A Novel Synthesis of Diaminomethanes

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Diaminomethanes have been synthesized by reaction of 1,3-benzodioxole and 1,3-benzoxathiole with a double amount of sodium dialkyl and alkyl aryl amides.

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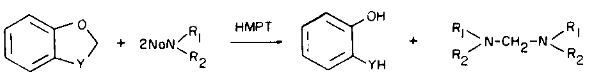
In previous research we have seen that sodium diethylamide cleaves ethereal and thioethereal bonds in alkyl aryl ethers and alkyl aryl sulfides to yield, respectively, phenols and benzenethiols (1,2).

The cleavage of both the C-O ethereal and the C-S thioethereal bonds prompted us to set up a novel synthesis of diaminomethanes using 1,3-benzodioxole (I) and 1,3-benzoxathiole (II). The reaction has been carried out treating the aforementioned heterocycles with a double molar amount of sodium amide (IIIa-e) in a mixture of benzene and hexamethylphosphoric triamide. All the products we obtained in fairly good yields (see Table).

Scheme



I Y = O
II Y = S

IIIa-e

IV Y = O
IV Y = S

VIa-e

a, $R_1 = R_2 = C_2H_5$
b, $R_1 = R_2 = n\text{-}C_3H_7$
c, $R_1 = CH_3$, $R_2 = C_6H_5$
d, $R_1 = C_2H_5$, $R_2 = C_6H_5$
e, $R_1 + R_2 = -(CH_2)_4-$

EXPERIMENTAL

General Procedure for the Preparation of Diaminomethanes (VIa-e).

To a well-stirred mixture of sodium hydride (80 mmoles) in dry benzene (15 ml) and hexamethylphosphoric triamide (80 mmoles) the amine (IIIa-e, H instead of Na) (80 mmoles) was added dropwise at 45° under nitrogen. After 30 minutes, the starting material (I or II) (40 mmoles) in dry benzene (6 ml) was added dropwise and the resulting mixture was heated under reflux for 24 hours. After cooling, the mixture was poured into 10% aqueous sodium hydroxide (100 ml) and steam distilled. The diaminomethane derivatives VIa-e were extracted from the aqueous mixture with diethyl ether and dried over sodium sulfate. The solvent was removed and the residue chromatographed on a neutral alumina column using benzene/petroleum ether (bp 40-60°) (1:4) as eluent.

Table

Starting Material	Amide	Products	Yield (%)	Bp/mm Hg, °C
I	IIIa	VIa	69	63-65/15 (a)
II	IIIa	VIa	77	
I	IIIb	VIb	65	77-78/2 (b)
II	IIIb	VIb	73	
I	IIIc	VIc	67	145-146/2 (c) mp 34-35°
II	IIIc	VIc	76	
I	IIId	VId	68	mp 77-78° (d)
II	IIId	VId	74	
I	IIIe	VIe	61	75-76/2 (e)
II	IIIe	VIe	68	

(a) Lit (3) bp 66-67/20 mm. (b) Lit (3) bp 66/0.6 mm. (c) Lit (4) bp 137-149/2 mm, mp 33-34°. (d) Lit (5) mp 79°. (e) Lit (6) bp 88/4.6 mm.

The glc analysis (conditions: 1 m × 0.2 cm column, 5% SE-52 on 80/100 chromosorb W) of the products indicated a purity of ≅98%. The products VIa-e were identified by comparison of their ir and ^{1}H nmr spectra with those of authentic samples (see Table).

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