

Electrophilic Aromatic *N*-Substitution by Ethoxycarbonylnitrenium Ion generated from Ethyl Azidoformate in the Presence of Trifluoroacetic Acid †

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Thermal reactions of ethyl azidoformate with aromatic compounds in the presence of trifluoroacetic acid (TFA) gave ethyl *N*-arylcarbamates. Toluene, nitrobenzene, or naphthalene was selectively attacked on the *ortho*- and *para*-positions, on the *ortho*- and *meta*-positions, or on the 1- and 2-positions, respectively. The yields were *ca.* twice as high as those for thermolysis (a nitrene-azepine route) in the absence of TFA with the subsequent addition of TFA at room temperature. The positional selectivities for toluene and naphthalene were lower for the former thermolysis than for the latter. The reactivity of cyclohexane or toluene relative to benzene was greater in the latter thermolysis than the former. A Hammett plot with $\rho = -1.7$ was obtained for the formation of ethyl *N*-arylcarbamates in the former thermolysis in TFA-nitrobenzene (8:2 v/v); the value was more negative than that (-1.32) for the disappearance of substituted benzenes in the reaction with ethoxycarbonylnitrene. The results suggest that the thermolysis in the presence of TFA involves an electrophilic aromatic *N*-substitution by ethoxycarbonylnitrenium ion.

Nitrenium ions containing divalent nitrogen with a positive charge have not been extensively studied, but none the less have been shown to occur as reactive intermediates.¹ Electrophilic aromatic substitution by nitrenium ions has not been established although it is of great interest in organic chemistry as it represents an amination not proceeding through nitro compounds. We recently found the presence of an ethoxycarbonylnitrenium ion intermediate in the decomposition of ethyl azidoformate in acetic acid,² but aromatic *N*-substitution by the nitrenium ion did not occur (see Results and Discussion section), possibly because of its competing reaction with the neighbouring acetate anion or the solvent. We selected trifluoroacetic acid (TFA) instead of acetic acid to avoid this difficulty, and achieved the desired aromatic *N*-substitution; the adoption of TFA was based on its high ionizing power and low nucleophilicity.³

Results and Discussion

Reactions of Ethyl Azidoformate with Benzene in the Presence of Acetic Acid, Trichloroacetic Acid, TFA, or Trifluoromethanesulphonic Acid.—The reaction of the azide with benzene in the presence of the acid yielded ethyl *N*-phenylcarbamate (**1a**) (Table 1). The yield from the reaction with benzene in the presence of acetic acid (run 2) was lower than that from the thermolysis (run 6) in benzene, followed by the addition of TFA. The product (**1a**) in run 2 presumably results from the rearrangement caused by acetic acid of 1-ethoxycarbonyl-1*H*-azepine which is formed by the reaction of ethoxycarbonylnitrene with benzene,⁴ while in run 6 (**1a**) is obtained from the rearrangement brought about by TFA. The fact that almost no product (**1a**) was formed by photolysis in acetic acid-benzene (run 1) supports the proposal that ethoxycarbonylnitrenium ion² generated in acetic acid does not bring about aromatic *N*-substitution.

Thermolysis in the presence of trichloroacetic acid or trifluoromethanesulphonic acid enhanced the yield of (**1a**) compared with that in run 6, but the yield was lower than that obtained in the presence of TFA. We therefore investigated reactions in the presence of TFA after this.

Table 1. Reaction of ethyl azidoformate with benzene in the presence of acetic acid, trichloroacetic acid, TFA, or trifluoromethanesulphonic acid

Run	[Azide]/ M	Acid (% v/v)	<i>T</i> /°C	<i>t</i> /h	% Azide decom- posed	Yield ^a [% of (1a)]
1 ^b	0.5	CH ₃ CO ₂ H(90)	25	8	64	0.3
2	0.5	CH ₃ CO ₂ H(60)	109	2	56	18
3	0.5	CCl ₃ CO ₂ H(35)	109	2	79	47
4	0.6	CF ₃ SO ₃ H(10)	109	2	100	<i>c</i>
5	0.5	CF ₃ CO ₂ H(30)	109	2	60	63
6	0.5	<i>d</i>	109	2	54	28

^a Yields are based on decomposed azide. ^b Photolysis. ^c 41% Yield of aniline. ^d TFA (30% v/v) was added at 25 °C after thermolysis.

