Inter- and Intra-molecular Aromatic N-Substitution by Arylnitrenium–Aluminium Chloride Complexes generated from Aryl Azides in the Presence of Aluminium Chloride †

Hiroshi Takeuchi,* Munenori Maeda, Michiharu Mitani, and Kikuhiko Koyama
Department of Synthetic Chemistry, Faculty of Engineering, Shinshu University, 500 Wakasato, Nagano 380, Japan

Reactions of phenyl azide with aromatic compounds (*i.e.* benzene, toluene, ethylbenzene, cumene, anisole, and bromobenzene) in the presence of $AlCl_3$ gave diarylamines, whereas those of phenyl azides with an electron-donating group such as Me and OMe yield little of the corresponding diarylamines (tar formation takes place). The reaction of 4-nitrophenyl azide with benzene in the presence of $AlCl_3$ gave 4-nitrophenyl(phenyl)amine and a *C*-substitution product, 2-amino-5-nitrobiphenyl. Decomposition of 2-azidophenyl(phenyl)methane and 2-azidobiphenyls in CH_2Cl_2 in the presence of $AlCl_3$ underwent an *N*-cyclization to afford 9,10-dihydroacridine and carbazoles, respectively, in good yields. The kinetic data on the decomposition of aryl azides and a Hammett plot (with ρ −6.0) for the formation of diarylamines suggest that the products are formed by an aromatic *N*-substitution of arylnitrenium–$AlCl_3$ complexes *via* azide–$AlCl_3$ complexes. We further argue the character of arylnitrenium–$AlCl_3$ complexes.

Since the work of Gassman and his group the chemistry of divalent positive charged species, nitrenium ions, has been actively investigated, from both the mechanistic and the synthetic points of view. We have reported that a phenylnitrenium ion is generated from phenyl azide in the presence of trifluoroacetic acid (TFA) or trifluoromethanesulphonic acid (TFSA).[1–5] It is known that the reaction of phenyl azide (1a) with aromatic substrates in the presence of a Lewis acid such as $AlCl_3$ gives diarylamines in yields of 30—40%.[6] Phenylnitrenium–aluminium complexes have been assumed to be present where $AlEt_3$[7] and $AlBr_3$ have been used,[8] but to date there is no unequivocal evidence supporting their existence. We here propose that arylnitrenium–$AlCl_3$ complexes which are formed *via* azide–$AlCl_3$ complexes in the decomposition of aryl azides in the presence of $AlCl_3$ brings about the aromatic *N*-substitution.

Although we expected that decomposition of 2-azidophenyl(phenyl)methane (1h) or 2-azidobiphenyl (1i) in the presence of TFA or TFSA would lead to formation of 9,10-dihydroacridine (2h) or carbazole (2i) by intramolecular aromatic *N*-substitution of the arylnitrenium ion, such a cyclization failed to occur effectively,[5] even in the presence of hydrogen halides.[9] The use of $AlCl_3$ as an acid however achieved the desired cyclization and this reaction should have wide synthetic applications. We discuss below the behaviour of arylnitrenium–$AlCl_3$ complexes by contrast with arylnitrenium ions formed from aryl azides in the presence of protonic acids.

Results and Discussion

Inter- and Intra-molecular Aromatic N-*Substitution in the Presence of* $AlCl_3$.—Reactions of the azide (1a) with benzene, toluene, ethylbenzene, cumene, anisole, and bromobenzene in the presence of $AlCl_3$ yielded 2- and 4-substituted diarylamines (2a—f) and (3a—f) after work-up with aqueous NaOH (Table 1 and Scheme 1). 3-Nitrophenyl(phenyl)amine was not isolated however in the reaction with nitrobenzene. A similar reaction between *p*-tolyl azide (1b) and benzene yielded phenyl(*p*-

Table 1. Reactions of aryl azide $(4\text{-}XC_6H_4N_3)$ with aromatic compounds (PhY) in the presence of $AlCl_3$

X of $4\text{-}XC_6H_4N_3$ (1)	Y of PhY	Yield[a] (%)		
		(2)	(3)	(6)
a, H	a, H	19	—	Trace
a, H	b, Me	12	58	8
a, H	c, Et	23	45	
a, H	d, Pr^i	18	47	
a, H	e, OMe	18	23	
a, H	f, Br	6	17	
a, H	g, NO$_2$	0	0[b]	
b, Me	H	—	Trace[c]	Trace
e, OMe	H	—	0[d]	Trace
g, NO$_2$	H	—	49[e]	Trace

