Addition of Phenylnitrenium Ion to Olefins. Reactions of Phenyl Azide with Some Olefins in the Presence of Trifluoroacetic Acid †

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Addition to cyclohexene, cis- or trans-4-methylpent-2-ene, or hex-1-ene of a singlet phenylnitrenium ion, generated from phenyl azide in the presence of trifluoroacetic acid, gave stereo- or regio-specifically N-phenyl-β-hydroxyamines (after work-up with aqueous Na_2CO_3) via aziridinium ions together with N-allyl- and 2- and/or 4-allylanilines. Use of methyl acrylate or methyl crotonate as an electron-deficient olefin led to the formation of N-phenylserine or N-phenylthreonine methyl ester (after work-up with aqueous Na_2CO_3), respectively. In the reaction with 1,1-disubstituted ethylene or styrene derivatives, N-substituted anilines were formed through an attack of either tertiary alkyl or benzylic cations on phenyl azide.

It is known that the phenylnitrenium ion is generated in the reactions of N-hydroxy- and N-chloro-aniline derivatives under neutral conditions [1] and in the decomposition of phenyl azide in the presence of strong acid,[2] or acetic acid.[3] The phenylnitrenium ion has been shown to be reactive to nucleophiles at the para- and ortho-positions rather than at the nitrogen atom. However, we have recently discovered preferential attack on the nitrogen position of the phenylnitrenium ion formed from phenyl azide in the presence of trifluoroacetic acid (TFA)[4] or trifluoromethanesulphonic acid.[5]

We describe here an investigation of the reaction of phenyl azide with olefins in the presence of TFA in an attempt to find a stereo- or regio-specific formation of N-phenyl-β-hydroxy-amines via the singlet phenylnitrenium ion, and the application of this to a useful synthesis of N-phenyl-β-hydroxyamino acid esters from the reaction with α,β-unsaturated carboxylic acid esters. Such intermolecular reactions of nitrenium ion with olefins have scarcely been investigated so far, although it is known that nitrenium ions [6] or amino radical species [7] may add to double bonds in an intramolecular reaction. We also describe the formation of N-substituted anilines in the reaction with 1,1-disubstituted ethylene or styrene derivatives.

Results and Discussion

Reactions of Phenyl Azide with Cyclohexene, cis- and trans-4-Methylpent-2-enes, and Hex-1-ene in the Presence of TFA.—The reaction of phenyl azide with cyclohexene yielded trans-2-(phenylamino)cyclohexan-1-ol (1), 3-(phenylamino)cyclohexene (2), and 3-(2-aminophenyl)cyclohexene (3) (Table 1 and Scheme 1). The reaction with cis-4-methylpent-2-ene instead of cyclohexene gave 2-hydroxy-4-methyl-3-(phenylamino)pentane (4), 4-methyl-3-(phenylamino)pent-1-ene (5), and cis-2-isopropyl-3-methyl-1-phenylaziridine (6), and with trans-4-methylpent-2-ene gave compound (5), 3-hydroxy-4-methyl-2-(phenylamino)pentane (7), and 2-methyl-4-(phenylamino)pent-2-ene (8), as shown in Scheme 2. The results are summarized in Table 2. The reaction with hex-1-ene produced 2-hydroxy-1-(phenylamino)hexane (9) (14%), 1-(phenylamino)hex-2-ene (10) (1%), and 1-(2- and 4-aminophenyl)hex-2-enes (11) and (12) (5 and 6%) (Scheme 3).

Table 1. Reaction of phenyl azide with cyclohexene in the presence of TFA at room temperature for 1 day

[Azidel]/M	[Cyclo-hexene]/M	TFA/% v/v	Yield[a]/%		
			(1)	(2)	(3)
0.45	4.9	45	63	11	10
0.46	1.0	85	43	9	9
0.32	0.33	94	28	6	6

[a] Yields were based on azide used.

Table 2. Reactions of phenyl azide (0.45M) with cis- and trans-4-methylpent-2-enes in the presence of TFA at room temperature for 1 day

[Alkene]/M	TFA/% v/v	Yield[a]/%				
		(4)	(5)	(6)	(7)	(8)
3.7[b]	48	48	9	6		
1.6[b]	75	20	7	14		
3.7[c]	48		18		54	4
1.6[c]	75		12		34	2

[a] Yields were based on azide used. [b] cis-4-Methylpent-2-ene was used. [c] trans-4-Methylpent-2-ene was used.

We have previously reported that the decomposition of phenyl azide in benzene–TFA proceeds via a conjugate acid of the azide, forming a phenylnitrenium ion.[4] For the reaction with alkenes, there are two possibilities at first sight (see Scheme 1); one involves the addition of the phenylnitrenium ion to alkene, and the other involves an S_N2-like attack of the alkene on the azide conjugate acid. If the reaction occurs through the latter route, the azide decomposition in cyclohexene–TFA rather than in benzene–TFA should be accelerated because cyclohexene is more nucleophilic than benzene. The first-order rate constant for this decomposition in cyclohexene (50% v/v)–TFA (50% v/v) at 21 °C is, however, slightly lower than in benzene (50% v/v)–TFA (50% v/v) at 21 °C.‡ Thus, the conjugate acid of azide must spontaneously lose a nitrogen

