Reactions of Isocyanates with Carbonyl Azides and Carbonylnitrenes[1]

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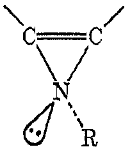
Received January 31, 1973

Photolysis and thermolysis of alkyl azidoformates in isocyanates leads to two reactions: a nitrene addition to the C=N bond of the isocyanate, forming 2-alkoxy-4-alkyl-1,3,4-oxadiazolin-5-ones, and an azide addition to the isocyanate, followed by attack of a second molecule of isocyanate and resulting in the formation of 1,4-dialkyl-2-alkoxycarbonylurazoles. The latter reaction predominates in the azidoformate system, but is not detected when aroyl azides are decomposed in alkyl isocyanates. A formal retro Chapman rearrangement takes place when 1,4-dialkyl-3-alkoxy-1,2,4-triazolin-5-ones are passed over a vpc column.

Carbonylnitrenes, RCON, are known to add to a variety of unsaturated functions with the formation of three- or five-membered rings.[2] For example, olefins give aziridines, alkynes give oxazoles, and nitriles give oxadiazoles. The formation of three-membered rings by addition to triple bonds has not been observed, perhaps because the resulting systems, such as 1 and 2, would be antiaromatic. In such cases inclusion of the carbonyl group leads to stable five-membered rings, *e.g.*, 3 and 4.



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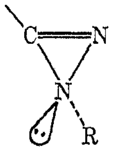

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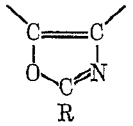

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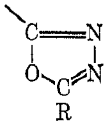

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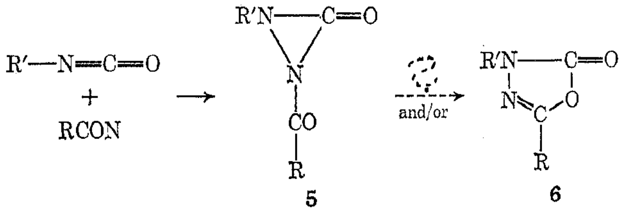
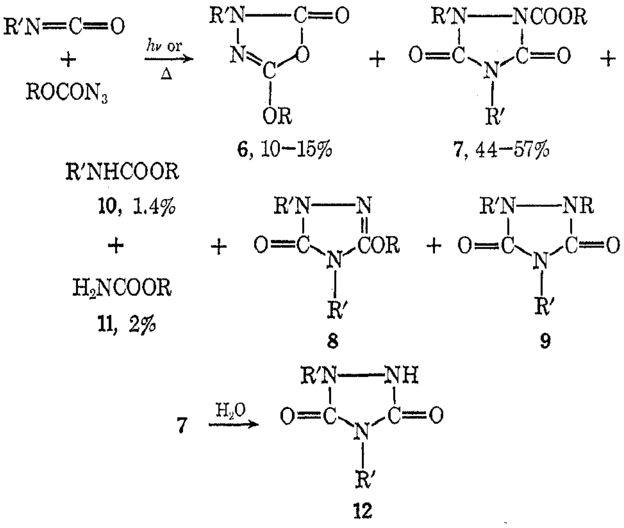
The addition of carbonylnitrenes to isocyanates, however, seemed to allow the formation of stable three-membered as well as five-membered rings. We report here on the decomposition of various nitrene precursors in the presence of aliphatic isocyanates.



Results

Alkyl Azidoformates.—Thermolyses and photolyses of methyl azidoformate, dissolved in alkyl isocyanates, gave mixtures of six products in ratios dependent on the reaction conditions. Ethyl azidoformate gave entirely analogous products and product ratios. Scheme I summarizes the products and Table I gives the yields (measured by vpc) of the products under various conditions, together with those obtained when alkoxycarbonylnitrenes were generated by α-elimination, rather than by azide decomposition (see below).

SCHEME I[a]



[a] The yields given are for R = CH_3 and R' = C_2H_5 (*cf.* text).

TABLE I

REACTIONS OF ISOCYANATES WITH ALKOXYCARBONYLNITRENE PRECURSORS

		Yield, % (based on the precursor)		
Product	Conditions	R = Me; R' = Et	R = R' = Et	R = Et; R' = Me
6	hν, 254 nm	10–15	13.2	9.4
	hν, 300 nm	4.5		
	Thermolysis, 120°	7		
	α-Elimination	2.7		7
7	hν, 254 nm	50	52	48
	hν, 300 nm	46		
	Thermolysis, 120°	68		
	α-Elimination	0		0
8[a]	hν, 254 nm	*b*	0.2	*b*
9[a]	hν, 254 nm	*b*	1.8	*b*
10	hν, 254 nm	1.4	1.5	*b*
	hν, 300 nm	1.0		
	Thermolysis, 120°	1.0		
	α-Elimination	1.8		
11	hν, 254 nm	2.2	2.5	
	hν, 300 nm	2.0		
	Thermolysis, 120°	2.6		
	α-Elimination	6.7		

[a] A secondary product; exact yields depend on the vpc conditions used in work-up; see text. [b] Not determined.

