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ON THE REACTIVITY OF THIOPHENE AS A TRAP FOR BENZYNE

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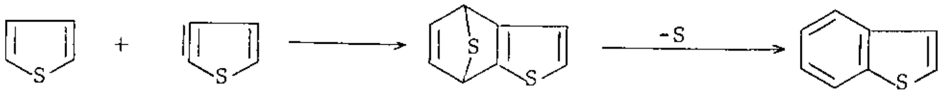
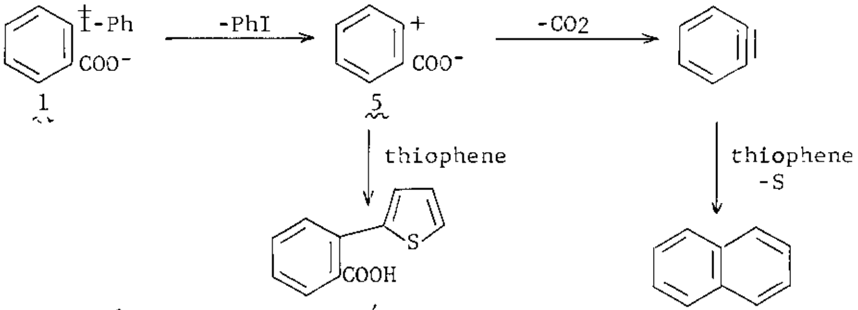
Abstract -- The thermal decomposition of diphenyliodonium-2-carboxylate in thiophene solution gives naphthalene as the major product thereby demonstrating the effectiveness of thiophene as a trap for benzyne in solution.

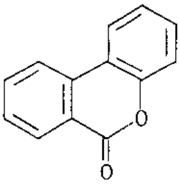
The surprising ability of thiophene to serve as a superior trap for the aryne 2,3-didehydrothiophene[1] raises the question of whether this observation is due to some unique property of the five-membered hetaryne,[2] or to some previously unappreciated Diels-Alder reactivity of thiophenes with arynes. Whereas the very reactive tetrahalobenzynes are well-known to react with thiophenes in this way,[3] benzyne itself apparently fails,[4] except under very high temperature, gas-phase conditions.[5] Since other reactive dienophiles have recently been shown to react with thiophenes in solution,[6] it seemed possible that it was the intervention of side reactions, and not a lack of diene reactivity, which was responsible for the failure of thiophene to react with benzyne. Accordingly, an investigation was undertaken of the reaction of thiophene with benzyne generated from a variety of precursors. The preliminary results reported in this Communication represent the first solution trapping of benzyne itself by thiophene.



Of several tested,[7] the most successful benzyne precursor for this reaction appears to be diphenyliodonium-2-carboxylate (1),[8-10] which gives naphthalene in up to 33% yield. In a typical run, dry 1 and thiophene are heated in a vacuum-sealed glass vial for 15 minutes at 220°. The yield of napthalene was determined by vpc, and its identity was established by ms and uv of a vpc-isolated sample.

Depending on the reaction conditions, major side-products include the expected[8] lactone (2) and xanthone (3), along with o-(2-thienyl)-benzoic acid (4),[11] formed in up to 16% yield, presumably by reaction of thiophene with a prebenzyne intermediate such as 5.





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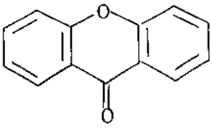

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The reaction conditions have been optimized with respect to temperature and concentration. A decreased temperature results in a lower yield of naphthalene due to the occurrence of known non-benzyne forming reactions of the precursor 1.[8] Increasing the initial concentration of precursor also lowers the yield of naphthalene. For example, at 190°, the yield drops from 29% at $1.2x10^{-2}$M to 13% at $2x10^{-1}$M, due to the consumption of 1 in the formation of xanthone 3 and of the lactone 2. On the other hand, at very low concentrations (10^{-3}M), an additional limiting factor is apparently side-reactions with residual water in the precursor and/or solvent.

These studies therefore support the hypothesis that reactions of the precursor or nonbenzyne intermediates are a major reason for the apparent failure of benzyne to react with thiophene in a Diels-Alder manner. Thus, if care is taken to minimize these competing reactions by the proper selection of precursors and conditions, thiophene can be an effective solution trap for benzyne. The influence of substituents on the scope of this reaction is presently under investigation.

ACKNOWLEDGEMENTS

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