Evidence for the Formation of a Guanidinium Ylide

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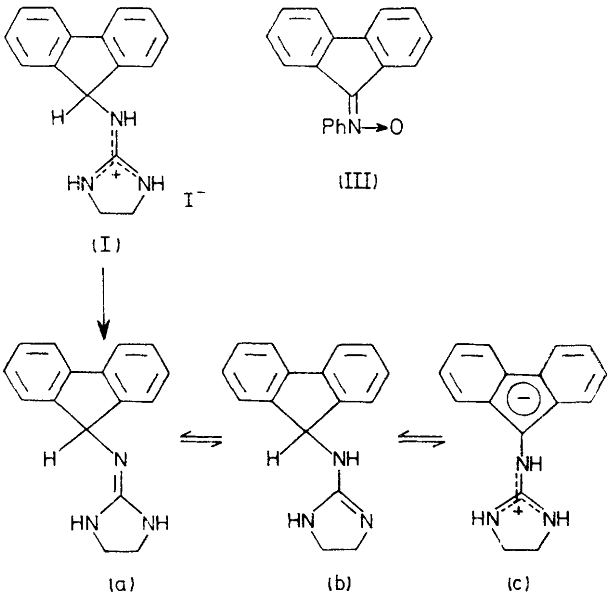
Summary Evidence is presented for the formation of a guanidinium fluorenylide which reacts with nitrosobenzene to give *N*-fluoren-9-ylideneaniline *N*-oxide.

Although ylides with many different heteronium groups have been described,[1] we believe that to date there has been no report of the formation of a guanidinium ylide.

When the fluorenylguanidinium salt (I) was treated with 1 equiv. of phenyl-lithium, aqueous work-up of the reaction mixture provided a base (II) [*m/e* 249·126,($C_{16}H_{13}N_3$, M^+)]. Reaction of (I) with concentrated aqueous sodium hydroxide also gave (II) but in much lower yield. Compound (II) could be formulated as an *N*-fluorenylguanidine (IIa or b) or as a guanidinium fluorenylide (IIc); the latter structure would be stabilised by the delocalisation of charge in both the carbanionic and heteronium portions of the molecule.

Spectroscopic evidence is inconclusive concerning the contributions of these forms, but the chemical behaviour indicates that the ylide form must contribute to this possible tautomeric equilibrium. Compound (II) reacted rapidly with nitrosobenzene to give products, for the most part unidentified, but among them was the anil oxide (III), identical with an authentic sample.[2] Formation of this product necessitates the presence of the ylide tautomer (IIc). This ylide thus resembles another *N*-fluorenylide, pyridinium fluorenylide,[3] and also sulphonium[3,4] and arsonium[5] fluorenylides, in giving an anil oxide on reaction with nitrosobenzene, whereas phosphonium fluorenylides instead give fluorenylidene anil.[6]

Compound (II) is resistant to alkaline hydrolysis or methanolysis, but was partially decomposed when recrystallisation from ethanol was attempted. It underwent extensive decomposition when kept at room temperature under nitrogen for a week, but could be kept for a longer time at −40 °C. Fluorenone imine was detected as a decomposition product, presumably formed by loss of the stable dihydroimidazole ring.



(I) (III)

(a) (b) (c)

(II)

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[1] A. Wm. Johnson, 'Ylid Chemistry', Academic Press, New York, 1966.
[2] H. Staudinger and K. Miescher, *Helv. Chim. Acta*, 1919, **2**, 578.
[3] A. Wm. Johnson and R. B. LaCount, *J. Amer. Chem. Soc.*, 1961, **83**, 417.
[4] A. Wm. Johnson, *J. Org. Chem.*, 1963, **28**, 252.
[5] A. Wm. Johnson and J. O. Martin, *Chem. and Ind.*, 1965, 1726.
[6] A. Schonberg and K. H. Brosowski, *Chem. Ber.*, 1959, **92**, 2602.