

Reactions of Aryl Azides with Alkenes in the Presence of Aluminium Trichloride. Formation of Novel Aziridines fused to Seven- and Eight-membered Rings†

Hiroshi Takeuchi,* Yukihiro Shiobara, Hideyuki Kawamoto, and Kikuhiko Koyama

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

Reactions of aryl azides (1) with cyclohexene gave 3-(arylamino)cyclohexenes (2) and *trans*-1-chloro-2-(arylamino)cyclohexanes (3), whereas that of (1) with cycloheptene or *cis*-cyclo-octene afforded novel aziridines, 8-aryl-8-azabicyclo[5.1.0]octanes (4), or 9-aryl-9-azabicyclo[6.1.0]nonanes (5), respectively. The reaction of phenyl azide (1a) with *cis*-4-methylpent-2-ene yielded 3-anilino-2-chloro-4-methylpentane (10), but that with the *trans*-alkene gave 4-anilino-2-methylpent-2-ene (7) and 3-anilino-4-methylpent-1-ene (8). The similar reaction of (1) with 3-trimethylsilylcyclohexene or 3-trimethylsilyl-*cis*-cyclo-octene produced only (2) or 3-(arylamino)-*cis*-cyclo-octenes (2'). The formation of the aziridines or the ring-opened products was explained by a mechanism *via* an aziridinium-AlCl₃ complex formed from an azide-AlCl₃ complex.

It is known that the reaction of phenyl azide with cyclohexene, *trans*-cyclo-octene, or oct-1-ene gives an aziridine derivative, but that with cyclopentene, cycloheptene, or *cis*-cyclo-octene yields the *N*-phenyliminocycloalkane.¹ Aromatic Friedel-Crafts *N*-substitution by either hydrazoic acid² or organic azides³⁻⁸ has literature precedent. We have recently reported that aromatic *N*-substitution occurs *via* arylnitrenium-AlCl₃ complexes generated from aryl azides in the presence of AlCl₃.^{9,10} This work has now been extended to the formation of novel aziridines fused to 7- and 8-membered rings. Ring-opened products were formed in those cases in which aziridines were not produced. The difference between the formation of aziridines and that of ring-opened products is discussed from a mechanistic point of view.



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|--|---|
| a; Ar = Ph | e; Ar = 2,6-Me ₂ C ₆ H ₃ |
| b; Ar = 4-MeC ₆ H ₄ | f; Ar = 4-ClC ₆ H ₄ |
| c; Ar = 4-MeOC ₆ H ₄ | g; Ar = 4-EtC ₆ H ₄ |
| d; Ar = 2-MeC ₆ H ₄ | |

Results and Discussion

Reactions of Aryl Azides with Alkenes in the Presence of Aluminium Trichloride.—Reaction of phenyl azide (1a) or 4-tolyl azide (1b) with cyclohexene gave 3-(arylamino)cyclohexene (2a) or (2b) and *trans*-1-chloro-2-(arylamino)cyclohexane (3a) or (3b) after addition of aqueous Na₂CO₃ to the reaction mixture (Table 1). Products (3a) and (3b) were not obtained pure, but identified by spectral data. The yields of (2) and (3) were increased with an excess of cyclohexene. The other products were tars. The reaction of 4-methoxyphenyl azide (1c) did not produce the corresponding compounds, and gave only tar. The results are shown in Table 1.

In contrast, the reaction of (1) with cycloheptene or *cis*-cyclo-octene in the presence of AlCl₃ gave the novel aziridine derivatives 8-aryl-8-azabicyclo[5.1.0]octane (4) or 9-aryl-9-azabicyclo[6.1.0]nonane (5), respectively (Table 2). The other products were tars.

A similar reaction with *cis*-4-methylpent-2-ene yielded 3-

anilino-2-chloro-4-methylpentane (10) along with tar and only traces of 4-anilino-2-methylpent-2-ene (7) and 3-anilino-4-methylpent-1-ene (8) were observed (Table 1). However, with the *trans*-alkene, compounds (7) and (8) and tar were formed without (10) (Table 1). Compound (10) was not obtained pure, but the structure was confirmed by spectral results. The reaction with hex-1-ene produced tar and a trace of 1-anilinohex-2-ene (9) (3.6%).

(a) *Induced decomposition of azide-AlCl₃ complex by alkene.* Phenyl azide (1a) completely decomposed in the presence of AlCl₃ in CH₂Cl₂ at room temperature, although the azide usually decomposes in aromatic solvents only at temperature > 130 °C. The AlCl₃ catalysed decomposition suggests that the azide decomposes in the presence of AlCl₃ *via* the conjugate acid of the azide. The decomposition rate for (1a) was measured in the presence of AlCl₃ at 8 °C; the rate in cyclohexene-CH₂Cl₂ was much faster than that in benzene-CH₂Cl₂ (the former rate was not measured because the azide was almost immediately decomposed by addition of 1.36M cyclohexene). This indicates that the decompositions occur *via* different mechanisms. Since the mechanism of decomposition of benzene is believed to involve the rate-determining formation of a nitrenium ion-AlCl₃ complex from the azide-AlCl₃ complex,^{9,10} the mechanism in the presence of the more nucleophilic cyclohexene could involve the elimination of a molecule of N₂ by induced decomposition corresponding to attack of an alkene on the azide-AlCl₃ to form the aziridinium-AlCl₃ complex (Scheme 1). The yields of (2a) and (3a) are increased as the concentration of cyclohexene is raised (see Table 1). This also supports the induced decomposition. However, 4-methoxyphenyl azide (1c) decomposes very quickly in benzene-CH₂Cl₂ and cyclohexene-CH₂Cl₂ in the presence of AlCl₃. This probably means that the decompositions in the two mixtures take place *via* an ArN⁺-AlCl₃^{9,10} complex stabilised by the electron-donating methoxyphenyl group. Thus, the reaction of (1c) may bring about polymerisation *via* the nitrenium-AlCl₃ complex to form a tar.

