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A NEW APPROACH TO THE DIBENZ[b,f]AZEPINE AND [b,f]OXEPINE SYSTEM

by Ernst D. Bergmann, I. Shahak and Z. Aizenshtat

Department of Organic Chemistry, Hebrew University, Jerusalem

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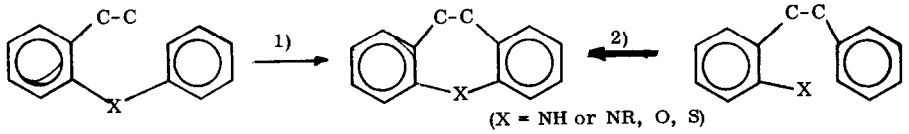
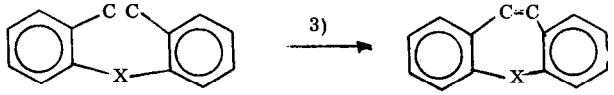
The systems of dibenz[b,f]azepine, dibenz[b,f]oxepine and dibenzo[b,f]thiepine have been synthesized until now mainly by two general methods symbolized by the following schemes:



(X = NH or NR, O, S)

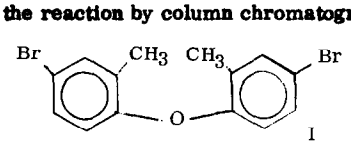
The third possibility, symbolized by

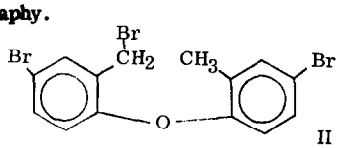


has, on the whole, failed so far (1,2), and only recently have Bestmann and co-workers (3) succeeded in making the unsaturated analogs of such systems according to this scheme.

We wish to report a general method, utilizing scheme 3, for the synthesis of 10,11-dihydro-N-acetyl-dibenz[b,f]azepine and 10,11-dihydrodibenz[b,f]oxepine. 4,4'-Dibromo-2,2'dimethyldiphenyl ether (I), obtained from the 2,2'-dimethyl compound (4) and bromine in glacial acetic acid (yield 94%; b.p. 170-175° (1 mm)) gave with N-bromosuccinimide in the presence of benzoyl peroxide only the tribromo compound (II) (80%; m.p. 126° (from hexane)). However, the reaction of 2,2'-dimethyldiphenyl ether with a large excess (6 mole) of NBS in the presence of the peroxide gave 4,4'-dibromo-2,2'-di(bromomethyl)-diphenyl ether (III) (45%; m.p. 178° (from cyclohexane)). Treatment of the latter with 6 mole of phenyl lithium gave a 66.5% yield of the unknown 10,11-dihydrodibenzo[b,f]oxepine (IV) (m.p. 154°, from benzene-hexane) and 2.3% of 10,11-dihydro-2,8-dibromodibenzo[b,f]oxepine (V) (m.p. 210°); they could be separated in pure form by column chromatography on alumina, benzene-ether (95:5) serving as eluent.

When analogously N-acetyl-2,2'-dimethyldiphenylamine (VI) (5) (b.p. 149-156° (1 mm); m.p. 82-83°) was treated with NBS, the 2,2'-di(bromomethyl)-derivative (VII) was not stable enough to be isolated in pure form; it was directly treated with an excess of phenyl lithium and gave a 66.5% yield of N-acetyl-10,11-dihydrodibenz [b,f] azepine (m.p. 96°) (VIII) (6) and a 3.5% yield of N-acetyl-dibenz [b,f] azepine (XI) (m.p. 120°) (6); they could be separated from each other and from biphenyl formed in the reaction by column chromatography.


I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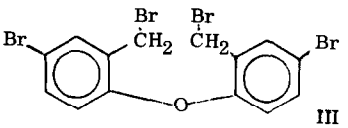
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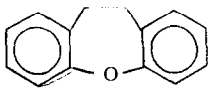
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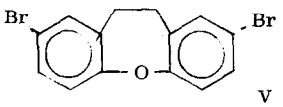
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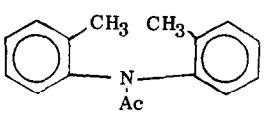
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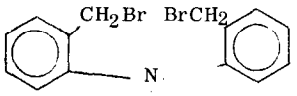
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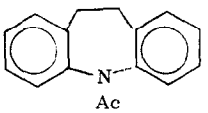
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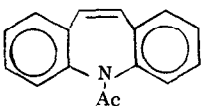
IX

The n.m.r. spectra of 2,2'-dimethyl-diphenylether and VI show an interesting difference: in the former, there exists free rotation around the O-(o-tolyl) bonds (singlet at $\delta = 2.3$), whilst in VI a doublet appears at $\delta = 2.2$, indicating steric repression of the free rotation through the acyl group, even at room temperature. This difference in the spectra reflects the differences easily recognised in models of the two compounds.

The analyses of all compounds were satisfactory. A detailed paper will appear in due course.

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