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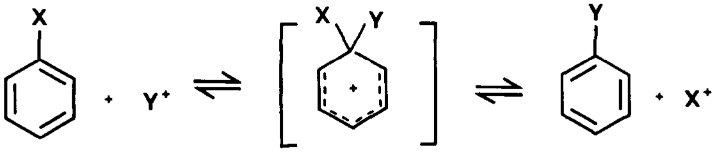
PROTODEALKYLATION OF BIS(AMINOPHENYL)METHANES

by Peter J. Whitman*, Floro F. Frulla,
George H. Temme, and Fred A. Stuber
Dow Chemical U.S.A., North Haven Laboratories
North Haven, Connecticut 06473

Abstract: Contrary to earlier reports, the formation of bis(aminophenyl)methanes in the acid-catalyzed condensation of aniline and formaldehyde can result in carbon-carbon bond cleavage proceeding via an ipso protodealkylation mechanism.

Ipso electrophilic aromatic substitution reactions have been the subject of several monographs and reviews.[1-4] It has been recognized that ipso attack is not unique, but merely another facet of the same reaction in which the leaving group is a moiety other than hydrogen, as illustrated in equation 1.



Equation 1

Several types of dealkylation reactions have been reported including replaclement of the alkyl group by hydrogen (protodealkylation),[5-7] halide (halodealkylation),[5,8-10] or nitro (nitrodealkylation).[11-13] Enhanced stabilization of the resultant carbonium ion, X^+ in equation 1, should result in increased ipso substitution.

As shown in Figure I, previous studies of the acid-catalyzed aniline-formaldehyde condensation have reported[14,15] that the carbon-nitrogen bonds in aminobenzylanilines 1 and 2 may break, but the transformation of aminobenzylanilines to bis(aminophenyl)methanes is irreversible, hence bis(aminophenyl)methanes are terminal products. Our results show that the final step is indeed reversible due to a carbon-carbon bond cleavage proceeding via an ipso attack.

Protodealkylation of para and ortho substituted bis(aminophenyl)methanes 4 and 5 were studied. The aminobenzyl cations 3a and 3b, the X^+ leaving group in equation 1, can react with aniline or other aromatic amines in the system. By heating with hydrochloric acid or acidic clays in excess aniline, isomerization was observed. Treatment of p,p'-bis(aminophenyl)methane 4 with aniline, water, and acids resulted in the formation of the