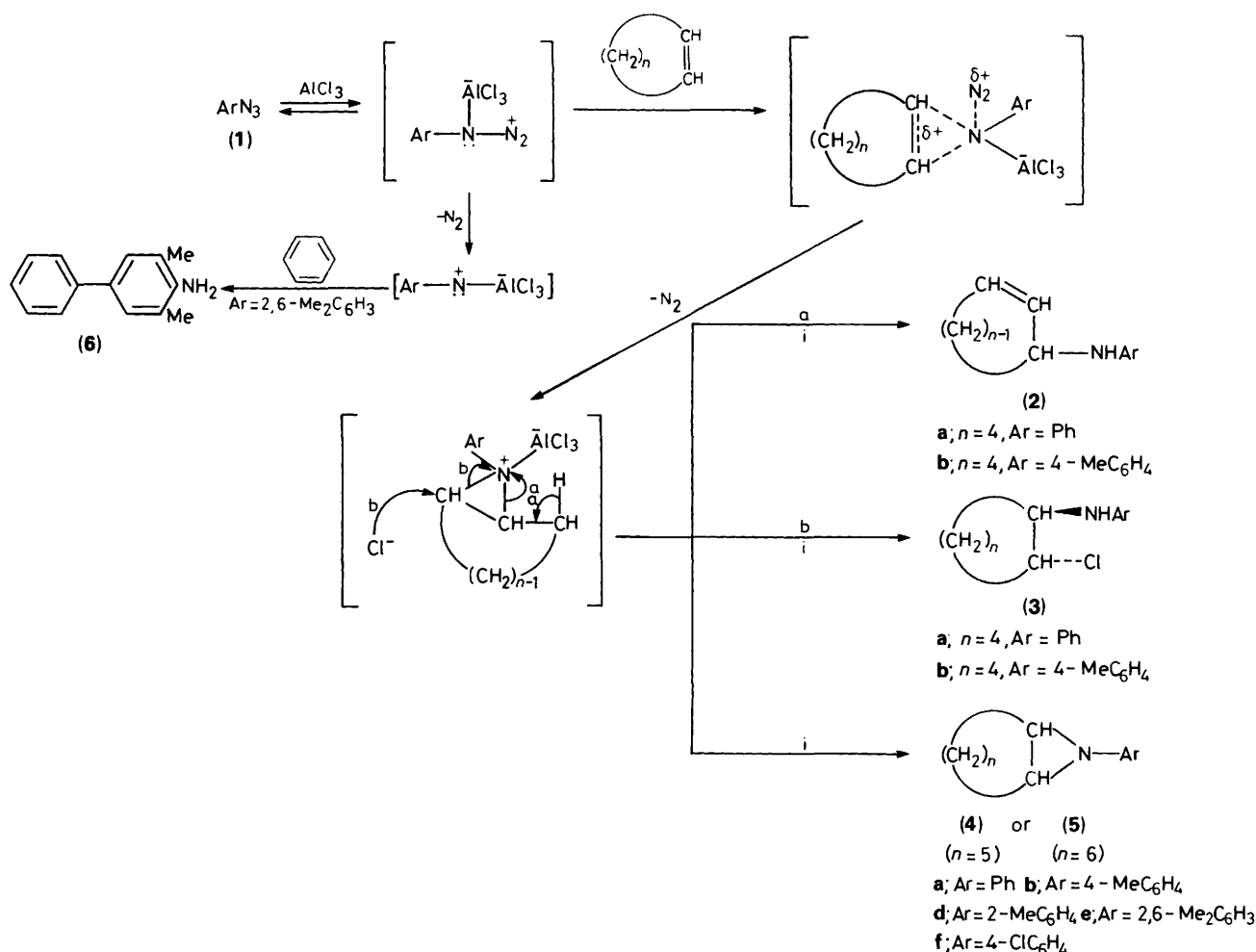
The reaction of (1a) with cyclohexene did not give aromatic substitution products like 3-(2- and 4-aminophenyl)cyclo-

† Preliminary report, H. Takeuchi, Y. Shiobara, M. Mitani, and K. Koyama, *J. Chem. Soc., Chem. Commun.*, 1985, 1251.

Table 1. Reactions of *para*-substituted aryl azides $p\text{-XC}_6\text{H}_4\text{N}_3$ (1) with cyclohexene or *cis*- and *trans*-4-methylpent-2-enes in the presence of AlCl_3 .

X in (1)	Azide/ mmol	Alkene/ ml	AlCl_3 / mmol	% Yield ^a				
				(2)	(3)	(7)	(8)	(10)
(1a), H ^b	2.3	1.8 ^c	2.6	49	43	—	—	—
(1a), H ^d	2.3	0.8 ^c	2.3	7	14	—	—	—
(1b), Me ^b	2.2	1.8 ^c	2.6	18	81	—	—	—
(1b), Me ^d	2.1	1.1 ^c	2.5	7	16	—	—	—
(1c), OMe ^b	2.3	1.8 ^c	2.6	0	0	—	—	—
(1a), H	4.6	3.0 ^e	5.1	—	—	trace	trace	31
(1a), H	4.6	3.0 ^f	5.1	—	—	23	20	0

^a Yields are based on the azide used, and the other products were tars. ^b The reaction was carried out by Method 1 described in the Experimental section. ^c Cyclohexene was employed. ^d Method 2 mentioned in the Experimental section was used. ^e *cis*-4-Methylpent-2-ene was used. ^f *trans*-4-Methylpent-2-ene was used.

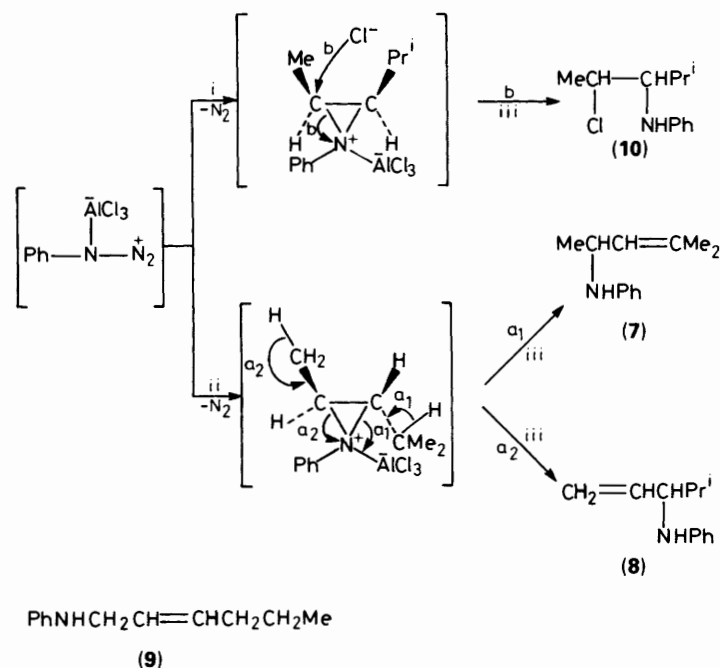


hexene,¹¹ and that of (1) with cycloheptene or *cis*-cyclo-octene also did not produce the analogous products or cyclopropane derivatives. If the reaction with alkene proceeds *via* the nitrenium species, some attack on the aromatic ring would have been expected.^{11,12} In fact, 4-amino-3,5-dimethylbiphenyl (6) was obtained in the reaction of (1e) with benzene in the presence of AlCl_3 or AlBr_3 (see Scheme 1 and Experimental section). The absence of aromatic substitution products in the present cases suggests that attack of an aryl nitrenium ion- AlCl_3 complex on the alkene does not occur.