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† A preliminary report of the reaction with cyclohexene or with cis- and trans-4-methylpent-2-enes has appeared; H. Takeuchi and R. Ihara, *J. Chem. Soc., Chem. Commun.*, 1983, 175.
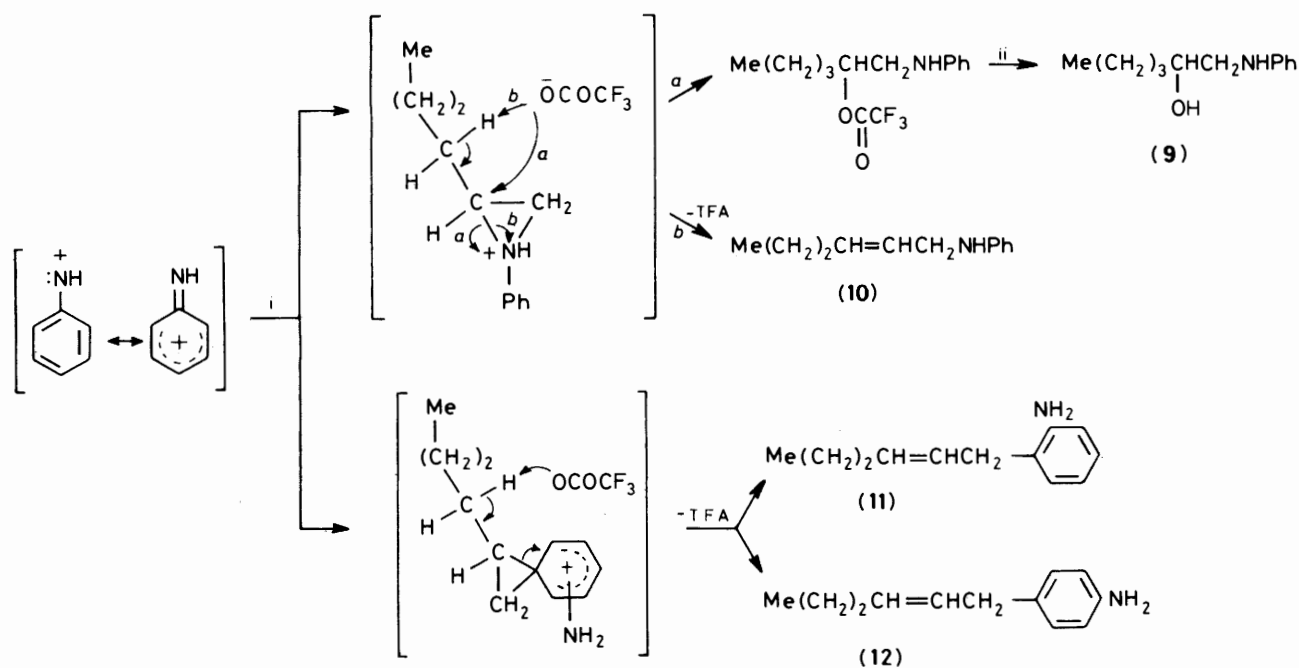
‡ The charge-transfer interaction between TFA and cyclohexene is stronger than that between TFA and benzene, so that the formation of the azide conjugate acid may be suppressed in the presence of cyclohexene rather than benzene.
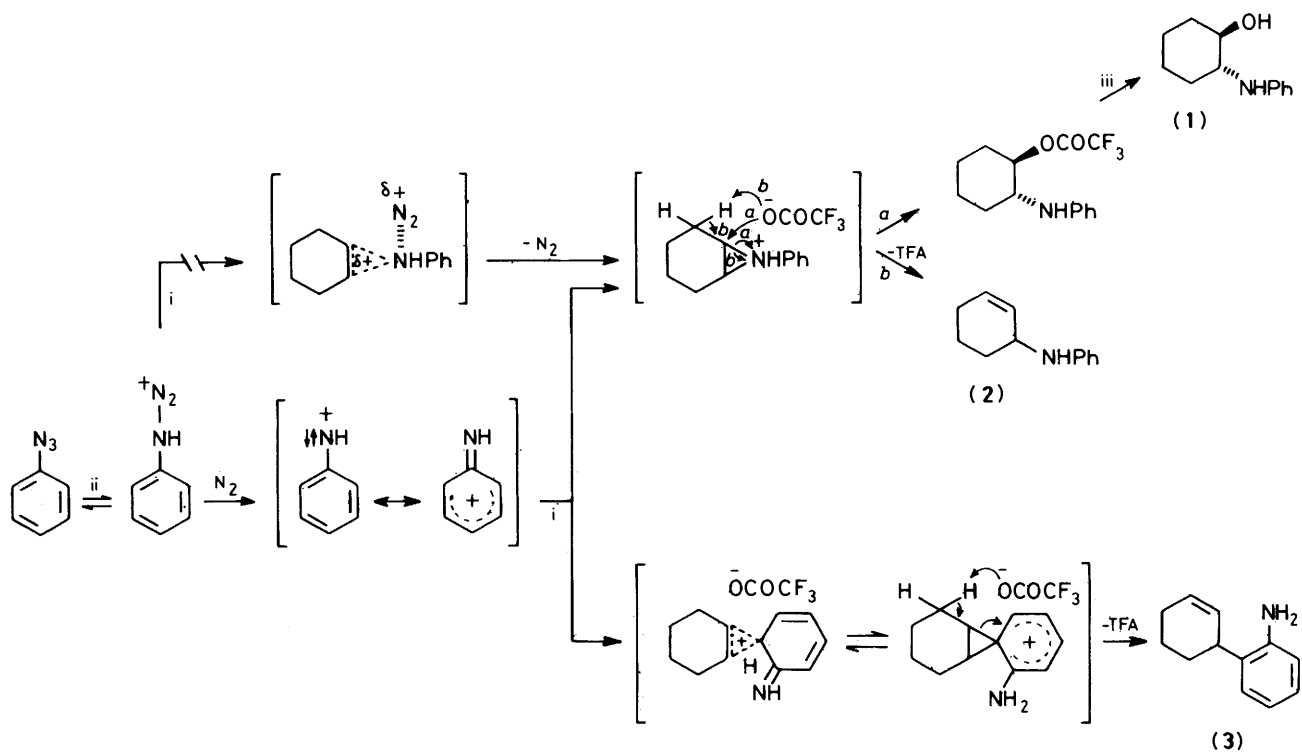
Scheme 1. *Reagents:* i, cyclohexene; ii, TFA; iii, aq.NaOH
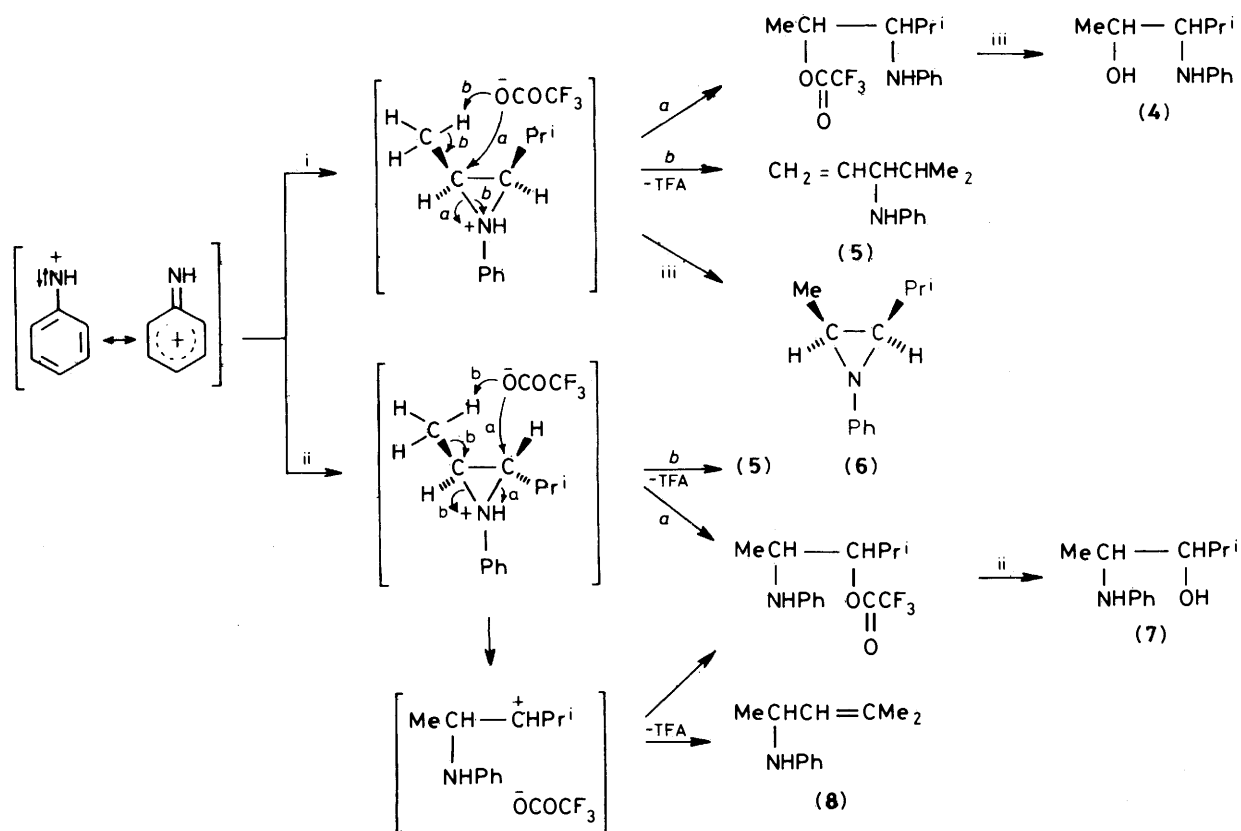
Scheme 2. *Reagents:* i, *cis*-4-methylpent-2-ene; ii, *trans*-4-methylpent-2- ene; iii, aq.Na₂CO₃

Scheme 3. *Reagents:* i, hex-1-ene; ii, aq.NaOH

molecule to give the phenylnitrenium ion which is reactive to the alkenes.

