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AN UNUSUAL REACTION OF AZIDE WITH NITROOLEFINS

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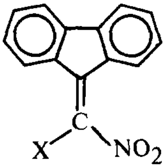
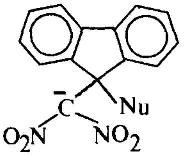
Abstract: The reaction of sodium azide in DMSO with 9-dinitromethylenefluorene (DNF) and 9-bromonitromethylenefluorene (BNF) results in the formation of N-cyano-9-iminofluorene (2). The overall reaction time is two minutes at room temperature.

When reacted with nucleophiles such as CN^-, MeO^-, $PhCH_2S^-$ etc., 9-dinitromethylenefluorene (DNF) quantitatively furnishes the stable carbanion 1.[1] However when DNF (200 mg) is allowed to react with NaN_3 (ca. 250 mg) in DMSO (10 ml) at ambient temperature, an unexpected product, namely N-cyano-9-iminofluorene (2) is obtained.[2] The reaction is accompanied by vigorous gas evolution and reaches completion within two minutes. This same product is also obtained in the reaction of 9-bromonitromethylenefluorene[3] (BNF) with NaN_3 under similar conditions.[2] The structure of 2 was determined on the basis of the following data: Anal. ($C_{14}H_8N_2$) C,H,N; MS, m/e 204 (M^+); IR ($CHCl_3$), 2190, 1640, 1590 cm^{-1}; ^1H NMR ($CDCl_3$), δ 7.8 (d-1H), 7.3-7.6 (m-7H); both basic and acidic hydrolysis of the product resulted in fluorenone, indicating that the aromatic nucleus remains unchanged.



DNF: X=NO_2 BNF: X=Br



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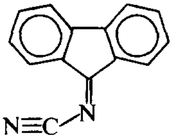
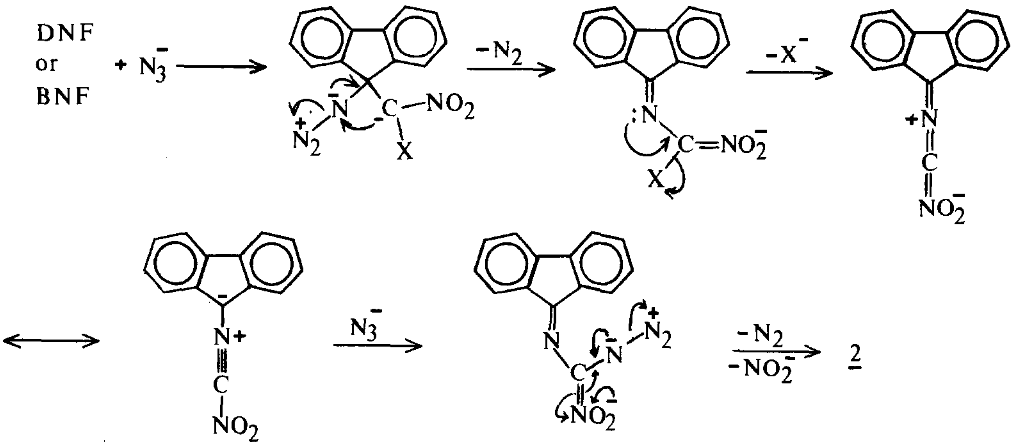


2

The mechanism of this reaction is not entirely clear. However, the good correlation obtained between the rate of disappearance of DNF and Ritchie's nucleophilicity constant N_+,[1] clearly indicates that the first step is a nucleophilic attack of the azide ion on C-9 of the fluorene system. The release of NO_2^- to the reaction mixture as evidenced by the iodide-starch paper test,[4] implicates the azide as the source of the cyano nitrogen.

A tentative mechanism for this reaction is given in the scheme. The formation of the imino moiety is probably coupled with the elimination of N_2 thus avoiding the intermediacy of a highly energetic nitrene. Departure of NO_2 from a carbanion has been previously suggested.[5] Although dinitrocarbanions usually do not undergo decomposition reactions (eg. 1), the presence of the imino group in this case undoubtedly facilitates the expulsion of X to give the resonance stabilized nitrile ylide. C-1 of nitrile ylides was shown by several investigators to be prone to nucleophilic attacks.[6] This is much more so in this case where the nitrile ylide is further activated by the electron-withdrawing nitro group. Thus a nucleophilic attack of the azide anion on the nitrile ylide followed by the splitting off of



Scheme: X = NO_2 or Br

nitrogen and the expulsion of the remaining nitro group yields the product 2.

It is interesting to compare this reaction with that reported by Smolinsky[7] in which a carbonitrile moiety was also formed by the reaction of azide anion with an olefinic compound. In his reaction, Smolinsky reacted 9-dichloromethylenefluorene (3) with NaN_3 in DMF. In spite of the structural similarities between this compound and the two reported here, another product, namely 9-cyano-9-azidofluorene was obtained. The origin of this difference apparently derives from the differing sites of the first nucleophilic attack. While the structure of DNF and BNF dictates nucleophilic attack on C-9 of the fluorene system, the first step in the reaction of 3 is probably a nucleophilic vinylic substitution of one of the chlorine atoms by N_3^- on the α-carbon of 3.

References and Notes

1) S. Hoz and D. Speizman, Tetrahedron Lett. 1775 (1978).

2) The product was usually precipitated by addition of water. In some cases extraction by ether and water was used. The yield of the first crop after recrystallization from ethanol is about 10% starting with DNF and ca. 40% starting from BNF, tlc analysis of the mother liquor shows that it still contains relatively large quantities of 2.

3) BNF (m.p. 96°C; Anal. ($C_{14}H_8N_1O_2Br$) C,H,N,Br) is prepared by bromination of 9-nitromethylenefluorene and consecutive dehydrobromination of the dibromide (m.p. 113-114°C).

4) F. Feigl, "Spot Tests", Vol. 1, Elsevier, London 1954, p 304.

5) H.U. Blank and J.J. Fox, J. Am. Chem. Soc., 90, 7175 (1968).
C. Shin, Y. Yonezawa and J. Yoshimura, Tetrahedron Lett. 7 (1974).

6) P. Caramella and N.K. Houk, J. Am. Chem. Soc., 98, 6397 (1976), A. Padwa and H.J. Carlsen, ibid., 99, 1514 (1977), A. Padwa and N. Kamigata, ibid., 99, 1871 (1977).

7) G. Smolinsky and C.A. Pryde, J. Org. Chem., 33, 2411 (1968).

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