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FORMATION OF PUMMERER'S KETONE FROM 4-METHYLPHENOXENIUM ION. AN ACID-CATALYZED SOLVOLYSIS OF N-p-TOLUENESULFONYL-O-(4-TOLYL)-HYDROXYLAMINE IN p-CRESOL

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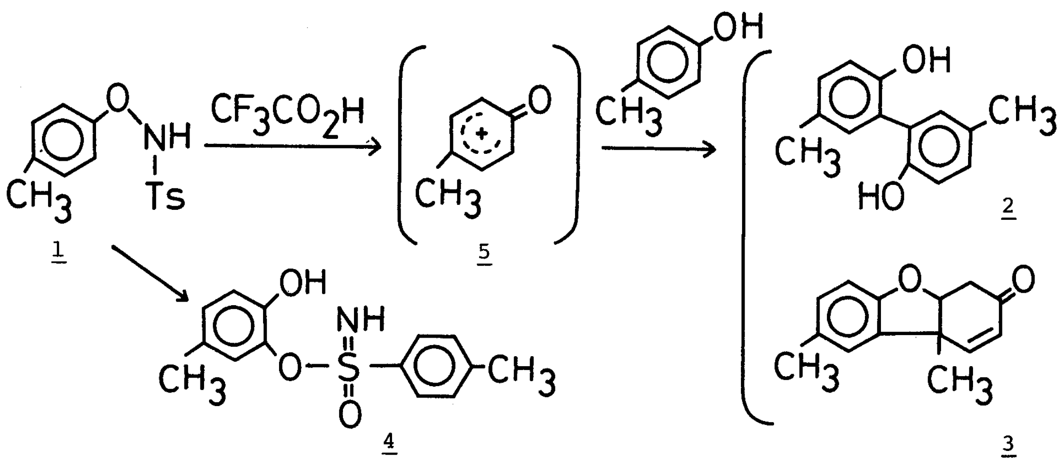
N-p-Toluenesulfonyl-O-(4-tolyl)hydroxylamine (1) reacts with p-cresol in the presence of trifluoroacetic acid to yield biscresol (2) and Pummerer's ketone (3).

KEYWORDS —— phenoxenium ion; Pummerer's ketone; oxidation; oxidative coupling

Aryloxenium ions have received considerable interest in recent years particularly in connection with phenol oxidation[1] and biosynthetic-type oxidative coupling reactions.[2] Previously, we have shown that aryloxenium ions can be generated in the acid-catalyzed solvolysis of N-acyl-O-arylhydroxylamines.[3] We now report an acid-catalyzed reaction of N-p-toluenesulfonyl-O-(4-tolyl)-hydroxylamine (1) with p-cresol: Pummerer's ketone is formed from 4-methyl-phenoxenium ion and cresol.

Reaction of (1) with p-cresol (25 equiv.) in the presence of trifluoroacetic acid (6.5 equiv.) at 20°C for 1 h gave 2,2'-dihydroxy-5,5'-dimethylbiphenyl (2) 24%, mp 152-153°C,[4] 2,9a-dimethyl-5a,6,7,9a-tetrahydro-7-oxodibenzofuran (Pummerer's ketone; (3), 9%, mp 124-125°C,)[5] which was stable under the acidic conditions if the workup process is careful enough,[6] and 2-hydroxy-5-methylphenyl p-toluenesulfonimidate (4)[7] (39%). Thus, biscresol (2) by ortho-ortho coupling and Pummerer's ketone (3) by ortho-para coupling was isolated. In this reaction, however, 2-hydroxy-4',5-dimethyldiphenylether was not produced by O-ortho coupling.



The mechanism for the reaction involves initial N-O bond heterolysis to the 4-methylphenoxenium ion (5), which attacks as an electrophilic species upon the aromatic nucleus of p-cresol.3) We suggest that the reaction is a model for C-C bond formation in phenol oxidative coupling reactions. This suggestion is consistent with the Waters' view that PhO^+ participates in the C-C coupling reactions.1a)

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6) The reaction mixture was poured into 5% aqueous sodium hydroxide at 0°C, and the solution was extracted with dichloromethane. The organic layer was dried and evaporated to give a sole product (3). The aqueous layer was acidified with concentrated hydrochloric acid and was extracted with dichloromethane. The dried dichloromethane extract was evaporated and p-cresol was removed under vacuum. The residue was chromatographed on a column of silica gel to give acidic products; (2) and (4).

7) The rearranged product (4) can be reasonably explained by acid-catalyzed [3,3]-sigmatropic-like rearrangement, which competes with the formation of the free aryloxenium ion. See Y.Endo, K.Shudo and T.Okamoto, Synthesis, 1980, 461.

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