The expected 4-ethyl-2-methoxy-1,3,4-oxadiazolin-5-one (6a) was formed in 10–15% yield when methyl azidoformate was photolyzed in ethyl isocyanate solution, using light of 254-nm wavelength. Using light with a peak intensity at 300 nm, only a 4.5% yield

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[1] A preliminary account of this work was given in a lecture reprinted in the *Trans. N. Y. Acad. Sci., Ser. II*, **33**, 259 (1971). This paper is based in part on a part of the Ph.D. Thesis by S. M. A. Hai, New Mexico State University, 1969.

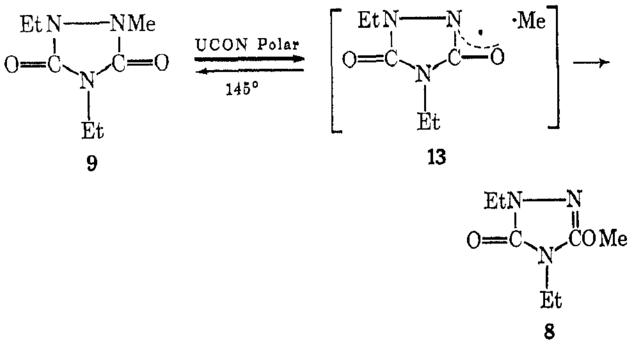
[2] *Cf.* W. Lwowski in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, Chapter 7.

of **6a** was obtained, and thermolysis of the azide at 120° gave only a 7% yield. The structures of **6a** (R = Me; R′ = Et), **6b** (R = R′ = Et), and **6c** (R = Et; R′ = Me) were derived from their elemental analyses, ir, nmr, and mass spectra, and chemical degradation. Catalytic hydrogenation failed, making unlikely the diaziridinone structure **5**. Hydrolysis of **6a** with 0.1 *N* NaOH gave methyl 2-ethylcarbazate in quantitative yield, establishing the presence of a N–N bond. Treating **6a** with sodium methoxide gave quantitatively the expected dimethyl *N*-ethylhydrazinedicarboxylate. Furthermore, **6a** and **6b** were independently synthesized from the corresponding 2-alkylcarbazates and phosgene.[3,4]

The major product, **7**, contains the elements of one ROOCN plus two R′NCO. Thermolytic reactions favor the formation of **7** and disfavor that of **6**. Photolysis of **6a** in dichloromethane and in ethyl isocyanate solutions failed to produce any **7a**. Also, subjecting a mixture of **6a** and ethyl isocyanate to our work-up procedure, including vpc, did not produce any **7a**. During one photolysis run, eight samples were withdrawn and analyzed by vpc. The yields of **6a** and **7a** (based on the nitrogen evolved at the particular sampling time) stayed virtually constant over 41 hr. We thus conclude that both **6** and **7** are primary products.

The structure of **7a** was derived from its elemental analysis and ir, nmr, and mass spectra and by chemical degradation and independent synthesis as that of 1,4-diethyl-2-methoxycarbonyl-1,2,4-triazolidine-3,5-dione. Mild hydrolysis gave 1,4-diethyl-1,2,4-triazolidine-3,5-dione (**12**) (commonly called 1,4-diethylurazole) (see Scheme I). Compound **12** was synthesized independently by pyrolysis of 1,1,4-triethyl-1,2,4-triazolidine-3,5-dion-1,2-ylide,[5] and also by exhaustive diazoethane ethylation of urazole, followed by separation of the isomeric (N and O) triethylurazoles. Their structures can be unequivocally assigned by nmr spectroscopy. Hydrolysis of the 1,4-diethyl-*O*-ethylurazole gave the desired **12**.[6] Treating **12** with potassium sand and then methyl chloroformate gave **7a**.

Separation by vpc (UCON Polar, 140°) of the reaction mixtures gave two minor products possessing the 1,2,4-triazole skeleton. However, careful scrutiny of the spectra of the crude reaction mixtures before vpc showed the absence of these two products, **8** and **9**. They are produced during vpc from **7**, by loss of the elements of carbon dioxide. Treating **12** with diazomethane gave **8** and **9** in approximately equal amounts. This result, together with the nmr, ir, and mass spectra, led to the structure assignments of 1,4-diethyl-2-methylurazole for **9**, and 1,4-diethyl-3-methoxy-1,2,4-triazolin-5-one for **8**. Both compounds are stable to heating, by themselves, to 150–160° for a few hours. However, **9** is converted to a small extent (0.5%) to **8** when passed through an 8-ft 20% UCON Polar column at 145°. This reaction is formally a retro Chapman rearrangement. It might involve dissociation of **9** to a paired intermediate, such as the radical pair **13**. Recombination would then give **8** and **9**. Loss of methyl is prominent in the mass spectral fragmentation of **9**, but could also arise from processes other than the formation of a dissociated form of **13**. The formation of **8** and **9** from **7** might well involve an intermediate common to that in the retro Chapman rearrangement, perhaps **13**.