Thermal Reactions of Ethyl Azidoformate with Aromatic Compounds in the Presence of TFA.—The thermal reaction of ethyl azidoformate with benzene, toluene, nitrobenzene, or naphthalene in the presence of TFA [thermolysis (i)] afforded compound (**1a**), ethyl *N*-(*o*- and *p*-tolyl)carbamates (**1b**) and (**1c**), ethyl *N*-(*o*- and *m*-nitrophenyl)carbamates (**1d**) and (**1e**), or ethyl *N*-(1- and 2-naphthyl)carbamates (**4a**) and (**4b**), respectively. These are summarized in Table 2. G.l.c. peaks for other products were insignificant, perhaps because of the formation of polymers.

In the reactions with benzene, the presence of 30% v/v of TFA and a reaction temperature of *ca.* 110 °C seemed to be effective for the formation of compound (**1a**). Similar conditions were therefore employed in the reactions with other aromatic compounds (Table 2).

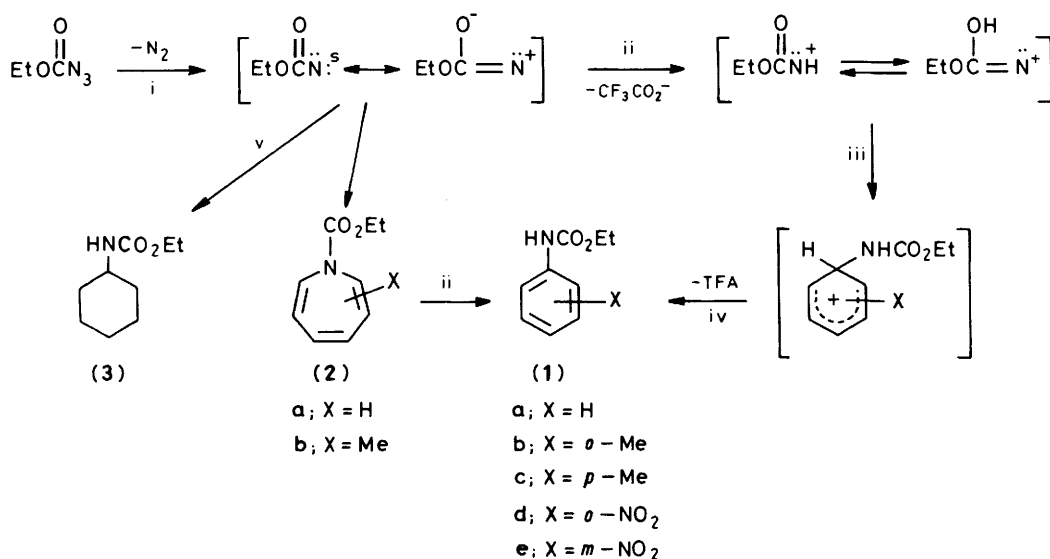
The products (**1a**–**c**), (**4a**), and (**4b**) were also formed on thermolysis in the absence of TFA with the subsequent addition of TFA (30% v/v) at 25 °C [thermolysis (ii)]. The data for this thermolysis are given in parentheses in Table 2. The rearrangement of the azepine (**2a**) or (**2b**), which is produced by the attack of the nitrene on benzene or toluene⁴ (see Scheme 1), went to completion in the presence of TFA (30% v/v) at 25 °C for 1 h. The yields of (**1a**–**c**) from thermolysis (i) were about twice as high as those from the azepine route *via* nitrene. For thermolysis (ii), the carbamates (**1d**) and (**1e**) were not produced even at 25 °C for 10 days after TFA (30% v/v) had been added,

† Preliminary report, H. Takeuchi and K. Koyama, *J. Chem. Soc., Chem. Commun.*, 1982, 226.

