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INTERCHANGE OF HYDROGEN AND OXYGEN ATOMS IN o-NITROTOLUENE AT HIGH TEMPERATURES

Ellis K. Fields

Research and Development Department
Amoco Chemicals Corporation
Whiting, Indiana

Seymour Meyerson

Research and Development Department
American Oil Company
Whiting, Indiana

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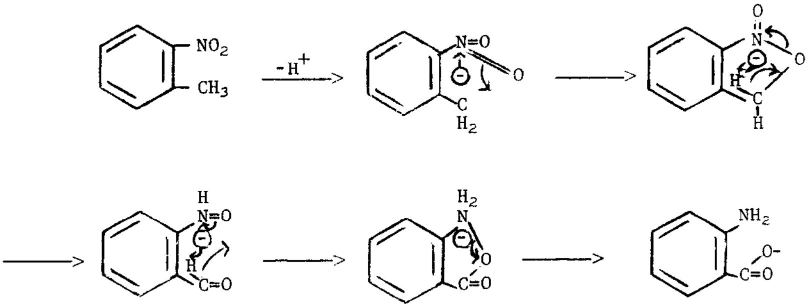
In a study of arylation by aromatic nitro compounds at high temperatures,[1] we had occasion to examine the reactions of _o_-nitrotoluene with benzene. A solution of 6.14 ml. (0.05 mole) of _o_-nitrotoluene in 8.88 ml. (0.1 mole) of benzene was passed through a Vycor tube, filled with Vycor chips, at 600° under dry nitrogen flowing at the rate of 20 cc./minute. The contact time was 16 seconds. Distillation of the products boiling below 165° left a residue of 5.3 g. which was analyzed by gas chromatography and low voltage (7.5 volts, uncorrected) mass spectrometry. The major components, accounting for 87% of the material, were aniline, _o_-cresol, and biphenyl in about the ratio 2:1:1.

By analogy to the reaction of nitrobenzene with benzene,[1] we had anticipated that _o_-nitrotoluene would give mainly _o_-methylbiphenyl and its dehydrogenation product, fluorene. These were indeed formed, but only in trace amounts. Evidently the favored process for _o_-nitrotoluene thermolysis involved reduction of the nitro- and loss of the methyl group.

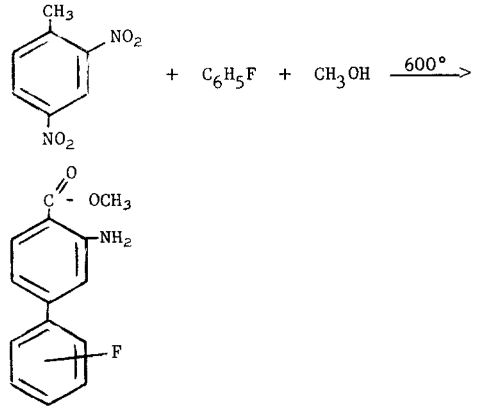
To clarify the mechanism, we pyrolyzed a solution of 0.05 mole of _o_-nitrotoluene in 0.5 mole of methanol at 600° with a contact time of 11 seconds. The main product, determined by gas chromatography, proved to be methyl anthranilate in 48 mole % yield. At high temperatures, therefore, _o_-nitrotoluene undergoes intramolecular oxidation and reduction to give anthranilic acid; in the absence of methanol to esterify and stabilize it, the carboxyl group is lost to yield aniline.[2]

A complex mixture of products containing _inter alia_ anthranil and anthranilic acid has resulted by treatment of _o_-nitrotoluene with concentrated alkali.[3] The mechanism seems therefore to involve formation of a carbanion species at the high temperature, followed by a series of hydrogen and oxygen shifts:



The proton and carbon or nitrogen anions are probably never separated to any extent, as the reaction occurs in the gas phase. Interchange of hydrogen and oxygen atoms has been postulated to account for the sequential loss of OH, CO, and HCN from labeled and unlabeled o-nitrotoluene under electron impact in the mass spectrometer[4]; the two processes thus resemble each other closely. Numerous examples of parallel behavior in pyrolysis and under electron impact have been found in other contexts.[5] Our high-temperature formation of anthranilic acid also resembles to some extent the thermal elimination of sulfur dioxide from o-methyldiarylsulfones to give diarylmethanes.[6]

Substituted methyl anthranilates result under the same conditions from o-nitrotoluenes containing nuclear substituents. Thus, 4-fluoro-2-nitrotoluene, 4-chloro-2-nitrotoluene, 3-nitro-o-xylene, and nitro-p-xylene gave methyl 4-fluoro-, 4-chloro-, 3-methyl- and 4-methylanthranilates respectively, in yields of about 35 mole %. 2,4-Dinitrotoluene with methanol and fluorobenzene gave a rather complex mixture, as was anticipated; however, among the products was an appreciable amount of the isomers of methyl 4-fluorophenylanthranilate:



A wide variety of substituted methyl anthranilates hitherto unknown or difficult to prepare can therefore be made in one step by our new synthesis from _o_-nitrotoluenes. We are presently investigating the high-temperature reactions of nitro compounds having ortho substituents other than methyl.

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