The two open-chain products **10** and **11** were identified by comparison with authentic samples. Carbamates **11** ($ROOCNH_2$) are always found in alkoxycarbonylnitrene reaction and arise by hydrogen abstraction.[3] The origin of the *N*-alkylcarbamates **10** is not clear, except that the group on nitrogen must come from the isocyanate.

Methoxycarbonylnitrene Generated by α-Elimination.—The base-induced decomposition of methyl *N*-(*p*-nitrobenzenesulfonyloxy)carbamate (**14**, $MeOOCNHOSO_2C_6H_4NO_2$-*p*) is known[3] to give the nitrene MeOOCN in its singlet state (by analogy with the well-studied EtOOCN system). In order to test for the intervention of ROOCN in the formation of **6** or **7** or both, **14** was decomposed by triethylamine in a 1.6 *M* solution of ethyl isocyanate in dichloromethane, and also in undiluted ethyl isocyanate. Small yields of **6a**, **10a**, and **11a** were formed (see Table I and Experimental Section), but no trace of **7a** could be detected. In a control experiment, added **7a** survived the whole reaction process and 90% of it was recovered. Thus, we conclude that **7a** is formed from the azide, but not from the corresponding nitrene, while **6a** is the product of a nitrene reaction.

Aroyl Azides.—Horner[7] has shown that the photolysis of aroyl azides gives mixtures of aryl isocyanates and aroylnitrenes. Photolysis of benzazide in a tenfold molar excess of ethyl isocyanate at −16° gave a 93% yield of nitrogen, about a 50% yield of phenyl isocyanate, and 4-ethyl-2-phenyl-1,3,4-oxadiazolin-5-one (**15**) in about 25% yield. The novel aryloxadiazolinones **16** and **17** (from *p*-methoxybenzazide and *p*-nitrobenzazide, respectively) were formed analogously in 11.5 and 10% yields, respectively. Their identities were established by independent synthesis using Freund's method.[3,4] Compounds with the spectral characteristics of the urazoles (corresponding to **7**) were not found among the products of the aroyl azide–ethyl isocyanate photolyses. One, 1,4-diethyl-2-*p*-nitrobenzoylurazole (**18**), was prepared independently. It could have been easily detected in the photolysis reaction mixture. As expected from Horner's results,[7] thermolysis of our aroyl azides in ethyl isocyanate gave neither oxadiazolinones nor urazoles, only the aryl isocyanates.

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[3] M. Freund and B. B. Goldsmith, *Ber.*, **21**, 1240, 2456 (1888).

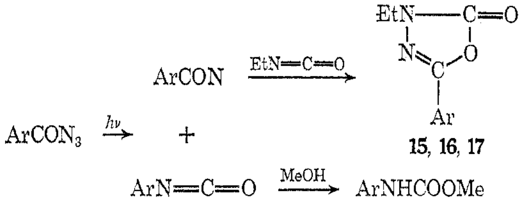
[4] A. Stern, *J. Prakt. Chem.*, **60**, 235 (1899); A. Dornow and K. Bruncke, *Chem. Ber.*, **82**, 121 (1949).

[5] W. Lwowski, R. A. de Mauriac, R. A. Murray, and L. Lünow, *Tetrahedron Lett.*, 425 (1971).

[6] R. A. de Mauriac, Ph.D. Thesis, Yale University, 1967.

[7] L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963); L. Horner, G. Bauer, and J. Dörges, *ibid.*, **98**, 2631 (1965).

Photolysis of benzazide in equimolar mixtures of ethyl isocyanate and cyclohexane gave the oxadiazolinone **15** and *N*-cyclohexylbenzamide (**19**), the C–H insertion product from C_6H_5CON and cyclohexane. The average ratio of **15**:**19** was 1.42, not much affected by the reaction conditions or by addition of nitrobenzene or *m*-dinitrobenzene. The latter two compounds, added in small quantities, raise the yields of some C–H insertion reactions of ethoxycarbonylnitrene.[8] Typically, one run gave yields of 13.9% of **15**, 10.5% of **19**, and 48.3% of phenyl isocyanate (determined as its methanol adduct). If one neglects the ethyl group (insertion products into which were not detected), the 12 C–H bonds of the cyclohexane compete with each isocyanate function of the ethyl isocyanate. Thus, the relative reactivity of the functions –NCO *vs.* C–H is about 17.



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The aroyl azide systems were not studied in any more detail, because of their apparently limited synthetic utility and because of external circumstances.

