Nuclear Magnetic Resonance Investigation of Restricted Rotation of Some Vinylogous Amides

By JANUSZ DABROWSKI* and LECH KOZERSKI

(*Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw* 42)

OUR previous i.r. data[1,2] showed that different types of amide vinylogues contain a mixture of the s-*cis* and s-*trans* forms, due to restricted rotation around the C–C bond in the O=C—C=C—N system. Several related papers have recently been published on vinylogous amides[3a] amides,[3b] 2-furanaldehyde,[3c] and acryl fluoride.[3d] Other investigators[4,6] reported n.m.r. data on restricted rotation around the C–N bond in *NN*-disubstituted β-aminoacroleins containing the same structural element, whereas no sign of the s-*cis*–s-*trans* isomerism was observed.

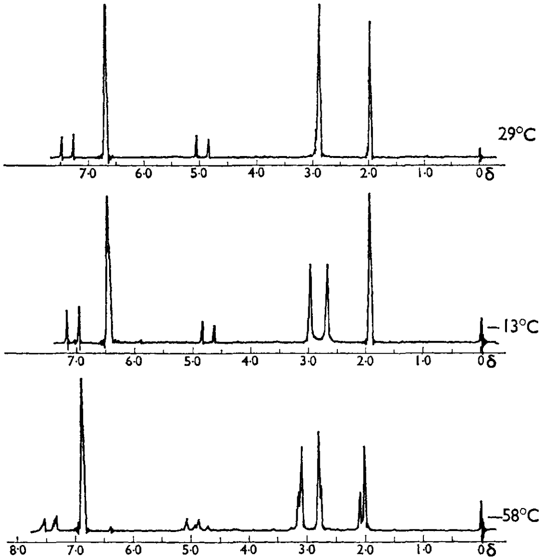


FIGURE 1. *Effect of temperature on the n.m.r. spectrum of 4-dimethylaminobut-3-en-2-one in trichloroethylene* (1M *solution*)

Both types of restricted rotation are shown to occur simultaneously in 4-dimethylaminobut-3-en-2-one (I), while only the s-*cis*–s-*trans* isomerism can be detected in 4-methylaminobut-3-en-2-one (II) (see Scheme) and 4-aminobut-3-en-2-one (III). There are sharp signals for all protons in the spectrum of (I) recorded at 29° (the temperature of the probe of the Varian HR-60 spectrometer), which points to rapid rotation in all parts of the molecule (Figure 1). At −13° the signals of the two *N*-methyl groups appear separately at δ 2·68 and 2·98 (Me_4Si as internal reference) due to lowering of the rotation rate around the C–N bond. At −60° all signals are additionally split because the rotation around the single C–C bond in the O=C—C=C system is frozen. The populations of rotamers change within wide limits when solvents of different polarity are used.

With molecules containing bulky substituents at the carbonyl group no appreciable amount of the s-*trans* rotamer exists at room temperatures.[1] The n.m.r. spectrum of 1-dimethylamino-4,4-dimethylpent-1-en-3-one shows that this is also

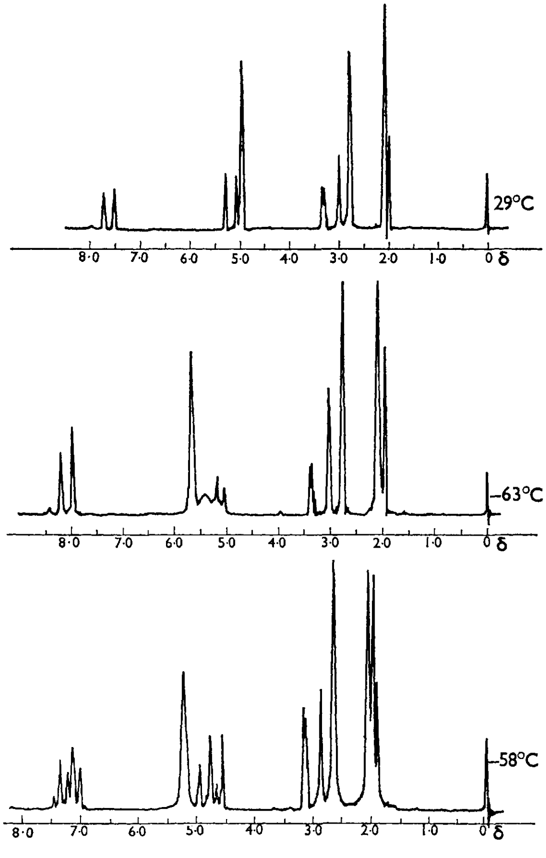
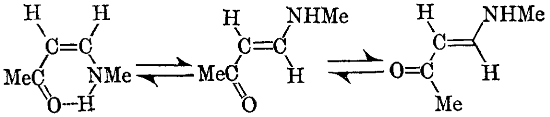


