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N.M.R. SPECTRA OF N-NITROSOAMINES AND CARBONIUM IONS

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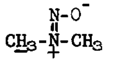
A recent problem of product identification (1) led us to obtain n.m.r. data for some model N-nitrosoamines, but certain features of the data prompted an extension of the scope of our inquiry. Coincident with our collection of data, an excellent paper analyzing n.m.r. data for several acyclic N-nitrosoamines appeared (2). The juxtaposition of that paper (2) and another on acyl cations (3) leads us to call attention at this time to a potentially useful correlation that has not, to our knowledge, been pointed out before and is responsible in part for our extended interest in N-nitrosoamines.

The chemical shifts of hydrogen in carbonium ions (4), particularly acyl cations (3), and in N-nitrosoamines (2) are nearly the same. Some examples are quoted here; numbers beneath the formulas refer to chemical shifts of the hydrogens indicated, in p.p.m. downfield from tetramethylsilane (TMS).

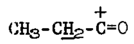
$$C\underline{H}_3-\overset{+}{C}=O$$

3.93 (3)



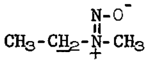
$$C\underline{H}_3-\underset{+}{\overset{N-O^-}{\overset{\|}{N}}}-CH_3$$

3.82 (2)



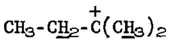
$CH_3\text{-}C\underline{H_2}\text{-}\overset{+}{C}{=}O$

4.06 (3)



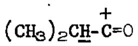
$CH_3\text{-}C\underline{H_2}\text{-}\overset{\overset{\text{N-O}^-}{\|}}{\underset{+}{N}}\text{-}CH_3$

4.15 (2)



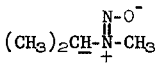
$CH_3\text{-}C\underline{H_2}\text{-}\overset{+}{C}(C\underline{H_3})_2$

4.90 (5) 4.50 (5)



$(CH_3)_2C\underline{H}\text{-}\overset{+}{C}{=}O$

4.23 (3)
4.33 (6)



$(CH_3)_2C\underline{H}\text{-}\overset{\overset{\text{N-O}^-}{\|}}{\underset{+}{N}}\text{-}CH_3$

4.85 (2)

Although the evidence for the existence of carbon cations is now compelling (3-6), the experimental conditions for studying them are not convenient (oleum, SbF_5 or SO_2 solvent) and sometimes promote extensive rearrangement. *N*-nitrosoamines are easily prepared from secondary amines without danger of skeletal rearrangements, and n.m.r. studies in a variety of solvents can be made (2). With the electron-deficient atom being trigonal in both species, *N*-nitrosoamines may serve as useful models for n.m.r. studies of carbonium ions under conditions or with structures not suitable for the carbonium ions themselves. Although hyperconjugation may be important for carbonium ions, expectations of such contributions in *N*-nitrosoamines are not reasonable. Larger hyperconjugative contributions from CH_3 than from CH_2 and CH may account for the opposite relative positions of the chemical shifts of CH_3 on one hand and CH_2 and CH on the other in acyl cations and *N*-nitrosoamines.

We have included in our study (7) some cyclic compounds for which n.m.r. data have not been reported. Adjacent CH_2 hydrogens in *N*-nitrosomorpholine (8) are detected at 4.20 (*trans* (2)) and 3.67 (*cis* (2)) p.p.m., those in *N*-nitroso-3-azabicyclo[3.2.2]nonane (9) at 4.43 (*trans* (2)) and 3.82 (*cis* (2)) p.p.m. downfield from TMS (benzene solvent). These last signals are farther downfield than those reported for any other all-aliphatic *N*-nitrosoamine (2), suggesting that the bicyclononane framework particularly favors contributions from the dipolar structure $>\overset{+}{N}=N\diagdown_{O}^{-}$. We might expect similar influence on carbonium ion formation and predict rapid ionization of 3-substituted-bicyclo[3.2.2] nonanes.

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(7) A Varian HR-60 n.m.r. instrument was used. We express our appreciation to Mr. George Sexton and Mr. Ralph Seab of these laboratories for technical assistance in obtaining the data.

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(9) Y. L. Chow, *Tetrahedron Letters*, 2333 (1964), mentions this compound without description. Our sample was poorly crystalline and waxy even after several recrystallizations and vacuum sublimations, but it gave satisfactory analyses; m.p. imprecise, 166.5-168.5°.