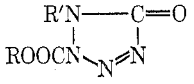
Discussion

Our results indicate that the oxadiazolinones **6**, and their aroyl analogs, are produced from carbonylnitrenes and isocyanates, while the formation of the urazoles **7** is not a nitrene reaction and occurs only with azidoformates, not with aroyl azides. No urazoles were found when alkoxycarbonylnitrenes were generated by α-elimination, and none were found in the aroyl azide photolyses, where the presence of aroylnitrenes is demonstrated by the formation of the C–H insertion product **19**. The urazole formation must be a reaction peculiar to the azidoformates, with which competing thermal reactions are relatively slow. Such reactions are nitrene formation and the Curtius rearrangement (with migration of RO from C to N). This Curtius rearrangement is about 10–20 times slower than nitrene formation.[9] In the aroyl azides, thermal Curtius rearrangement (with aryl migration) is the most facile reaction, to the exclusion of all other reaction paths. In the aroyl azide photolyses, rearrangement and nitrene formation seem to compete about evenly.[7]

Photolysis of methyl azidoformate in ethyl isocyanate gives more of the urazole **7a** and less of the oxadiazolinone **6a** when light of 300- rather than 254-nm wavelength is used. This agrees with the assumption that short-wavelength light produces more of the nitrene (and from it **6a**), than light of longer wavelength. Pending more intensive studies, one might conclude that the vibrationally highly excited state of the first excited singlet of the azide preferentially undergoes nitrogen elimination to the nitrene, while the cooler electronically excited azide, produced by absorption of 300-nm light, does not dissociate equally readily but undergoes internal conversion to a highly vibrationally excited molecule in its electronic ground state. Since the ethyl isocyanate (used as the solvent) is the most abundant quencher for the vibrationally hot ground state azide, the same reaction occurs (formation of **7a**) as is observed by merely heating the azide–isocyanate mixture. Earlier work indicates that alkoxycarbonylnitrenes, once formed, do not reflect in their reactions the wavelength of the light used to generate them.[10] For example, the stereospecificity of the addition of ethoxycarbonylnitrene to *cis*-4-methylpent-2-ene does not change when the photolysis wavelength is changed over the range from 250 to 300 nm. The nitrene seems to equilibrate thermally before it reacts, a contention well in accord with the selectivity observed for the nitrene.[2]

The mechanism of the oxadiazolinone formation might well be straightforward 1,3-cycloaddition. The intermediacy of a three-membered ring adduct **5** cannot be ruled out by our data, but in view of Greene's work,[11] we feel that we should have been able to detect diaziridinones if they had been present. Comparison of the ir and nmr spectra of the crude reaction mixtures before and after molecular distillation and then vpc (collecting all peaks together) showed that the final products **6**, **7**, **10**, and **11** were present in the crude mixtures, while **8** and **9** were formed during the vpc separation. No major product could have disappeared during this work-up.

The formation of the urazoles **7** must involve an intermediate 1:1 adduct which is not an oxadiazolinone **6** (see above). The tetrazolinones **20** and **21** are excluded as intermediates by L'abbé,[12] who obtained 1,4-disubstituted tetrazolinones from isocyanates and azides. He found **21** and similar compounds to be stable at temperatures higher than those used in this work. Furthermore, cycloreversion at 150° resulted in equilibria between starting materials and adduct, not in loss of nitrogen and urazole formation. This does not rigorously exclude **20** as a possible cyclic intermediate. However, L'abbé always found the N_α of the azide group bound to the isocyanate carbonyl, and his compounds (such as **21**) formed in slow reactions (*e.g.*, 30 days at 55°). It is therefore unlikely that in our cases rapid formation of **20** should take place, and be followed by rapid decomposition. Formation of **7** *via* prior trimerization of the isocyanate, followed by attack of the azide, is also unlikely; no trimer was observed, although the reactions were run in an excess of isocyanate. The mechanism that seems most likely to us involves successive nucleo-



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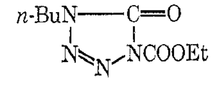

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[8] D. S. Breslow and E. I. Edwards, *Tetrahedron Lett.*, 2123 (1967); D. S. Breslow, T. J. Prosser, A. F. Marcantonio, and C. A. Genge, *J. Amer. Chem. Soc.*, **89**, 2384 (1967).

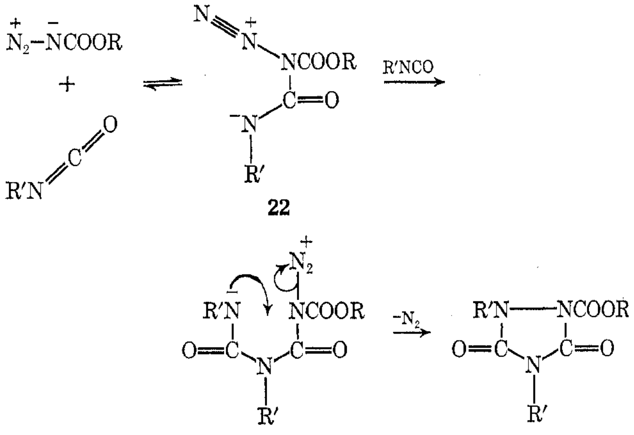
[9] W. Lwowski, R. de Mauriac, T. W. Mattingly, Jr., and E. Scheiffele, *Tetrahedron Lett.*, 3285 (1964).