[a] Yields are based on azide used. [b] No 3-nitrophenyl(phenyl)amine was detected. [c] Tarry material and a trace of 2-amino-5-methylbiphenyl (4b) were formed. [d] Major product was tar. [e] As a *C*-substitution product, 2-amino-5-nitrobiphenyl (4g) was formed in 12% yield.
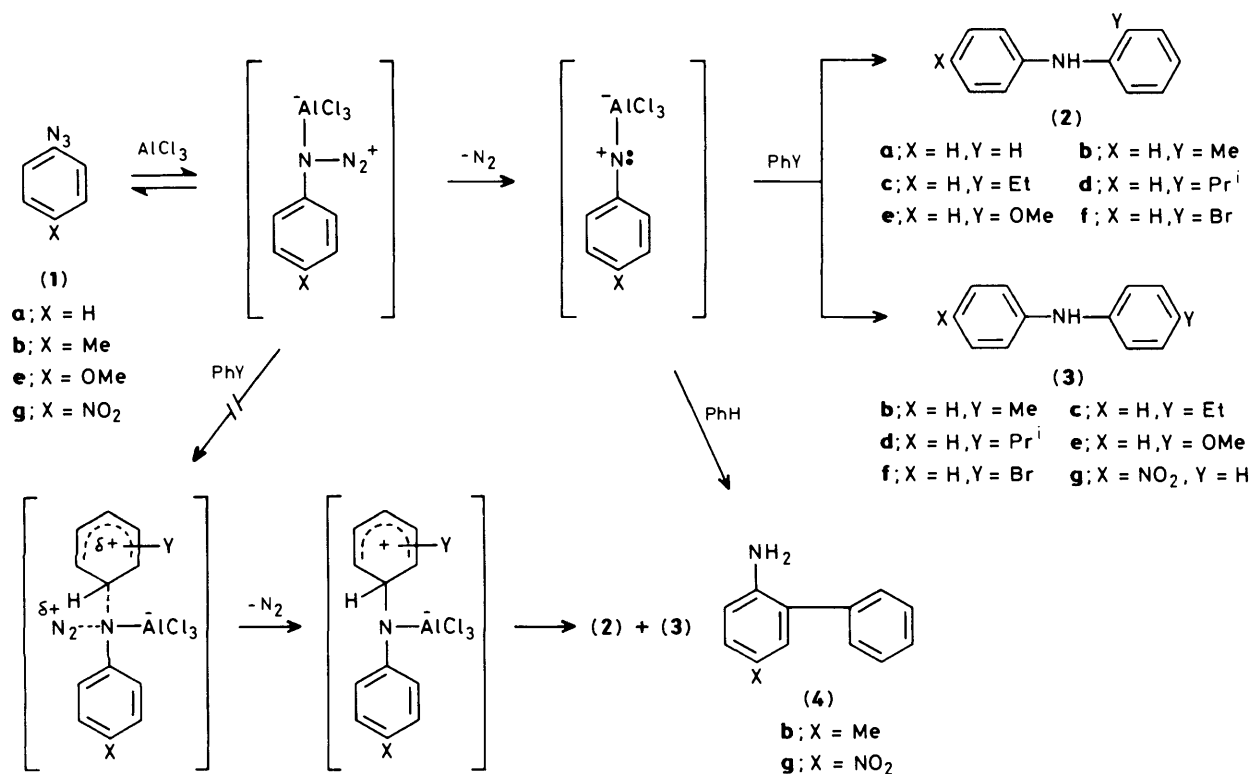
Table 2. Decomposition of aryl azides in CH_2Cl_2 in the presence of $AlCl_3$

