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NUCLEAR MAGNETIC RESONANCE EVIDENCE ON ANIONIC ADDUCT BETWEEN METHOXIDE ION AND CARBON-NITROGEN DOUBLE BOND

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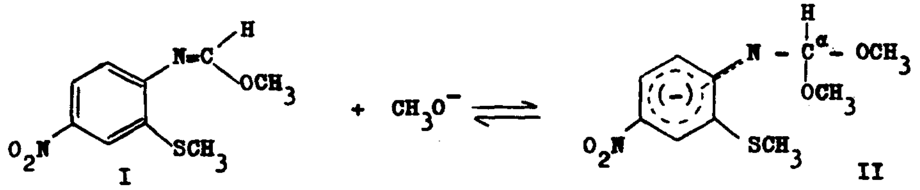
While anionic adducts originated by action of bases on C=C bond have been characterized in several cases,[1] the corresponding adducts on C=N bond have been only postulated as intermediates in the base-catalyzed addition of nucleophiles to Shiff bases[2].

The present report gives ^{1}H n.m.r.. evidence on the anionic adduct (II) arising from the interaction between methoxide ion and 2-methoxymethyleneamino -5-nitrophenyl methyl sulphide (I)[3] in DMSO at room temperature.



The addition of anhydrous potassium methoxide to a solution of I in DMSO produces immediately a deep red colour. When less than one equivalent of MeOK is added, the ^{1}H n.m.r. spectrum of the red mixture shows a new set of bands together with those of I. An additional amount of methoxide ion increases the new resonances and decreases those of the starting compound.

The resonances of (I) can be assigned as follows: τ(60MHz): 1.78 (2H, m, 4H- and 6-H); 1.9 (1H, s, N=CH); 2.73 (1H, d.d., 3-H); 6.20 (3H, s, -OMe) and 7.50 (3H, s, -SMe). Those of the red species consist of: d.d. at 2.27 τ (1H), d. at 3.92 τ (1H), s. at 4.53 τ (1H), s. at 6.73 τ (6H), s. at 7.78 τ (3H). The assignments of the new set of bands (all shifted at higher field as we would expect for an anionic adduct) can be made on the basis of the coupling state and relative intensities, and with the aid of the compound (I)deuteriated at the formiminic carbon. The multiplets at 2.27, 2.50 and 3.92 τ are assigned respectively to 4-H, 6-H and 3-H, while singlets at 4.53, 6.73 and 7.78 τ are assigned respectively to H_α, to two equivalent -OMe and to -SMe groups. The presence of two equivalent methoxy groups and the shift value of H_α are very consistent with the anionic adduct (II). This hypothesis is also strongly supported by comparison with the proton chemical shift (4.33 τ) reported by Ogata and Kawasaki for the $>N{-}\overset{|}{\underset{|}{C}}{-}H$ hydrogen in the addition product of methanol to N-benzylidene-m-nitroaniline.

The red mixture is stable for several hours when the DMSO is rigorously dried and MeOK is free of methanol. After neutralization of the base it gives back the starting material without any products arising from N-C cleavage or from nucleophilic attack to the $-SCH_3$ group carbon.

References

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