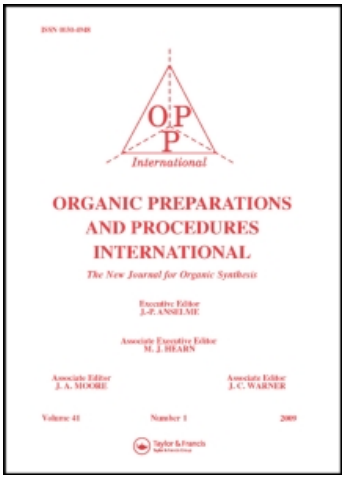

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NEW SYNTHESIS OF 2-AMINOBIPHENYLS

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NEW SYNTHESIS OF 2-AMINOBIPHENYLS

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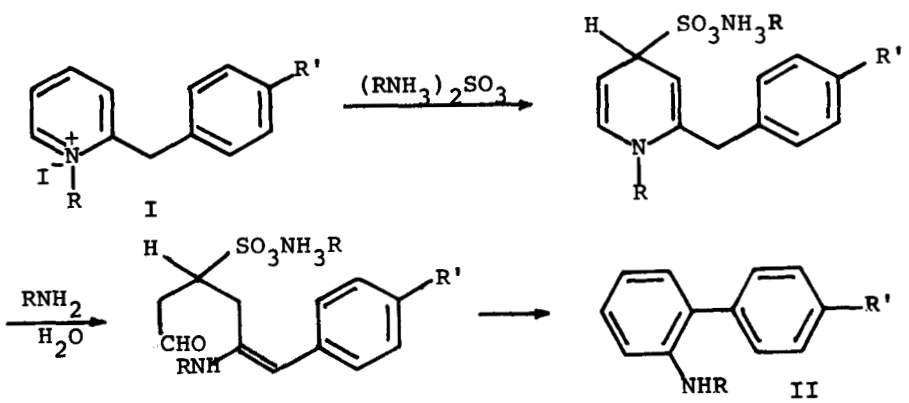
2-Aminobiphenyl is usually obtained by the reduction of 2-nitrobiphenyl.[1-4] Recently, we have discussed the ring opening and recyclization of 1,2-dimethylpyridinium salts to substituted N-methylanilines by the action of bases.[5-8] We now report that N-alkyl-2-benzylpyridinium salts (I)[9] recyclize to o-aminobiphenyl derivatives (II) by the action of aqueous alkylamine sulphite solution. Identification of the compounds was achieved on the basis of their NMR spectra and by the preparation of their N-acetyl derivatives III.

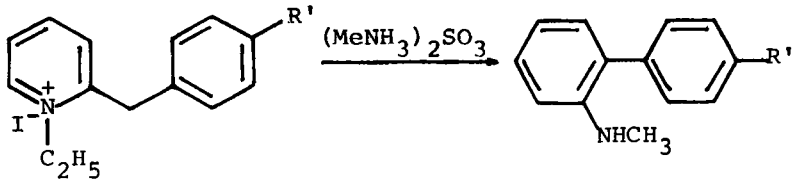


a) R = Me, R' = H b) R = Et, R' = H

c) R = Me, R' = AcO d) R = Me, R' = Et

† Deceased

When N-ethyl-2-benzylpyridinium iodide (Ib) and aqueous methylammonium sulphite solution are used as starting materials, this leads to exchange of the ethylamine by a methylamine group and 2-(N-methylamino)biphenyl (IIa) is obtained.



EXPERIMENTAL

The reaction products were shown to be single compounds by TLC (benzene as solvent). The NMR spectra were obtained on a Varian T-60 instrument for solutions in CCl_4 with hexamethyldisiloxane or tetramethylsilane as internal standard. Melting points are uncorrected.