(b) Formation of aziridinium- AlCl_3 complexes as inter-

mediates. Additions to *cis*- and *trans*-4-methylpent-2-enes give different compounds as expected (see Scheme 2). This means that the additions lead to aziridinium- AlCl_3 complexes in which the alkyl groups have the same geometry as in the alkenes. The formation of aziridines (4) and (5) without contamination by ring-opening products also supports the formation of aziridinium- AlCl_3 complexes.

(c) Ring-opening reactions of aziridinium- AlCl_3 complexes. The reaction with cyclohexene gave *N*-allylaniline (2), but did not yield *N*-cyclohexylideneaniline which can conceivably be formed *via* a stable secondary carbocation. This observation,



Scheme 2. Reagents: i, *cis*-4-methylpent-2-ene; ii, *trans*-4-methylpent-2-ene; iii, aqueous Na₂CO₃. Only traces of (7) and (8) were formed from i.

Table 2. Reactions of the aryl azides ArN₃ (1) with cycloheptene or *cis*-cyclo-octene (2.1 ml) in the presence of AlCl₃ (2.6 mmol).

Ar in (1)	Azide/ mmol	Alkene	% Yield ^a	
			(4)	(5)
(1a), Ph	2.3	A ^b	13	—
(1a), Ph	2.3	B ^c	—	47
(1b), 4-MeC ₆ H ₄	2.2	A	59	—
(1b), 4-MeC ₆ H ₄	2.2	B	—	93
(1d), 2-MeC ₆ H ₄	2.3	A	21	—
(1d), 2-MeC ₆ H ₄	2.3	B	—	6
(1e), 2,6-Me ₂ C ₆ H ₃	2.3	A	44	—
(1e), 2,6-Me ₂ C ₆ H ₃	2.3	B	—	42
(1f), 4-ClC ₆ H ₄	2.2	A	63	—
(1f), 4-ClC ₆ H ₄	2.2	B	—	65

^a Yields are based on the azide used, and the other products were tars.

^b A = cycloheptene. ^c B = *cis*-cyclo-octene was used.

Table 3. Reactions of the aryl azides ArN₃ (1) with 3-trimethylsilylcycloalkenes (3.6 mmol) in the presence of AlCl₃ (2.6 mmol).

Ar in (1)	Azide/mmol	Alkene	% Yield ^a
			of (2)
(1b), 4-MeC ₆ H ₄	2.3	A ^b	24
(1b), 4-MeC ₆ H ₄	2.3	B ^c	21
(1f), 4-ClC ₆ H ₄	2.3	A	14
(1f), 4-ClC ₆ H ₄	2.3	B	26
(1g), 4-EtC ₆ H ₄	2.3	A	18
(1g), 4-EtC ₆ H ₄	2.2	B	26

^a Yields are based on the azide used, and the other products were tars.

^b A = 3-trimethylsilylcyclohexene. ^c B = 3-trimethylsilyl-*cis*-cyclo-octene.

the *trans*-addition giving (3), and at the less sterically hindered position producing (10) may eliminate an S_N1 ring-opening mechanism.

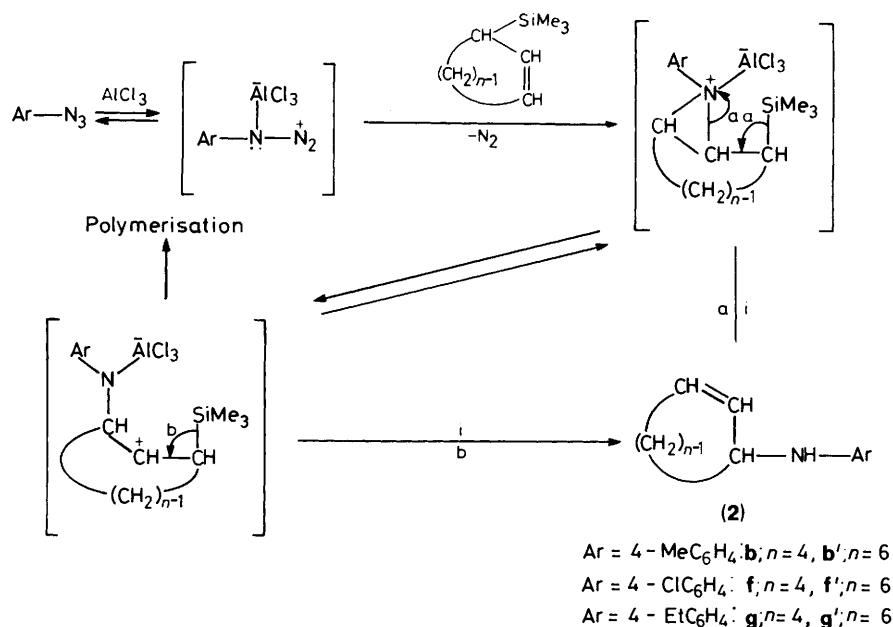
The reaction with cycloheptene or *cis*-cyclo-octene yielded the aziridines (4) or (5) whereas that with cyclohexene gave the

ring-opened products (2) and (3). This interesting difference can be explained as follows. The ring-strain in the three-membered ring of the aziridinium-AlCl₃ complex is greater with fusion of the aziridine to a five- or six-membered ring than for seven- or eight-membered rings, because of the interactions between the substituents on the nitrogen and the adjacent hydrogens (at nearly axial positions) close to the aziridine ring in the cyclohexene complex. Molecular models of the aziridinium-AlCl₃ complexes support this idea. Thus, the cyclohexene complex undergoes concerted ring opening to lead to (2) (see path a in Scheme 1), and S_N2 ring-opening by Cl⁻ to yield the *trans*-adduct (3) (path b in Scheme 1), while the cycloheptene and *cis*-cyclo-octene complexes would be inert to the ring-opening reaction. Compound (3a) was not converted to the corresponding (2a) under the reaction conditions without the azide and alkene, so that (2) would be the primary ring-opened products from the aziridinium-AlCl₃ complexes.

