Observation of Dynamic Nuclear Polarization in the Reaction of *N*,*N*-Dimethylaniline Oxide with Acetic Anhydride

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The mechanism of the reaction of *N*,*N*-dimethylaniline oxide (I) with acetic anhydride has been a subject of controversy.[1] Although the free radical pair mechanism seems to have been concluded by an ellegant ^{18}O-labelling experiment,[2] recent findings that 3,3-sigmatropic shift predominates in scrambling the oxygen atoms of acetyl peroxide,[3] and that even 1,3-sigmatropic rearrangement is operative in heteroatomic systems[4] prompted the present authors to reconsider these mechanistic possibilities[5] for the reaction of I to give *o*-acetoxy-*N*,*N*-dimethylaniline (II). A method of detecting the chemically induced dynamic nuclear polarization (CIDNP)[6] in the NMR spectrum of the reaction mixture has been employed as an operational test.

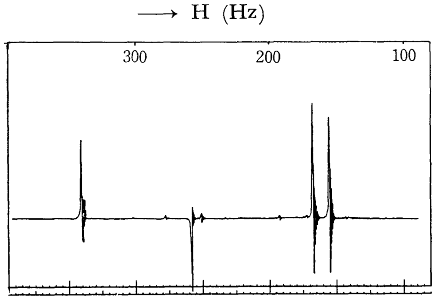

Fig. 1. The NMR spectrum of a mixture of I and acetic anhydride in benzene.

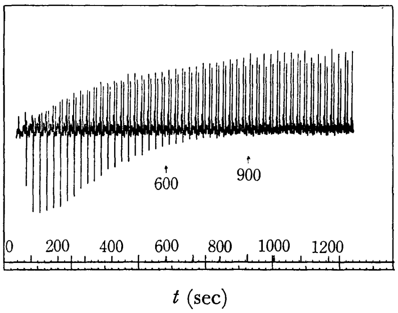

Fig. 2. Plot of signal intensities *vs*. time. The upper envelopes represent the formation of II and *N*-methylacetanilide, while the lower one demonstrates the CIDNP in III.

In a typical run, 32 mg of I was dissolved in a solution of 58 mg of acetic anhydride in 0.5 m*l* of benzene. The NMR trace obtained on a Varian HA 100 D spectrometer at 60 sec after mixing is reproduced in Fig. 1. In the course of the reaction which could be followed by decrease of the *N*-methyl signal at 341 Hz of I and was completed in 30 min at room temperature, a strong emission of radiation was observed at 258 Hz which decayed as shown in Fig. 2. Peaks at 196, 251 and 280 Hz increased exponentially with the progress of the reaction. It was found by comparison with the spectra in benzene of the authentic samples that the origin of the emitting line was the *N*-methyl protons of *N*,*N*-dimethylaniline (III) formed in 5% yield. Similarly the absorption peaks were unambiguously assigned to the methyl protons of II and *N*-methylacetanilide. Under no circumstances was observed any sign of either emission or enhanced absorption for these signals of the main reaction products. Thus the evidence is not in favor of the intermediacy of the free radical pair for the formation of II.[2] It might be argued that in the intimate radical pair in the solvent cage the singlet spin correlation between the two fragments will be kept throughout the rearrangement and there will be no chance of dynamic nuclear polarization. Mechanistically, however, the situation is indistinguishable from, and had better be described as, 1,3- and 3,3-sigmatropic rearrangements.

On the other hand, it was confirmed by the observation of CIDNP that III is indeed formed by a free radical reaction[7] and is independent of the rearrangement to give II.

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