The reaction with cyclohexene yielded the *trans*-addition compound (1) without contamination by the corresponding *cis*-isomer, and the addition giving compounds (4) and (7) from *cis*- and *trans*-4-methylpent-2-enes is regiospecific. The results show that the singlet phenylnitrenium ion probably adds stereospecifically to alkenes to form aziridinium ions, followed by ring-opening reactions; if the reaction involves the triplet nitrenium ion, the *cis*-isomer of compound (1) along with (1) itself should be produced, and the regiospecific addition forming compounds (4) and (7) would not be expected to occur. These ring-opening reactions of aziridinium ions agree well with the results for the ring-opening reactions of *cis*- and *trans*-1-ethoxycarbonyl-2-isopropyl-3-methylaziridines by acetic acid.[8]

An S_N2 attack of trifluoroacetate anion on the backside of the breaking C–N bond of the aziridinium ion (step *a* in Schemes 1—3) may give compound (1), (4), (7), or (9), while proton abstraction by the anion (step *b* in Schemes 1—3) would produce compound (2), (5), or (10). The isolation of the *cis*-aziridine (6) [the *trans*-isomer of (6) was relatively unstable under the reaction conditions] after neutralization of the reaction mixture with aqueous Na_2CO_3 supports the formation of aziridinium ions as intermediates.

N-Cyclohexylidenephenylamine, a tautomer of 1-(phenylamino)cyclohexene, was not produced from cyclohexene, and compound (8) was not detected in the reaction with *cis*-4-methylpent-2-ene. These both indicate that the reaction with cyclohexene or *cis*-4-methylpent-2-ene does not proceed *via* an S_N1 ring-opening reaction of aziridinium ions. However, the aziridinium ion from *trans*-4-methylpent-2-ene may cause the S_N1 ring-opening reaction to yield compound (8) and some of the product (7) based on the following: according to the ^{1}H and ^{13}C n.m.r. spectra and g.l.c. analyses, compound (7) was a mixture of two diastereoisomers, but (4) was a single isomer, and compound (8) was produced from the *trans*-olefin but not the *cis*-isomer.

Compounds (3), (11), and (12) might be formed *via* an intermediate, a phenylium ion, arising from an attack of

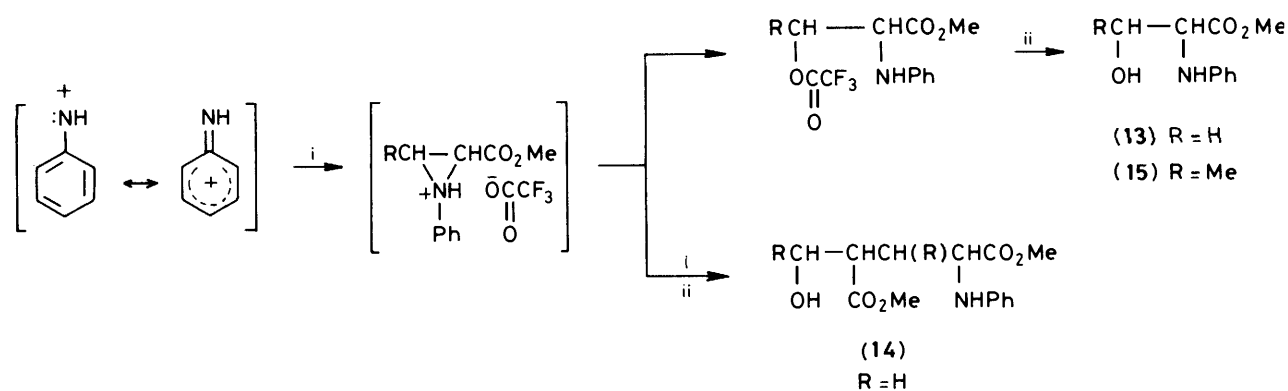**Table 3.** Reaction of phenyl azide with methyl acrylate or methyl crotonate in the presence of TFA

[Azide]/M	[Olefin]/M	TFA/% v/v	$T/^{\circ}C$	t/h	Yield[a]/% (13)	(14)	(15)
0.46	6.1[b]	40	25	47	96	4	
1.7	3.4[b]	50	25	46	86	1	
0.23	3.1[b]	80	25	24	Trace	3	
0.46	5.9[c]	35	25	72			Trace
1.0	6.5[c]	22	48	40			17
1.0	6.5[c]	11[d]	90	4			30

[a] Yields were based on azide used. [b] Methyl acrylate was employed. [c] Methyl crotonate was employed. [d] TFA, diluted to 50% v/v with CH_2Cl_2, was used.

cyclohexene or hex-1-ene on the positive ring positions of the phenylnitrenium ion (see Schemes 1 and 3). Such an attack is perhaps impossible for the reaction with *cis*- and *trans*-4-methylpent-2-enes because of the steric hindrance to the formation of a three-membered ring attached to a phenylium ion.

The Reaction of Phenyl Azide with Methyl Acrylate or Methyl Crotonate in the Presence of TFA.—The reaction of phenyl azide with methyl acrylate in the presence of TFA afforded *N*-phenylserine methyl ester (13) and dimethyl 2-(hydroxymethyl)-4-(phenylamino)glutarate (14). The analogous reaction with methyl crotonate gave *N*-phenylthreonine methyl ester (15). The results are summarized in Table 3 and Scheme 4.

It has been reported that phenyl azide adds to α,β-unsaturated carboxylic acid esters to yield 4,5-dihydro-1-phenyl-1,2,3-triazole-4-carboxylic acid esters.[9] On the other hand, phenylnitrene has been observed to add to an alkene such as cyclohexene, giving an aziridine in a very low yield.[10] Thus, the phenylamination of α,β-unsaturated carboxylic esters as elec-

Scheme 4. *Reagents:* i, $RCH=CHCO_2Me$; ii, $aq.Na_2CO_3$

Table 4. Reactions of phenyl azide with ethylene or styrene derivatives in the presence of TFA

Olefin	[Olefin]/M	[Azide]/M	TFA/% v/v	$T/°C^a$	t/min	Yield[b]/%					
						PhNHEt (16a)	PhNHPr (16b)	PhNHMe (16c)	PhNHPh (16d)	PhNHC₆H₄Me-4 (16e)	PhNHPr^i (16f)
$CH_2=C(Me)Et$	2.0	1.0	67	25—65	3	23		0.5			
$CH_2=C(Me)Pr$	1.8	1.0	67	25—85	3	0.9	24	0.5			
$CH_2=C(Me)Ph$	1.7	1.0	67	25—65	3			0	4.3		
$CH_2=CHPh$	2.2	1.1	62	25—85	3				24		
$CH_2=CHC_4H_4Me-4$	1.7	1.0	67	25—75	3					17	
$CH_2=CPh_2$	0.85	0.7	77	25	30				2.2^c		
$Me_2C=CMe_2$	1.8	1.0	67	25—80	3			0			43

^{a} The temperature rose to the higher one owing to the heat of reaction on adding TFA to a mixture of azide and olefin. ^{b} Yields were based on azide employed. ^{c} Besides (16d), acetophenone was produced in 1.2% yield based on the amount of azide used.

