

Cyclisation of 2-Azidodiphenylmethane and 2-Azidobiphenyls by Regiospecific *N*-Attack of Arylnitrenium–Aluminium Chloride Complexes

Hiroshi Takeuchi,* Munenori Maeda, Michiharu Mitani, and Kikuhiko Koyama

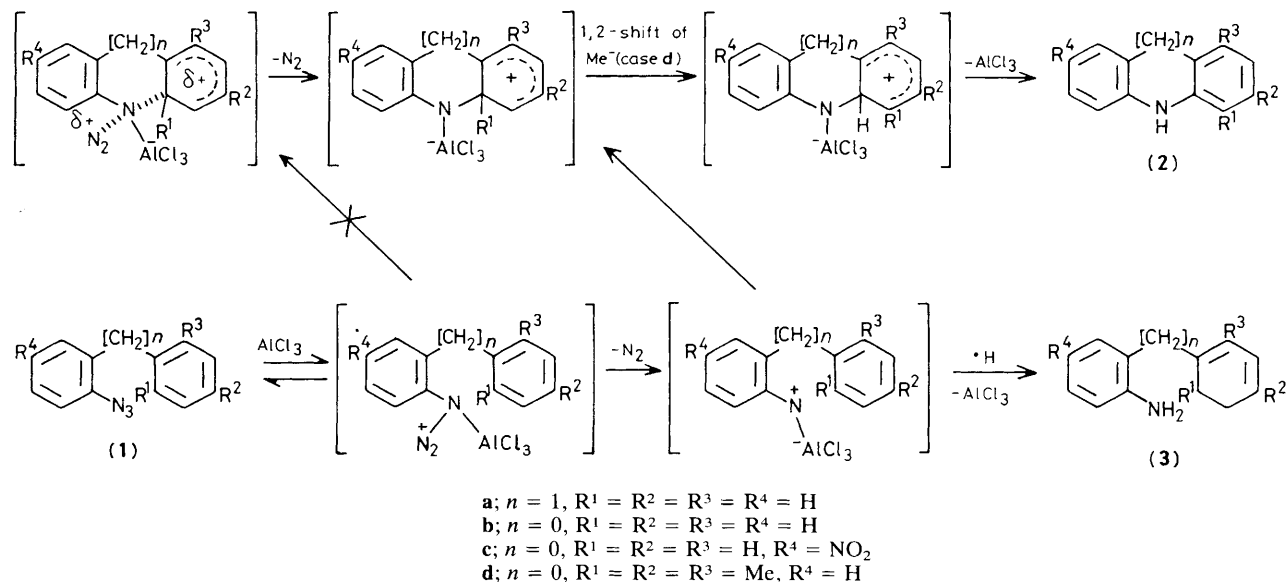
Department of Synthetic Chemistry, Faculty of Engineering, Shinshu University, 500 Wakasato, Nagano 380, Japan

Decomposition of 2-azidodiphenylmethane and 2-azidobiphenyls in CH_2Cl_2 in the presence of AlCl_3 gave 9,10-dihydroacridine and carbazoles, respectively, in reasonable yields by regiospecific *N*-attack of an arylnitrenium– AlCl_3 complex.

We have reported that a phenylnitrenium ion generated from phenyl azide in the presence of trifluoroacetic acid (TFA) or trifluoromethanesulphonic acid (TFSA) brings about an aromatic *N*-substitution.^{1,2} Thus, we expected that the decomposition of 2-azidodiphenylmethane (**1a**) or 2-azidobiphenyl (**1b**) in the presence of TFA or TFSA would lead to a favourable formation of 9,10-dihydroacridine (**2a**) or carbazole (**2b**) by an intramolecular aromatic *N*-substitution of the

arylnitrenium ion. But, such a cyclisation could not occur effectively because the selectivity for *N*- or *C*- attack of substituted phenylnitrenium ions depends upon the electronic character of substituents.[†] The cyclisation failed in the

[†] An intra- or inter-molecular aromatic *N*-substitution by phenylnitrenium ions occurred preferentially with electron-withdrawing groups but did not take place with electron-donating groups.



Scheme 1

presence of acids such as the hydrogen halides.³ The use of $AlCl_3$ as an acid achieved the desired cyclisation *via* an arylnitrenium- $AlCl_3$ complex. This cyclisation should have wide synthetic applications.

To a stirred suspension of $AlCl_3$ (2.2 mmol) in CH_2Cl_2 (5.0 ml) a solution of azide (**1a**) (2.1 mmol) in CH_2Cl_2 (2.0 ml) was added slowly at room temperature. After the evolution of N_2 gas ceased aqueous NaOH solution was added. From the resulting organic layer (**2a**) (89%) and 2-aminodiphenylmethane (**3a**) (4%) were isolated by column chromatography and the yields determined by g.l.c. analysis. Similar reaction of azide (**1b**), 2-azido-5-nitrobiphenyl (**1c**), or 2-azido-2',4',6'-trimethylbiphenyl (**1d**) with $AlCl_3$ afforded (**2b**) (83%), 3-nitrocarbazole (**2c**) (98%), or 1,2,4-trimethylcarbazole (**2d**) (51%),[‡] respectively, together with a small amount of 2-aminobiphenyls (**3b**–**3d**).

