

References

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Faculty of Pharmaceutical Sciences,
University of Tokyo,
Bunkyo-ku, Tokyo,

College of General Education,
University of Tokyo,
Meguro-ku, Tokyo

FUMIYA KUROSAKI
SOSHIRO TAKAHASHI
KOICHI SHUDO
TOSHIHIKO OKAMOTO*
YO ISOGAI

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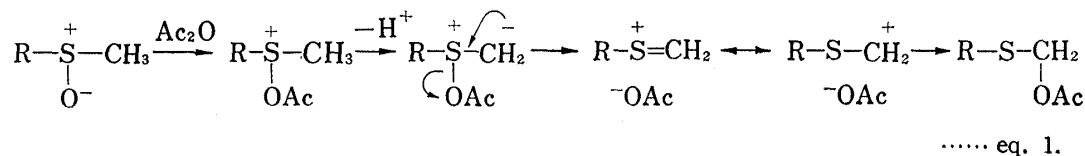
Reaction of Benzene with Diphenyl Sulfoxides

Diphenyl sulfoxide reacted with benzenes in the presence of trifluoroacetic anhydride and trifluoromethanesulfonic acid to yield triphenylsulfonium ions in good yields. A new electrophilic species was proposed.

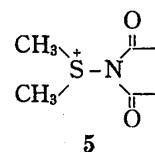
Keywords—electrophilic aromatic substitution; diphenyl sulfoxide; triphenylsulfonium salt; trifluoromethanesulfonic acid; benzene

The most widely known reaction of benzene is the substitution by electrophilic species.¹⁾ The quest for new electrophiles has been overcome by employing strong acids or suitable leaving groups.¹⁾ The iminium-benzenium dication produced from N-phenylhydroxylamine in the reaction catalyzed by trifluoromethanesulfonic acid (TFSA) is an example of new electrophiles which react with benzene under mild conditions.²⁾ The phenoxenium ion prepared by elimination of sulfonamide as the nucleofugal leaving group, also reacts with benzene.³⁾ This paper describes a discovery of a new electrophilic species which can react with benzene easily.

Sulfoxide, on acylation, gives an acyloxysulfonium ion. In the Pummerer type reactions, a proton abstraction on α -carbon atom and the subsequent elimination of an acyloxy group gives ion pairs; carbonium ion and acetate anion. A nucleophilic attack of acetate anion to the carbonium ion gives the product (eq. 1).⁴⁾



Among known methods for synthesis of triarylsulfonium ions,⁸⁻¹⁰⁾ the simplest is the aluminum halides-catalyzed reaction of sulfoxide with benzene.⁸⁾ Though the reaction conditions are drastic, the mechanism may be closely related to the present reaction. An example of a sulfonium ion postulated as an intermediate attacking arenes is dimethylsulfonium ion of type 5.¹¹⁾ However, the reagent reacts only with phenol, and the mechanism is preferably interpreted by an intramolecular rearrangement of a sulfonium ion formed by the attack of phenolic oxygen.¹²⁾ From a synthetic stand-point, the reaction found here is the most promising method for synthesis of triarylsulfonium salts.



References and Notes

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Faculty of Pharmaceutical Sciences,
University of Tokyo,
Bunkyo-ku, Tokyo 113, Japan

YASUYUKI ENDO
KOICHI SHUDO
TOSHIHIKO OKAMOTO*

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High Performance Liquid Chromatographic Analysis of Sulfite using Malachite Green

A selective, sensitive and accurate determination of sulfite was proposed by high performance liquid chromatography (HPLC). The sulfite was converted quantitatively to an adduct by reacting with a triphenylmethane dye, malachite green (MG). The formation of adduct was complete, and the adduct was stable at the experimental conditions. Then, the adduct was submitted to HPLC. The working curve for sulfite was linear in the range from 2.0×10^{-12} mol upto 1.2×10^{-9} mol.