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Formation and Cycloaddition Reactions of Substituted *N*-Ethoxycarbonyl-1(1*H*)-azepine Derivatives[1]

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The formation of substituted *N*-ethoxycarbonyl-1(1*H*)-azepine derivatives is reinvestigated in the thermal reactions of benzene derivatives with ethyl azidoformate. The rate-determining step in these reactions is determined by kinetic experiments to be the decomposition of the azide. The (4+2) π cycloadducts of these azepine derivatives are obtained by thermal reactions with tetracyanoethylene (TCNE) as a dienophile. The formation of compounds **22**, **23**, **24**, **25**, **26**, and **27** is confirmed by the spectral evidence.

Previously, we reported on the photosynthesis of substituted 1(1*H*),2-diazepines and their reactivities in the cycloaddition reactions.[2] In view of the interest in the theoretical aspects of the cycloaddition reactions of seven-membered cyclic non-benzenoid heteroaromatic hydrocarbons, the above-mentioned new 1(1*H*),2-diazepines would seem to be of timely interest. At the same time, substituted 1(1*H*)-azepines are also considered to comparable with the diazepines in the cycloaddition reactions. Furthermore, recent works[3,4] along these lines have prompted us to report our different preliminary observations concerning the

1) Presented in part at the symposium on Synthetic Organic Chemistry of the Chemical Society of Japan, Tokyo, Nov., 1969. Studies of Heteroaromaticity. XL. Part XXXIX, T. Sasaki, K. Kanematsu and K. Hayakawa, *Chem. Commun.*, **1970**, 82.

2) T. Sasaki, K. Kanematsu, A. Kakehi, I. Ichikawa, and K. Hayakawa, *J. Org. Chem.*, **35**, 426 (1970).

3) Recently, the structures of the adducts from the reactions of *N*-ethoxycarbonyl- and *N*-methoxycarbonylazepines with TCNE have been rigorously established; see a) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **87**, 4819 (1965); *J. Org. Chem.*, **32**, 3511 (1967). b) A. S. Kende, P. T. Izzo and J. E. Lancaster, *J. Amer. Chem. Soc.*, **87**, 5044 (1965).

4) While this paper was being prepared, a report of the cycloadditions reactions of 1(1*H*)-azepine derivatives has been published: see L. A. Paquette, D. E. Kuhla, J. H. Barrett and L. M. Lwichter, *J. Org. Chem.*, **34**, 2889 (1969).

Table 1. Reaction of ethoxycarbonylnitrene with benzene derivatives

Benzene derivatives	Reaction conditions		Absolute yields (%)**	
	a) and b)*	(°C)	Azepines	Urethans
Benzene	a	80	10	0
	b	120	40	0
Toluene	a	110	30	0
	b	120	50	0
o-Xylene	a	120	40—50	0—10
	b	120	20—30	30—40
m-Xylene	a	120	40—50	0—10
	b	120	20—30	30—40
p-Xylene	a	120	40—50	0—10
	b	120	20—30	30—40
Mesitylene	a	120	25	30
	b	120	0	70

* a) in an open flask for 3 hr. b) in a sealed-tube for 2 hr.
** Absolute yields based on ethyl azidoformate.

cycloaddition reactions of 1(1*H*)-azepine derivatives.

This paper will deal with the thermal formation of azepine derivatives from benzene derivatives and ethyl azidoformate under various conditions in both open and sealed-tube systems. To obtain further information concerning the mechanisms for these reactions, we carried out kinetic experiments in the formation of azepines from *p*-xylene and ethyl azidoformate. Subsequently, we investigated the isomeric structures of the reaction adducts between ethyl azidoformate and benzene derivatives in the presence of TCNE.

Results and Discussion

Thermal Reaction of Benzene Derivatives and Ethyl Azidoformate. Although substituted *N*-ethoxycarbonyl-1(1*H*)-azepines have been prepared by the photolysis or pyrolysis of ethyl azidoformate in aromatic substrates such as toluene, anisole, and halobenzenes,[5] we reinvestigated the thermal reaction under various conditions.

