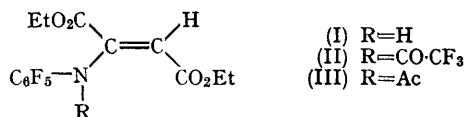


A New Carbanion Rearrangement

By G. M. BROOKE and R. J. D. RUTHERFORD

(Chemistry Department, Science Laboratories, South Road, Durham)

THE reaction of the sodium salt of pentafluoroaniline with diethyl acetylenedicarboxylate has been shown to give the aminofumarate¹ (I).

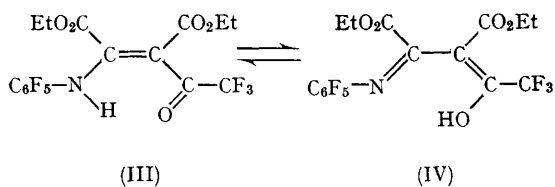


We have now treated the *N*-trifluoroacetyl derivative of pentafluoroaniline² with sodium hydride, reacted the resulting sodium salt with diethyl acetylenedicarboxylate at -70° , and then heated the mixture under reflux for 5 hr. Two products, isolated by distillation, fractional sublimation, and chromatography on alumina were both shown by accurate mass measurements in a mass spectrometer to have the same molecular formula $\text{C}_{16}\text{H}_{11}\text{F}_8\text{NO}_5$. The liquid product (b.p. $103^\circ/0.05$ mm., 5% yield) was shown to be the

N-trifluoroacetylaminofumarate (II) from its ¹H n.m.r. spectrum. There were three areas of absorption: a singlet at τ 2.9 due to one olefinic proton; two overlapping quartets at τ 5.7, and two overlapping triplets τ 8.7 due to the methylene and methyl protons respectively in two ethyl groups. Isomerisation of (II) with ultraviolet light shifted the olefinic peak up-field to τ 3.9, the other features of the spectrum remaining essentially unchanged. The olefinic protons in aminomaleate derivatives have been shown to be more shielded than the isomeric fumarates.³

The second reaction product, a solid (m.p. $81-81.5^\circ$, 22% yield) was assigned the structure (III) and when dissolved in carbon tetrachloride was in equilibrium with its tautomer (IV). The infrared spectrum of (III) in the solid phase (KBr disc) showed strong absorptions at 3150 cm^{-1} due to the N-H stretch [*cf.* 3225 cm^{-1} for N-H stretch in (I)] and at 1680 cm^{-1} due to the carbonyl stretch in the conjugated CF_3CO group;

there was no evidence for absorption by O—H. In carbon tetrachloride, the relative intensity of the i.r. absorption in the region of the N—H stretch was reduced by about a half, and considerably broadened due to the presence of hydrogen-bonded O—H from (IV). The ^1H n.m.r. of (III) dissolved in carbon tetrachloride showed no absorption in the olefinic region, but two absorptions at τ -0.4 and -1.6 were assigned to the N—H and O—H protons of a mixture consisting of (III) and tautomer (IV) in the ratio of *ca.* 3:1. The sum of these two low-field absorptions accounted for one proton, and the overlapping quartets at τ 5.8 and overlapping triplets at τ 8.7 were due to four protons from methylene groups and six protons from methyl groups respectively. The ^{19}F n.m.r. of (III) in carbon tetrachloride showed sharp absorptions in the ratio of *ca.* 3:1 at 74 and 73 p.p.m. up-field from CFCl_3 as internal reference, assigned to the CF_3 groups in (III) and (IV) respectively.



The position of keto-enol equilibria of a number of $\alpha\beta$ -unsaturated γ -keto-amines has been reported

¹ G. M. Brooke and R. J. D. Rutherford, *J. Chem. Soc.*, in the press.

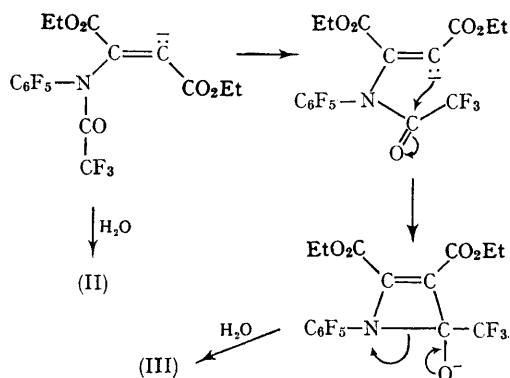
² G. M. Brooke, E. J. Forbes, R. D. Richardson, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1965, 2088.

³ E. Winterfeldt and H. Preuss, *Chem. Ber.*, 1966, 99, 450.

⁴ G. O. Dudek and R. H. Holm, *J. Amer. Chem. Soc.*, 1962, 84, 2691.

previously and shown to lie largely towards the ketamine structure.⁴ Chemical evidence for the structure of the rearranged material was provided by the formation of fluoroform on treatment of (III) with caustic soda solution. It is of interest that reaction of the aminofumarate (I) with trifluoroacetic anhydride also gave (III) whereas acetylation of (I) gave the *N*-acetylaminofumarate (V).¹

The formation of (III) can readily be explained on the basis of a carbanion rearrangement in which the initially formed carbanion isomerises and can then effect an intramolecular nucleophilic addition-elimination reaction at the carbonyl of the *N*-trifluoroacetyl group:



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