

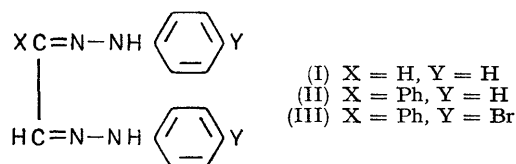
## The Monoacetyl Derivatives of Phenylglyoxal Bisarylhydrazones

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Comparison of the  $^1\text{H}$  n.m.r. spectra of phenylglyoxal bisarylhydrazones and their monoacetyl derivatives in hexamethylphosphoramide shows that acetylation occurs at the NH group of the  $-\text{CH}=\text{N}-\text{NHAr}$  system, and hence that this NH group is that involved in intermolecular rather than intramolecular hydrogen bonding in the phenylglyoxal bisarylhydrazone.

PHENYLGLYOXAL BISARYLHYDRAZONES form only monoacetyl derivatives under conditions where most glyoxal bishydrazones are easily di-acetylated.<sup>1</sup> The determination of which NH system is acetylated provides a good example of the utility of n.m.r. solvent effects.

We recorded the 60 MHz  $^1\text{H}$  n.m.r. spectra of glyoxal bisphenylhydrazone (I), phenylglyoxal bisphenylhydrazone (II), phenylglyoxal bis-*p*-bromophenylhydrazone (III), and the monoacetyl derivatives of (II) and (III) in a number of solvents in order to discover a



medium in which the two NH groups gave separate signals. Hexamethylphosphoramide (HMPA) had the desired properties, and the spectra of *ca.* 10% solutions in this solvent are given in the Table.

$^1\text{H}$  Chemical shifts ( $\delta$  values) of phenylhydrazones in HMPA

Compound	NH	CH	ArH
Glyoxal bisphenylhydrazone (I)	10.8, 10.3	7.8	8.1—6.8
Phenylglyoxal bisphenylhydrazone (II)	13.3, 12.1	8.7	8.1—6.8
<i>N</i> -Acetylphenylglyoxal bisphenylhydrazone	13.3	7.8	8.3—7.0
Phenylglyoxal bis- <i>p</i> -bromophenylhydrazone (III)	13.1, 12.2	8.6	8.1—7.0
<i>N</i> -Acetylphenylglyoxal bis- <i>p</i> -bromophenylhydrazone	12.9	7.6	8.1—7.3

The three low-field signals observed for the bishydrazones (I)—(III) are assigned, in order of increasing

<sup>1</sup> H. El Khadem, M. M. El-Sadik, and M. H. Meshreki, *J. Chem. Soc. (C)*, 1968, 2097.

field strength, to the intramolecularly hydrogen-bonded NH, the intermolecularly hydrogen-bonded NH, and the methine proton. This assignment is based on the similar appearance of three signals in the low-field portion of spectra of glyoxal bisphenylhydrazone in acetone and in dimethyl sulphoxide, and on previous assignments<sup>2</sup> for the low-field signals in the spectra of solutions of sugar osazones in dimethyl sulphoxide. The NH resonances are distinguished from those due to CH by their greater width, and the two NH signals were differentiated by the change in chemical shift experienced on dropwise addition of HMPA to a solution of the hydrazone in [ $^2\text{H}$ ]chloroform. When sufficient HMPA has been added to separate all three signals, further addition of HMPA leaves the lowest field signal little changed, whereas the other two signals are strongly shifted to low field. The breaking of intermolecular hydrogen bonds is thus accompanied by a downfield shift of the signal due to the methine proton. It is evident that this methine proton in compounds (II) and (III) is adjacent to the intermolecularly hydrogen-bonded NH, which one would expect to be replaced on acetylation.

This is confirmed by the spectra of the acetyl derivatives of (II) and (III) in which the methine proton signal is strongly shifted to higher field. A shift of this magnitude would be observed only if *N*-acetylation of the  $-\text{CH}=\text{N}-\text{NHAr}$  system occurred. This result agrees with the previous assumption that the other NH proton would form the intramolecular hydrogen bond preferentially and hence be less reactive.

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<sup>2</sup> H. El Khadem, M. L. Wolfrom, and D. Horton, *J. Org. Chem.*, 1965, **30**, 838.