When ethyl azidoformate was decomposed in *o*-, *m*- and *p*-xylene in an open flask or in a sealed-tube at 120°C, the corresponding azepines were obtained, together with aromatic urethans. However, when ethyl azidoformate was refluxed in benzene (at 80°C) and toluene (at 110°C) or in a sealed-tube at 120°C, only the corresponding azepines were obtained. On the other hand, when ethyl azidoformate was decomposed in mesitylene at 120°C in an open flask, the corresponding azepines and aromatic urethans were produced in 25 and 30% yields respectively, but at 120°C in a sealed-tube, only the aromatic urethan was produced in about a 60% yield. These results are summarized in Table 1.

These results indicate that ethyl azidoformate was not thermolyzed appreciably at the reflux temperatures of benzene and toluene, as has been reported by Baldwin and Smith.[6]

Substituted aromatic urethans were obtained conveniently by the thermal isomerization of dimethyl and trimethyl-substituted azepines under more drastic conditions. Especially, because of the thermal instability of the tri-substituted azepine skeleton, 1-ethoxycarbonyl-2,4,6-trimethylazepine was readily converted to the aromatic urethans and no seven-membered ring compounds could

Table 2. The number and the ratio of 1(1*H*)-azepines produced

Azepine precusor	Number of azepines	Ratio of azepines* (Comp. No.)
Toluene	3	40 (**9**) : 35 (**8**) : 25 (**10**)
o-Xylene	4	50** : 30** : 15** : 5**
m-Xylene	3	15 (**15**) : 50** : 35**
p-Xylene	2	20 (**18**) : 80 (**19**)

* These ratios were determined by glpc and NMR spectra.
** Structures of isomeric azepines were difficult to determine.

5) a) W. Lwowski and R. L. Jahnson, *Tetrahedron Lett.*, **1967**, 891, and the refs. cited therein. b) R. J. Cotter and W. F. Beach, *J. Org. Chem.*, **29**, 751 (1964). c) K. Hafner, D. Zinser and K. L. Moritz, *Tetrahedron Lett.*, **1964**, 1733. d) R. A. Smith, J. E. Baldwin and I. C. Paul, *J. Chem. Soc., B*, **1967**, 112.

6) Ethoxycarbonylnitrene and ethoxycarbonylcarbene have been generated by the thermal decomposition of ethyl azidoformate and ethyl diazoacetate at 129.6°C in a solution of benzene and anisole, toluene, chlorobenzene or of fluorobenzene in an unreactive perfluorinated polyether: see J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **89**, 1886 (1967).

be detected. The relative ratio of the yielded isomeric ethoxycarbonylazepine derivatives was determined by gas-chromatographic and spectroscopic means. However, the reaction mixture was difficult to separate by means of column chromatography and molecular distillation. These results[7] are shown in Table 2.

In order to obtain kinetic information concerning the above-mentioned reactions, we investigated the reaction of *p*-xylene with ethyl azidoformate in an open flask. The thermolysis of ethyl azidoformate was done at 100, 120, and about 140°C in pure *p*-xylene, and the reactants were then analyzed by glpc. The products were identified as di-substituted *N*-ethoxycarbonylazepines by their retention times and IR and NMR spectra, given in Table 3. The amounts of unchanged ethyl azidoformate at different reaction times were measured by glpc in the reactions of the heating of the mixture of *p*-xylene and ethyl azidoformate at 120°C. These results are shown in Fig. 1. Thus, the following zeroth-order rate constants were determined: $k_{100°}=1.7\times10^{-3}$ min^{-1}; $k_{120°}=6.3\times10^{-3}$ min^{-1}; $k_{138°}=1.7\times10^{-2}$ min^{-1}. On the other hand, the rate of the decomposition of ethyl azidoformate was calculated to be -6.3×10^{-3} min^{-1} at 120°C. These results can be explained in terms of a ethoxycarbonylnitrene which

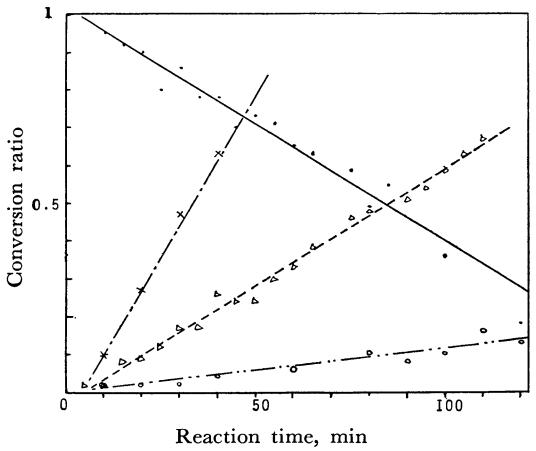


Fig. 1. Kinetic experiments in the reactions of ethyl azidoformate with *p*-xylene.

