene as the solvent. Further work is in progress attempting to extend this reaction to include other halogens and active methylene compounds.

### Experimental

All of the reactions reported above were carried out under similar experimental conditions. The most convenient procedure is described below for the conversion of acetophenone to α-chloroacetophenone.

**α-Chloroacetophenone.**—In a 200-ml. round-bottom flask was placed 100 ml. of benzene and 2 g. (0.2 mole) of acetophenone. The flask was cooled in an ice bath and 16.6 g. (0.1 mole) of selenium oxychloride was slowly added, cooling the flask as necessary. After allowing the solution to stand at room temperature for about 1 hr., precipitation of the organoselenium adduct was essentially complete. The flask was then equipped for distillation and all of the benzene removed. The crystalline mass was heated with a free flame and the α-chloroacetophenone collected along with other pyrolysis products. Redistillation gave 16.7 g. (54%) of pure α-chloroacetophenone b.p. 139–140° (14 mm.).

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[1] E. J. Corey and J. P. Schaefer, *J. Am. Chem. Soc.*, **82**, 918 (1960); J. P. Schaefer, *ibid.*, **84**, 713, 717 (1962).

[2] J. P. Schaefer and E. J. Corey, *J. Org. Chem.*, **24**, 1825 (1959).

[3] R. E. Nelson and R. N. Jones, *J. Am. Chem. Soc.*, **52**, 1588 (1930).

[4] The same adduct is reported to be formed with selenium tetrachloride.[5]

[5] A. Michaelis, *Ber.*, **30**, 2821 (1897); A. Michaelis and F. Kunckell, *ibid.*, **30**, 2823 (1897).

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## The Wittig Reaction Using Methylsulfinyl Carbanion–Dimethyl Sulfoxide[1]

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Recently a brief account was given of an efficient and very convenient procedure for effecting the Wittig reaction.[2] In this note examples are presented which illustrate the utility and merits of this simplified method. The methylsulfinyl carbanion is first formed from dimethyl sulfoxide–sodium hydride (75–80°). The solution is cooled and treated with a phosphonium salt to yield the alkylidene phosphorane or Wittig reagent almost instantaneously. Subsequent addition of the carbonyl component, and appropriate reaction temperature, time, and product isolation complete the process.

The Wittig reaction appears to proceed more rapidly in dimethyl sulfoxide than in the customary solvents and, further, the yields obtained are frequently superior Thus, the yield of methylenecyclohexane obtained by our procedure is twice that obtained by the Organic Syntheses method of Wittig.[3] Camphor, a rather unreactive ketone, presents no special problem. In addition, these conditions allow highly selective reaction with the ketonic function of keto esters.

The examples presented in the Experimental illustrate the modification in a variety of instances which serve to outline appropriate conditions and isolation procedures. Lastly, it is worthy of note that our simplified procedure is excellent for small-scale work. In connection with other synthetic problems in these Laboratories, as little as 5 mg. of ketone has been converted to olefin in high yield by using careful

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[1] Research supported by the National Institutes of Health.

[2] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

[3] G. Wittig and U. Schoellkopf, *Org. Syn.*, **40**, 66 (1960).