The aziridinium-AlCl₃ complex formed from the *cis*-4-methylpent-2-ene is attacked by Cl⁻ preferentially at the less hindered carbon (*i.e.* C-3) to produce (10) (path b, Scheme 2). However, the complex formed from the *trans*-isomer is less susceptible to such an attack because of steric interference between the attacking anion and the 2-Prⁱ substituent (the interference is greater than in the reaction of the *cis*-isomer), so that the former complex may undergo ring-opening to lead to (7) and (8) (paths a₁ and a₂ in Scheme 2). The lack of susceptibility to attack on C-3 in the *trans*-isomer of 1-substituted-2-isopropyl-3-methylaziridines has also been observed in ring-opening reactions of 1-ethoxycarbonyl-2-isopropyl-3-methylaziridines by acetic acid¹³ and those of 1-phenyl-2-isopropyl-3-methylaziridines by trifluoroacetic acid.¹¹

The low yield of (9) from hex-1-ene is probably due to the difficulty in formation of the aziridinium-AlCl₃ complex because of the low nucleophilic character of the terminal alkene.¹⁴

Reaction of Aryl Azides with 3-Trimethylsilylcycloalkenes in the Presence of Aluminium Trichloride.—The reaction of the aryl azides (1b) (1f), and (1g) with 3-methylsilylcyclohexene or 3-methylsilyl-*cis*-cyclo-octene afforded only 3-(arylamino)cyclohexene (2b), (2f), and (2g) or 3-(arylamino)-*cis*-cyclo-octene



Scheme 3. Reagent: i, aqueous Na_2CO_3 .

(2b'), (2f'), and (2g'), respectively (Table 3). Both fast (in the case of SiMe_3) and slow (in the case of H) pathways for electrophilic group loss are available. Thus, we expected that the aziridinium- AlCl_3 complexes formed in these reactions would exclusively undergo concerted ring opening to give compounds (2) in good yields (see path a in Scheme 3). In fact, only compounds (2) were formed, but the yields were low. Polymerisation probably occurs *via* a carbocation generated from the aziridinium- AlCl_3 complex (see Scheme 3). The carbocation might be stabilised by σ - π conjugation caused by interaction between a $\sigma_{\text{Si-C}}$ orbital and a vacant p_π orbital at the β -position with respect to the Si atom.

Experimental

IR spectra were obtained on a Hitachi model EPI-G3 spectrometer. ^1H and ^{13}C NMR spectra were taken with a Nippondenshi JNM-FX-60Q instrument with Me_4Si as internal standard. Analytical GLC was performed on a Shimadzu GC-6A chromatograph using a glass column (1 m \times 3 mm) (column A, 10% silicone SE-30 on 60-80 Chromosorb W; column B, 5% silicone DC-550 on 60-80 Chromosorb W). Preparative GLC was carried out with a Hitachi model 063-0012 unit using a column (2 m \times 3 mm) packed with 10% silicone SE-30 on 60-80 Chromosorb W. The analyses of products agreed within <3% on two runs.

Cyclohexene, cycloheptene, *cis*-cyclo-octene, *cis*- and *trans*-4-methylpent-2-enes, hex-1-ene, dichloromethane, and benzene were purified by standard methods before use. AlCl_3 and AlBr_3 were reagent grade (Wako), and used without further purification. *o*- and *p*-Tolyl azides (1d) and (1b), 4-methoxyphenyl azide (1c), 2,6-dimethylphenyl azide (1e), 4-chlorophenyl azide (1f), and 4-ethylphenyl azide (1g) were prepared by diazotisation of the corresponding anilines followed by addition of sodium azide.¹⁵⁻¹⁷

The following compounds were prepared by the methods described in the literature. Phenyl azide (1a),¹⁸ 3-anilinocyclohexene (2a),¹¹ 4-anilino-2-methylpent-2-ene (7),¹¹ 3-anilino-4-methylpent-1-ene (8),¹¹ 1-anilinohex-2-ene (9),¹¹ 3-trimethylsilylcyclohexene,¹⁹ 3-trimethylsilyl-*cis*-cyclo-octene,¹⁹ and *N*-cyclohexylideneaniline.²⁰

Reactions of Phenyl Azide (1a) and *p*-Tolyl Azide (1b) with Cyclohexene in the Presence of Aluminium Trichloride.—To a stirred suspension of AlCl_3 (ca. 2.6 mmol) in cyclohexene (0.7 ml)- CH_2Cl_2 (2.0 ml) a solution of (1a) or (1b) (ca. 2.3 mmol) in cyclohexene (1.1 ml)- CH_2Cl_2 (1.0 ml) was added during ca. 5 min (Method 1). The temperature rose from 15 to ca. 30 °C, and then the evolution of N_2 gas ceased. Aqueous Na_2CO_3 was added until the solution reached pH > 7, the organic layer was extracted with CH_2Cl_2 , and the products were isolated by column chromatography using silica gel (Wakogel C-300) and CCl_4 - CH_2Cl_2 as eluant. The yields of the products were determined by GLC using column A. When the initial suspension of AlCl_3 did not contain cyclohexene (Method 2), the yields were decreased. Use of (1c) instead of (1a) or (1b) led only to tar. The results are summarized in Table 1. The product (2a) was identified by comparison (IR; ^1H NMR) with an authentic sample, and the following compounds were identified by their spectroscopic data.