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tron-deficient olefins, which gives N-phenyl-β-hydroxyamino acid esters, is of great interest from the synthetic point of view. Aziridinium ions which are formed by the reaction of phenylnitrenium ion with the unsaturated esters undergo ring-opening by trifluoroacetate anion to give trifluoroacetates of compounds (13) and (15), and then the trifluoroacetates are converted into (13) and (15) after work-up with aqueous Na_2CO_3 (Scheme 4). An attack of phenylnitrenium ion on two molecules of methyl acrylate, followed by the work-up, yields compound (14) (Scheme 4).

With an increased amount of TFA the yields of compounds (13)—(15) were lowered because of polymerization. When we employed methyl crotonate, secondary carbocations formed during the polymerization, so that the yield of compound (15) was lower the higher the concentration of TFA. The conditions necessary, lower concentration of TFA and higher temperature, were comparatively suitable for the formation of compound (15) (see Table 3).

The Formation of N-*Substituted Anilines in the Reaction of Phenyl Azide with* 1,1-*Disubstituted Ethylene or Styrene Derivatives in the Presence of TFA.*—Reactions of phenyl azide with 2-methylpent-1-ene, 2-methylbut-1-ene, α-methylstyrene, styrene, 4-methylstyrene, 1,1-diphenylethylene, and 2,3-dimethylbut-2-ene in the presence of TFA produced the N-substituted anilines (16) as shown in Table 4 (Scheme 5). The reaction with 2-methylbut-1-ene or 2-methylpent-1-ene gave N-(1,1-dimethylpropyl)-2- and -4-(1,2-dimethylprop-1-enyl)anilines (17a) (1%) and (18a) (4%) or N-(1,1-dimethylbutyl)-2- and -4-(1-ethyl-2-methylprop-1-enyl)anilines (17b) (4%) and (18b) (8%), respectively (Scheme 6).

The reaction of phenyl azide with propylbenzene in the

presence of TFA did not yield compounds (16a—c), but only a trace of (16d).* This means that the presence of a double bond plays an important role in the formation of the N-substituted anilines (16). Unlike the olefins used in the previous sections of the paper, all the olefins described in this section would give tertiary alkyl or benzylic cations on protonation. Phenyl azide immediately decomposed exothermically on the addition of TFA to a mixture of azide and the olefin (see Table 4). We therefore suggest that carbocations which are formed on protonation attack phenyl azide, and that a nitrogen molecule is eliminated by a 1,2-migration of a substituent to the nitrogen atom to give compound (16) after work-up with aqueous NaOH (Scheme 5).

The relative yields, (16a)/(16c) = 46, (16b)/(16c) = 48, (16d)/(16c) = ∞, and (16f)/(16c) = ∞, were calculated from the experiments using 2-methylbut-1-ene, 2-methylpent-1-ene, α-methylstyrene, and 2,3-dimethylbut-2-ene, respectively (see Table 4). From these values, we showed the migratory aptitudes to be in the following order: Ph and Pr^i ≫ Pr > Et > Me. The formation of acetophenone from 1,1-diphenylethylene after work-up with aqueous NaOH supports this mechanism.

The formation of a small amount of N-ethylaniline (16a) from 2-methylpent-1-ene is equivocal mechanistically, but perhaps arises from the following equilibrium:

$$Me_2\overset{+}{C}-CH_2Et \rightleftharpoons Me_2CH-\overset{+}{C}HEt$$
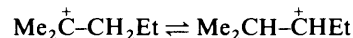
We invoke a comparable isomerization of the alkenes to account for the formation of compounds (17) and (18) in

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* The formation mechanism of compound (16d) is ambiguous, but appears to be *via* an attack of phenylnitrenium ion or the conjugate acid of azide on the benzene ring of propylbenzene.

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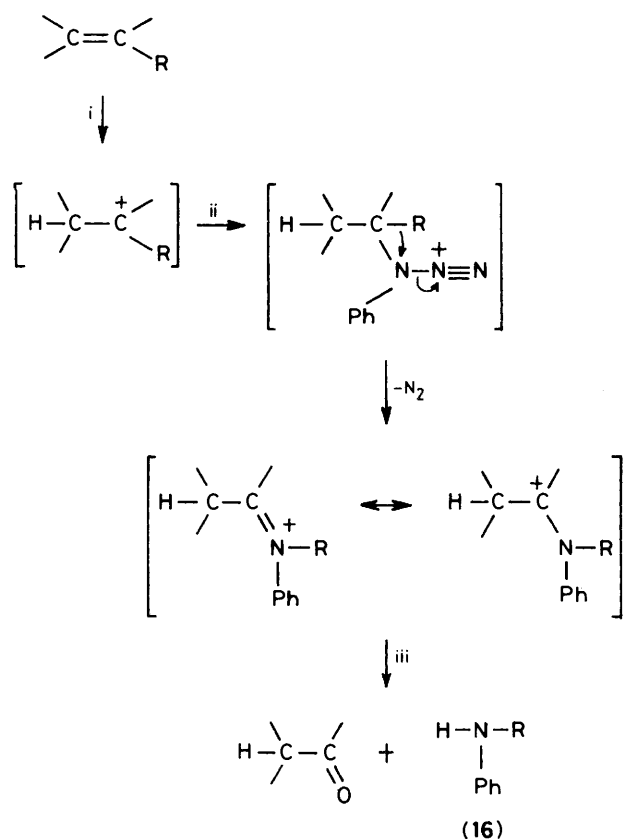
Scheme 5. *Reagents:* i, H+; ii, PhN₃; iii, aq.NaOH

Scheme 5; 2-methylpent-1-ene isomerizes to 2-methylpent-2-ene under the reaction conditions (confirmed by g.l.c.). Such isomerized olefins attack the phenyl ring of the phenylnitrenium ion, and compounds (**17**) and (**18**) are produced *via* an alkylation by a cation, Me₂ĊR¹ (see Scheme 6).

The low yield of the products (especially in the cases where the reagents are aromatic) is due to the significant tar formation.

Experimental

I.r. spectra were measured with a Hitachi model EPI-G3 spectrometer. ¹H and ¹³C N.m.r. spectra were obtained on a Nippondenshi JNM FX60Q instrument with Me₄Si as internal standard. Mass spectra were recorded on a Hitachi RMU-6E spectrometer. G.l.c. analyses were carried out with a Shimazu GC-6A unit using a glass column (1m × 3 mm) [column A, 10% polyethylene glycol (20M) on 60—80 Uniport KS; column B, 10% silicone DC-550 on 60—80 Uniport KS; column C, 10% silicone SE-30 on 60—80 Uniport KS]. The analyses of products agreed within <3% on two runs, and the products did not decompose under the g.l.c. conditions. Preparative g.l.c. was performed with a Hitachi model 063-0012 unit using a column (2 m × 3 mm).

Phenyl azide,[11] cyclohexene,[12] N-cyclohexylidenephenylamine,[13] and 4-methylphenylamine (**16e**)[14] were prepared by methods described in the literature.

