Degenerate Group Movements. Degenerate Acyl Migrations in Pyrazole Chemistry

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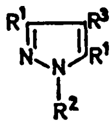
Summary Variable-temperature n.m.r. studies show the existence of degenerate *NN*-acyl migration in 1-anilinocarbonyl-3,5-dimethylpyrazole (Ia).

WE present here evidence for degenerate *NN*-acyl migration in the pyrazole (Ia), which, to the best of our knowledge, is the first example of degenerate *NN*-group movement in an uncharged species; there are a few reported examples[1] of the related degenerate *OO*-migration and recently the trimethylsilyl *NN*-exchange in the anion from tris(trimethylsilyl)-hydrazine has been reported.[2]

At 29°, the pyrazole (Ia) shows† two narrow methyl n.m.r. peaks at τ 7·57 and 8·05; at 130° the spectrum remains substantially unchanged but at 170° considerable broadening of the bands is observed and at 195° the two methyl absorptions coalesce. At 215°, the spectrum shows a single band at τ 7·80 ($\omega_{\frac{1}{2}}$ 32 Hz), corresponding to a rapid (n.m.r. time-scale) transfer of the acyl group. On cooling, there is no change in the original spectrum.

No fast exchange was observed in the n.m.r. spectra of the pyrazoles (Ib—d) up to 200°; however, (Id), at *ca.* 200°, showed some broadening of the ring t-butyl peaks.

When mixed samples of the pyrazoles (Ie) and (If) and of (Ia) and (Ig) are heated at *ca.* 200° in α-chloronaphthalene, mixtures of all four pyrazoles are obtained (n.m.r. spectroscopy). These crossing experiments indicate that intermolecular acyl exchange takes place, but do not exclude the possibility of a simultaneous intramolecular migration; furthermore, it is not yet established if the intermolecular exchange is direct or if it takes place through reversible dissociation of the arylaminocarbonylpyrazoles into pyrazole and arylisocyanate.[3]



	R^1	R^2	R^3
(I) a;	Me	CONHPh	H
b;	Me	*p*-CO·C_6H_4·NO_2	H
c;	Me	CO·$C_6H_3(NO_2)_2$-(2,4)	H
d;	Bu^t	COBu^t	H
e;	Me	*p*-CONH·C_6H_4Me	H
f;	Me	CONHPh	Me
g;	Me	*p*-CONH·C_6H_4Me	Me

M.p.s in agreement with literature values and spectral data consistent with the proposed structures (Ia—g) were obtained.

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† All spectra were recorded in α-chloronaphthalene.

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[2] R. West and B. Bichlmeir, *J. Amer. Chem. Soc.*, 1972, **94**, 1649.

[3] W. Otting and H. A. Staab, *Annalen*, 1959, **622**, 23.