——— Decomposition curve of ethyl azidoformate at 120°C.
— — — Formation curve of azepines at *ca.* 138°C.
------ Formation curve of azepines at 120°C.
—··— Formation curve of azepines at 100°C.

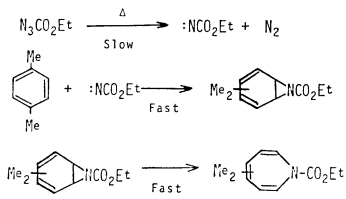


Chart 1.

is generated by the thermal decomposition of ethyl azidoformate in the rate-determing step (slow); it is added to *p*-xylene to form the bicyclic aziridine intermediate, and they converted to the valence-bond isomerization products rapidly (Fig. 1 and Chart 1).

On the basis of the above facts, in summary it can be said that 1*H*-azepines are formed by the kinetically-controlled and aromatic urethans by the thermodynamically-favored reaction pathway shown in Chart 2.

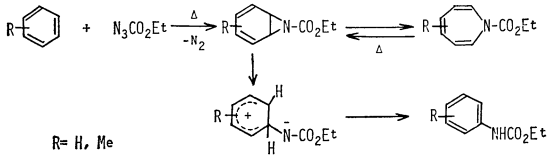


Chart 2.

The structures of a representative number of 1(1*H*)-azepines thus formed from the corresponding benzene substrates are illustrated in Table 3.

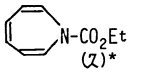
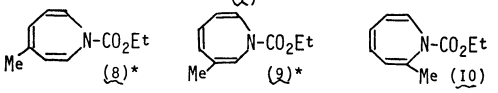
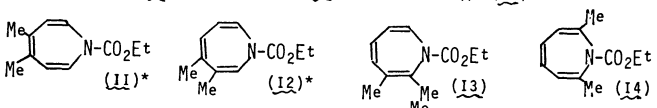
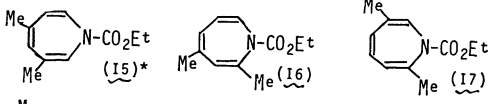
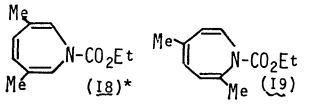
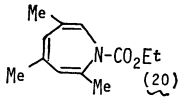
The structural assignments for the produced azepines and aromatic urethans were determined by means of their spectral characteristics. In the infrared spectra, the azepines (**7**—**20**) show two strong absorptions due to the carbonyl ester in the ranges of 1700—1720 cm^{-1} and 1320—1340 cm^{-1}, and medium absorptions due to the carbon-carbon double bond in the range of 1610—1660 cm^{-1}. On the other hand, the aromatic urethans exhibit absorptions at 3240—3320 cm^{-1} (NH) and at 1600 cm^{-1} (C_6H_5). More significantly, the isomeric azepine mixture was confirmed by NMR inspection.[8]

From their NMR assignments for substituted 1*H*-azepines, the structures of the isomeric mixture of methyl-substituted 1*H*-azepine derivatives were confirmed. In the 2- and 7-methyl isomers, methyl protons appeared at the lowest field, while in the 3- and 6-methyl isomers, methyl protons appeared at the highest field. The spectrum of a mixture of **18** and **19** showed signals at τ 7.93 (C_2-Me, almost singlet), 8.09 (C_5-Me, almost

7) These results were different from the preliminary observations in the reactions of the ethoxycarbonylnitrene and methoxycarbonylcarbene with substituted benzene derivatives; a) K. Hafner, D. Zinter and K. L. Moritz, *Tetrahedron Lett.*, **1964**, 1733. b) K. Alder, R. Munders and P. Wirtz, *Ann. Chem.*, **627**, 59 (1959).