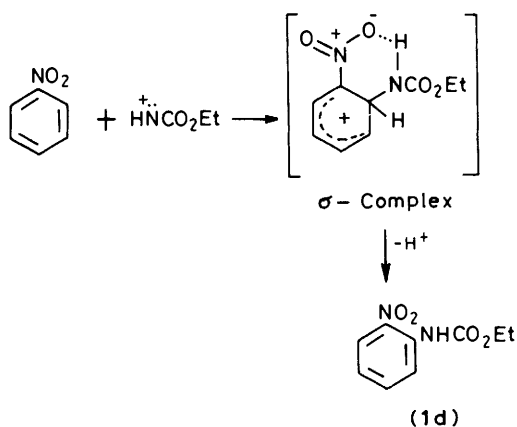
Table 2. Reactions of ethyl azidoformate (0.5M) with aromatic compounds either in the presence of TFA or in the absence of TFA with later addition of TFA (30% v/v) at 25 °C^a

Substrate	TFA/ % v/v	T/°C	t/h	% Azide decom- posed	Yield ^b (%)						o:p Ratio (1b):(1c)	1:2 Ratio (4a):(4b)	
					(1a)	(1b)	(1c)	(1d)	(1e)	(4a)			(4b)
Benzene	10	125	1	88	49								
Benzene	30	125	1	98(83)	57(25)								
Benzene	40	125	1	94	47								
Benzene	30	109	2	60(54)	63(28)								
Benzene	30	100	2	33	44								
Toluene	30	125	1	93(83)		33(22)	20(8.6)					1.7(2.6)	
Toluene	30	109	2	60(54)		42(24)	24(9.3)					1.8(2.6)	
Nitrobenzene	30	125	1	93(93)			17(ca. 0)	11(ca. 0)					
Nitrobenzene	30	109	2	70(65)			16(ca. 0)	10(ca. 0)					
Naphthalene	c	109	2	82(94)						42(67)	12(3.0)		3.5(22)

^a The data in parentheses refer to thermolysis (ii). ^b Yields are based on decomposed azide. ^c The azide and naphthalene (1.1M) were dissolved in TFA or in CH₂Cl₂. TFA (50% v/v) was added to the thermal mixture in CH₂Cl₂.



Scheme 1. Reagents: i, heat; ii, TFA; iii, PhX; iv, CF₃CO₂⁻; v, cyclohexane



Scheme 2.

or after the mixture had been heated in the presence of TFA (30% v/v) at 110 °C for 2 h. These results suggest that an electrophile, more reactive towards aromatic compounds than the nitrene, is involved in thermolysis (i). This electrophile must

be the ethoxycarbonylnitrenium ion, since attack by a cation takes place at the *ortho*- and *para*-positions in toluene and at the *meta*-position⁵ in nitrobenzene. The attack at the *ortho*-position in nitrobenzene may be explained by the high stability of the resulting σ -complex (Scheme 2).

