Site of Protonation of α-Diazo-ketones in Super-acids

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Summary When dissolved in the mixture $FSO_3H-SbF_5-SO_2$, α-diazo-ketones are protonated on oxygen, and not on carbon as previously reported.

IN the mixture $FSO_3H-SbF_5-SO_2$, protonated diazoacetone has the n.m.r. spectrum shown in the Figure. Two species are obviously present, neither of which can be regarded as the cation $CH_3-CO-CH_2-N_2^+$, that would be expected to show only two signals in the ratio 3 : 2. These species can, however, be identified with the two possible conformers, *cisoid* and *transoid*, corresponding to those whose existence has been proved by Kaplan and Meloy[1] for non-protonated diazoacetone. To the conformer exhibiting a long-range coupling between C-1–H and OH, is assigned the only conformation allowing a W-arrangement[2–4] of the bonds, *i.e.* the *cisoid* conformation (a).

Data obtained from diazoacetone and other diazo-ketones are shown in the Table. The n.m.r. spectrum patterns reported exclude the possibility of protonation on carbon in diazoacetone and *p*-nitro-α-diazoacetophenone. In view of the similarity of the chemical shifts of the added proton (8·78 to 9·90 p.p.m.) it can probably be safely assumed that protonation on carbon is also excluded for diazobutanone† and diazocamphor. These chemical shifts are in good agreement with those, which we reported in 1968[5] for 2-diazo-5α-cholestan-3-one (9·3 p.p.m.) and its 4,4-dimethyl derivative (9·4 p.p.m.). Therefore, our statement that these diazo-ketones were stereospecifically protonated on carbon should be withdrawn. The linewidth (about 5 Hz) exhibited by these protonated diazo-ketones at −70° may probably be ascribed to the viscosity of the solutions.

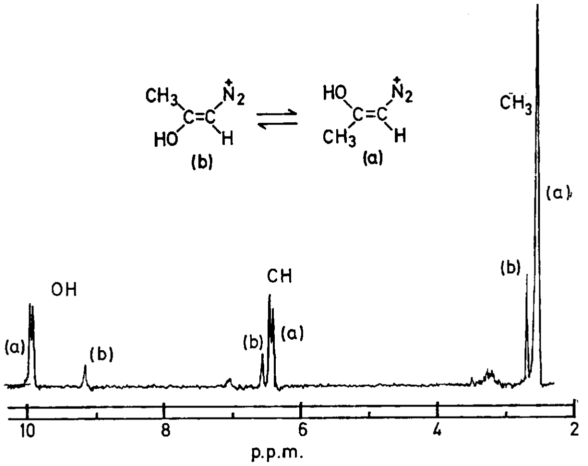
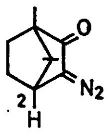


FIGURE. *N.m.r. spectrum of diazoacetone in* $FSO_3H-SbF_5-SO_2$ *at* − 60°.

TABLE

*N.m.r. data on diazo-ketones**

		Non-protonated			Protonated	
Diazoketone		C-1–H	C-2–H	C–OH	C-1–H	C-2–H
$CH_3CO{\cdot}CHN_2$	*cisoid*	5·35	1·80	9·90 d (*J* 2·5)	6·45 d (*J* 2·5)	2·56
2 1	*transoid*	4·91	1·99	9·05	6·60	2·73
$CH_3CO{\cdot}CN_2CH_3$	*cisoid*	1·58	1·88	9·00	2·17	2·54
2 1	*transoid*	1·80	1·83	8·78	2·18	2·42
p-NO_2-C_6H_4-$COCHN_2$ 1		5·90		9·99 d (*J* 2)	6·85 d (*J* 2)	
			2·80 d (*J* 3)	9·70		3·27 d (*J* 3)

* Chemical shifts in p.p.m. from Me_4Si; *J* in Hz.

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† The coupling pattern in protonated diazobutanone also excludes protonation on carbon.

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