[10] G. R. Felt, Ph.D. Thesis, New Mexico State University, 1971.

[11] F. D. Greene and J. C. Stowell, *J. Amer. Chem. Soc.*, **86**, 3569 (1964); F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969).

[12] J-M. Vandensavel, G. Smets, and G. L'abbé, *J. Org. Chem.*, **38**, 675 (1973).

philic attacks on isocyanate carbonyls by the N_α of the azides. Apparently, the intermediate 1:1 adduct 22 does not cyclize to a five-membered ring (similar to 21), or to a three-membered one (the diaziridinone 5). Rather, 22 attacks a second isocyanate molecule at its carbonyl group, to give a second intermediate in which cyclization to a five-membered ring is favored.



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Operation of this mechanism depends on a delicate balance. Competing thermal reactions must be relatively slow, and the azide N_α must be sufficiently nucleophilic, so that the equilibrium between starting materials and 22 contains enough of the latter. This might account for our failure to observe urazole formation using phenyl azide and benzenesulfonyl azide with ethyl isocyanate.

Experimental Section

Photolyses were carried out in silica vessels equipped with cooling fingers, in Rayonet photochemical reactors. Unless specified, low-pressure mercury lamps were used, emitting most of their light at 254 nm. The 300-nm irradiations were carried out using fluorescent lamps (RPR-3000), emitting light in a band from 280 to 340 nm. Infrared spectra were taken in carbon tetrachloride solution, nmr spectra in deuteriochloroform. Quantitative vpc analyses were evaluted planimetrically, after calibration of the detector response by injecting weighed pure samples.

Photolyses of Alkyl Azidoformates.—Typically, 6.66 g (66 mmol) of methyl azidoformate in 50 ml of redistilled ethyl isocyanate was irradiated until 70–90% of the calculated volume of nitrogen was evolved (24 hr). Removal *in vacuo* of the volatile constituents left 7.77 g of a viscous liquid. Tlc on silica gel with acetone–nitromethane–benzene (1:3:10) eluent separated **6a** (R_f 0.278), identified by comparison with an authentic sample. Vpc on a 20% UCON Polar 50HB2000 on 50/60 mesh Anakrom ABS (4 ft × 0.25 in.) separated all the components, in the order **10**, **11**, **6**, **8**, **9**, **7**.

Thermolyses of Alkyl Azidoformates.—Typically, 1.01 g (0.01 mol) of methyl azidoformate and 8.98 g (0.128 mol) of ethyl isocyanate in a 50-ml stainless steel cylinder were heated to 120°. After removal of the excess ethyl isocyanate, vpc separation (as above) was used to determine the yields (*cf.* Table I).

Alkoxycarbonylnitrenes by α-Elimination.—Adding slowly 1.25 ml (0.1 mol) of triethylamine to a solution of 2.67 g (0.01 mol) of methyl *N*-(*p*-nitrobenzenesulfonyloxy)carbamate (**14**) in 7.1 g (0.1 mol) of ethyl isocyanate, evaporation of the excess isocyanate and triethylamine, and vpc analysis (as above) gave **6a** in 2.7%, **10** in 1.8%, **11** in 6.7%, and dimethyl hydrazodiformate in 19% yield. The urazole **7a** could not be detected. Running the reaction in dichloromethane solution (typically 170 ml of dichloromethane and 60 ml of ethyl isocyanate) gave lower yields of **6a**.

4-Ethyl-2-methoxy-1,3,4-oxadiazolin-5-one[13] (**6a**), isolated from the reaction mixtures as described above, shows characteristic ir absorption at 1805 and 1660 cm^{-1}, nmr signals at δ 1.30 (t, 3 H), 3.67 (q, 2 H), and 4.0 (s, 3 H), and in the mass spectrum P 144 (42%), P + 1/P 6.38% (calcd, 6.41%). Major cleavages are to *m/e* 59 (100%, $MeOCO^+$) and 85 (13.5%, EtN_2CO^+), the latter cleavaging further. A metastable ion peak at *m/e* 115.5 corresponds to P − CH_3. In the uv spectrum only end absorption near 200 nm was observed. In the synthesis of **6a** by Freund's method,[8] 0.673 g (5.7 mmol) of methyl 3-ethylcarbazate in 100 ml of benzene was treated with 240 ml (10 mmol) of phosgene gas and heated to reflux for 30 min. After washing with sodium bicarbonate solution, drying, and removal of the solvent, the brown residue was subjected to vpc separation (as above) to give a 34% yield of **6a**, identical in all respects with the material obtained from methyl azidoformate and ethyl isocyanate.