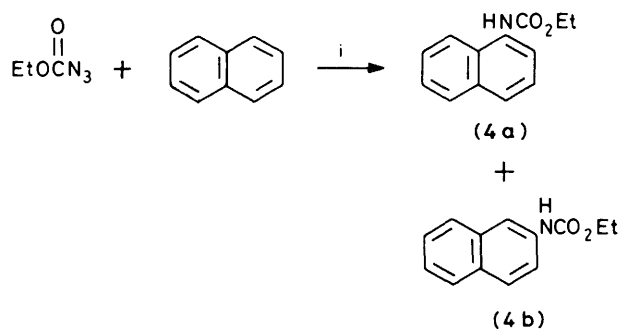
The carbamates (**4a**) and (**4b**) were formed in 67 and 3% yields on thermolysis in dichloromethane at 109 °C in the absence of TFA [Scheme 3]. This is consistent with the fact that the direct formation of *N*-aryluurethanes takes place on reaction of ethoxycarbonylnitrene with anthracene⁶ or pyrene.⁷ As shown in Table 2, the relative reactivities of positions 1 and 2 in naphthalene and the *ortho*:*para* ratios for the reaction with toluene were lower for thermolysis (i) than for thermolysis (ii). The low selectivities support the idea that the nitrenium ion is more reactive than the nitrene.

Relative Reactivity of Cyclohexane or Toluene with respect to Benzene.—The relative reactivity of cyclohexane with respect to benzene was determined by comparing the yield of ethyl *N*-cyclohexylcarbamate (**3**) with that of (**1a**) in reactions using cyclohexane and benzene as substrates (Table 3). The relative reactivity for thermolysis (ii) was *ca.* five times greater than that for thermolysis (i). This difference in relative reactivity cannot

Table 3. Relative reactivity (r) of cyclohexane or toluene with respect to benzene for reaction of ethyl azidoformate in the presence of TFA (30% v/v) and that in the absence of TFA with subsequent addition of TFA (30% v/v) at 25 °C^a

Substrate (70% v/v)	$T/^\circ\text{C}$	t/h	% Azide decomposed	r (cyclohexane)	r (toluene)	
					o_f	p_f
Benzene-cyclohexane	109	2	60(53)	0.36(1.9)		
Benzene-cyclohexane	79	24	35(21)	0.36(2.0)		
Benzene-toluene	109	2	59(41)		2.8(3.9)	3.0(3.1)
Benzene-toluene	79	24	35(15)		2.6(4.5)	2.9(3.7)

^a The data in parentheses refer to thermolysis (ii) (see the text).



Scheme 3. Reagents: In CH_2Cl_2 , 109 °C

be explained by the change in the nitrene multiplicity because the singlet nitrene, but not the triplet nitrene, reacts with cyclohexane⁸ and benzene⁹ to give the carbamate (3) and the azepine (2a), respectively. Therefore, the result agrees with the idea that thermolysis (i) involves the nitrenium ion intermediate which is more reactive towards benzene than cyclohexane.

ortho- and *para*-Attacking partial rate factors (o_f and p_f) for toluene were determined from the thermolysis employing benzene and toluene as substrates (Table 3). The low partial rate factors for thermolysis (i) compared with those for thermolysis (ii) supports the above idea. In view of the evidence that the formation of the carbamate (3) through the nitrene is not negligible in thermolysis (i), the carbamates (1a–c) may be formed *via* both the nitrene and the nitrenium ion in thermolysis (i).

The Hammett Plot for Electrophilic Aromatic N-Substitution by the Nitrenium Ion.—The partial rate factors (k_f), *i.e.* p_f for toluene, m_f for acetophenone, and m_f for nitrobenzene, were determined for the formation of the ethyl *N*-arylcarbamates in TFA–nitrobenzene (8:2 v/v) containing toluene, acetophenone, and benzene (each <3% v/v), respectively. The mixed solution permits us to assume the exclusive transformation of the nitrene into the nitrenium ion since the nitrene is not active enough to react with nitrobenzene (Table 2). The correlation¹⁰ between $\log k_f$ and σ^+ give a linear plot with $\rho = -1.7$ (Figure). The ρ value is more negative than that (-1.32) obtained from the correlation with σ_p for the disappearance of substituted benzenes in the reactions of nitrene with aromatic compounds.¹¹ The less negative ρ value than that usually obtained for aromatic substitution, *i.e.* showing a low substrate selectivity for the reaction with the nitrenium ion, may be rationalized by postulating an early transition state resembling a π -complex,¹² because the nitrenium ion is highly reactive. The nitrenium ion is therefore characterized by the apparently unreconcilable low substrate and high positional selectivities (with the latter selectivity compare the selective attack at the *ortho*- and *para*-positions in toluene with that at the *ortho*- and *meta*-positions in nitrobenzene). However, this observation is in good agreement

