Tetrahedron. Vol. 25, pp. 4873 to 4874. Pergamon Press 1969. Printed in Great Britain

NMR DEMONSTRATION OF THE REARRANGEMENT OF ^{15}N-LABELLED *p*-ANISOLEDIAZONIUM ION*

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(*Received in USA 26 April* 1969; *Received in the UK for publication* 16 *June* 1969)

Abstract—The conversion of p-$CH_3OC_6H_4N_2^+$ to the hydrazine and then to the benzaldehyde hydrazone gave a stable substance in which the proton NMR could be used to locate a ^{15}N label. In contrast to an earlier study on benzenediazonium ion by a similar method, this analysis showed that the α-^{15}N label in the diazonium salt migrates during hydrolysis to the β position to about the extent indicated by a degradative method.

THE observation[1] of the rearrangement of ^{15}N labelled benzenediazomium ion was questioned in a study using thd change in NMR spectrum of a phenyl hydrazone on ^{15}N substitution, which failed to detect any rearrangement of benzenediazonium-α-^{15}N ion accompanying hydrolysis.[2] However, the original work, which was based upon a degradation of the diazonium salt with azide ion,[3] has been extended with studies on the kinetic order, substituent effects, and temperature dependence.[4] The possibility of an experimental error in the degradation became correspondingly less, and the existence of the reaction hardly seems open to question. The disagreement between the two methods of analysis for position of ^{15}N is nevertheless vexing, and we have therefore used a NMR analysis similar to that of Bose and Kugajevsky[2] to study the possible rearrangement of *p*-methoxybenzenediazomium-α-^{15}N, reaction (1). The *p*-methoxy compound was chosen because the study by the other method showed that it rearranged more than the unsubstituted compound.[4a]

$$p\text{-}CH_3OC_6H_4\text{—}{}^{15}\overset{+}{N}\equiv N \rightarrow p\text{-}CH_3OC_6H_4\text{—}\overset{+}{N}\equiv{}^{15}N$$

EXPERIMENTAL

p-*Methoxybenzenediazonium ion*-α-^{15}N *fluoborate*. This material was prepared exactly as described before[4b] except that the ^{15}N content was higher (>98%).

p-*Methoxyphenylhydrazone of benzaldehyde*. The diazonium salt was reduced with $SnCl_2$ in ethanolic HCl,[5] and the resulting soln was directly treated with benzaldehyde, precipitating the hydrazone. After recrystallization from EtOH, it had m.p. 121–123° (lit.[6] 123°), although it decomposed perceptibly over 105°.

The NMR spectrum of the hydrazone I. In ordinary DMSO soln at 60m Hertz, I showed a complex multiplet, δ 6·8–7·8 (from TMS) assigned to the aromatic protons *b*, a sharp singlet, δ 3·72, assigned to the OMe protons *a*, a broad singlet (half width ca. 9 Hz), δ 10·1 assigned to the NH proton *c*, and a fairly sharp singlet, δ 7·87, assigned the benzal proton *d*.

$$p\text{-}\overset{a}{CH_3O}\overset{b}{C_6H_4}\overset{c}{NH}N{=}\overset{d}{CH}\overset{b}{C_6H_5}$$

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[*] This is Part XVI in the series *The Reaction of Diazonium Salts with Nucleophiles*; Part XV, E. S. Lewis, R. E. Holliday, and L. D. Hartung, *J. Am. Chem. Soc.* **91**, 430 (1969).

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The assignment of the important proton *c* was confirmed in two ways. When the hydrazone was made by reduction of diazonium salt in D_2O, the peak at 10·1 showed a major loss of intensity. When the hydrazone was made by reduction of *p*-methoxybenzenediazonium-α-^{15}N, the peak at δ 10·1 was replaced by a sharp doublet ($J_{^{15}NH}$ = 91 Hz) and the peak at δ 7·87 was replaced by a sharp doublet ($J_{^{15}NH}$ = 6·5 Hz). One of the peaks in the aromatic group (*b*) was also slightly split; presumably it was one if the *ortho* hydrogens, but further assignment was not attempted. In the α-^{15}N compound, there was a small residual peak at δ 10·1 amounting to about 2% of the protons in the split peak. This may have been due to some unlabelled I, to some labelled I which had been rearranged on storage, or to an impurity. It did not disappear on recrystallization.

Partial hydrolysis of diazonium salt. The diazonium salt was dissolved in 0·01 M sulfuric acid and heated as before[6b] to 80% hydrolysis at 90°. The resulting soln was concentrated at 33° in a rotary evaporator in the dark to prevent photolysis, then converted as above to the hydrazone. The extent of hydrolysis was computed from the rate constants, neglecting the small ^{15}N isotope effect.[1,7]

RESULTS AND DISCUSSION

The NMR of benzaldehyde *p*-methoxyphenylhydrazone made from the labelled diazonium salt after 80% hydrolysis differed from that made from the original labelled diazonium salt in the peak centred at 10·1 δ. This contained both the sharp peaks split by the ^{15}N and a larger central peak. The magnitude of this central peak was estimated by from two different spectra. One was an accumulation of 49 scans on a Varian A-60 spectrometer, using the Varian 1024 computer,* and the electronic integrator, a planimeter intergration and a trapezoid rule integration showed it to have 5·1% of the area of the major split peaks. The spectrum was also taken on the more sensitive Varian HA100 spectrometer with a single scan, which showed an area 7·3% of the main peaks (by trapezoid rule or planimeter intergration). The latter spectrum also showed a small splitting of the central peak of questionable significance. If real, it suggests a coupling from the β-^{15}N to the proton on the α-nitrogen with $J = 3$ Hz.† The stability of the A-60 was not sufficient to show the splitting after enough scans to bring it well above noise. The presence of the central peak was clearly visible on a single A-60 scan, however.

The values of 5·1 and 7·3% rearrangement are in satisfactory agreement with the value of 5·82% from the degradative experiments.[4a] We find no source of the disagreement on the unsubstituted compound,[2] except to note that we would have had difficulty seeing a third as much rearrangement with our NMR instrument, which would be necessary on this compound to detect the rearrangement. Our earlier explanation that the splitting by the β-^{15}N was sufficient to cause the spectrum to be lost is untenable; the very uncertain value of $J_{\beta^{15}N=H}$ = 3 Hz would have caused no difficulty and is in a reasonable range for published values.[8]

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* This instrument was purchased with a National Science Foundation Research Equipment Grant to the Chemistry Department of Rice University, which we acknowledge with thanks.

† We thank Professor M. R. Willcott and the University of Houston Chemistry Department for this spectrum.