8) Coincidentally, a general synthetic entry to 1*H*-azepine derivatives has been reported in which structures of substituted 1*H*-azepines have been elucidated by their NMR and Mass spectra: L. A. Paquette, D. E. Kuhla, J. H. Barrette and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).

Table 3. Structures of 1(1*H*)-azepines from corresponding benzene derivatives

Azepine precursor	Possible structure of formed 1(1*H*)-azepines
Benzene (**1**)	
Toluene (**2**)	
o-Xylene (**3**)	
m-Xylene (**4**)	
p-Xylene (**5**)	
Mesitylene (**6**)	

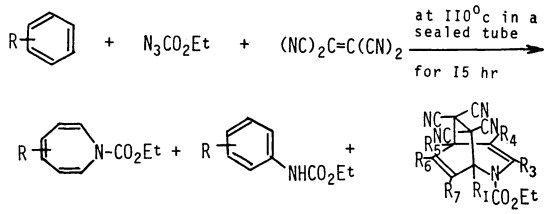
* The positions of substituents of the 1(1*H*)-azepine derivatives were determined by confirmation of NMR spectra of thier adducts to TCNE.

singlet), and 8.34 (C_3- and C_6-Me, doublet $J=1.5$ Hz) with relative intensities of 2 : 2 : 1. However, the chemical shifts of the C_3- and C_4-Me of the mixture (**8**—**17**) showed approximate values in the range of τ 8.05—8.30, and the signals often overlap. Aromatic urethans, of course, showed a broad signal at about τ 3.60 due to the amino group and at τ 7.65—7.85 attributable to methyl protons attached to the benzene ring.

Thermal Reaction of Ethyl Amidoformate and Aromatic Substrates in the Presence of TCNE. The adducts from tetracyanoethylene and 1-ethoxycarbonylazepines[9] have already been reported to arise from (4+2) π Diels-Alder cyclo addition reactions.[3]

We investigated a series of cycloaddition reactions of ethyl azidoformate and aromatic substrates in the presence of TCNE under thermal conditions (in a sealed-tube at 110°C for 15 hr.).

A dark solution of the reaction mixture was carefully chromatographed in order to obtain the adducts. Thus, four 1 : 1 adducts, **21**,[3] **22**, **26**, and **27**, were isolated. These adducts were structurally elucidated through a consideration of their NMR



Adduct Comd. No.	R_1	R_3	R_4	R_5	R_6	R_7
21	H	H	H	H	H	H
22	H	H	H	H	Me	H
23	H	H	H	H	H	Me
24	H	H	H	Me	Me	H
25	H	H	H	H	Me	Me
26	H	H	Me	H	Me	H
27	H	H	Me	H	H	Me

Chart 3.

Table 4. Reaction of ethoxycarbonylnitrene and bnzenee derivatives in the presence of TCNE

Benzene derivatives	Absolute yield (%) azepines+Urethans	Cycloadducts (Comp. No.)
Benzene	24*	18 (**21**)
Toluene	20	61 (**22**+**23**)
o-Xylene	16	39 (**24**+**25**)
m-Xylene	20	11 (**26**)
p-Xylene	22	11 (**27**)
Mesitylene	73**	—

* In this case, urethan was not detected.
** In this case, azepine was not detected.

9) The (4+2) π cycloadditions of *N*-substituted azepines to various dienophiles such as tetracyanoethylene,[3] 4-phenyl-1,2,4-triazoline-3,5-dione,[1] *N*-phenylmaleimide,[4] and isobenzofurans,[4] have already been studied. In addition, *N*-carbethoxyhomoazepine and a TCNE adduct were obtained in a similar fashion: T. Sasaki, K. Kanematsu and A. Kakehi, *Chem. Commun.*, in press.

