BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN　VOL. 42　2359—2361 (1969)

Benzyne Addition Induced Rearrangement to *N*-Methyl-*N*-(1-phenethyl)aniline*[1]

Angelo G. GIUMANINI

Istituto di Chimica Organica ed Industriale, Università di Bologna, 40136 Bologna, Italy

and Arthur R. LEPLEY

Department of Chemistry, Marshall University, Huntington, West Virginia 25701, U.S.A.

(Received April 25, 1968)

In a continuing interest in the chemistry of α-dialkylamino carbanions and nitrogen ylids, we have studied the reaction between *N,N*-dimethylbenzylamine (DMBA) and benzyne, the latter being generated *in situ* by means of the reaction of a phenyl halide (Hal=F or Cl) and *n*-butyllithium. This technique, previously applied by the present authors to the system fluorobenzene/*n*-butyllithium/*N,N*-dimethylaniline,(1) allowed to predict that an *ortho*-ylid I formed which, in turn, could quickly isomerize to the *N*-ylids II and III by a prototropic shift. The ylids II and III are the postulated intermediates to the observed products IV and V of the reaction of the benzyldimethylanilinium ion VI with *n*-butyllithium(2) (Scheme 1). In the frame of this schematic and simplified picture, the environmental and physicochemical conditions for the generation of II and III should be closely similar for the two routes. It was therefore expected that the rates of the possible reactions involved(2) would closely parallel for the two cases, a fact that must be reflected into final product distribution. In a series of experiments with VI and *n*-butyllithium, we found(2) V to VI ratios between 0.81: 1 and 9.4 : 1 depending on experimental conditions.

In a related work by Jones *et al.* using VI and sodamide, only V was detected.(4)

We have now found in a preliminary study of the reaction in question that the benzyne generated betaine I affords practically a single (Stevens) rearrangement product, IV, as inequivocably shown by vapour phase chromatographic analysis(5) of the crude mixture combined with product separation and conventional analytical techniques. It also appears that no significant amounts of *o*-rearranged amine VII (Sommelet rearrangement) are present. Infrared and nuclear magnetic resonance spectral evidences ruled out that the isolated amine contained either product of 1,3 migration directly derived from the primary betaine I, apparently a very elusive compound, namely VIII and IX. Authentic IV was synthetized through an independent route(6) for definitive comparison.

There still remain the possibilities of direct displacement of the halogen atom by metallated

---

*[1] This work was supported by U. S. Public Health Service grant GM-09136 from the National Institute of General Medical Science and the National Research Council of Italy. Parts of the work were presented before the 145th National Meeting of the American Chemical Society and the 10th National Meeting of the Italian Chemical Society.

1) A. R. Lepley, A. G. Giumanini, A. B. Giumanini and W. A. Khan, *J. Org. Chem.*, **31**, 2051 (1966).

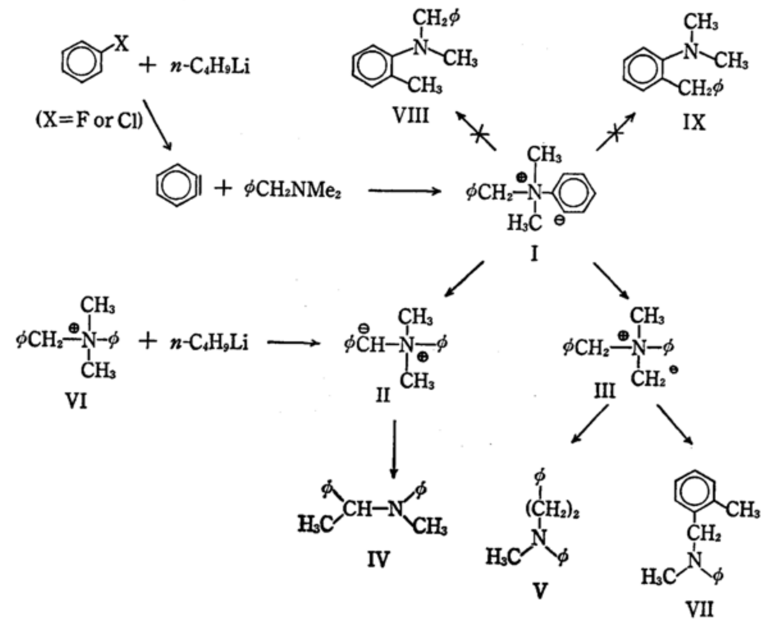
2) A. G. Giumanini and A. R. Lepley, X Congresso Nazionale della Società Chimica Italiana, Padova 1968, comm. XIII/25 (1968).