2-Ethoxy-4-ethyl-1,3,4-oxadiazolin-5-one (**6b**)[13] was synthesized independently by the same method as used for **6a**, in 38% yield. The ir spectrum showed absorptions at 1805 and 1640 cm^{-1}, and the nmr spectrum had signals at δ 1.28 (t), 1.43 (t), 3.6 (q), and 4.3 (q). The parent peak in the mass spectrum was at *m/e* 158 (40.9%); P + 1/P = 7.82% (calcd 7.52%); base peak at 130, metastable ion peak at 107 (P − C_2H_4 = 130).

2-Ethoxy-4-methyl-1,3,4-oxadiazolin-5-one (**6c**)[13] was not synthesized independently. Its properties were analogous to those of **6a** and **6b** and its methanolysis gave ethyl 3-methyl-3-methoxycarbonylcarbazate, ir spectrum 1805 and 1640 cm^{-1}, nmr spectrum δ 1.43 (t, 3 H), 3.28 (s, 3 H), 4.3 (q, 2 H).

Hydrolysis of 6a.—A 114-mg (0.79 mmol) portion of **6a** in 5 ml of dioxane was refluxed for 10 hr with 1 equiv of sodium hydroxide. The residues of ether and chloroform extracts of the neutralized reaction mixture upon vpc (20% silicone gum SE-30, 5 ft, 100°) gave methyl 3-ethylcarbazate, identical with an authentic sample.[9]

Methanolysis of 6a.—A 127-mg (0.88 mmol) portion of **6a** in 15 ml of ether was treated with 88 ml of 0.1 *N* methanolic sodium hydroxide for 4.5 hr. Neutralization, extraction with ether, and vpc separation (SE-30, 142°) gave dimethyl *N*-ethylhydrazodiformate identical with an authentic sample.[14]

Methanolysis of 6c, in the same manner, gave ethyl 3-methyl-3-methoxycarbonylcarbazate, ir 1709 cm^{-1}, nmr spectrum δ 1.28 (t, 3 H), 3.12 (s, 3 H), 3.71 (s, 3H), 4.14 (q, 2 H), 7.5 (broad, 1 H).

1,4-Diethyl-2-methoxycarbonylurazole (**7a**),[13] a colorless oil, was isolated as described above: ir spectrum 1828, 1802, and 1730 cm^{-1} (all strong); nmr spectrum δ 1.10 (t), 1.25 (t), 3.08 (q), 3.55 (q), 3.92 (s); integrals of these overlapping signals, $CH_3 + 2CH_2$, 7 H, $2CH_3$, 6 H; mass spectrum P = 215, P + 1/P = 10.0% (calcd 9.88%); major fragmentations P − CH_3COO, P − CO_2, P − (CH_3COO + EtNCO), P − ($CO_2 + C_2H_4$).

Synthesis of 1,4-Diethylurazole.[5,6]—Irradiation (254 nm) of 3.16 g (22.3 mmol) of diethylcarbamoyl azide in 35.5 g of ethyl isocyanate to give 47% of the calculated amount of nitrogen and removal of the volatile components gave, after recrystallization from ether, a 24% yield of 1,1,4-triethylurazole-1,2-ylide. Its pyrolysis (160°, 8 hr) gave 0.6 g of 1,4-diethylurazole. This was treated with potassium sand in refluxing benzene, followed by methyl chloroformate, to give **7a**, identical in all respects with the material obtained from methyl azidoformate and ethyl isocyanate. Very mild hydrolysis of **7a**, such as upon tlc on wet silica gel, led back to 1,4-diethylurazole.

1,4-Diethyl-2-ethoxycarbonylurazole (**7b**)[13] was isolated as described above from the photolysis reaction mixtures from ethyl azidoformate and ethyl isocyanate, in 52.3% yield: ir spectrum 1824, 1800, and 1738 cm^{-1}; nmr spectrum (overlapping signals) δ 1.12 (t), 1.27 (t), 1.42 (t) (9 H), 3.58 (q), 3.84 (q) (4 H), 4.38 (q, 2 H); mass spectrum P = 229, P + 1/P 10.52% (calcd 10.98%); major fragmentations P − (CO_2, C_2H_4) = 157 (100%), 157 − NH = 142 (48%, metastable ion peak 128.3), 142 − CO = 114 (metastable ion peak at 91.5), P − 28 = 129 (metastable ion peak at 106), 129 − EtNCO; 129 − 28 (metastable ion peak at 79.0).

1,4-Dimethyl-2-ethoxycarbonylurazole (**7c**)[13] was isolated as described from photolyses of ethyl azidoformate in methyl isocyanate in 48% yield: ir spectrum 1825, 1805, and 1725 cm^{-1}; nmr spectrum δ 1.42 (t, 3 H), 3.16 (s, 3 H), 3.30 (s, 3 H), 4.37 (q, 2 H).

Decomposition of 7a upon gas chromatography on a 8 ft × 0.25

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[13] Compound gave elemental analysis within ±0.3% of the calculated value.