(in $CDCl_3$) and mass spectral menas. The NMR spectrum of the adduct from *m*-xylene shows signals at τ 3.30 (bs, 1H, H_3), 4.03 (bd, 1H, H_7 overlapped with H_1), 4.11 (bs, 1H, H_1 overlapped with H_7), 5.66 (q, 2H, J=7.0 Hz, $COC\underline{H}_2$-), 6.93 (d, 1H, J=7.5 Hz, H_5), 7.90 (d, 3H, J=1.5 Hz, C_6-Me), 8.07 (d, 3H, J=1.5 Hz, C_4-Me), and 8.66 (t, 3H, J=7.0 Hz, $COCH_2C\underline{H}_3$), which was assigned as **26**. Similarly, the spectrum of the adduct from *p*-xylene shows characteristic signals at τ 3.30 (bs, 1H, H_3), 3.59 (bd, 1H, J=7.5 Hz, H_6), 4.30 (bs, 1H, H_1), 5.61 (q, 2H, J=7.0 Hz, $COC\underline{H}_2$-), 6.71 (d, 1H, J=7.5 Hz, H_5), 7.89 (d, 3H, J=1.5 Hz, C_7-Me), 8.06 (d, 3H, J=1.5 Hz, C_4-Me), and 8.62 (t, 3H, J=7.0 Hz, $COCH_2C\underline{H}_3$). The cycloaddition product in this case was then concluded to be **27**. On the other hand, the adduct fraction from toluene afforded a 61% yield of a mixture of **22** and **23**[10] in a 4 : 6 ratio (NMR). The mixture was then recrystallized from chloroform - *n*-hexane to give a 1 : 1 adduct with a mp of 131—133°C (**22**) and which shows signals at τ 3.12 (bd, 1H, J=9.0 Hz, H_3), 3.95 (bd, 1H, J=8.0 Hz, H_7), 4.02 (be, 1H, J=8.0 Hz, H_1), 4.99 (t, 1H, J=9.0 Hz, H_4), 5.66 (q, 2H, J=7.0 Hz, $COC\underline{H}_2$), 6.75 (bd, 1H, J=9.0 Hz, H_5), 7.88 (d, 3H, J=1.5 Hz, C_6-Me), and 8.66 (t, 3H, J=7.0 Hz, $COCH_2C\underline{H}_3$). From the mother liquor, however, **23** was obtained by further recrystallization, but it was still mixed with **22**. The spectrum of the crude adduct, **23**, shows weak signal at τ 3.95, but it exhibited characteristic signals at 3.62 (bd, 1H, J=7.5 Hz, H_6), 4.02 (bs, 1H, H_1), and τ 6.75 (bt, J=7.5 and 8.0 Hz, H_5). For the adducts from *o*-xylene, a mixture of **24** and **25** was produced in a 3 : 7 ratio, but it could not be separated by column chromatography. However, the NMR spectrum of the mixture showed C-methyl groups at τ 8.00 and 8.33 with relative intensities of 17 : 3. Because of the abnormality of the chemical shift

Table 5. NMR Spectral data of cycloadducts at 60 MHz in $CDCl_3$

Cycloadduct	Chemical shifts (τ-value)						$COOCH_2CH_3$	
	R_1	R_3	R_4	R_5	R_6	R_7	$-CH_2-$	$-CH_3$
21	4.23	3.20	5.03	6.60	3.26	3.75	5.71	8.67
22	4.25	3.12	4.99	6.73	7.88	3.95	5.66	8.66
23	4.36	3.18	4.94	6.60	3.62	7.89	5.64	8.65
24	4.32	3.23	5.51	8.33	8.00	4.02	5.71	8.68
25	4.43	3.23	5.03	6.88	8.00	8.00	5.71	8.68
26	4.11	3.30	8.07	6.93	7.90	4.03	5.66	8.66
27	4.30	3.30	8.06	6.71	3.59	7.89	5.61	8.62