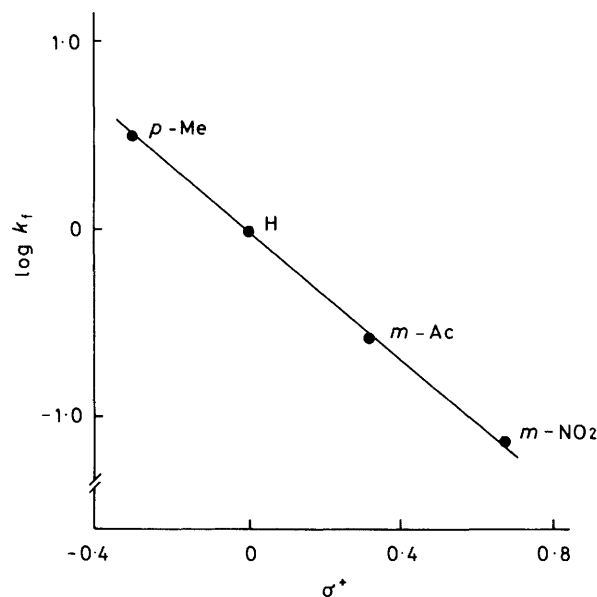


Figure. Plot of $\log k_f$ against σ^+ for reaction of ethyl azidoformate with substituted benzenes in TFA–nitrobenzene (8:2 v/v) at 109 °C for 1 h

with the suggestion^{12a,b} that the transition state with the highest energy (which determines the substrate selectivity) has a π -complex nature, and is followed by σ -complex formation, which determines the positional selectivity.

The Decomposition of Ethyl Azidoformate in TFA.—The rate of the thermal decomposition of ethyl azidoformate in TFA or in benzene was determined by measurement of the amount of azide as a function of time (a_t). Linear plots of $\ln a_0/a_t$ versus t were obtained and indicate that the decomposition is first order in azide. Rate constants were determined from the slopes of the plots, and the activation parameters, ΔH^\ddagger and ΔS^\ddagger , were calculated from the equation derived from transition state theory. The results are summarized in Table 4.

The activation parameters in benzene and in TFA do not differ much and the ΔH^\ddagger values are same in both solvents. The results show that the thermolysis in TFA does not proceed *via* an azide conjugate acid, but *via* the nitrene.² Thus, the nitrenium ion with its equilibrated keto and enol forms would be formed not *via* the conjugate acid but by proton abstraction² by the nitrene from TFA (the 1,3-dipole in the nitrene may abstract a proton at the negative oxygen to give the enol, see Scheme 1). The evidence that the thermolysis in TFA does not proceed through the conjugate acid rules out the possibility that an acid-catalysed S_N2 type reaction (attack of the aromatic compound on the conjugate acid) is involved in the thermolysis. Therefore, the TFA-catalysed aromatic *N*-substitution by the nitrenium

Table 4. Rate constants and activation parameters for the decomposition of ethyl azidoformate

Solvent	$T/^\circ\text{C}$	$10^5 k/s^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$ ^a	$\Delta S^\ddagger/\text{cal mol}^{-1} \text{K}^{-1}$ ^a
Benzene	99.3	2.9	32.0	3.5
	109.0	9.6		
	125.0	46		
TFA	99.3	6.5	32.0	1.7
	109.0	23		
	125.0	117		

^a 1 cal is 4.184 J.

ion takes place in the usual way, and the ethyl *N*-arylcarbamates (**1a–c**), (**4a**), and (**4b**) are formed by substitution as well as by the nitrene–azepine route (Scheme 1).