3-(*p*-Tolylamino)cyclohexene (2b), liquid; ν_{max} (neat) 3 400 (NH), 3 010, 2 920, and 2 850 (C-H), 1 620 (C=C) 1 580 and 1 520 (ArC=C) 1 300 (C-N), and 810 cm^{-1} (*para*-substituted phenyl); δ_{H} (CCl_4 - CDCl_3) 1.2-2.5 (6 H, m, CH_2), 2.3 (3 H, s, Me), 3.7-4.3 (1 H, m, 3-CH), 5.0-5.5 (1 H, br, NH), 5.7-6.1 (2 H, br, 1- and 2-CH), and 6.35-7.2 (4 H, ABq, C_6H_4); δ_{C} (CCl_4 - CDCl_3) 19.5, 24.9, and 28.2 (CH_2), 20.4 (Me), 49.9 (3-CH), 115.3 and 129.5 (ArC-2 and -3), and 127.5 and 130.4 ($\text{CH}=\text{CH}$) (Found: C, 83.7; H, 9.15; N, 7.2. $\text{C}_{13}\text{H}_{17}\text{N}$ requires C, 83.35; H, 9.15; N, 7.5%).

trans-2-Anilino-1-chlorocyclohexane (3a), liquid; ν_{max} (neat) 3 400 (NH), 3 020, 3 050, 2 920, and 2 850 (C-H), 1 600 and 1 500 (C=C of Ph), 1 450 (C-H), 1 305 (C-N), 750 and 695 cm^{-1} (Ph); δ_{H} (CCl_4 - CDCl_3) 0.6-2.7 (8 H, m, CH_2), 3.2-3.7 (1 H, m, NCH), 3.7-4.3 (1 H, m, ClCH), 4.0-4.8 (1 H, br, NH), and 6.4-7.6 (m, 5 H, Ph); δ_{C} (CCl_4 - CDCl_3) 22.9, 23.7, 30.7, and 33.9 (CH_2), 57.4 (NCH), 61.5 (ClCH), and 113.3, 117.2, 117.8, and 128.9 (phenyl C-2, -1, -4, and -3). Elemental analysis was not performed because the product contained some impurities (NMR). The coupling constant between 1-H and 2-H, $J_{1,2}$ 8 Hz, shows the protons to be axial (*i.e.* *trans*-geometry).

trans-1-Chloro-2-(*p*-tolylamino)cyclohexane (3b), liquid, ν_{max} (neat) 3 400 (NH), 3 050, 2 930, and 2 955 (C-H), 1 615 and 1 520 (Ar C=C), 1 470 (C-H), 1 300 (C-N), 810 (*para*-

substituted phenyl), and 750 cm^{-1} (C–Cl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.6–2.8 (8 H, br, CH_2), 2.3 (3 H, s, Me), 3.0–3.6 (1 H, m, NCH), 3.6–4.2 (1 H, m, ClCH), 4.7–5.6 (1 H, br, NH), and 6.25–7.45 (4 H, ABq, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 20.3 (Me), 22.8, 23.7, 30.3, and 33.9 (CH_2), 58.4 (NCH), 61.2 (ClCH), and 114.6, 126.4, and 129.4 (ArC-2, -1, and -3). Elemental analysis was not carried out because impurities were present. The coupling constant between 1-H and 2-H, $J_{1,2}$ 8 Hz, also indicates the product to have the *trans*-geometry.

Reactions of Aryl Azides (1) with Cycloheptene in the Presence of Aluminium Trichloride.—Reactions of the azides (**1a**), (**1b**), (**1d**), (**1e**), and (**1f**) with cycloheptene were carried out under conditions similar to those in the foregoing Method 1 (but the initial suspension contained 1.0 ml of alkene) for the reaction of (**1**) with cyclohexene. Products were isolated and analysed as just described. Conditions and results are in Table 2. The structures of the products were characterised by the following data.

8-Phenyl-8-azabicyclo[5.1.0]octane (4a), liquid; $v_{\text{max}}(\text{neat})$ 3 020, 2 910, and 2 840 (C–H), 1 600 and 1 490 (C=C of Ph), 1 260 (C–N), 1 450 (C–H), and 770 and 690 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.7–2.6 (12 H, m, CH_2 and NCH) and 6.6–7.6 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 24.9, 29.2, 30.6 (3-, 2-, and 4- CH_2), 42.5 (NCH), and 118.8, 120.4, and 127.5 (PhC-2, -4, and -3) (Found: C, 83.7; H, 9.25; N, 7.25. $\text{C}_{13}\text{H}_{17}\text{N}$ requires C, 83.35; H, 9.15; N, 7.50%).

8-(p-Tolyl)-8-azabicyclo[5.1.0]octane (4b), liquid; $v_{\text{max}}(\text{neat})$ 3 010, 2 910, and 2 830 (C–H), 1 610 and 1 510 (Ar C=C), 1 725 and 1 220 (C–N), 1 450 (C–H), and 820 cm^{-1} (*para*-substituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.9–2.4 (12 H, m, CH_2 and NCH), 2.3 (3 H, s, Me), and 6.4–7.4 (4 H, ABq, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 20.6 (Me), 25.9, 30.2, and 31.6 (3-, 2-, and 4- CH_2), 43.4 (NCH), and 119.6, 128.9, 130.1, and 153.4 (ArC-2, -3, -4, and -1) (Found: C, 83.9; H, 9.5; N, 6.65. $\text{C}_{14}\text{H}_{19}\text{N}$ requires C, 83.55; H, 9.5; N, 6.95%).

8-(o-Tolyl)-8-azabicyclo[5.1.0]octane (4d), liquid; $v_{\text{max}}(\text{neat})$ 3 000, 2 900, and 2 840 (C–H), 1 600 and 1 490 (Ar C=C), 1 290 and 1 250 (C–N), 1 450 (C–H), and 760 cm^{-1} (*ortho*-substituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 1.0–2.7 (12 H, m, CH_2 and NCH), 2.3 (3 H, s, Me), and 6.6–7.5 (4 H, m, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 18.2 (Me), 25.8, 29.7, and 31.8 (3-, 2-, and 4- CH_2), 43.2 (NCH), and 118.6, 121.4, 126.1, 129.6, 130.0, and 153.0 (Ar C-6, -4, -5, -2, -3, and -1) (Found: C, 83.8; H, 9.65; N, 6.65. $\text{C}_{14}\text{H}_{19}\text{N}$ requires C, 83.55; H, 9.5; N, 6.95%).