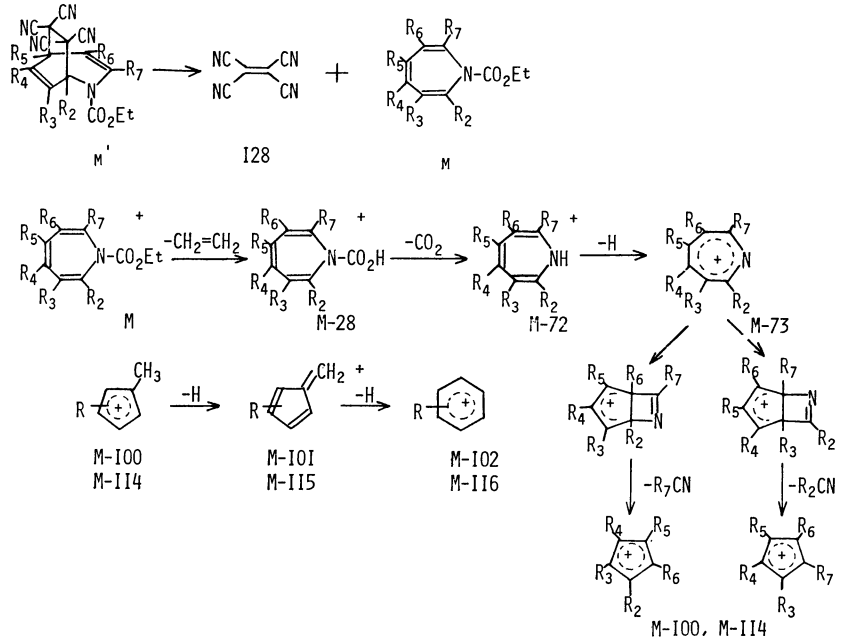


Chart 4.

10) The 4-methyl isomer was observed as a minor product by NMR (τ 8.06, 3H, d, J=1.5 Hz $C\underline{H}_3$)

Table 6. Mass spectral data for various fragment ions and the relative abundance (%) of 1(1*H*)-azepines and its diels-alder adducts

Comp. No.	Ions, rel. int. (%)								
	M′	128	M	M-28	M-72	M-73	M-106	M-101	M-102
7	—	—	58	16	26	100	60	4	5
21	5	19	100	45	41	88	45	23	24
22	20	21	100	55	26	50	51	96	82
26	5	3	100	28	11	56	14	4	9
27	7	5	100	57	28	71	27	10	30

of methyl protons at τ 8.33, the structure of the adduct **24** was tentatively identified as that of a 5,6-dimethyl isomer. The chemical shifts of these compounds are shown in Table 5.

These results suggest the importance of both steric and inductive effects on the 1*H*-azepine reactivity and that it is difficult for the methyl substitution of the adduct to proceed at a bridgehead position excepting that of **24** and at an α-position adjacent to nitrogen.[11] Furthermore, the mass spectra of **21**, **22**, **26**, and **27** show molecular ion peaks, and strong at M′-128 (=M) by the loss of a C_6N_4-molecule from the molecular ion; this fragment may arise from a retro-Diels-Alder fragmentation. Further fragmentations are pararelled to those of substituted azepinium ions,[4] as is shown in Chart 4 and Table 6.

On the basis of the above facts, we could determine the positions of the substituted 1(1*H*)-azepine derivatives (**7**, **8**, **9**, **11**, **12**, **15**, and **18**) by confirming the structures of their adducts (**21**—**27**) with TCNE. Other azepine derivatives (**10**, **13**, **14**, **16**, **17**, **19** and **20**) had been confirmed only partially by spectral and glpc data because of the difficulty of forming their adducts.

Experimental[12]

Preparation of Azepine Derivatives. Method A. A solution of ethyl azidoformate (2.3 g) and an excess of the respective benzene derivatives (10 g) was heated in an oil bath for 3 hr. The solution was then evaporated *in vacuo*, and the residue was separated by chromatography (silica gel), using chloroform as the eluent. The resulting crude red or orange azepine derivatives were purified by fractional distillation.

Method B. Ethyl azidoformate (4.0 g) and an aromatic compound (20 g) were mixed in a 100 m*l* stainless tube. The reaction was carried out in a sealed system at 120°C for 2 hr, after which the reaction mixture was treated much as with method A. These results are summarized in Tables 1 and 2.

These azepine derivatives were isomerized to the aromatic urethans under thermal conditions at 150—200°C in an oil bath for 4—5 hr.[13]

The relative ratio of the produced isomeric *N*-ethoxycarbonylazepine derivatives was determined by glpc and spectroscopic means. Especially, the structures of the mixture of azepine derivatives were determined by the NMR data in the following regions: 3.70—4.65 (olefinic-ring protons), τ 7.90—8.00 (C_2- and C_7-methyl protons), 8.10—8.30 (C_3-, C_4-, C_5- and C_6-methyl protons), and 5.60—6.00 and 8.60—8.90 (ethyl protons of the carbethoxyl group).