[14] D. C. Morrison, *J. Org. Chem.*, **23**, 1072 (1958).

in. 20% UCON Polar 50 HB 2000 column at 145° led to 90% recovery of **7a** and the formation of **8a** (1.3%) and **9** (6–7%).

1,4-Diethyl-3-methoxy-1,2,4-triazolin-5-one (**8a**),[13] a colorless oil, showed no ir absorption above 3000 cm^{-1} but bands at 1718 and 1608 cm^{-1}; nmr spectrum δ 1.27 (m, 6 H), 3.6 (m, 4 H), 3.95 (s, 3 H); mass spectrum P = 171, P + 1/P = 9.09% (calcd 8.78%); major fragmentations P − CH_3 = 156 (100%), 156 − EtNCO = 85 (75%), 156 − 28 = 128 (18%), P − 29 = 142 (18%), 142 − 28 = 114 (4%), P − 28 = 143 (16%), 143 − 28 = 115 (18%, metastable ion peak at 92.5), 115 − MeOCN = 58 (36%). Heating **8a** to 158° for 4 hr or passing it through the UCON Polar column (as above) left it unchanged, as indicated by its vpc and tlc.

1,4-Diethyl-2-methylurazole (**9a**),[13] a colorless liquid, had no ir absorption above 3000 cm^{-1} but bands at 1770 and 1710 cm^{-1}; nmr spectrum δ 1.17 (m, 6 H), 3.5 (m, 4 H), 3.03 (s, 3 H); mass spectrum P = 171, P + 1/P = 8.90 (calcd 8.78%); major fragmentations P − CH_3 = 156 (52%), 156 − EtNCO = 85 (95%), P − 28 = 143 (60%), 143 − 28 = 115 (83%), 115 − MeNCO = 58 (33%), MeNCO = 57 (17%). Heating to 150° for 2.5 hr in a sealed tube did not change **9a**, but passing it over a UCON Polar vpc column at 145° converted 0.5% of it to **8a**.

Synthesis of 8a and 9a was accomplished by treating 1,4-diethylurazole (**12a**) with diazomethane in ether solution. About equal amounts of **8a** and **9a** were formed; they were separated by vpc and identified by comparison with the compounds described above.

1,4-Diethyl-3-ethoxy-1,2,4-triazolin-5-one (**8b**)[13] was separated as described from the reaction mixture from the photolysis of ethyl azidoformate in ethyl isocyanate. It had no ir absorption above 3000 cm^{-1}, carbonyl absorption at 1720 cm^{-1}, C═N at 1605 cm^{-1}; nmr spectrum δ 1.28 (m, 9.6 H), 3.6 (m, 3.9 H), 4.3 (q, 2.0 H). The compound was identical in its properties with a sample synthesized by exhaustive diazomethane treatment of urazole, separation of the triethyl urazules by vpc, and identification by the unequivocal nmr spectra.[6]

1,2,4-Triethylurazole (**9b**)[13] was separated as described from the reaction mixture from the photolysis of ethyl azidoformate in ethyl isocyanate. The ir spectrum showed no absorption above 3000 cm^{-1}, but bands at 1770 and 1705 cm^{-1}; nmr spectrum δ 1.2 (m), 3.52 (m). The compound was independently synthesized by exhaustive treatment of urazole with diazoethane and vpc separation on a 5 ft × 0.25 in. 15% QF-1 fluorosilicon column at 135°.[6]

Aroyl azides were photolyzed with light of 254 nm as described above, in ethyl isocyanate, at −16°. Aryl isocyanates were formed in about 40% yield. These isocyanates were converted to methyl *N*-arylcarbamates by treatment of the reaction mixture with an excess of methanol for 12 hr at 35°, and were determined as such by vpc analysis on 2 ft × 0.25 in. 20% UCON Polar or 2 ft × 0.25 in. 15% OV-3 silicone columns at 140°. No aroyl amides were detected in the reaction mixtures, nor any of the urazoles (2-aroyl-1,4-diethyl-1,2,4-triazolidine-3,5-diones) or their conversion products. Products were identified by comparison of their spectra and vpc retention times with those of authentic samples. The oxadiazolinones were synthesized independently by Freund's method[4] (see above).

Benzazide, photolyzed at −16° in a tenfold excess of ethyl isocyanate, gave a 25.9% yield of **4-ethyl-2-phenyl-1,3,4-oxadiazolin-5-one** (**15**), a 43% yield of phenyl isocyanate (determined as methyl *N*-phenylcarbamate), and a 93% yield of nitrogen. No product with the spectral characteristics of an arylurazole was detected. The 4-ethyl-2-phenyl-1,3,4-oxadiazolin-5-one (**15**),[13] mp 46–47°, showed in the ir spectrum CH at 3072, 2988, 2984, and 2880 cm^{-1}, other bands at 1865 (w), 1800 (s), 1780 (s), 1612 cm^{-1}; nmr spectrum δ 1.40 (t, 3 H), 3.85 (q, 2 H), 7.53 (m, 3 H), 7.83 (m, 2 H); mass spectrum P = 190 (100%), P + 1/P = 12% (calcd 11.8%); major fragmentations P − EtN_2CO = 105 (41%), P − EtN_2H_2 = 131 (48%), P − 28 = 146 (5%); major fragments C_6H_5 = 77 (39%), CO, C_2H_4 = 28 (93%).