8-(2,6-Dimethylphenyl)-8-azabicyclo[5.1.0]octane (4e), m.p. 60.9–61.0 °C; $v_{\text{max}}(\text{Nujol})$ 3 060, 3 030, and 3 010 (C–H), 1 595 and 1 480 (Ar C=C), 1 280, 1 270, and 1 230 (C–N), and 765 and 740 cm^{-1} (1,2,3-trisubstituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 1.0–2.4 (12 H, m, CH_2 and NCH), 2.3 (6 H, s, Me), and 6.7–7.15 (3 H, m, C_6H_3); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 19.3 (Me), 25.7, 29.2, 31.9 (3-, 2-, and 4- CH_2), 44.3 (NCH), and 120.7, 128.1, 128.6, and 151.5 (ArC-4, -2, -3, and -1) (Found: C, 83.55; H, 9.8; N, 6.6. $\text{C}_{15}\text{H}_{21}\text{N}$ requires C, 83.65; H, 9.85; N, 6.5%).

8-(4-Chlorophenyl)-8-azabicyclo[5.1.0]octane (4f), liquid; $v_{\text{max}}(\text{neat})$ 3 020, 2 920, and 2 840 (C–H), 1 590 and 1 490 (Ar C=C), 1 280 and 1 250 (C–N), 1 450 (C–H), 1 095 (ClC₆H₄), and 830 (*para*-substituted phenyl), and 650 cm^{-1} (C–Cl); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.0–2.6 (12 H, m, CH_2 and NCH), and 6.75–7.55 (4 H, ABq, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 25.7, 29.9, and 31.5 (3-, 2-, and 4- CH_2), 43.8 (NCH), and 120.6, 126.3, 128.4, and 154.4 (ArC-2, -4, -3, and -1) (Found: C, 70.8; H, 7.25; N, 6.0. $\text{C}_{13}\text{H}_{16}\text{ClN}$ requires C, 70.4; H, 7.25; N, 6.3%).

Reactions of Aryl Azides (1) with cis-Cyclo-octene in the Presence of Aluminium Trichloride.—*cis*-Cyclo-octene was used in place of the cycloheptene used in the foregoing experiments. The procedure for isolation and analysis was almost same as

that just described. Conditions and results are in Table 2. The products were identified as follows.

9-Phenyl-9-azabicyclo[6.1.0]nonane (5a), liquid; $v_{\text{max}}(\text{neat})$ 3 000, 2 950, and 2 850 (C–H), 1 600 and 1 500 (C=C of Ph), 1 450 (C–H), 1 320 (C–N), 1 450 (C–H), and 755 and 670 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.7–1.9 (12 H, m, CH_2), 1.9–2.6 (2 H, m, NCH), and 6.7–7.5 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 26.4, 27.0, 27.1 (CH_2), 43.1 (NCH), and 119.8, 121.4, 128.4, and 155.2 (Ph C-2, -4, -3, and -1). This compound was dissolved in acetic acid, and the solution was refluxed for 5 h. The mixture was treated with aqueous Na_2CO_3 , and extracted with benzene. The following compound was isolated by evaporation [this acetolysis suggests the structure of (**5a**) to be correct]: 1-acetoxy-2-anilino-*cis*-cyclo-octane (**5a'**); liquid, $v_{\text{max}}(\text{neat})$ 3 400 (NH), 3 000, 2 950, and 2 850 (C–H), 1 720 (C=O), 1 600 and 1 500 (C=C of Ph), 1 450 (C–H), 1 365 and 1 310 (C–N), 1 240 and 1 020 (C–O), and 740 and 690 cm^{-1} (mono-substituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.7–2.3 (12 H, m, CH_2 and NCH), 1.8 (3 H, s, Me), 3.3–3.9 (1 H, m, OCH), 4.7–5.2 (1 H, br, NH), and 6.3–7.4 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 19.9 (Me), 23.4, 23.8, 24.7, 25.0, 28.4, and 29.2 (CH_2), 55.7 (NCH), 76.0 (OCH), 111.9, 115.8, 127.9, 146.2 (PhC-2, -4, -3, and -1), and 169.4 (C=O).

9-(p-Tolyl)-9-azabicyclo[6.1.0]nonane (5b), liquid; $v_{\text{max}}(\text{neat})$ 3 000, 2 900, and 2 840 (C–H), 1 610 and 1 510 (Ar C=C), 1 465, 1 440, and 1 430 (C–H), 1 270 and 1 220 (C–N), and 820 cm^{-1} (*para*-substituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.9–2.5 (14 H, m, CH_2 and NCH), 2.3 (3 H, s, Me), and 6.65–7.25 (4 H, ABq, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 20.6 (Me), 26.4, 27.0, and 27.1 (CH_2), 43.2 (NCH), and 119.7, 129.0, 130.4, and 152.8 (ArC-2, -3, -4, and -1) (Found: C, 83.7; H, 9.95; N, 6.3. $\text{C}_{15}\text{H}_{21}\text{N}$ requires C, 83.65; H, 9.85; N, 6.5%).

9-(o-Tolyl)-9-azabicyclo[6.1.0]nonane (5d), m.p. 62.3–62.9 °C; $v_{\text{max}}(\text{Nujol})$ 2 950 and 3 000 (C–H), 1 600 and 1 490 (Ar C=C), 1 270 and 1 220 (C–N), and 750 cm^{-1} (*ortho*-substituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.7–2.5 (14 H, m, CH_2 and NCH), 2.3 (3 H, s, Me), and 6.4–7.4 (4 H, m, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 18.4 (Me), 26.4, 26.6, and 27.0 (CH_2), 43.1 (NCH), and 118.8, 121.6, 126.0, 129.8, 130.0, and 152.4 (ArC-6, -4, -5, -2, -3, and -1) (Found: C, 83.95; H, 9.85; N, 6.2. $\text{C}_{15}\text{H}_{21}\text{N}$ requires C, 83.65; H, 9.85; N, 6.5%).

9-(2,6-Dimethylphenyl)-9-azabicyclo[6.1.0]nonane (5e), m.p. 97.5–98.0 °C, $v_{\text{max}}(\text{Nujol})$ 3 050 and 3 020 (C–H), 15 90 (Ar C=C), 1 270 and 1 220 (C–N), and 760 and 740 cm^{-1} (1,2,3-trisubstituted phenyl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 1.0–2.7 (14 H, m, CH_2 and NCH), 2.3 (3 H, s, Me), and 6.7–7.5 (3 H, m, C_6H_3); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 19.6 (Me), 26.3, 26.5, and 27.1 (CH_2), 44.6 (NCH), and 120.9, 128.4, 128.7, and 151.2 (ArC-4, -2, -3, and -1) (Found: C, 83.4; H, 10.0; N, 5.9. $\text{C}_{16}\text{H}_{23}\text{N}$ requires C, 83.8; H, 10.1; N, 6.1%).

