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THE REACTION OF 2,3-DIAMINO-BUTADIENES WITH 1,2-DIIMMONIUM DIBROMIDES: A DIRECT SYNTHESIS OF 1,2,4-TRIAMINO BENZENES

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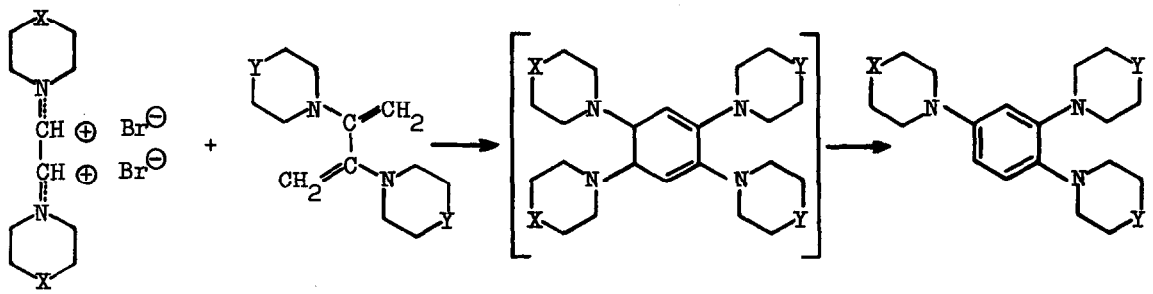
Summary. A new benzene ring synthesis is reported: 1,2-diimmonium dibromides react in mild conditions with 2,3-diamino-butadienes affording 1,2,4-triamino benzenes with yields of preparative interest.

The diimmonium dibromides 1, which are easy to prepare from 1,2-diamino-ethenes 2 by addition of bromine[1] or, more practically, by reaction of 1,1,2,2-tetraaminoethanes 3 with acetyl bromide[2], have proven to be useful intermediates for the preparation of some nitrogen-containing five-membered ring heterocycles such imidazoles[3], indoles[4] and pyrroles[5].

We now wish to report that these salts react with 2,3-diamino-butadienes[6] 4 yielding 1,2,4-triamino-benzenes 5 (40-70%). The reaction was carried out in dichloromethane at a temperature ranging between -30°C and -15°C and in the presence of a bimolecular amount of triethylamine.



1a : X = O
1b : X = CH_2
1c : X = NCH_3

4a : X = O
4b : X = CH_2

6

5

The products were isolated by standard procedures and their structure was assigned on the basis of analytical (C,H,N) and spectral data (IR, ^{1}H n.m.r. and mass spectrometry). In the table are summarized the amino-benzenes synthesized in the preliminary study.

The reaction probably proceeds via an unstable tetraamino-dihydrobenzene 6 which is the product of a double electrophilic attack of 1 upon the electron-rich carbon atoms of enamine 4.

Compound	X	Y	Yield[a)]	m.p. (°C)[b)]
5a	O	O	50	126 (lit[7] 130)
5b	CH_2	O	55	123-124
5c	N-CH_3	O	70	132
5d	O	CH_2	58	129-130
5e	CH_2	CH_2	46	105
5f	N-CH_3	CH_2	62	95

a) Of analytically pure compounds and based on enamine 3.

b) All products were recrystallized from diisopropylether.

At present, further work is in progress to explore the extension of the reaction to other electron-rich conjugated dienes.

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(5) Results to be published.

(6) 2,3-Diamino-butadienes 4a (b.p. 100-105/0.5 torr, m.p. 88°C) and 4b (b.p. 95-100/0.5 torr) were prepared by the method of H. Weingarten[8].

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