Competition reactions were performed as described above, except that 10 mmol of benzazide and 100 mmol each of ethyl isocyanate and cyclohexane (purified) were used. Analysis by vpc (2 ft × 0.25 in. 15% OV-13 on Anachrom ABS at 140°), using weighed authentic samples for calibration, gave a 1.42 ratio of *N*-cyclohexylbenzamide to **15**. Addition of 1 mmol of *m*-dinitrobenzene or hydroquinone, or 100 mmol of nitrobenzene or hydroquinone, did not affect the ratio. However, yields decreased at the 100-mmol addend level.

2-Anisyl-4-ethyl-1,3,4-oxadiazolin-5-one (**16**) was obtained in 11.5% yield from the photolysis of 1.77 g (10 mmol) of anisoyl azide in 7.1 g (100 mmol) of ethyl isocyanate at −20°, together with a 49% yield of anisyl isocyanate. No 2-anisoyl-1,4-diethylurazole could be detected. The oxadiazolinone **16** (colorless crystals, mp 92°) was prepared for comparison, as described above: ir spectrum bands at 3080, 3000, 2945, 2845, 1790 (sh), and 1780 cm^{-1} (s); nmr spectrum δ 1.40 (t, 3 H), 3.87 (q) and 3.90 (s) (5 H), 6.9–7.9 (m, 4 H).

p-**Nitrobenzoyl azide** photolyzed until 39% of the calculated amount of nitrogen had been evolved, and gave four major products, none of them 1,4-diethyl-2-*p*-nitrobenzoylurazole. The isocyanate was formed in 10.7% yield, and **4-ethyl-2-*p*-nitrophenyl-1,3,4-oxadiazolin-5-one** (**17**) in 10% yield. Treating 1-ethyl-2-*p*-nitrobenzoylhydrazine with phosgene also gave **17**, ir spectrum 1775 (s), 1785 (sh), 1525, 1505, 1350, and 1330 cm^{-1}.

1,4-Diethyl-2-*p*-nitrobenzoylurazole (**18**) was prepared by treating 0.85 g (5.4 mmol) of 1,4-diethylurazole with 0.211 g of potassium sand in refluxing benzene for 4 hr, then with 5.4 mmol of *p*-nitrobenzoyl chloride, followed by vpc: ir spectrum 3110, 3052, 2980, 2875, 1770, 1715, 1540, and 1355 cm^{-1}; nmr spectrum δ 1.26 (2 t, 6 H), 3.4–4.2 (2 q, 4 H), 11.67 (m, 4 H). The compound could not be detected in the reaction mixture from the *p*-nitrobenzoyl azide–ethyl isocyanate photolysis. Thermolysis of 1.92 g (10 mmol) of *p*-nitrobenzoyl azide in 14.2 g (200 mmol) of ethyl isocyanate (132°, 24 hr) in a steel cylinder gave neither **17** nor **18**, just *p*-nitrophenyl isocyanate.

Registry No.—**6a**, 39636-00-5; **6b**, 39636-01-6; **6c**, 39636-02-7; **7a**, 39636-03-8; **7b**, 39636-04-9; **7c**, 39636-05-0; **8a**, 39636-06-1; **8b**, 39636-07-2; **9a**, 39636-08-3; **9b**, 39636-09-4; **10a**, 6135-31-5; **10b**, 623-78-9; **11a**, 598-55-0; **11b**, 51-79-6; **12a**, 39636-12-9; **15**, 21816-80-8; **16**, 39636-14-1; **17**, 39636-15-2; **18**, 39636-16-3; methyl isocyanate, 624-83-9; ethyl isocyanate, 109-90-0; methyl azidoformate, 1516-56-9; ethyl azidoformate, 817-87-8; ethyl 3-methyl-3-methoxycarbonylcarbazate, 39636-17-4; diethylcarbamoyl azide, 922-12-3; 1,1,4-triethylurazole-1,2-ylide, 32515-29-0; 1,4-diethylurazole, 39636-12-9; diazomethane, 334-88-3; benzazide, 582-61-6; *p*-anisoyl azide, 3532-17-0; *p*-nitrobenzoyl azide, 2733-41-7; 1-ethyl-2-*p*-nitrobenzoylhydrazine, 39636-23-2; phosgene, 75-44-5; *p*-nitrobenzoyl chloride, 122-04-3.

Acknowledgments.—We are greatly indebted to the National Institutes of Health for support of this work under Grant GM14638.