2,5-Dimethyl-*N*-ethoxycarbonylaniline. This compound was obtained by the reaction described above when *p*-xylene was employed; mp 95—96°C; NMR τ 2.47 (bs, 1H, H_6), 3.30 and 3.25 (each bd, 2H, J=7.0 Hz, H_3- and H_4), 3.60 (bd, 1H, NH), and 7.69 and 7.81 (each broad singlet, 6H, C_2- and C_5-Me).

Found: C, 68.30; H, 7.95; N, 7.00%. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25%.

2,4,6-Trimethyl-*N*-ethoxycarbonylaniline. This compound was obtained by the reaction described above when mesitylene was employed; mp 90—92°C (lit,[5c] 90°C); mass *m/e* 207: NMR 3.23 (bs, 2H, H_3 and H_5), 3.63 (bs, 1H, NH), and 7.77—7.83 τ (two singlets, 9H, C_2-, C_4- and C_6-Me).

Kinetics in the Reaction of *p*-Xylene and Ethyl Azidoformate. Solutions for the "nitrene" runs were prepared by adding *p*-xylene (10 g, 0.094 mol) an ethyl azidoformate (2.3 g, 0.02 mol) from a 10-μ*l* syringe to a 20-m*l* volumetric flask at 100, 120, and 138°C (in oil baths). The contents of the reaction solution were then analyzed by glpc. Each analysis was carried out at least three times. The relative rate ratios thus determined are given in Fig 1. The peaks of azepine derivatives were calculated by the half-width method, but the amounts of the side-formed aromatic urethan were not calculated because the yields were low

11) Recently, the adduct of 2-methyl-*N*-methoxycarbonylazepine has been reported to give the 3-methyl compound, but only in a 2.5% yield.[4]

12) The melting points were measured with a Yanagimoto micro-melting-point apparatus and are uncorrected. The microanalyses were performed on a Yanagimoto C.H.N.-Corder, Model MT-1. The NMR spectra were taken with a Japan Electric Optics Lab. Co., Ltd, Model JNN-MH-60 NMR spectrometer and with a Varian A-60 recording spectrometer, with tetramethylsilane as the internal standard. The chemical shifts are expressed in τ values. The mass spectra were obtained on a Hitachi RMU-D double-focussing mass spectrometer operating at an ionization potential of 70 eV. The IR spectra were taken with a JASCO Model IR-S spectrophotometer. The glpc was done isothermally with a Hitachi K-23 Gas Chromatograph on a 3-ft, 5 wt% SE 30 (Chromosorb G NAW) column (flame-ionization detector).

13) *Cf.* L. A. Paquette, D. E. Kuhla and J. H. Barette, *J. Org. Chem.*, **34**, 2879 (1969).

(below 3%).

Reaction of Benzene and Ethyl Azidoformate in the Presence of TCNE. In a stainless steel tube benzene (10 g), ethyl azidoformate (1.15 g, 0.01 mol) and TCNE (0.005 mol) were mixed. The closed tube was heated at 100—110°C in an oil bath for 15 hr and then cooled. After the reaction mixture had been concentrated *in vacuo*, the residue was purified by column chromatography (silica gel) using *n*-hexane, benzene, and chloroform successively as eluents. A red oil (0.51 g, 24%) was obtained from the first fraction; it was identical in all respects with *N*-ethoxycarbonyl-1-(1*H*)-azepine (**7**).[5c] Subsequently, white crystals **21** (0.54 g, 24%) were obtained from the second fraction, mp 156—158°C; they were identical with a specimen prepared by the method of Kende *et al.*[3b]

Reaction of Toluene and Ethyl Azidoformate in the Presence of TCNE. In a closed tube toluene (10 g), ethyl azidoformate (1.15 g), and TCNE (1.28 g, 0.01 mol) were mixed. The reaction was then carried out under the conditions described above. The reaction mixture was concentrated *in vacuo*, and the tarry residue was purified by column chromatography (silica gel). Red, oily compounds (0.35 g, 20%) were obtained from the first fraction, but they were found to consist of azepine derivatives and aromatic urethans (by IR and NMR). On the other hand, a yellow, oily adduct (1.88 g,61%) was obtained from the second fraction; its NMR spectra showed that it consisted of **22** and **23** in a 40 : 60 ratio, together with the 4-methyl isomer as a minor product. However, the mixture was recrystallized from *n*-hexane - chloroform to give colorless crystals, **22**; mp 131—133°C; IR ν_{max}^{KBr} 1645 (C=C), 1710 (C=O), 2280 cm^{-1} (w, C≡N); mass *m/e* 307.