The Reaction of Phenyl Azide with Cyclohexene in the Presence of TFA.—A mixture of phenyl azide, cyclohexene, and TFA was allowed to react under the conditions indicated in Table 1. The reaction mixture was diluted with benzene (10 ml), and the solution was basified with aqueous NaOH. After evaporation of the solvent, the following materials were isolated
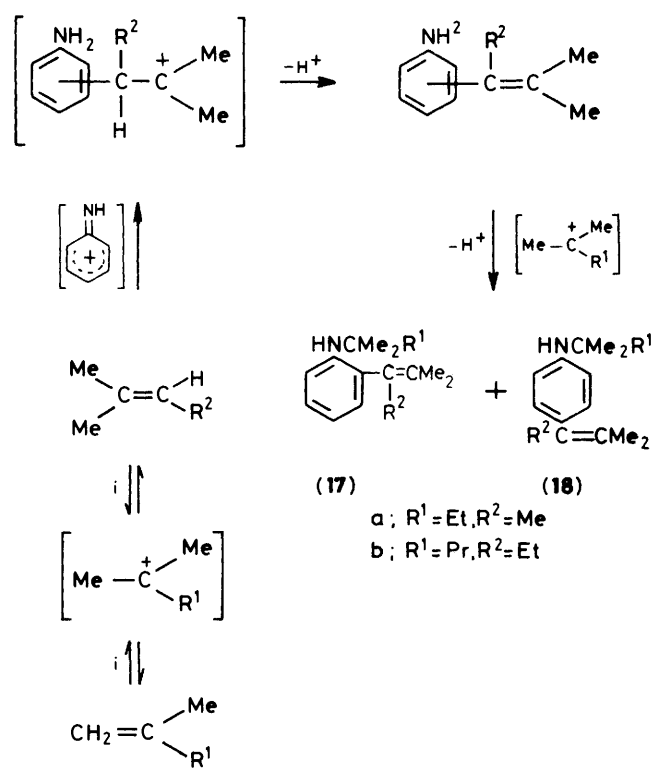
Scheme 6. *Reagents:* i, H+

by preparative g.l.c. using 10% polyethylene glycol (20M) on 60—80 Uniport KS. The yields were obtained by g.l.c. employing column A.

trans-2-(Phenylamino)cyclohexan-1-ol (**1**). This compound * had the same m.p. (58 °C) and ¹H and ¹³C n.m.r. and i.r. spectra as those of the product[15] from the reaction of cyclohexene oxide (0.1 mol) with aniline (0.1 mol) in ethanol (25 ml) at 130 °C for 1 day.

3-(Phenylamino)cyclohexene (**2**). This compound was a liquid, δ_C(CCl₄-CDCl₃) 19.6 (5-CH₂), 25.1 (4-CH₂), 28.8 (6-CH₂), 47.6 (3-CH), 112.9, 117.0, and 128.9 (2-, 4-, and 3-phenyl C), and 128.6 and 129.6 (CH=CH); identical i.r. and ¹H n.m.r. spectra with those of an authentic sample.[10]

3-(2-Aminophenyl)cyclohexene (**3**). This compound was a liquid, ν_max.(neat) 3 370 and 3 450 (NH₂), 3 010, 2 920, and 2 850 (CH), 1 620 (NH₂), 1 605 and 1 495 (C=C of Ph), 1 450 (CH), 1 290 (C–N), and 750 (strong) and 690 cm⁻¹ (weak) (*ortho*-substituted Ph); δ_H(CCl₄-CDCl₃) 0.5—2.5 (6 H, m, CH₂), 2.8—3.8 (2 H, br, NH₂), 3.5—4.0 (1 H, s, CH), 5.5—6.2 (2 H, m, CH=CH), and 6.5—7.5 (4 H, m, Ph); δ_C(CCl₄-CDCl₃) 21.1 (5-CH₂), 24.9 (4-CH₂), 28.1 (6-CH₂), 37.9 (3-CH), 115.8, 118.5, 128.5, and 128.8 (3-, 5-, 4-, and 6-phenyl C), and 126.7 and 129.9 (CH=CH). The i.r. and ¹H n.m.r. spectra are almost the same as those described in the literature.[16]

The Reaction of Phenyl Azide with cis- and trans-4-Methylpent-2-enes in the Presence of TFA.—A mixture (10 ml) containing *cis-* or *trans*-4-methylpent-2-ene was made to react as described in Table 2. After being basified with aqueous Na₂CO₃, 2-hydroxy-4-methyl-3-(phenylamino)pentane (**4**), 4-methyl-3-

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* The evidence that ¹J_C₍₁₎-H(141 Hz) and ¹J_C₍₂₎-H(137 Hz) of (**1**) are similar to ¹J_C-H(139 Hz) of cyclohexanol and ¹J_C-H(133 Hz) of phenylaminocyclohexane, respectively, for the C–H attaching functional group apparently shows 1-H and 2-H of (**1**) to be axial (*i.e. trans*-configuration).

(phenylamino)pent-1-ene (5), and the cis-aziridine (6) were isolated from the cis-olefin, and the pentene (5), 3-hydroxy-4-methyl-2-(phenylamino)pentane (7), and 2-methyl-4-(phenylamino)pent-2-ene (8) from the trans-olefin. The yields were determined by g.l.c. using column B. The isolation of the compounds was carried out by preparative g.l.c. using 10% silicone DC-550 on 60—80 Uniport KS, and the products were identified as follows: 2-hydroxy-4-methyl-3-(-phenylamino)pentane (4), liquid, v_{max}(neat) 3 100—3 700 (OH and NH), 3 030, 2 940, and 2 850 (CH), 1 590 and 1 495 (C=C of Ph), 1 460 and 1 370 (CH), 1 210—1 340 (C-O and C-N), 1 150 (C-O), and 740 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.95 [6 H, d, (CH$_3$)$_2$CH], 1.2 [3 H, d, CH$_3$CH(OH)], 1.5—2.3 [1 H, m, (CH$_3$)$_2$CH], 2.1—3.2 (2 H, br, NH and OH), 3.0 (1 H, t, NCH), 3.8 (1 H, quintet, OCH), and 6.3—7.6 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 16.0(CH$_3$CH), 20.2 and 21.1 [(CH$_3$)$_2$CH], 30.8 [(CH$_3$)$_2$CH], 65.2 (NCH), 64.2 (OCH), and 114.0, 118.2, and 130.2 (2-, 4-, and 3-phenyl C) (Found: C, 74.6; H, 9.6; N, 7.5. C$_{12}$H$_{19}$NO requires C, 74.55; H, 9.9; N, 7.25%).

4-Methyl-3-(phenylamino)pent-1-ene (5), liquid, v_{max}(neat) 3 400 (NH), 3 040, 2 950, and 2 850 (CH), 1 600 and 1 505 (C=C of Ph), 1 460 and 1 430 (CH), 1 320 (C-N), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 1.0 (6 H, d, CH$_3$), 1.8—2.6 [1 H, septet, (CH$_3$)$_2$CH], 2.6—3.8 (1 H, br, NH), 3.5—3.8 (1 H, br NCH), 5.4—5.8 (2 H, br t, CH$_2$=CH), and 6.3—7.6 (5 H, m, Ph and CH$_2$=CH); δ_C(CCl$_4$-CDCl$_3$) 22.3 (CH$_3$), 30.7 [(CH$_3$)$_2$CH], 45.9 (NCH), 112.6, 117.1, and 128.8 (2-, 4-, and 3-phenyl C), and 123.7 and 139.9 (CH$_2$=CH) (Found: C, 82.2; H, 9.85; N, 7.95. C$_{112}$H$_{17}$N requires C, 82.25; H, 9.8; N, 8.0%).

cis-2-Isopropyl-3-methyl-1-phenylaziridine (6), liquid, v_{max}(neat) 3 020, 2 950, and 2 850 (CH), 1 595 and 1 490 (C=C of Ph), 1 460 and 1 360 (CH), 1 260 (C-N), and 740 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.96 (3 H, d; CH$_3$CH), 1.25 [6 H, d, (CH$_3$)$_2$CH], 1.4—1.8 (2 H, m, 2- and 3-CH), 1.8—2.4 [1 H, m, (CH$_3$)$_2$CH], and 6.4—7.5 (5 H, m, Ph). The ^{13}C n.m.r. spectrum was not taken because the aziridine (6) underwent ring-opening under the measurement conditions. This aziridine was unstable when the reaction mixture was treated with aqueous NaOH presumably because of the ring-opening.

