The Chlorinium Ion as an Intermediate in Chlorination of Aromatic Compounds by Hypochlorous Acid

BY C. GARDNER SWAIN AND ARTHUR D. KETLEY

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Chlorinations of phenol, anisole, methyl *p*- or *m*-tolyl ether or mesitylene by hypochlorous acid in aqueous or aqueous dioxane solution containing excess silver perchlorate at 25° have the kinetic form

$$-\frac{d[\mathrm{HOCl}]}{dt} = k[\mathrm{HOCl}] + k'[\mathrm{H}^+][\mathrm{HOCl}] + k''[\mathrm{H}^+][\mathrm{HOCl}][\mathrm{ArH}]^1$$

The first two terms might represent slow steps forming H_2OCl^+ (from H_2O and HOCl or H_3O^+ and HOCl)[2] and the third term, which is relatively more important with the most reactive aromatic compounds, might represent a termolecular reaction. Alternatively it has been suggested[1] that the first two terms represent slow steps forming Cl^+ (from HOCl or H_2OCl^+) and that the third term represents direct chlorination by H_2OCl^+. There has been no experimental evidence to discriminate between these two alternative interpretations but the second interpretation requires a concentration of Cl^+ intermediate much too high to be consistent with the equilibrium constant $[Cl^-][Cl^+]/[Cl_2] = 10^{-60}$ calculated by Bell and Gelles.[3]

To decide experimentally between these two interpretations we compared rates in light and heavy water (protium and deuterium oxides). Methyl *p*-tolyl ether was used because the third term is negligibly small for this compound. The second term was made to predominate strongly over the first by using a high concentration (0.5 *M*) of perchloric acid. If the second term represents a rate-determining proton transfer to form H_2OCl^+ as an intermediate, the rate should be faster in light than in heavy water, because of the difference in zero-point energies of H_3O^+ and D_3O^+.[4] If it represents a rate-determining fission of H_2OCl^+ to form Cl^+ as an intermediate, the rate should be slower in light than in heavy water, because the acid dissociation constants of protium-protonated substrates (such as H_2OCl^+) are generally higher than those of deuterium-protonated substrates (such as D_2OCl^+), hence the hypochlorous acidium ion would be in lower concentration in the light solvent.[5]

We found that the rate in light water was only 52% of that in heavy water. Using 0.044 *M* methyl *p*-tolyl ether, 0.0008 *M* hypochlorous acid, 0.052 *M* silver perchlorate and 0.50 *M* perchloric acid in a solvent of 37.5% light or heavy water–62.5% dioxane at 25°, the rate constant was 4.9×10^{-2} min.$^{-1}$ with light water and 9.46×10^{-2} min.$^{-1}$ with heavy water.

This experimental result requires the interpretation[1] involving chlorinium ion, Cl^+, as an intermediate.

Experimental

Procedures were those previously described[1] except as noted below. All standard solutions were prepared with either light or heavy water. Methyl *p*-tolyl ether (Eastman Kodak) was purified by fractional distillation, b.p. 174–175° at 762 mm. Total volume of reacting solutions was 100-ml. and 10-ml. portions were removed for titration.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

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Friedel–Crafts Condensations of Benzenesulfonyl Chloride with Thiophenes

BY WILLIAM E. TRUCE AND FREDERICK J. LOTSPEICH

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Although the Friedel–Crafts process represents one of the general methods for preparing aryl sulfones,[1] it has not been applied successfully to the condensation of sulfonyl chlorides with simple heterocyclic compounds. Accordingly, it seemed of interest to study such applications, particularly with thiophene and its derivatives, in view of the greater stability toward acids of the thiophene nucleus over furan and pyrrole nuclei.