Experimental

I.r. spectra were obtained on a Hitachi model EPI-G3 spectrometer. N.m.r. spectra were taken with a Nippondens JNM FX-60Q instrument. G.l.c. analyses were carried out with Shimadzu GC-6A unit using a glass column (1 m × 3 mm) (column A, 10% polyethylene glycol 20M on 60–80 Uniport KS; column B, 10% silicone DC 550 on 60–80 Uniport KS). Photolysis was performed externally in a quartz tube (25 cm × 1.8 cm) with a 300-W high-pressure mercury lamp (Halos PIH-300). Ether refers to diethyl ether.

Acetic acid, benzene, toluene, nitrobenzene, cyclohexane, and dichloromethane were purified by standard methods before use. Trichloroacetic acid, trifluoroacetic acid (TFA), trifluoromethanesulphonic acid, and ethyl *N*-phenylcarbamate (**1a**) are commercially available materials (Wako). The following materials were prepared by the methods described in the literature: ethyl azidoformate,¹³ ethyl *N*-(*o*-tolyl)carbamate (**1b**),¹⁴ ethyl *N*-(*p*-tolyl)carbamate (**1c**),¹⁵ ethyl *N*-(*o*-nitrophenyl)carbamate (**1d**),¹⁶ ethyl *N*-(*m*-nitrophenyl)carbamate (**1e**),¹⁷ ethyl *N*-cyclohexylcarbamate (**3**),¹³ ethyl *N*-(1-naphthyl)carbamate (**4a**),¹⁵ and ethyl *N*-(2-naphthyl)carbamate (**4b**).¹⁸

Ethyl *N*-(*m*-acetylphenyl)carbamate (**1f**) which was employed as a standard material in the Hammett plots was synthesized by the reaction of *m*-aminoacetophenone (2 mol equiv.) with ethyl chloroformate (1 mol equiv.) in ether at room temperature; m.p. 113–114 °C (recrystallized from benzene), v_{max} (Nujol) 3 300 (NH), 1 730 and 1 680 (C=O), 1 540 (C–N), 1 230 and 1 070 (C–O), and 900, 795, and 690 cm^{-1} (*meta*-substituted Ph); $\delta(\text{CDCl}_3\text{--CCl}_4)$ 1.32 (3 H, t, CH_2CH_3), 2.62 (3 H, s, COCH_3), 4.28 (2 H, q, CH_2CH_3), 7.1–8.0 (4 H, m, Ph), and ca. 7.9–8.4 (1 H, br, NH); $\delta_{\text{C}}(\text{CDCl}_3\text{--CCl}_4)$ 14.5 (CH_2CH_3), 26.6 (COCH_3), 61.4 (CH_2CH_3), 118.2, 123.1, 137.8, and 138.7 (2-, 4- and 6-, 5-, 3-, and 1-phenyl carbons from nitrogen), 153.7 ($\text{NHCO}_2\text{CH}_2\text{CH}_3$), and 198.0 p.p.m. (COCH_3) (Found: C, 63.95; H, 6.3; N, 6.55. $\text{C}_{11}\text{H}_{13}\text{NO}_3$ requires C, 63.75; H, 6.30; N, 6.75%).

Photolysis of Ethyl Azidoformate in Acetic Acid–Benzene.—Ethyl azidoformate (21 mmol) was dissolved in acetic acid–benzene (9:1 v/v) to give a total volume of 10 ml. Dry nitrogen was bubbled through the solution for 1 h, and then it was irradiated at 25 °C for 8 h. Unchanged azide (36%) and the products, ethyl *O*-acetyl-*N*-hydroxycarbamate (20%), (**1a**) (0.3%), and 1-ethoxycarbonyl-1*H*-azepine (**2a**) (2%), were analysed by g.l.c. using column A, the amounts being calculated from the peak areas in the usual manner. The product yields

were based on the amount of azide decomposed, and authentic samples of the hydroxycarbamate² and the azepine⁴ were prepared by methods described in the literature. A 0.1% yield could be detected by the analytical conditions. A non-photolysed mixture did not yield the above products, and none of the g.l.c. peaks of the starting materials and products overlapped.