3-Hydroxy-4-methyl-2-(phenylamino)pentane (7), liquid, v_{max}(neat) 3 400—3 650 (OH and NH), 3 030, 2 940, and 2 850 (CH), 1 600 and 1 495 (C=C of Ph), 1 465, 1 425, and 1 380 (CH), 1 300 (C-N), 1 250 (C-O), and 745 and 690 cm^{-1} (monosubstituted Ph) (Found: C, 74.6; H, 9.7; N, 7.5. C$_{12}$H$_{19}$NO requires C, 74.55; H, 9.9; N, 7.25%). ^{1}H and ^{13}C N.m.r. and g.l.c. analyses indicate that the product (7) consists of two diastereoisomers (7a) and (7b) in 66 and 34%, respectively. Compound (7a); δ_H(CCl$_4$-CDCl$_3$) 0.98 [6 H, d, (CH$_3$)$_2$CH], 1.2 (3 H, d, CH$_3$CH), 1.4—2.0 [1 H, m, (CH$_3$)$_2$CH], 2.8—3.5 (3 H, br, OH, NH, and NCH), 3.95 (1 H, t, OCH), and 6.3—7.4 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 18.8 (CHCH$_3$), 19.0 and 20.2 [CH(CH$_3$)$_2$], 32.0 [CH(CH$_3$)$_2$], 56.0 (NCH), 58.8 (OCH), and 113.6, 117.6, and 129.6 (2-, 4-, and 3-phenyl C). Compound (7b); δ_C(CCl$_4$-CDCl$_3$) 0.94 [6 H, d, (CH$_3$)$_2$CH], 1.15 (3 H, d, CH$_3$CH), 1.4—2.0 [1 H, m, (CH$_3$)$_2$CH], 2.8—3.5 (3 H, br, OH, NH, and NCH), 3.9 (1 H, t, OCH), and 6.3—7.4 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 17.2 (CHCH$_3$), 18.8 and 19.7 [CH(CH$_3$)$_2$], 31.2 [CH(CH$_3$)$_2$], 50.0 (NCH), 78.5 (OCH), and 113.6, 117.6, and 129.6 (2-, 4-, and 3-phenyl C). On the other hand, the ring-opening reaction of trans-4-methylpent-2-ene oxide by aniline in ethanol at 130—140 °C gave (7a) and (7b) in 27 and 78% yields, respectively. The oxide was prepared by the reaction between trans-4-methylpent-2-ene and m-chlorobenzoic peroxide at room temperature. The product (7a) had shorter retention time than (7b) in g.l.c.

2-Methyl-4-(phenylamino)pent-2-ene (8), liquid, v_{max}(neat) 3 400 (NH), 3 040, 2 950, and 2 850 (CH), 1 600 and 1 500 (C=C of Ph), 1 450, 1 425, and 1 370 (CH), 1 320 (C-N), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 1.2 (3 H, d, CH$_3$CH), 1.4—1.95 [6 H, br s, (CH$_3$)$_2$C=C], 2.6—3.6 (1 H, br, NH), 4.1 (1 H, quintet, CH), 4.8—5.3 (1 H, br d, CH=C), and 6.2—7.5 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 18.0 (CH$_3$CH), 21.9 and 25.5 [(CH$_3$)$_2$C=C], 47.0 (CH$_3$CH), 113.0, 116.9, and 128.8 (2-, 4-, and 3-phenyl C), and 129.5 (CH=C) (Found: C, 82.3; H, 9.8; N, 7.9. C$_{12}$H$_{17}$NO requires C, 82.25; H, 9.8; N, 8.0%).

The Reaction of Phenyl Azide with Hex-1-ene in the Presence of TFA.—Phenyl azide (4.6 mmol) was dissolved in hex-1-ene (5 ml) and TFA (5 ml), and the solution was allowed to stand for 10 h at room temperature. After being basified with aqueous NaOH as described above, 2-hydroxy-1-(phenylamino)hexane (9), 1-(phenylamino)hex-2-ene (10), 1-(2-aminophenyl)hex-2-ene (11), and 1-(4-aminophenyl)hex-2-ene (12) were isolated by preparative g.l.c. using 10% silicone SE-30 on 60—80 Uniport KS. These materials were identified as shown below: 2-hydroxy-1-(phenylamino)hexane (9), m.p. 46—50 °C, 14% yield, v_{max}(Nujol) 3 600—3 100 (OH and NH), 3 040 (CH), 1 600 and 1 500 (C=C of Ph), 1 310 (C-N), 1 250, 1 220, 1 140, and 1 080 (C-O), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.9 (3 H, t, CH$_3$), 1.1—1.8 (6 H, br, CH$_2$), 2.4—3.4 (4 H, br, NCH$_2$, OH, and NH), 3.4—4.1 (1 H, m, OCH), and 6.3—7.6 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 14.0 (CH$_3$), 22.8 (5-CH$_2$), 28.0 (4-CH$_2$), 35.1 (3-CH$_2$), 51.0 (NCH$_2$), 70.8 (OCH), and 113.7, 118.6, and 129.6 (2-, 4-, and 3-phenyl C) (Found: C, 74.75; H, 10.15; N, 6.95. C$_{12}$H$_{19}$NO requires C, 74.55; H, 9.9; N, 7.25%). This compound had the identical ^{1}H and ^{13}C n.m.r. and i.r. spectra with those of an authentic sample which was synthesized by the reaction of hex-1-ene oxide with aniline under the similar conditions as described in the preparation of compound (1).

1-(Phenylamino)hex-2-ene (10), liquid, 1% yield, v_{max}(neat) 3 400 (NH), 3 040, 2 950, and 2 850 (CH), 1 615 (C=C), 1 600 and 1 500 (C=C of Ph), 1 455 and 1 430 (CH), 1 320 (C-N), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.95 (3 H, t, CH$_3$), 1.0—1.8 (4 H, br, 4-CH$_2$ and 5-CH$_2$), 3.0—4.5 (3 H, br, NH and 1-CH$_2$), 4.9—6.1 (2 H, m, CH=CH), and 6.5—7.5 (5 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 13.9 (CH$_3$), 19.0 (5-CH$_2$), 37.6 (4-CH$_2$), 56.2(1-CH$_2$), 113.8, 117.8, and 128.7(2-,4-, and 3-phenyl C), and 115.2 and 139.3 (CH=CH) (Found: C, 82.35; H, 9.9; N, 7.75. C$_{12}$H$_{17}$N requires C, 82.25; H, 9.8; N, 8.0%).

1-(2-Aminophenyl)hex-2-ene (11), liquid, 5% yield, v_{max}(neat) 3 440 and 3 350 (NH$_2$), 3 010, 2 950, 2 920, and 2 850 (CH), 1 620 (NH$_2$), 1 605 (C=C), 1 580 and 1 495 (C=C of Ph), 1 280 (C-N), and 750 (strong) and 690 cm^{-1} (weak) (ortho-substituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.90 (3 H, t, CH$_3$), 1.0—1.8 (2 H, br, 5-CH$_2$), 1.8—2.4 (2 H, br, 4-CH$_2$), 3.0—3.4 (2 H, br, 1-CH$_2$), 3.5—4.0 (2 H, br, NH$_2$), 5.2—5.7 (2 H, m, CH=CH), and 6.5—7.4 (4 H, m, Ph); δ_C(CCl$_4$-CDCl$_3$) 13.6 (CH$_3$), 22.4 (5-CH$_2$), 34.4 (4-CH$_2$), 35.2 (1-CH$_2$), 115.7, 118.9, 127.0, 129.7 (3-, 5-, 4-, and 6-phenyl C), and 127.4 and 131.6 (CH=CH) (Found: C, 82.55; H, 9.7; N, 7.75. C$_{12}$H$_{17}$N requires C, 82.25; H, 9.8; N, 8.0%).