Found: C, 62.60; H, 4.26; N, 22.70%. Calcd for $C_{16}H_{13}N_5O_2$: C, 62.53; H, 4.26; N, 22.79%.

The mother liquor afforded crude **23**, which was still mixed with **22** and the 4-methyl isomer (τ 8.06, d, J=1.5 Hz, 3H, C_4-Me distinguish between C_6- and C_7-methyl protons) even after further purification by recrystallization from benzene.

Reaction of *o*-Xylene and Ethyl Azidoformate in the Presence of TCNE. In a closed tube *o*-xylene (10 g), ethyl azidoformate (0.75 g), and TCNE (0.83 g, 0.065 mol) were mixed. The reaction was then carried out under the conditions described above. After the reaction mixture had been concentrated *in vacuo*, the residue was separated by column chromatography (silica gel), using *n*-hexane and benzene successively as eluents. Red, oily compounds (0.20 g, 16%) were obtained from the first fraction; they were determined by NMR and IR inspections to be mixtures of aromatic urethans (major products) and azepine derivatives (minor products).

The second fraction afforded colorless crystals (0.78 g, 39%) of **24** and **25** in a 30 : 70 ratio, but no further purification was undertaken. On the other hand, when two equimolar portions of ethyl azidoformate were employed in the reaction, a mixture of **24** and **25** was obtained in a 22% yield, while the aromatic urethans were given in a 22% yield.

Reaction of *m*-Xylene and Ethyl Azidoformate in the Presence of TCNE. In a closed tube *m*-xylene (10 g), ethyl azidoformate (2.3 g, 0.02 mol), and TCNE (1.28 g, 0.01 mol) were mixed. The reaction was then carried out under the conditions described above. From the reaction mixture, aromatic urethans and **26** were obtained in 10 and 11% yields respectively. The adduct was recrystallized from benzene; mp 200—201°C; IR ν_{max}^{KBr} 1660 (C=C), 1705 (C=O), 2280 cm^{-1} (w, C≡N); mass *m/e* 321.

Found: C, 63.60; H, 4.75; N, 21.90%. Calcd for $C_{17}H_{15}N_5O_2$: C, 63.54; H, 4.70; N, 21.80%.

Reaction of *p*-Xylene and Ethyl Azidoformate in the Presence of TCNE. In a closed tube *p*-xylene (10 g), ethyl azidoformate (2.3 g, 0.02 mol) and TCNE (1.28 g, 0.01 mol) were mixed, and the reaction was carried out under the conditions described above. From the reaction mixture, 2,5-dimethylethoxycarbonylaniline and **27** were obtained in 22 and 11% yields respectively. **22** was recrystallized from ether - *n*-hexane, mp 147—149°C; ν_{max}^{KBr} 1668 (C=C), 1716 (C=O), 2280 cm^{-1} (w, C≡N); mass *m/e* 221.

Found: C, 63.64; H, 4.56; N, 21.99%. Calcd for $C_{17}H_{15}N_5O_2$: C, 63.52; H, 4.70; N, 21.80%.

Reaction of Mesitylene and Ethyl Azidoformate in the Presence of TCNE. In a closed tube mesitylene (10 g), ethyl azidoformate (2.3 g), and TCNE (0.25 g, 0.002 mol) were mixed, and the reaction was carried out under the conditions described above. After the reaction mixture had been under concentrated *in vacuo*, the residue was recrystallized from benzene to give 2,4,6-trimethyl-ethoxycarbonylaniline (3.04 g, 73%), mp 90—92°C (lit,[5] 90°C), while TCNE (0.25 g) was recovered from the mother liquor.