Thermal Reactions of Ethyl Azidoformate with Aromatic Compounds in the Presence or Absence of Acetic Acid, Trichloroacetic Acid, TFA, or Trifluoromethanesulphonic Acid.—A solution (10 ml) containing the azide, the aromatic compound, and the acid was placed in a sealed tube, and heated; the results are shown in Tables 1 and 2. The thermal reactions of the azide with the aromatic compound in the absence of acid were carried out similarly, and then TFA (30% v/v) was added to the reaction mixture at room temperature for 1 h to complete the rearrangement of the azepine into the *N*-arylcarbamate. The yields of the products (**1a–c**), (**4a**), and (**4b**) were determined by g.l.c. using column A as described above, and those of (**1d**) and (**1e**) using column B. The product aniline in the presence of trifluoromethanesulphonic acid was analysed similarly after neutralization of the reaction mixture with aqueous sodium hydrogen carbonate. The analyses of these products agreed within <3% on two runs, and the products did not decompose under the g.l.c. conditions.

Relative Reactivity of Cyclohexane or Toluene with respect to Benzene.—Ethyl azidoformate (2.6 mmol) was dissolved in benzene (28.8 mmol)–cyclohexane (20.6 mmol) to give a total volume of 5.0 ml. The solution and an equivalent solution but containing TFA (30% v/v) were heated at 109 °C for 2 h or at 79 °C for 24 h. To the reaction mixture in the absence of TFA, TFA (30% v/v) was added at 25 °C after 1 h to bring about the rearrangement of the azepine (**2a**) into the carbamate (**1a**).

A solution containing ethyl azidoformate (4.9 mmol), benzene (49.8 mmol), and toluene (47.0 mmol) was heated either in the presence or absence of TFA (30% v/v) at 109 °C for 2 h or at 79 °C for 24 h, and the reaction mixture not containing TFA was treated as above to bring about the rearrangement of the azepines. The yields of (**1a–c**) and (**3**) were determined as described above, employing column A. The relative reactivity of cyclohexane or toluene with respect to benzene was calculated from the yields and the initial concentrations of cyclohexane, toluene, and benzene. When a mixture of (**1a–c**) and (**3**) was heated in benzene–TFA (7:3 v/v) at 109 °C for 2 h, each component was consumed to a very small extent, and ratios, (**1b**):(**1a**) and (**1c**):(**1a**), were almost constant during the reaction. However, a decrease of ca. 20% was observed in the ratio (**3**):(**1a**).

Hammett Plot.—A solution containing ethyl azidoformate (0.25M) in TFA–nitrobenzene (8:2 v/v) was heated in the presence of benzene, toluene, or acetophenone (<3% v/v) at 109 °C for 1 h. The ratios, (**1e**):(**1a**), (**1e**):(**1c**), and (**1e**):(**1f**), were determined by g.l.c. analysis using column B as described above. The partial rate factor (k_f), m_f for nitrobenzene, p_f for toluene, or m_f for acetophenone, was obtained from the above ratio and the initial concentration of the aromatic compound. Treatment of a mixture of (**1a**), (**1c**), (**1e**), and (**1f**) in TFA–nitrobenzene (8:2 v/v) at 109 °C for 1 h caused almost no change in the relative ratios of the compounds.

Kinetic Measurements.—Ethyl azidoformate (0.5M) was dissolved in TFA or in benzene. The solution (2 ml) was placed in a sealed tube, and heated at three temperatures. Six identical mixtures were made up for the reaction at each temperature, and the azide remaining in the reaction mixture at various times

was followed by g.l.c. using column A (column temperature, 80 °C; injection and detector temperature, 90 °C).

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