Thermal decomposition of azide (**1a**) does not produce (**2a**), but 10*H*-azepino[1,2-*a*]indole.⁴ Thermolysis or photolysis of azide (**1b**) to (**2b**) is a well-studied arylnitrene reaction.⁵ The yield of carbazoles (**2b**) and (**2c**) in our experiment was slightly better than in the thermal and photochemical cases.⁶ Pyrolysis of azide (**1d**) gives 2,4,9-trimethylcarbazole and 8,10-dimethylphenanthridine,⁷ not the carbazole (**2d**).

A stable solution[§] was formed at $-30^\circ C$ in the reaction of (**1b**) with $AlCl_3$; N_2 gas was evolved upon warming to $0^\circ C$. This suggests the existence of a complex of the azide with $AlCl_3$ below $-30^\circ C$.

Borsche and Hahn⁸ have reported that the reaction of phenyl azide with aromatic compounds in the presence of $AlCl_3$ gives diarylamines. We have determined relative rate constants, k_x/k_H , for the formation of *para*-substituted diphenylamines with respect to diphenylamine ($< 1:10$ molar ratio of the azide to benzene or other aromatic compound). Using anisole, toluene, ethylbenzene, and cumene as the aromatic compound, the correlation between $\log(k_x/k_H)$ and

σ_p gives a linear plot with $\rho = -6.0$. If the large negative ρ value comes from an S_N2 reaction involving attack of aromatic compound on the complex of azide with $AlCl_3$, the first-order rate constant k_{obs} for the decomposition of phenyl azide compared with that in benzene. The value obtained for k_{obs} at $20^\circ C$, $1.0 \times 10^{-3} s^{-1}$, in toluene is, however, the same as that in benzene [azide (0.33 g) and $AlCl_3$ (0.41 g) were added to 22 ml of aromatic compound]. The data in both solvents are sufficiently meaningful since the solubility of $AlCl_3$ in toluene is almost identical with that in benzene. The observations clearly rule out the S_N2 reaction, so instead the complex of azide with $AlCl_3$ must spontaneously lose a molecule of N_2 in a rate-determining step to form a nitrenium- $AlCl_3$ complex, and the complex reacts with the aromatic compound to yield diarylamines. Thus, a similar intramolecular reaction would take place in the formation of (**2**) from (**1**) (Scheme 1).

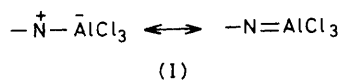
Phenylnitrenium-aluminium complexes have been assumed in the case using $AlEt_3$ ⁹ and $AlBr_3$,¹⁰ but to date there is no unequivocal evidence supporting their existence. The regio-specific *N*-attack^{††} of arylnitrenium- $AlCl_3$ complexes presumably arises from the greater delocalization of the positive charge between the nitrogen and aluminium atoms than is possible on the phenyl ring. The more negative ρ value (-6.0) obtained from the phenylnitrenium- $AlCl_3$ complex over that (-4.5)^{1,2} from the phenylnitrenium ion suggests that the reaction *via* the Al complex proceeds through a later transition state (*i.e.* more similar to a σ -complex) than that *via* the

[¶] Regarding the S_N2 mechanism, $k_{obs} = k_x K [AlCl_3] [ArH]$ where k_x is the rate constant for the formation of diarylamines from the complex of azide with $AlCl_3$, and K is the equilibrium constant for the formation of the complex. Thus, the relative ratio of k_{obs} in toluene to that in benzene is equal to $(k_{Me}/k_H) \cdot \{[toluene]/[benzene]\} = 20$, where k_{Me}/k_H is the relative rate constant for the formation of 2- and 4-methyldiphenylamines with respect to diphenylamine, since K and $[AlCl_3]$ in toluene are nearly the same as those in benzene, respectively (k_{Me}/k_H was determined by competitive reaction).

^{††} In the reaction of phenyl azide with benzene in the presence of $AlCl_3$, the regioselectivity, *N*-*C*-attack = 95, was obtained from the relative yield of diphenylamine to 2- and 4-aminobiphenyls.

[‡] In the experiment using (**1d**), a brown oil was eluted with CH_2Cl_2 -EtOH using column chromatography, but could not be purified by further chromatography.

[§] The solution was blue in CH_2Cl_2 , but yellow in toluene.



nitrenium ion. In other words, the nitrenium-AlCl₃ complex is more stable than the nitrenium ion in accord with the Hammond postulate, the stability probably being due to resonance as in (1).

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