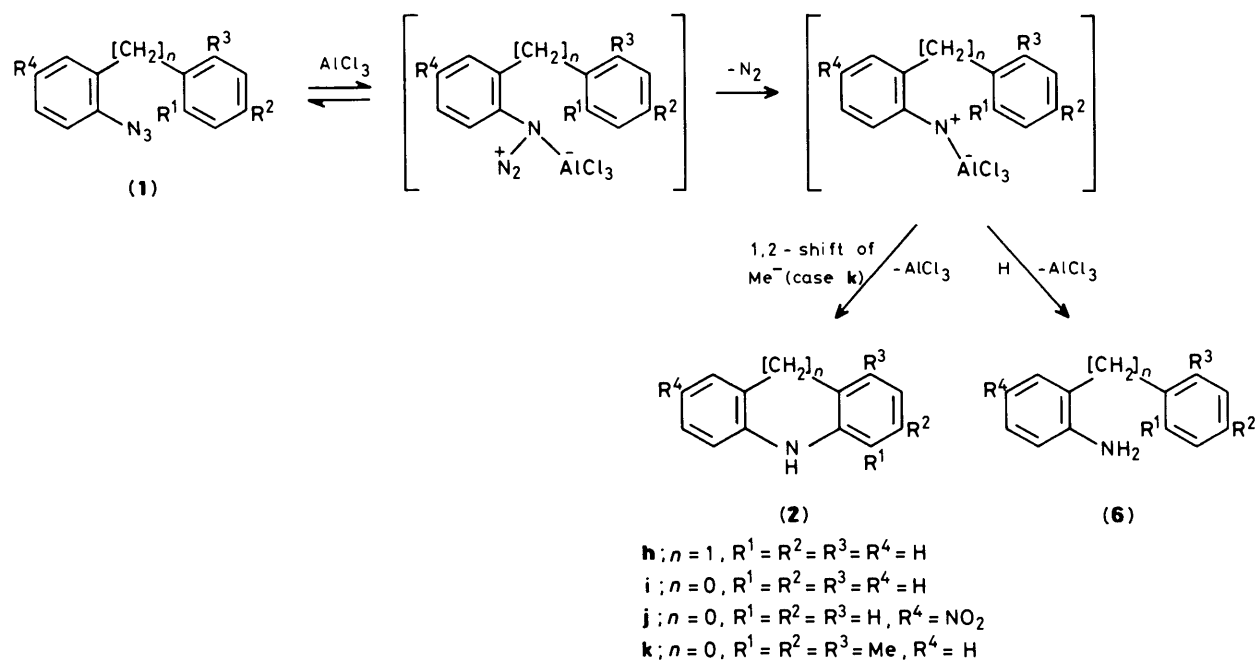| Azide	Yield[a] (%)	
	(2)	(6)
(1h)	89	4
(1i)	83	2
(1j)	98	2
(1k)[b]	51	3

[a] Yields are based on azide used. [b] In the experiment employing azide (1k), a brown oil was eluted with CH_2Cl_2–EtOH using column chromatography, but could not be purified by further chromatography.

tolyl)amine (3b) (trace), 2-amino-5-methylbiphenyl (4b) (trace), and tar as a major product, and that with 4-methoxyphenyl azide (1e) mainly a tar without contamination by 4-methoxyphenyl(phenyl)amine (3e) (Table 1). The reaction between 4-nitrophenyl azide (1g) and benzene in the presence of $AlCl_3$ gave both an *N*-substitution product, 4-nitrophenyl(phenyl)amine (3g), and a *C*-substitution product, 2-amino-5-nitrobiphenyl (4g) (Table 1).

---

† A preliminary report of the cyclisation of 2-azidophenyl(phenyl)-methane and 2-azidobiphenyls; H. Takeuchi, M. Maeda, M. Mitani, and K. Koyama, *J. Chem. Soc., Chem. Commun.*, 1985, 287.

Scheme 1.

Scheme 2.

Although Borsche and Hahn[6] have found only 4-substituted diphenylamines in the reaction of the azide (**1a**) with toluene and anisole, we isolated both 2- and 4-substituted diphenyl-amines in the reaction with alkylbenzene or anisole. The reaction with bromobenzene also occurred preferentially at the *ortho* and *para-* positions, but there was no reaction with nitrobenzene.

Decompositions of (**1h**), (**1i**), 2-azido-5-nitrobiphenyl (**1j**), and 2-azido-2′,4′,6′-trimethylbiphenyl (**1k**) in CH_2Cl_2 in the

presence of $AlCl_3$ afforded (**2h**), (**2i**), 3-nitrocarbazole (**2j**), and 1,2,4-trimethylcarbazole (**2k**), respectively, together with a small amount of the corresponding 2-amino-substituted products (**6h**—**k**) (Table 2 and Scheme 2).