1-Alkyl-2-benzylpyridinium Salts (I). General Procedure.- A mixture of 0.02 mol of 2-benzylpyridine or its derivative and methyl iodide (5.5 g, 0.03 mol) was allowed to stand at room temperature for one day. The yellow crystals formed were recrystallized from 3:1 ethanol-ether (see Table 1).

1-Ethyl-2-benzylpyridinium Iodide (Ib).- A mixture of 3.4 g. (0.02 mol) of 2-benzylpyridine and 4.7 g (0.03 mol) ethyl iodide was heated in a sealed tube at 100° for 1.5 hr, the product was recrystallized from ethanol-ether (3:1) to give 6.0 g (92%) of yellow crystals of IB (see Table 2).

Methylammonium Sulfite.- Gaseous sulfur dioxide was passed through 100 ml of a 25% aqueous solution of methylamine until the weight was increased by 50 g. The bisulfite produced was

mixed with twice its volume of 25% aqueous methylamine to produce methylammonium sulfite. Similarly ethylammonium sulfite can be obtained from aqueous ethylamine.

TABLE 1. 1-Alkyl-2-benzylpyridinium Iodides (I)

Cmpd	mp (°C)	Yield (%)	Elemental Analyses Calcd (Found) C	H	N
Ia	116-118[9]	95	-	-	-
Ib	140	92	51.71 (51.53)	4.96 (4.92)	4.31 (4.29)
Ic	165-167	82	48.78 (48.53)	4.33 (4.31)	3.79 (3.65)
Id	145-147	71	53.09 (53.00)	5.30 (5.12)	4.12 (4.10)

Ring Opening and Recyclization of 1-Alkyl-2-benzylpyridinium Salts (I) to 2-(N-Alkylamino)biphenyls (II). General Procedure.- Aqueous methylammonium sulfite (30 ml) was added to salt I (0.018 mol). The mixture was heated in a sealed tube at 150° for 20-25 hrs; the product was extracted with ether, dried over magnesium sulfate and chromatographed on silica gel (L 100/160 μ) using benzene as eluent. The benzene solution was dried and benzene removed under vacuum to give 2-(N-alkylamino)biphenyls (Table 2). For identification and analysis of liquid 2-(N-alkylamino)biphenyls, their acetyl derivatives were prepared by reaction with acetic anhydride or acetyl chloride (Table 3).

2-(N-Methylamino)biphenyl (IIa) from Ib.- A mixture of 0.018 mol of Ib and 30 ml of methylammonium sulfite solution was heated under the condition given in the general procedure to

afford IIa in 63% yield.

TABLE 2. 2-(Alkylamino)biphenyls (II)

Cmpd	Yield %	Rf	NMR Spectral Data
IIa	73	0.72	2.8 (s, N-CH), 3.9 (s, NH), 6.55-7.6 (aromatic)
IIb	68	0.82	1.1 (t, C-CH_3), 3.2 (q, N-CH_2), 4.0 (s, NH), 6.3-7.7 (aromatic)
IIc[a]	50	0.85	2.3 (s, $COCH_3$), 2.8 (s, N-CH_3), 3.2 (s, NH), 7.5-8.5 (aromatic)
IId	63	0.65	1.3 (t, C-CH_3), 2.6 (s, N-CH_3), 2.7 (q, C-CH_2), 3.8 (s, NH), 6.4-7.3 (aromatic)

a. mp. 136°, Anal. Calcd. for $C_{15}H_{15}NO$: C, 79.75; H, 6.45; N, 5.87
Found: C, 79.97; H, 6.70 N, 6.02

TABLE 3. Acetyl Derivatives of 2-(N-Alkylamino)biphenyls (III)

Cmpd	mp. (°C)	Analysis Calcd (Found) C	H	N
IIIa	98° (from EtOH)[10]	-	-	-
IIIb	90° (from EtOH)	80.33 (79.70)	7.11 (7.10)	5.85 (5.79)
IIId	80-82° (from C_6H_{14})	80.632 (80.05)	7.509 (7.57)	5.533 (5.39)

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