9-(4-Chlorophenyl)-9-azabicyclo[6.1.0]nonane (5f), m.p. 76.0–77.5 °C; $v_{\text{max}}(\text{Nujol})$ 3 080 and 3 020 (C–H), 1 590 and 1 490 (Ar C=C), 1 280 and 1 230 (C–N), 1 100 and 1 110 ($\text{C}_6\text{H}_4\text{Cl}$), 830 (*para*-substituted phenyl), and 650 cm^{-1} (C–Cl); $\delta_{\text{H}}(\text{CCl}_4\text{-CDCl}_3)$ 0.6–2.6 (14 H, m, CH_2 and NCH), and 6.75–7.55 (4 H, ABq, C_6H_4); $\delta_{\text{C}}(\text{CCl}_4\text{-CDCl}_3)$ 26.3, 27.0, and 26.9 (CH_2), 43.5 (NCH), and 121.1, 126.3, 128.5, and 153.8 (ArC-2, -4, -3, and -1) (Found: C, 71.35; H, 7.65; N, 5.95. $\text{C}_{14}\text{H}_{18}\text{ClN}$ requires C, 71.35; H, 7.7; N, 5.95%).

Reactions of Phenyl Azide (1a) with cis- and trans-4-Methyl-2-enes in the Presence of Aluminium Trichloride.—A solution of (**1a**) (4.6 mmol) in the *cis*- or *trans*-alkene (2.0 ml)– CH_2Cl_2 (1.0 ml) was added to a stirred suspension of AlCl_3 (5.1 mmol) in the *cis*- or *trans*-alkene (1.0 ml)– CH_2Cl_2 (5.0 ml) during *ca.* 5 min. The temperature rose from 15 to *ca.* 30 °C. The mixture was treated with aqueous Na_2CO_3 , and the products were isolated by preparative GLC. Yields of the products were determined by GLC using column B. Conditions and results are

in Table 1. The IR and ^1H NMR spectra of (7) and (8) are the same as those described in the literature,¹¹ and the structure of the following compound was confirmed by spectral data.

3-Anilino-2-chloro-4-methylpentane (10), liquid; ν_{max} (neat) 3 400 (NH), 3 045, 3 010, 2 960, 2 910, and 2 860 (C-H), 1 600 and 1 510 (C=C of Ph), 1 320 and 1 265 (C-N), 750 and 690 (Ph), and 665 cm^{-1} (C-Cl); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 1.0 (6 H, d, CHMe_2), 1.5 (3 H, d, ClCHMe), 1.6–2.6 (1 H, m, Me_2CH), 3.1 (1 H, br d, NCH), 3.3–4.1 (1 H, br, NH), 4.4 (1 H, br q, ClCH), and 6.4–7.4 (5 H, m, Ph); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 19.9 (Me_2CH), 23.2 (ClCHMe), 32.9 (Me_2CH), 60.7 (NCH), 63.6 (ClCH), and 112.2, 116.8, and 129.1 (PhC-2, -4, and -3). Elemental analysis was not carried out because a trace of impurity was present.

The Reaction of Phenyl Azide (1a) with Hex-1-ene in the Presence of Aluminium Trichloride.—A solution of (1a) (4.6 mmol) and hex-1-ene (3.0 ml) was added to a suspension of AlCl_3 (5.1 mmol) in CH_2Cl_2 (5.0 ml). The product (9) (3.6%) and tar were found by the method described above.

Reactions of Aryl Azides (1) with 3-Trimethylsilyl-cycloalkanes.—A suspension of AlCl_3 (ca. 2.6 mmol) in CH_2Cl_2 (3.0 ml) was refluxed. A solution of (1b), (1f), or (1g) (ca. 2.3 mmol), 3-trimethylsilyl-cyclohexene or -cis-cyclo-octene (ca. 3.6 mmol), and CH_2Cl_2 (1.0 ml) was added to the suspension during ca. 5 min. The mixture was treated with aqueous Na_2CO_3 and the organic layer extracted with CH_2Cl_2 . The products were isolated by column chromatography as mentioned above. The yields were determined by GLC using column A. Conditions and results are in Table 3. The structures of the products were confirmed as follows.

3-(4-Chlorophenylamino)cyclohexene (2f), liquid; ν_{max} (neat) 3 400 (NH), 3 020, 2 920, and 2 850 (C-H), 1 600 and 1 500 (Ar C=C), 1 450 and 1 400 (C-H), 1 315 and 1 240 (C-N), 1 090 (PhCl), 820 (*para*-substituted phenyl), 730 (CH=CH), and 660 cm^{-1} (C-Cl); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 0.8–2.4 (6 H, m, CH_2), 3.4–4.2 (2 H, br, NH and NCH), 5.6–6.2 (2 H, m, CH=CH), and 6.35–7.55 (4 H, ABq, C_6H_4); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 19.5, 25.0, and 28.6 (CH_2), 48.0 (NCH), 114.2, 121.9, 128.9, and 145.1 (ArC-2, -4, -3, and -1), and 128.0 and 130.1 (1- and 2-CH) (Found: C, 69.65; H, 6.85; N, 6.45; $\text{C}_{12}\text{H}_{14}\text{ClN}$ requires C, 69.4; H, 6.8; N, 6.75%).

3-(4-Ethylphenylamino)cyclohexene (2g), liquid; ν_{max} (neat) 3 390 (NH), 3 000, 2 920, and 2 840 (C-H), 1 610 and 1 510 (Ar C=C), 1 445 and 1 410 (C-H), 1 300 and 1 260 (C-N), 820 (*para*-substituted phenyl), and 720 cm^{-1} (CH=CH); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 0.8–2.2 (6 H, m, CH_2), 1.2 (3 H, t, Me), 2.55 (2 H, MeCH_2), 3.0–3.6 (1 H, br, NH), 3.7–4.2 (1 H, m, NCH), 5.6–6.1 (2 H, m, CH=CH), and 6.4–7.3 (4 H, ABq, C_6H_4); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 15.9 (Me), 19.6, 25.1, and 28.9 (4-, 5-, and 6- CH_2), 27.9 (MeCH_2), 48.1 (NCH), 113.3, 128.3, 132.6, and 144.7 (ArC-2, -3, -4, and -1), and 128.8 and 129.4 (1- and 2-CH) (Found: C, 83.75; H, 9.65; $\text{C}_{14}\text{H}_{19}\text{N}$ requires C, 83.55; H, 9.5; N, 6.95%).