3) G. C. Jones, W. Q. Beard and C. R. Hauser, *J. Org. Chem.*, **28**, 199 (1963).

4) Amine V is not stable in the presence of $NaNH_2$, which cleaves it to *N*-methylaniline and styrene. But this is the only source of these two compounds.(3)

5) A. H. Wagg, T. S. Stevens and D. M. Ostlo, *J. Chem. Soc.*, **1958**, 4057.

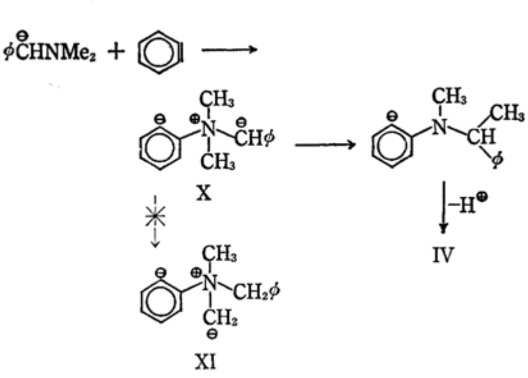
6) W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1396 (1964).



Scheme 1.

amine and of a benzyne reaction of the latter.[7] Indeed, BDMA reacts with *n*-butyllithium as evidenced by the bright colour appearing upon mixing with *n*-butyllithium. Once again the spectral characteristics of the separated amine ruled out such a hypothesis. The proton resonance spectrum indicated two methyls (a doublet centered at 1.46 ppm and split by methine with $J=6.7$ cps and a singlet at 2.56 ppm), a methine (quartet centered at 5.03 ppm and split by methyl with $J=7.0$ cps) and a phenyl (broad multiplet centered at 6.92 ppm) with relative intensities in the ratio 3/3/1/10.

Since the chromatic reaction between BDMA and *n*-butyllithium is instantaneous, it seems reasonable to conclude that either the metallated amine generates the benzyne to which it subsequently adds or the benzyne generated by excess butyllithium reacts with the metallated amine to yield the benzyl betaine anion X.



Scheme 2.

Since only a methyl shift occurs to produce IV, it is likely that the dianion X is involved in the rearrangement and at such a rate that prototropic shift to the methyl betaine anion XI cannot compete. Formation of ylid anions in the reactions of quaternary ammonium salts was previously advanced.[8]

To generate the benzyne, both chlorobenzene and fluorobenzene were used. The latter gave a better absolute yield in the rearranged amine (33% *vs.* 18%).

Experimental[9]

Chemicals. The best available grades of halobenzenes were used without purification. BDMA was a greatly appreciated gift of Miles Chemical Co. *n*-Butyllithium, 15% in hexane, was obtained from Foote Mineral Co. or prepared from 1-chlorobutane (Erba, Italy) and Li (Merk, W. Germany) in hexane under hydrogen.

Preparation of *N*-Methyl-*N*-(1-phenethyl)aniline (IV). *n*-Butyllithium (200 *ml*, 15%) was stirred and a solution of 200 *ml* BDMA in 400 *ml* anhydrous ether was rapidly added. The solution instantly turned bright yellow. Fluorobenzene (0.2 mol) in 150 *ml* ether

---

8) A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **32**, 1706 (1967).

9) Essential experimental data are presented here. Further details and progresses of the research will be given at a later date. Physical properties (infrared and PMR spectra, refractive indexes and specific gravities) were measured in the standardized method previously described, *loc. cit.* and related analytical methods: A. R. Lepley, *Anal. Chem.*, **34**, 322 (1962); A. R. Lepley and W. A. Khan, *J. Org. Chem.*, **31**, 2064 (1966).

was added in one lot. After 15 min a heavy precipitation of salt was observed. The stirring was continued at 26°C for 24hr. Then 150 m*l* of water was added slowly with cooling, the ether layer was separated, dried over potassium hydroxide and distilled. A 33% yield was obtained of product boiling 181—2°C/20 Torr, $n_D^{25°}$ 1.5946. Gas chromatography showed less than 3% impurity in this product. The product was identical with material prepared by reaction of 1-bromoethylbenzene and *N*-methylaniline.