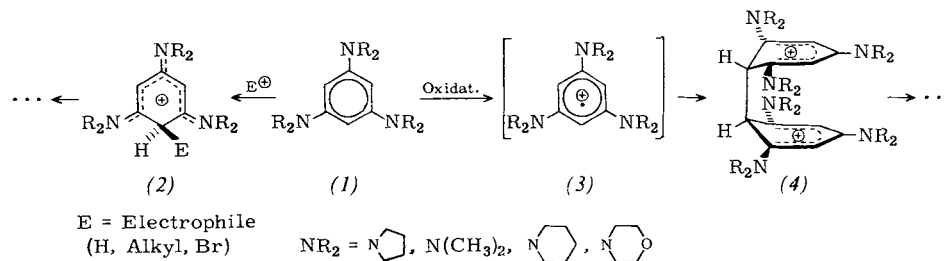


CONFERENCE REPORTS

Model Reactions for Electrophilic Substitution of Aromatic Compounds

By Franz Effenberger^[*]

Symmetrical triaminobenzenes are particularly suitable as model compounds for studying electrophilic aromatic reactions; due to the additive electron releasing influence of three mutually *meta* dialkylamino groups in (1), cationic intermediates are stabilized to such a degree that individual steps of electrophilic substitution can be separately studied. The stabilizing effect increases in the order morpholino < piperidino < dimethylamino < pyrrolidino. By HMO calculations, the mesomeric interaction of the individual amino groups with the



aromatic π system may be assessed quantitatively from the position of the $^1\text{H-NMR}$ ring proton signals if anisotropic effects are carefully eliminated.

The σ complexes (2) formed on protonation, alkylation, and bromination of tripyrrolidinobenzene prove to be isolable; in some cases, primary reaction at a dialkylamino nitrogen of (1) and subsequent rearrangement to (2) can be established. In contrast to the intermediates described by *Olah*, compounds (2) are true "Wheland intermediates", *i.e.* cationic analogs of the Meisenheimer complexes formed in the course of nucleophilic aromatic substitution.

Tris(dialkylamino)benzenes (1) may be oxidized readily; the isolable intermediates (4) are presumably formed by dimerization of (3). Spectra and model calculations offer unequivocal evidence for the "endo" conformation of (4); the preorientation thus indicated for dimerization of (3) is significant also with regard to the benzidine rearrangement.

[*] Prof. Dr. F. Effenberger
 Institut für Organische Chemie der Universität
 7 Stuttgart, Azenbergstrasse 14 (Germany)

In many cases the information gained from reactions of (1) can be successfully applied to the reactions of *N,N*-dialkylanilines. Although isolation of cationic intermediates is not feasible here under normal conditions, the product-determining steps may be influenced in a clearly defined way, based on the model concepts developed for (1). This principle is exemplified by the action of bromine on *N,N*-dialkylanilines and the reversibility of bromination of dialkylanilines.

Lecture at Tübingen on June 25, 1971 [VB 322 IE]
German version: *Angew. Chem.* 84, 37 (1972)