3-(*p*-Tolylamino)-cis-cyclo-octene (2b'), liquid; ν_{max} (neat) 3 390 (NH), 3 010, 2 920, and 2 850 (C-H), 1 620 and 1 520 (Ar C=C), 1 455 (C-H), 1 310 and 1 250 (C=N), 810 (*para*-substituted phenyl), and 760 and 720 cm^{-1} (CH=CH); δ_{H} (CDCl_3) 0.8–2.4 (10 H, m, CH_2), 2.25 (3 H, s, Me), 2.9–3.4 (1 H, br, NH), 3.9–4.4 (1 H, m, 3-CH), 5.1–6.1 (2 H, m, 1- and 2-CH), and 6.3–7.2 (4 H, ABq, C_6H_4); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 20.3 (Me), 24.3, 26.6, 26.9, 29.2, and 36.6 (CH_2), 51.0 (NCH), 113.2, 125.9, 129.3, and 145.2 (ArC-2, -3, -4, and -1), and 129.5 and 135.5 (1- and 2-CH) (Found: C, 83.8; H, 9.8; N, 6.3. $\text{C}_{15}\text{H}_{21}\text{N}$ requires C, 83.65; H, 9.85; N, 6.5%).

3-(4-Chlorophenylamino)-cis-cyclo-octene (2f'), liquid; ν_{max} (neat) 3 400 (NH), 3 010, 2 920, and 2 850 (C-H), 1 600 and 1 500 (Ar C=C), 1 450 (C-H), 1 320 and 1 250 (C-N), 1 090 ($\text{C}_6\text{H}_4\text{Cl}$), 820 (*para*-substituted phenyl), 760 and 720 (CH=CH), and 670 cm^{-1} (C-Cl); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 0.8–2.5 (10 H, m,

CH_2), 4.0–4.5 (1 H, m, NCH), 4.5–4.9 (1 H, br, NH), 5.15–6.15 (2 H, m, 1- and 2-CH), and 6.35–7.5 (4 H, ABq, C_6H_4); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 24.3, 26.5, 26.9, and 29.2 (CH_2), 51.9 (NCH), 115.1, 123.0, 128.8, and 144.8 (ArC-2, -4, -3, and -1), and 130.5 and 133.9 (1- and 2-CH) (Found: C, 71.35; H, 7.75; N, 5.75. $\text{C}_{14}\text{H}_{18}\text{ClN}$ requires C, 71.3; H, 7.7; N, 5.95%).

3-(4-Ethylphenylamino)-cis-cyclo-octene (2g'), liquid; ν_{max} (neat) 3 380 (NH), 3 000, 2 910, and 2 840 (C-H), 1 615 and 1 515 (Ar C=C), 1 450 (C-H), 1 300 and 1 260 (C-N), 820 (*para*-substituted phenyl), and 760 and 710 cm^{-1} (CH=CH); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 0.8–2.8 (10 H, m, 4-, 5-, 6-, 7-, and 8- CH_2), 1.2 (3 H, t, Me), 2.55 (2 H, q, MeCH_2), 3.0–3.55 (1 H, br, NH), 3.95–4.55 (1 H, m, NCH), 5.15–6.1 (2 H, m, 1- and 2-CH), and 6.4–7.24 (4 H, ABq, C_6H_4); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 15.8 (Me), 24.3, 26.6, 26.9, 29.2, and 36.6 (CH_2), 27.8 (CH_2Me), 51.0 (NCH), 113.3, 128.1, 132.6, and 145.4 (ArC-2, -3, -4, -1), and 129.5 and 135.5 (1- and 2-CH) (Found: C, 83.5; H, 9.95; N, 6.4. $\text{C}_{16}\text{H}_{23}\text{N}$ requires C, 83.8; H, 10.1; N, 6.1%).

The Reaction of 2,6-Dimethylphenyl Azide (1e) with Benzene in the Presence of Aluminium Trichloride or Tribromide.—A solution of (1e) (2.1 mmol) and benzene (1.0 ml) was added to a suspension containing ca. 3.7 mmol of AlCl_3 or AlBr_3 in benzene (4.0 ml). After reflux for 1 h, the mixture was treated with aqueous Na_2CO_3 , and extracted with CH_2Cl_2 . From the organic layer, the product was isolated by the method mentioned above. Yields were determined by GLC using column A; the yield was 8% or 69% in the presence of AlCl_3 or AlBr_3 , respectively. The structure of the product was confirmed as follows.

4-Amino-3,5-dimethylbiphenyl (6), liquid; ν_{max} (neat) 3 470 and 3 385 (NH_2), 3 050, 3 025, 2 960, and 2 850 (C-H), 1 625, 1 600, and 1 480 (Ar C=C), 1 450 (C-H), 1 330 (C-N), and 770 and 700 cm^{-1} (mono-substituted phenyl); δ_{H} ($\text{CCl}_4\text{-CDCl}_3$) 2.25 (6 H, s, Me), 3.0–3.9 (2 H, br, NH_2), and 6.9–7.8 (7 H, m, ArH); δ_{C} ($\text{CCl}_4\text{-CDCl}_3$) 17.6 (Me), 125.6, 126.2, 126.8, and 128.1 (ArC-4', -2', -3', and -2). (Found: C, 85.2; H, 7.6; N, 7.05; $\text{C}_{14}\text{H}_{15}\text{N}$ requires C, 85.25; H, 7.65; N, 7.1%).

Rates of Decomposition of Azide (1).—A solution containing the azide (1a) (4.6 mmol) and benzene (2.0 ml) was added to a suspension of finely powdered AlCl_3 (4.9 mmol) in CH_2Cl_2 (10.0 ml), and the rates of azide decomposition were determined at 8 °C by measurement of the volume of nitrogen gas evolved as a function of time. The decomposition obeyed pseudo-first-order kinetics with respect to the azide up to ca. 50% decomposition, $k_{\text{obs}} 7.5 \times 10^{-4} \text{ s}^{-1}$. Using cyclohexene in place of benzene, complete decomposition occurred in a few minutes. When (1c) was employed instead of (1a), the azide completely decomposed in a few minutes after mixing with AlCl_3 in the presence of benzene or cyclohexene.

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