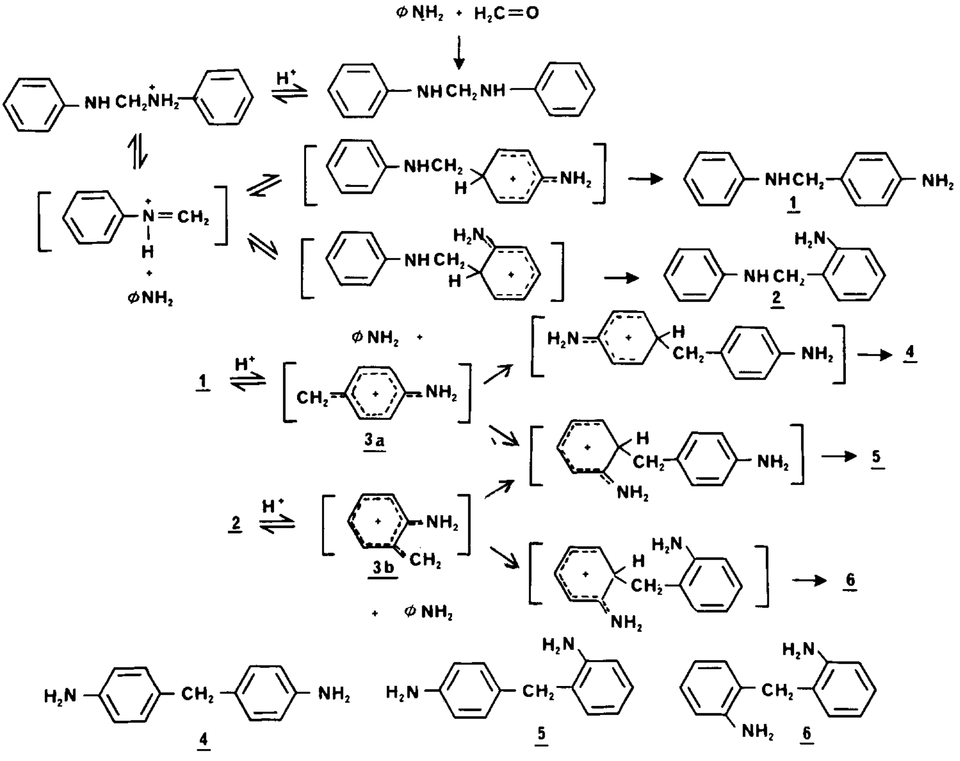


Figure I. Transformation of Aminals
to Aminobenzylanilines and Bis(aminophenyl)methanes

o,p'-isomer 5, along with higher oligomers. Likewise, similar treatment of 5 resulted in the slow formation of both 4 and the o,o'-isomer 6, as well as higher oligomers. This can be explained by an initial ipso protonation in the para or ortho positions, followed by elimination of cation 3a or 3b. Attack by the electrophile in a different position on the ring results in isomerization, according to Figure II. Protonation-deprotonation on the amine nitrogen atoms leads to no rearrangement. Best results were obtained with certain clay catalysts with small amounts of water. The p,p-isomer 4 was treated with Wyoming bentonite (IMC Corp.) in excess aniline containing 1% water (weight ratio; 4:catalyst:aniline=1.0:3.1:4.0) at 180°C for two hours. The diamine composition of the reaction mixture was 85% with an isomer ratio 4:5:6 = 38.4:57.4:2.2. A 15% yield of triamines and higher oligomers was obtained. Similar treatment of the o,p'-isomer 5 exhibited a much slower reaction, giving 99% diamines with an isomer ratio of

4:5:6: = 6.4:92.5:1.1 after 3.2 hours. Only 1% of triamines was obtained. Similar results were obtained with European montmorillonites (Sued-Chemie).

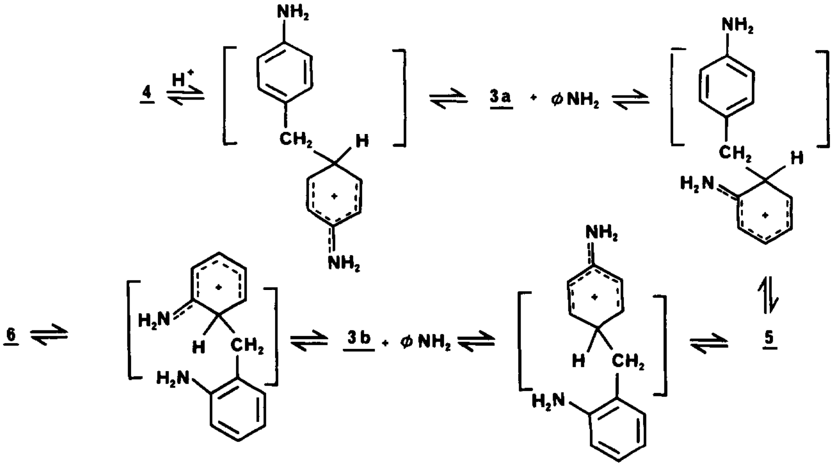
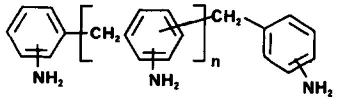
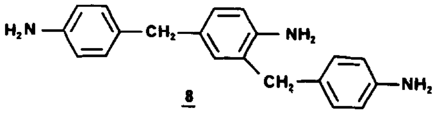


Figure II. Isomerization of Bis(aminophenyl)methanes

Recent studies have shown that reorganization of the oligomeric amines 7 in aniline takes place under a variety of conditions, giving diaminodiphenylmethanes enriched in the o,p-isomer.[16-21] Protodealkylation, involving an initial ipso C-protonation followed by loss of the aminobenzyl cation 3a or 3b is again a likely mechanism. A similar phenomenon has been observed with the triamine 2,4-bis(p-aminobenzyl)aniline 8 resulting in products derived from protodealkylation.



7; n≥1



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Thus, protodealkylation of bis(aminophenyl)methanes has been shown to proceed in positions para and ortho to the amine group. Isomerization or cracking results from this initial ipso attack.

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*Current address Upjohn Company, Fine Chemical Division, North Haven, CT 06473

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