Thermal decomposition of the azide (**1h**) does not produce (**2h**), but instead 10*H*-azepino[1,2-*a*]indole is formed.[10] Thermolysis or photolysis of the azide (**1i**) to the carbazole (**2i**) is a well studied arylnitrene reaction.[11] The yield of the carbazoles (**2i**) and (**2j**) in our experiment was slightly better
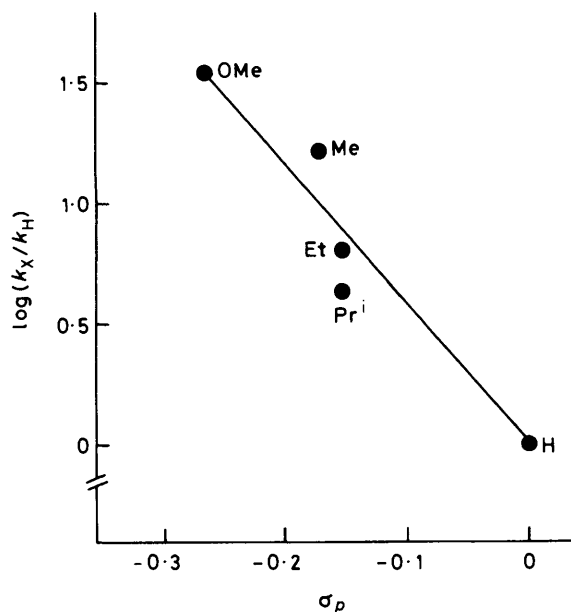
Figure. Hammett plot for the formation of diarylamines in the reaction of the azide (**1a**) with aromatic compounds in the presence of $AlCl_3$

than in the thermal and photochemical cases.[12] Pyrolysis of the azide (**1k**) gives 2,4,9-trimethylcarbazole and 8,10-dimethylphenanthridine,[13] not the carbazole (**2k**).

Formation of Arylnitrenium-$AlCl_3$ Complexes via Aryl Azide-$AlCl_3$ Complexes.—A stable solution which was blue in CH_2Cl_2 but yellow in toluene was formed at -30 to $-40\,°C$ in the reaction of (**1a**) or (**1i**) with $AlCl_3$; N_2 gas was evolved upon warming to *ca.* $0\,°C$. This indicates the existence of a complex between the azide and $AlCl_3$ below -30 to $-40\,°C$.

We have determined relative rate constants k_X/k_H, for the formation of *para*-substituted diphenylamines with respect to diphenylamine (**2a**) [$<1:10$ molar ratio of the azide (**1a**) to benzene or the other aromatic]. Employing 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 $\rho = -6.0$ (Figure 1).

The rate of evolution of N_2 in benzene is the same as that in toluene; pseudo first-order rate constants in both solvents were $1.0 \times 10^{-3}\ s^{-1}$ at $20\,°C$. The solubilities of $AlCl_3$ in these solvents are similar, and the reactivity of toluene is greater than that of benzene in the competition experiment using benzene and toluene (see Hammett plot). The results suggest that the aromatic compound is not involved in the step that leads to N_2 evolution; an S_N2 reaction involving attack of aromatic compound on the complex between the azide and $AlCl_3$ may be ruled out (see Scheme 1). These observations are in accord with the proposal shown in Scheme 1, for a rapid pre-equilibrium, a slow second step, and a fast third step. Thus, an intermediate which is formed in the slow step is likely to be a nitrenium-$AlCl_3$ complex (it is difficult to imagine what else could be formed on loss of N_2). The large negative ρ value and the *ortho*- and *para*-direction of the substitution may be reasonably explained in terms of electrophilic aromatic substitution *via* a nitrenium-$AlCl_3$ complex (Scheme 1). An analogous intramolecular reaction may take place in the formation of (**2h**—**k**) from (**1h**—**k**) (Scheme 2).
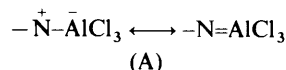
Character of Arylnitrenium-$AlCl_3$ Complexes.—In the reaction of the azide (**1a**) with benzene in the presence of $AlCl_3$,

the regiospecificity, *N*-/*C*-attack $= 95$, was obtained from the relative yield of (**2a**) compared with the yields of 2- and 4-aminobiphenyls (**4a**) and (**5a**). In contrast, the ratio of *N*-/*C*-attack was 4.6—4.7 for the reaction of the azide (**1a**) with benzene in the presence of TFSA or TFA.[5] There was no intramolecular *N*-substitution, and consequent cyclization, in the decomposition of the azides (**1h**) or (**1i**) in the presence of TFA,[5] TFSA,[5] or hydrogen halides.[9] The high regiospecificity of *N*-attack for 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. *N*-Attack would be less in the presence of competitive *C*-attack by a gegenion associated with the nitrenium ion in the presence of the above-mentioned protonic acid; such an attack by a gegenion may, however, be impossible for arylnitrenium-$AlCl_3$ complexes.