It has been reported that tars only are obtained on treating thiophene with benzenesulfonyl chloride in the presence of aluminum chloride.[2] Therefore, the more favorably disposed compound,[3] 2,5-dichlorothiophene, was considered first. Benzenesulfonyl chloride reacts with this substituted thiophene in the presence of aluminum chloride to give phenyl 2,5-dichloro-3-thienyl sulfone as determined by comparison with an authentic sample. Attempts to extend this reaction to thiophene, 2,5-dimethylthiophene, 2,5-diiodothiophene and 2-chloro-5-iodothiophene resulted in the formation of intractable tars, even when ferric chloride, stannic chloride or iodine were substituted for aluminum chloride. Furthermore, benzenesulfonic anhydride, which is superior to benzenesulfonyl chloride in the Friedel–Crafts synthesis,[4] also gave intractable tars with thiophene in the presence of aluminum chloride or phosphoric acid.

The greater difficulty of effecting sulfonylation in contrast to acylation is presumably related to the well-known greater tendency of the acyl chloride group to undergo nucleophilic displacement[5] as compared with the sulfonyl chloride group. Furthermore, it appears that electronegative substituents (chlorine) may sufficiently deactivate the thiophene nucleus toward polymerization to permit some sulfonylation.

Experimental

To a mixture of 17.6 g. (0.10 mole) of benzenesulfonyl chloride, 13.4 g. (0.10 mole) of aluminum chloride and 50

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[1] C. M. Suter, "Organic Chemistry of Sulfur," John Wiley & Sons, Inc., New York, N. Y., 1944, p. 673.

[2] H. Burton and W. A. Davy, *J. Chem. Soc.*, 525 (1948).

[3] H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 322.

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[5] J. M. Tedder, *Chem. and Ind.*, 630 (1954).

ml. of carbon disulfide was added slowly with stirring 15.3 g. (0.10 mole) of 2,5-dichlorothiophene. The mixture was stirred for 47 hours at room temperature and then slowly added to a mixture of ice and hydrochloric acid. The resulting precipitate was filtered and extracted with hot methanol. Evaporation of the methanol with the aid of an air jet yielded 4 g. of yellow crystals.

Meanwhile, the carbon disulfide layer was separated from the filtrate and evaporated to dryness. The solid residue was extracted with hot methanol and the extract was evaporated to dryness to yield an additional 5 g. of yellow crystals. The two crops of crystals were combined and dissolved in boiling glacial acetic acid. Treatment of the glacial acetic acid solution with Norit followed by partial evaporation and cooling, yielded 7 g. (24%) of phenyl 2,5-dichloro-3-thienyl sulfone, which melted at 126.5–128° after recrystallization from methanol; no depression resulted on admixture with an authentic sample prepared as described below.

Anal. Calcd. for $C_{10}H_{16}S_2O_2Cl_2$: C, 40.94; H, 2.07; Cl, 24.19; mol. wt., 293. Found: C, 41.18; H, 2.08; Cl, 24.10; mol. wt., 291.

Using the general procedure described by Hartough[6] for the preparation of 2-thiophenesulfonyl chloride, 15.3 g. (0.10 mole) of 2,5-dichlorothiophene was added slowly with stirring to 15.6 g. (0.134 mole) of chlorosulfonic acid cooled to 10°. The resulting solution was poured on ice, neutralized with 10% aqueous sodium hydroxide and evaporated to dryness. Extraction of the residue with boiling methanol yielded 17 g. (66%) of sodium 2,5-dichloro-3-thiophenesulfonate. A mixture of this sulfonate (17 g., 0.0664 mole) and 27.8 g. (0.134 mole) of phosphorus pentachloride was heated on the steam-bath for 8 hours, cooled and extracted with carbon tetrachloride. The carbon tetrachloride and phosphorus oxychloride were subsequently removed by reduced pressure distillation at 50°. A solution of this sulfonyl chloride in 50 ml. of dry benzene was added dropwise to a stirred mixture of 100 ml. of dry benzene and 10 g. (0.075 mole) of anhydrous aluminum chloride, and the reaction mixture was stirred for 15 hours at room temperature and 2 hours at 80°. The resulting solution was added to a mixture of ice and hydrochloric acid and the water layer was separated and extracted with benzene. The combined benzene extracts were evaporated to a solid residue. The residue was washed with cold methanol, dissolved in boiling methanol and treated with Norit. Partial evaporation of the methanol followed by cooling yielded 11 g. (56%) of phenyl 2,5-dichloro-3-thienyl sulfone, which melted at 126–128° after recrystallization from methanol and petroleum ether.

