Tetrahedron Letters No. 40, pp 3485 - 3486, 1975. Pergamon Press. Printed in Great Britain.

AZA-WITTIG REARRANGEMENT OF (9-LITHIO-9-FLUORENYL)-ALLYL-METHYL-AMINE

M.T. Reetz* and D. Schinzer

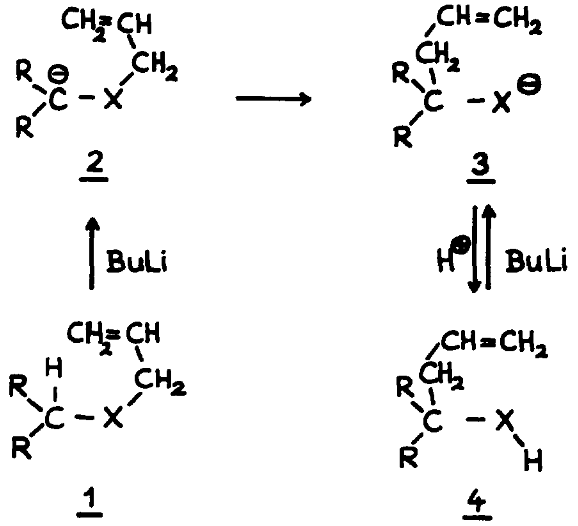
Fachbereich Chemie der Universität

355 Marburg, W-Germany

(Received in UK 11 July 1975; accepted for publication 22 August 1975)

Whereas the Wittig rearrangement of ethers to alcohols represents a well known reaction type1), the isoelectronic aza analog appears to be quite rare2). Scattered reports indicate that the nitrogen compounds react slowly, affording poor yields of rearrangement products3). Stevens, employing principally KOH and NaNH$_2$ as the metalating agent, attributed these observations to either sluggish deprotonation at the amine C$^{\alpha}$-position or to slow isomerization of the anionized species (or possibly to both)3).

In connection with our studies of dyotropic rearrangements, we sought a clean method of preparation of anions of type 2a. Since the oxygen analog 2b had been prepared previously and been shown to rearrange spontaneously to 3b at low temperatures1), the observation of 2a would allow a direct comparison between the O and N systems:



a) X = NCH$_3$

R + R = 2,2'-biphenylylene

b) X = O

R + R = 2,2'-biphenylylene

Addition of butyllithium to 1a[4)] in THF at room temp. immediately resulted in a deep red color, due to 2a. Quenching after 2 hours with D_2O afforded 1a with 95% deuterium incorporation at the fluorenyl C^9 position, as shown by NMR. Under these conditions no rearrangement product could be detected. Solutions of 2a can be kept at room temp. for at least one day without signs of rearrangement. In order to test whether an equilibrium 2a $\rightleftarrows$ 3a possibly prevails in favor of 2a, the anion 3a was prepared independently by metalation of 4a[4)]. However, 3a does not isomerize to 2a even after refluxing in THF for several hours. The failure of 2a and 3a to interconvert points to a high kinetic barrier. In order to induce a rearrangement nevertheless, 2a was refluxed in THF for 7 hours. Workup afforded a 44% yield of 4a, demonstrating that under such conditions allyl migration can indeed be induced. Our observations prove that metalation is fast[5)], and that the allyl shift is the rate determining step. They further show that within a comparable series the α-metalated amines rearrange considerably slower than the corresponding ethers. The reason for this dramatic difference is not clear at present, but may be due to the higher stability of RO^-Li^+ as compared to $R_2N^-Li^+$ [3)]. Further mechanistic studies designed to differentiate between a [2,3]-sigmatropic shift and a radical cleavage-recombination mechanism are planned.

Acknowledgement: This work was supported by the Deutsche Forschungsgemeinschaft.

References and Notes:

1) G.Wittig and E.Stahnecker, Liebigs Ann.Chem. 6o5, 69 (1957); U.Schöllkopf Angew.Chem. 82, 795 (197o); Angew.Chem.Int.Ed. 9, 763 (197o).

2) J.J.Eisch and C.A.Kovacs, J.Organomet.Chem. 3o, C 97 (1971).

3) H.Dahn and U.Solms, Helv.Chem.Acta 1o9, 9o9 (1951); R.A.W.Johnstone and T.S.Stevens, J.Chem.Soc. 3346 (196o).

4) All new compounds gave correct elemental analyses.

5) The aromaticity of the fluorenyl anion facilitates deprotonation. Amines are generally not easily anionized at the α-position; see D. Seebach and D. Enders, Angew.Chem. 87, 1 (1975); Angew.Chem.Int.Ed. 14, 15 (1975).