Arylnitrenium-$AlCl_3$ complexes generated from the azides (**1b**) and (**1e**) are presumably in the triplet state[5] as a result of an extended life-time arising from the electron-donating resonance effect of the substituents Me and OMe; tar formation may, therefore, occur *via* a triplet nitrenium ion-initiated polymerization. The triplet nitrenium ion may abstract hydrogen atoms[14] to produce amines (**6**).

Although we expect high reactivity at the *N*-position of both 4-nitrophenylnitrenium-$AlCl_3$ and 4-nitro-2-phenylphenylnitrenium-$AlCl_3$ complexes [*i.e.* the latter effectively produces (**2j**)], a *C*-substitution product (**4g**) (12%) was obtained along with an *N*-substitution product (**3g**) (49%) in the reaction of the azide (**1g**) with benzene; *N*-attack predominates to give (**3g**) in the reaction of (**1g**) with benzene in the presence of both TFA and TFSA.[5] For the 4-nitrophenylnitrenium-$AlCl_3$ complex the course of *C*-attack remains unclear because of the complexity of the substitution effect and the different reaction conditions, *etc.*

The more negative ρ value (-6.0) obtained from the phenylnitrenium-$AlCl_3$ complex over that (-4.5)[1,5] obtained 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 nitrenium ion. In other words, the nitrenium-$AlCl_3$ complex is more stable than the nitrenium ion in accord with the Hammett postulate, the stability probably being a result of resonance as in (A).

$$-\overset{+}{N}-\overset{-}{A}lCl_3 \longleftrightarrow -N{=}AlCl_3$$
(A)

Experimental

The general procedure for the analysis and characterization of the products and that for the preparation of azides as starting materials have been previously described.[5] Benzene, toluene, ethylbenzene, cumene, bromobenzene, nitrobenzene, and CH_2-Cl_2 were purified by standard method before use. $AlCl_3$ was reagent grade (Wako).

Reactions of Aryl Azides with Aromatic Compounds in the Presence of $AlCl_3$.—To a stirred suspension of $AlCl_3$ (3.1 mmol) in an aromatic solvent (5.0 ml) a solution of phenyl azide (**1a**), *p*-tolyl azide (**1b**), 4-methoxyphenyl azide (**1e**), or 4-nitrophenyl azide (**1g**) (2.8 mmol of each) in the same aromatic solvent (2.0 ml) was added over a period of *ca.* 5 min at room temperature. After the evolution of N_2 gas ceased aqueous NaOH solution was added. From the resulting organic layer 2- and 4-substituted diphenylamines (**2a**—**f**) and (**3a**—**f**) were isolated in the reaction of azide (**1a**), and 2-amino-5-methylbiphenyl (**4b**) and 2-amino-5-nitrobiphenyl (**4g**) in the reaction of (**1b**) and 4-nitrophenyl azide (**1g**), respectively (see Table 1). Tar production predominated in the reaction of (**1b**) or (**1e**), and we could find no

significant peak by g.l.c. analysis in the reaction of (1a) with nitrobenzene. For the reaction of (1a) with benzene, 2-amino-biphenyl (4a) (0.2%) was detected by g.l.c. analysis, but we could not find 4-aminobiphenyl (5a).

Intramolecular N-*Substitution of Aryl Azides in* CH_2Cl_2 *in the Presence of* $AlCl_3$.—A solution of 2-azidophenyl(phenyl)-methane (1h) 2-azidobiphenyl (1i), 2-azido-5-nitrobiphenyl (1j), or 2-azido-2',4',6'-trimethylbiphenyl (1k) (2.1 mmol of each) in CH_2Cl_2 (2.0 ml) was added slowly at room temperature to a stirred suspension of $AlCl_3$ (2.2 mmol) in CH_2Cl_2 (5.0 ml). The reaction mixtures were subsequently treated as mentioned above to give 9,10-dihydroacridine (2h), carbazole (2i), 3-nitrocarbazole (2j), or 1,2,4-trimethylcarbazole (2k) respectively, together with a small amount of 2-aminophenyl(phenyl)-methane (6h), 2-aminobiphenyl (6i), 2-amino-5-nitrobiphenyl (6j), or 2-amino-2',4',6'-trimethylbiphenyl (6k), respectively (Table 2).