1-(4-Aminophenyl)hex-2-ene (12), liquid, 6% yield, v_{max}(neat) 3 440 and 3 340 (NH$_2$), 3 000, 2 950, 2 920, and 2 850 (CH), 1 620 (NH$_2$), 1 600 (C=C), 1 580 and 1 510 (C = C of Ph), 1 450 (CH), 1 270 (C-N), and 820 cm^{-1} (para-substituted Ph); δ_H(CCl$_4$-CDCl$_3$) 0.90 (3 H, t, CH$_3$), 1.1—1.8 (2 H, br, 5-CH$_2$), 1.8—2.6 (2 H, br, 4-CH$_2$), 2.7—3.6 (4 H, br, 1-CH$_2$ and NH$_2$), 5.0—6.0 (2 H, m, CH=CH), and 6.2—7.4 (4 H, AB q, Ph); δ_C(CCl$_4$-CDCl$_3$) 13.5 (CH$_3$), 22.5 (5-CH$_2$), 34.4 (4-CH$_2$), 38.1 (1-CH$_2$), 115.1 and 128.8 (3- and 2-phenyl C), and 129.9 and 130.6 (CH=CH) (Found: C, 82.3; H, 9.65; N, 8.05. C$_{12}$H$_{17}$N requires C, 82.25; H, 9.8; N, 8.0%).

The Reaction of Phenyl Azide with Methyl Acrylate or Methyl Crotonate in the Presence of TFA.—A mixture (10 ml) of phenyl azide, TFA, and methyl acrylate or methyl crotonate was allowed to react under the conditions described in Table 3. After treating the reaction mixture with aqueous NaCO$_3$, N-

phenylserine methyl ester (13) and *dimethyl 2-(hydroxymethyl)-4-(phenylamino)glutarate* (14) or N-*phenylthreonine methyl ester* (15) were formed, respectively. These compounds were isolated by preparative g.l.c. employing 10% silicone SE-30 on 60—80 Uniport KS, and the yields determined by g.l.c. using column C. The products were identified as follows: N-*phenylserine methyl ester* (13), liquid, $v_{max.}$(neat) 3 100—3 700 (OH and NH), 3 030, 2 930, and 2 850 (CH), 1 730 (C=O), 1 600 and 1 500 (C=C of Ph), 1 450 and 1 430 (CH), 1 310 (C–N), 1 200, 1 150, and 1 070 (C–O), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$–CDCl$_3$) 3.2—3.6 (2 H, br s, OH and NH), 3.75 (3 H, s, OCH$_3$), 3.9 (2 H, d, OCH$_2$), 4.5 (1 H, t, NCH), 6.4—7.7 (5 H, m, Ph); δ_C(CCl$_4$–CDCl$_3$) 52.2 (OCH$_3$), 59.0 (NCH), 62.7 (OCH$_2$), 113.7, 118.9, 129.2, and 146.2 (2-, 4-, 3-, and 1-phenyl C), and 172.2 (C=O) (Found: C, 61.5; H, 6.6; N, 7.3. C$_{10}$H$_{13}$NO$_3$ requires C, 61.55; H, 6.7; N, 7.2%).

Dimethyl 2-(hydroxymethyl)-4-(phenylamino)glutarate (14), liquid, $v_{max.}$(neat) 3 160—3 700 (OH and NH), 3 100, 2 940, and 2 850 (CH), 1 730 (C=O), 1 600 and 1 500 (C=C of Ph), 1 435 and 1 360 (CH), 1 280 (C–N), 1 200 and 1 120 (C–O), and 750 and 690 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$–CDCl$_3$) 2.2—2.9 (2 H, br, OH and NH), 2.6 (2 H, t, CH$_2$), 3.7 (3 H, s, OCH$_3$), 3.8 (3 H, s, OCH$_3$), 3.0—4.2 (3 H, br, OCH$_2$ and NCH), 4.4 [1 H, quintet, C(=O)CHCH$_2$O], and 6.4—7.5 (5 H, m, Ph); δ_C(CCl$_4$–CDCl$_3$) 32.0 (CH$_2$), 48.0 (OCH$_3$), 52.0 (OCH$_2$CH), 52.8 (OCH$_3$), 54.6 (NCH), 70.0 (OCH$_2$), and 116.8, 121.6, and 133.2 (2-, 4-, 3-phenyl C). As the product isolated by preparative g.l.c. involved a small amount of impurity, the structure assignment was based solely on the spectroscopic data.

N-*Phenylthreonine methyl ester* (15), liquid, $v_{max.}$(neat) 3 200—3 600 (OH and NH), 3 050, and 2 950 (CH), 1 740 and 1 790 (C=O), 1 650 and 1 510 (C=C of Ph), 1 440 and 1 380 (CH), 1 320 (C–N), 1 225, 1 170, and 1 065 (C–O), and 755 and 695 cm^{-1} (monosubstituted Ph); δ_H(CCl$_4$–CDCl$_3$) 1.5 (3 H, d, CH$_3$CH), 3.7 (3 H, s, OCH$_3$), 3.8—4.4 (2 H, br s, OH and NH), 4.25 (1 H, d, NCH), 5.4 (1 H, quintet, OCH), and 6.2—7.5 (5 H, m, Ph); δ_C(CCl$_4$–CDCl$_3$) 15.8 (CH$_3$CH), 52.3 (OCH$_3$), 59.3 (NCH), 74.5 (OCH), and 113.7, 119.2, and 129.2 (2-, 4-, 3-phenyl C) (Found: C, 62.85; H, 7.1; N, 6.9. C$_{11}$H$_{15}$NO$_3$ requires C, 63.15; H, 7.25; N, 6.7%).

The Reaction of Phenyl Azide with 1,1-Disubstituted Ethylene or Styrene Derivatives in the Presence of TFA.—TFA was added to a mixture of phenyl azide and the olefin at room temperature. The detailed reaction conditions are shown in Table 4. The reaction mixture was diluted with benzene, and basified with aqueous NaOH. After evaporation of the solvent, the N-substituted anilines (16a)—(16f) were isolated by preparative g.l.c. using 10% silicone SE-30 on chromosorb W, and identified by comparison of the i.r. and ^{1}H n.m.r. spectra with those of an authentic specimen. The yields were determined by g.l.c. using column C. Acetophenone was produced in the reaction with 1,1-diphenylethylene, as confirmed by comparison of the retention time on g.l.c. using columns A and C with an authentic sample. In addition, compound (16), the N-(1,1-*dimethylpropyl*)-2- and -4-(1,2-*dimethylprop-1-enyl*)anilines (17a) and (18a), and N-(1,1-*dimethylbutyl*)-2- and -4-(1-*ethyl-2-methylprop-1-enyl*)anilines (17b) and (18b) were formed in the reaction with 2-methylbut-1-ene and 2-methylpent-1-ene, respectively. The products (17) and (18) were also isolated as described above, and identified as follows: N-(1,1-*dimethylpropyl*)-2-(1,2-*dimethylprop-1-enyl*)-*aniline* (17a), liquid, 1% yield, $v_{max.}$(neat) 3 400 (NH), 3 025, 2 960, and 2 850 (CH), 1 605 and 1 510 (C=C of Ph), 1 450 and 1 380 (CH), 1 320 (C–N), and 750 cm^{-1} (ortho-substituted Ph); δ_H(CCl$_4$–CDCl$_3$) 1.0 (3 H, t, CH$_3$CH$_2$), 1.25 [6 H, s, (CH$_3$)$_2$C], 1.3—1.6 (5 H, br, CH$_2$ and CH$_3$C=C), 1.5—2.0 (6 H, br s, CH$_3$C=C and PhCCH$_3$), 3.0—3.9 (1 H, br, NH), and 6.4—7.4 (4 H, m, Ph); δ_C(CCl$_4$–CDCl$_3$) 8.2 (CH$_3$CH$_2$), 19.5 and 19.7