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[6] H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 513.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

Disubstituted Phosphine Oxides and Disubstituted Phosphinic Acids. II. The Di-*n*-alkyl Series[1]

BY ROBERT H. WILLIAMS[2,3] AND LYLE A. HAMILTON[2]

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In the first paper of this series,[4] three members of the new class of organophosphorus compounds, the di-*n*-alkylphosphine oxides, and the corresponding phosphinic acids were reported. Eight new di-*n*-alkylphosphine oxides and seven new di-*n*-alkylphosphinic acids have since been synthesized.

The di-*n*-alkylphosphine oxides reported here are all neutral, moderately stable, white solids. The di-*n*-amyl-, di-*n*-heptyl- and di-*n*-nonylphosphine oxides are less stable than the other members of the series. This conclusion is based upon the following tests: (a) the samples were stored at room temperature and changes in melting points over periods of time varying from one week to two years noted, (b) a capillary tube containing the sample was placed in a bath maintained about three degrees below the melting point and the time required for the sample to partly decompose and melt was observed. The compounds with five, seven and nine carbon atoms in their alkyl groups showed signs of instability in one or both of these tests. For instance, their melting points decreased measurably in one to two weeks and as much as five to ten degrees in eight months. In test b, only five to seven minutes were required. In comparison, the di-*n*-hexyl- and di-*n*-octylphosphine oxides have maintained their original melting points over a period of one to two years and do not melt prematurely if held at temperatures just below their melting points. Di-*n*-undecylphosphine oxide showed no signs of instability in either of these tests. The melting points of the di-*n*-decyl-, di-*n*-dodecyl-, di-*n*-tetradecyl-, di-*n*-hexadecyl- and di-*n*-octadecylphosphine oxides have not decreased with time although all of these were prepared before any of the members with odd numbers of carbon atoms in an alkyl group.

The chemical properties of the di-*n*-alkylphosphine oxides were investigated only in connection with the preparation of the phosphinic acids. It was found that the lower members of the series were oxidized readily by 30% hydrogen peroxide. This reagent became less effective as an oxidizing agent with increasing molecular weight of the phosphine oxides, di-*n*-octadecylphosphine oxide being unaffected by it. This is probably due to mutual insolubility and lack of effective mixing. With chlorine or phosphorus pentachloride, a vigorous reaction took place, forming the di-*n*-alkylphosphinyl chlorides, $R_2P(O)Cl$. These were not isolated but were hydrolyzed *in situ* to the phosphinic acids.

A plot of the melting points of the di-*n*-alkylphosphine oxides against the number of carbon atoms in an alkyl group shows a gradual increase in melting point with increasing chain length. A smooth curve passes through all these points with the exception of that for di-*n*-undecylphosphine oxide.

The di-*n*-alkylphosphinic acids are white crystalline compounds of high stability. They are weak acids, the end-point in a potentiometric titration usually being taken at about *p*H 10.5. A plot of the melting points against the number of carbon atoms in an alkyl group reveals that, in contrast to the di-*n*-alkylphosphine oxides, the melting points alternate in a manner analogous to that characteristic of the normal fatty acids and the straight chain dicarboxylic acids. The effect decreases rapidly with increasing molecular weight. This is the first time that such an alternation has been observed in a series of organophosphorus compounds. The *n*-alkylphosphonic acids, $RP(O)(OH)_2$, are the only other fairly complete series, and the melting points of the members from *n*-butyl to *n*-octadecyl cluster around 100°.[5]

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(2) Socony-Vacuum Laboratories, Paulsboro, N. J.

(3) Socony-Vacuum Fellow at Temple University.

(4) Robert H. Williams and Lyle A. Hamilton, THIS JOURNAL, **74**, 5418 (1952).

(5) G. M. Kosolapoff, *ibid.*, **67**, 1180 (1945).