Rates of Decomposition of the Azide (1a).—The azide (1a) (0.33 g) and finely powdered $AlCl_3$ (0.41 g) were added to benzene or toluene (22 ml of each) and the rates of azide decomposition determined at 20 °C by measurement of the volume of nitrogen evolved as a function of time. The decomposition obeys pseudo-first-order kinetics in the azide up to *ca.* 50% decomposition. The first-order rate constant, k_{obs}. $1.0 \times 10^{-3} s^{-1}$, in benzene was the same as that in toluene. Two runs in each solvent gave the same rate constant under the careful temperature control. The data in both solvents are meaningful since the solubility of $AlCl_3$ in benzene is almost identical with that in toluene.

Hammett Plot.—A heterogeneous mixture of the azide (1a) (2.8 mmol), aromatic substrate [benzene (4.0 ml)–toluene (3.0 ml), benzene (5.5 ml)–ethylbenzene (1.5 ml), benzene (5.5 ml)–cumene (1.5 ml), or toluene (5.5 ml)–anisole (1.5 ml)], and finely ground $AlCl_3$ (3.1 mmol) was allowed to react at room temperature until the evolution of nitrogen gas ceased. The molar ratio of the azide to aromatic substrate was less than 1/10.

Subsequently, the reaction mixtures were treated as described above, the yields of the products being determined by g.l.c. analysis. The analyses of products agreed within <5% on two runs. From the competition experiments, relative rate constants, k_X/k_H for the formation of *para*-substituted diarylamines (3b—e) with respect to diphenylamine (2a) were calculated on the basis of the product ratios, (2a):(3b), (2a):(3c), (2a):(3d), and (3b):(3e), and the initial concentration of the aromatic compounds; $k_{Me}/k_H = $ [yield of (3b)]/[yield of (2a)] × [(initial concentration of benzene)/(initial concentration of toluene)] for example in the competitive reaction between benzene and toluene. The product ratios were unaffected by the treatment of a mixture of (2a) and (3b), (2a) and (3c), (2a) and (3d), and (2a) and (3e) under the reaction conditions. That the graph shown in the Figure does not represent the best straight line presumably arises from the heterogeneous nature of the reactions.

References

1 H. Takeuchi, K. Takano, and K. Koyama, *J. Chem. Soc., Chem. Commun.,* 1982, 1254.
2 H. Takeuchi and R. Ihara, *J. Chem. Soc., Chem. Commun.,* 1983, 175.
3 H. Takeuchi and K. Takano, *J. Chem. Soc., Chem. Commun.,* 1983, 447.
4 H. Takeuchi, K. Koyama, M. Mitani, R. Ihara, T. Uno, Y. Okazaki, Y. Kai, and N. Kasai, *J. Chem. Soc., Perkin Trans. 1,* 1985, 677.
5 H. Takeuchi, K. Takano, *J. Chem. Soc., Perkin Trans. 1,* 1986, 611.
6 W. Borsche and H. Hahn, *Chem. Ber.,* 1949, **82**, 260; R. Kreher and G. Jäger, *Angew. Chem., Int. Ed. Engl.,* 1965, **4**, 28.
7 K. Hoegler and P. E. Bulter, *Chem. Ind. (London),* 1964, 933.
8 R. A. Abramovitch and E. P. Kyba, 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, p. 244.
9 P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.,* 1951, **73**, 2438.
10 G. R. Cliff and G. Jones, *J. Chem. Soc. C,* 1971, 3418.
11 P. A. S. Smith, 'Nitrene,' ed. W. Lwowski, Interscience, New York, 1970, p. 99.
12 P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.,* 1951, **73**, 2435.
13 G. Smolinski, *J. Am. Chem. Soc.,* 1960, **82**, 4717.
14 P. S. Gassman and R. L. Cryberg, *J. Am. Chem. Soc.,* 1969, **91**, 5157.