(CH$_3$C=C), 21.6 (CH$_2$), 27.6 [(CH$_3$)$_2$C], 34.5 (PhCCH$_3$), 52.8 [(CH$_3$)$_2$C], 112.7, 116.2, 126.6, 128.2, 131.6, and 142.8 (6-, 4-, 5-, 3-, 2-, and 1-phenyl C), and 127.1 and 129.2 (C=C) (Found: C, 82.9; H, 11.0; N, 6.1. C$_{16}$H$_{25}$N requires C, 83.05; H, 10.9; N, 6.05%).

N-(1,1-*Dimethylbutyl*)-2-(1-*ethyl-2-methylprop-1-enyl*)-*aniline* (17b), liquid, 4% yield, $v_{max.}$(neat) 3 400 (NH), 3 040, 2 950, and 2 850 (CH), 1 600 and 1 500 (C=C of Ph), 1 460, 1 380, and 1 360 (CH), 1 320 (C–N), and 745 cm^{-1} (ortho-substituted Ph); δ_H(CCl$_4$–CDCl$_3$) 0.9 (6 H, t, CH$_2$CH$_3$), 1.25 [6 H, s, (CH$_3$)$_2$C], 1.1—1.6 (4 H, br, CH$_2$CH$_2$CH$_3$), 1.45 (3 H, s, CH$_3$C=C), 1.7 (3 H, s, CH$_3$C=C), 2.0—2.5 (2 H, q, CH$_2$C=C), 3.2—4.2 (1 H, br, NH), and 6.3—7.6 (4 H, m, Ph); δ_C(CCl$_4$–CDCl$_3$) 13.0 (CH$_3$CH$_2$CH$_2$), 14.0 (CH$_3$CH$_2$C=C), 17.6 (CH$_3$CH$_2$CH$_2$), 22.2 (CH$_3$CH$_2$CH$_2$), 26.0 (CH$_3$C=C), 28.3 (CH$_3$C=C), 28.4 [(CH$_3$)$_2$C], 45.4 (CH$_3$CH$_2$C=C), 53.1 [(CH$_3$)$_2$C], 118.8, 115.8, 126.8, and 129.0 (6-, 4-, 5-, and 3-phenyl C) (Found: C, 82.9; H, 11.3; N, 5.6. C$_{18}$H$_{29}$N requires C, 83.35; H, 11.25; N, 5.4%).

N-(1,1-*Dimethylpropyl*)-4-(1,2-*dimethylprop-1-enyl*)-*aniline* (18a), liquid, 4% yield, $v_{max.}$(neat) 3 400 (NH), 3 020, 2 950, and 2 850 (CH), 1 610 and 1 510 (C=C of Ph), 1 320 (C–N), and 820 cm^{-1} (para-substituted Ph); δ_H(CCl$_4$–CDCl$_3$) 0.9 (3 H, t, CH$_2$CH$_3$), 1.3 [6 H, s, (CH$_3$)$_2$C], 1.4—1.7 (5 H, br, CH$_2$ and CH$_3$C=C), 1.6—1.9 (3 H, br s, CH$_3$C=C), 1.8—2.0 (3 H, br s, PhCCH$_3$), 2.4—3.2 (1 H, br, NH), and 6.8—7.3 (4 H, AB q, Ph); δ_C(CCl$_4$–CDCl$_3$) 8.4 (CH$_3$CH$_2$), 20.6 and 20.7 (CH$_3$C=C), 22.1 (CH$_2$), 27.8 [(CH$_3$)$_2$C], 34.1 (PhCCH$_3$), 53.7 [(CH$_3$)$_2$C], 116.4, 125.6, 128.6, and 144.2 (2-, 4-, 3-, and 1-phenyl C), and 129.7 and 134.8 (C=C); m/z 231 (M^+), 216, 202, 160, and 146 (Found: C, 82.95; H, 11.1; N, 6.0. C$_{16}$H$_{25}$N requires C, 83.05; H, 10.9; N, 6.05%). The structure was also confirmed by X-ray analysis of the picrate (m.p. 143—146 °C).

N-(1,1-*Dimethylbutyl*)-4-(1-*ethyl-2-methylprop-1-enyl*)-*aniline* (18b), liquid, 8% yield, $v_{max.}$(neat) 3 400 (NH), 3 020, 2 950, and 2 850 (CH), 1 610 and 1 510 (C=C of Ph), 1 455, 1 380, and 1 360 (CH), 1 320 (C–N); and 820 cm^{-1} (para-substituted Ph); δ_H(CCl$_4$–CDCl$_3$) 0.85 (6 H, t, CH$_3$CH$_2$), 1.25 [6 H, s, (CH$_3$)$_2$C], 1.1—1.6 (4 H, br, CH$_2$CH$_2$CH$_3$), 1.5 (3 H, s, CH$_3$C=C), 1.65 (3 H, s, CH$_3$C=C), 2.0—2.6 (2 H, q, CH$_3$CH$_2$C=C), 4.5—5.0 (1 H, br, NH), and 6.4—7.4 (4 H, AB q, Ph); δ_C(CCl$_4$–CDCl$_3$) 12.9 (CH$_3$CH$_2$CH$_2$), 14.6 (CH$_3$CH$_2$C=C), 17.2 (CH$_3$CH$_2$CH$_2$), 19.8 (CH$_3$CH$_2$CH$_2$), 22.2 (CH$_3$C=C), 27.3 (CH$_3$C=C), 28.3 [(CH$_3$)$_2$C], 44.3 (CH$_3$CH$_2$C=C), 53.5 [(CH$_3$)$_2$C], 116.5, 125.2, 129.1, and 144.8 (2-, 4-, 3-, and 1-phenyl C), and 117.0 and 127.9 (C=C); m/z 259 (M^+), 244, 216, 175, and 146 (Found: C, 83.15; H, 11.3; N, 5.5. C$_{18}$H$_{29}$N requires C, 83.35; H, 11.25; N, 5.4%).

The Reaction of Phenyl Azide with Propylbenzene in the Presence of TFA.—To a mixture containing phenyl azide (4.6 mmol) and propylbenzene (1.0 ml), TFA (3.0 ml) was added at *ca.* 80 °C, and the reaction went to completion in a few minutes. The reaction mixture was diluted with benzene (10 ml), and basified with aqueous NaOH. The g.l.c. analyses using column C showed no formation of compounds (16a—c) but a trace of (16d).

Kinetic Measurements.—Phenyl azide (3.3 mmol) was dissolved in a mixture of benzene (5.0 ml) and TFA (5.0 ml), or in cyclohexene (5.0 ml) and TFA (5.0 ml). Each solution was kept at 21 °C, and the rate of decomposition of the azide was determined by measurement of the volume of nitrogen gas evolved as a function of time; the first-order rate constant in the presence of benzene, $k = 1.2 \times 10^{-4}$ s^{-1}, and that in the presence of cyclohexene, $k = 9.0 \times 10^{-5}$ s^{-1}, were obtained.

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