FIGURE 2. *Effect of temperature on the n.m.r. spectrum of 4-methylaminobut-3-en-2-one in* [$'H_4$]*methanol* (1M *solution*)

true at −60°, both in trichloroethylene and in [$^2H_4$]methanol solutions.

The spectrum of (II) is more complicated due to the admixture of the *cis*-isomer and the spin–spin coupling with the N-H proton. The latter disadvantage can easily be eliminated by using deuteriating solvents. The peaks of the *trans*-isomer were identified on the basis of the coupling constant of the *trans*-olefinic protons and the integration of all signals. The sharp peak at δ 2·08 in the spectrum recorded at 29° is assigned to COMe protons of the *trans*-isomer (Figure 2); it is split into two components of comparable intensity at −60°. In this case the s-*cis*–s-*trans* equilibrium also depends on the polarity of the solvent used. The N–Me signal is not split even at −60°; this may be accounted for either by a rapid rotation or a preferential existence of one of the C–NHMe rotamers.



SCHEME

Similarly, the spectrum of (III) recorded at room temperature exhibits one methyl signal of the *cis*-isomer at δ 2·00, and another at δ 2·05, due to the *trans*-isomer. At −60° rotation around the C–C bond is slow resulting in a splitting of the latter signal into two components, one of them being overlapped by the strong methyl signal of the *cis*-isomer.

It should be noted that with the vinylogues of acyl chlorides, *e.g.* 4-chlorobut-3-en-2-one lifetimes at −60° are too short for the s-*cis* and s-*trans* rotamers to be observable in n.m.r. although there was clear i.r. evidence[6] for their occurrence, even at elevated temperatures.

The different behaviour of the two types of vinylogue of acid derivatives is obviously due to a highly increased C–C bond order in amide vinylogues.

(*Received, March 1st,* 1968; *Com.* 279.)

---

[1] J. Dabrowski and K. Kamieńska-Trela, *Spectrochim. Acta*, 1966, **22**, 211; *Roczniki Chem.*, 1966, **40**, 831.

[2] J. Dabrowski and U. Dąbrowska, 9th European Congress on Molecular Spectroscopy, Madrid, September, 1967.

[3] (*a*) R. Parry, *Chem. Comm.*, 1967, 1294; (*b*) T. H. Siddall, tert., *Naturwiss.*, 1966, **53**, 502; (*c*) K. Dahlqvist and S. Forsén, *J. Phys. Chem.*, 1965, **69**, 4062; (*d*) D. F. Koster, *J. Amer. Chem. Soc.*, 1966, **88**, 5067.

[4] H. E. A. Kramer and Gompper, *Z. phys. Chem.* (*Frankfurt*), 1964, **43**, 242, 349; 1965, **44**, 82.

[5] M. Martin and G. Martin, *Compt. rend.*, 1963, **256**, 403.

[6] J. Dąbrowski and J. Terpiński, *J. Org. Chem.*, 1966, **31**, 2159; J. Dąbrowski and K. Kamieńska-Trela, *Bull. Chem. Soc. Japan*, 1966, **39**, 2565.