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### NEW SYNTHESIS OF 2-AMINOBIHENYLS

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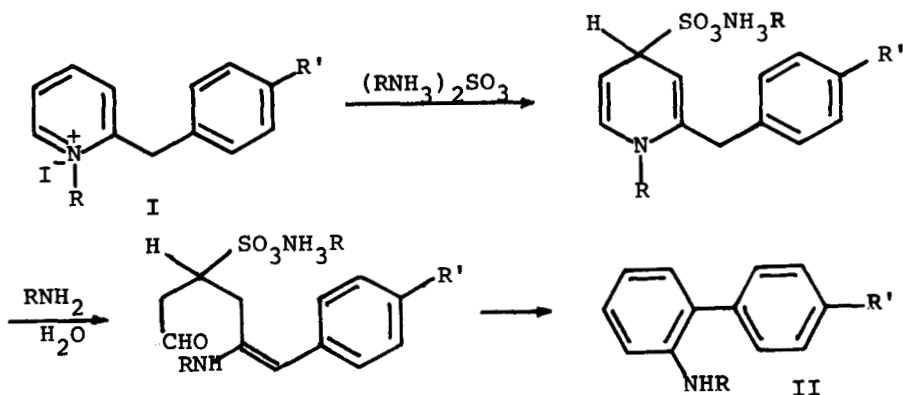
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NEW SYNTHESIS OF 2-AMINOBIPHENYLS

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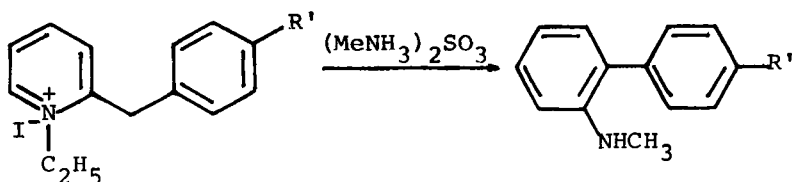
2-Aminobiphenyl is usually obtained by the reduction of 2-nitrobiphenyl.<sup>1-4</sup> Recently, we have discussed the ring opening and recyclization of 1,2-dimethylpyridinium salts to substituted N-methylanilines by the action of bases.<sup>5-8</sup> We now report that N-alkyl-2-benzylpyridinium salts (I)<sup>9</sup> 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

<sup>†</sup> 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  $\text{CCl}_4$  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  $100^\circ$  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 Sulphite.- 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              |
| Ia   | 116-118 <sup>9</sup> | 95        | -                  | -              | -              |
| Ib   | 140                  | 92        | 51.71<br>(51.53)   | 4.96<br>(4.92) | 4.31<br>(4.29) |
| Ic   | 165-167              | 82        | 48.78<br>(48.53)   | 4.33<br>(4.31) | 3.79<br>(3.65) |
| Id   | 145-147              | 71        | 53.09<br>(53.00)   | 5.30<br>(5.12) | 4.12<br>(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 <sub>3</sub> ), 3.2 (q, N-CH <sub>2</sub> ), 4.0 (s, NH), 6.3-7.7 (aromatic)                              |
| IIc <sup>a</sup> | 50      | 0.85 | 2.3 (s, COCH <sub>3</sub> ), 2.8 (s, N-CH <sub>3</sub> ), 3.2 (s, NH), 7.5-8.5 (aromatic)                              |
| IIId             | 63      | 0.65 | 1.3 (t, C-CH <sub>3</sub> ), 2.6 (s, N-CH <sub>3</sub> ), 2.7 (q, C-CH <sub>2</sub> ), 3.8 (s, NH), 6.4-7.3 (aromatic) |

a. mp. 136°, Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>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°<br>(from EtOH) <sup>10</sup>                 | -                 | -               | -               |
| IIIb  | 90°<br>(from EtOH)                               | 80.33<br>(79.70)  | 7.11<br>(7.10)  | 5.85<br>(5.79)  |
| IIIId | 80-82°<br>(from C <sub>6</sub> H <sub>14</sub> ) | 80.632<br>(80.05) | 7.509<br>(7.57) | 5.533<br>(5.39) |

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