DECOMPOSITION AND ADDITION REACTIONS OF ORGANIC AZIDES

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Received June 6, 1968

Contents

I. Introduction

The chemistry of azides has been the subject of intensive investigations in the last 10 years because of their importance in preparative heterocyclic chemistry. Indeed, many nitrogen-containing heterocycles such as carbazoles, furoxans, azepines, Δ^2-triazolines, triazoles,[1] tetrazoles,[2] aziridines,[3,4] azirines, and others have been obtained in good yield by decomposition or addition reactions of these substances. In this review the decomposition mechanisms of azides are described, and the addition reactions to unsaturated systems are classified on the basis of kinetic and structural evidence. The article includes alkyl and aryl azides, carboxazides, azidoformates, sulfonyl azides, and cyanogen azide. It could not be extended to carbamoyl azides because of lack of information. For the general behavior of these substances, the reader is referred to the review article of Lieber, Minnis, and Rao.[5]

II. Decomposition Reactions

A. NITRENES AS INTERMEDIATES

In most cases, loss of nitrogen from organic azides results in uncharged monovalent nitrogen intermediates (**1**)[6–8] variously called nitrenes, imidogens, imenes, imine radicals, azenes, azylenes, and azacarbenes. Today nitrene is generally used and will be employed in this article.

$$R{-}N_3 \xrightarrow{\Delta \text{ or } h\nu} N_2 + \underset{\mathbf{1}}{R{-}N}$$

The chemistry of nitrenes has been reviewed by Horner and Christmann[9] in 1963 and by Abramovitch and Davis[10] in 1964. Some of their important characteristics will be briefly summarized here.

1. Nitrenes have triplet ground states consistent with Hund's rule, as was clearly shown by electron spin resonance studies at very low temperatures.[11–16] The electronic ground states of two dinitrenes have also been reported: *p*-phenylenedinitrene (triplet state)[17] and *m*-phenylenedinitrene (quintet state).[18]

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2. At room or higher temperature they can behave as diradicals (triplet) as well as electrophilic (singlet) species, depending on the nature of the nitrene and on the reaction conditions.[19–34]

3. Nitrenes have a short lifetime (only several microseconds)[35,36] and undergo stabilization by the following reactions: isomerization to imines, dimerization to azo compounds, hydrogen abstraction followed by ring closure to heterocyclic compounds, bimolecular insertion into C–H bonds to secondary amines, addition to solvent yielding ylids, and addition to unsaturated systems yielding heterocyclic compounds. Table I[37–105] includes the reaction products and references for the different classes of nitrenes.

4. Relative reactivity studies with primary, secondary, and tertiary C–H bonds have revealed the following order of selectivity: phenylnitrene > carbethoxynitrene > sulfonylnitrene > carbene.[83, 106–109]

B. CONCERTED MECHANISM

Nitrene intermediates are formed in the thermal decomposition reactions of most alkyl azides, aryl azides, sulfonyl azides, and azidoformates. Some decompositions, however, must be regarded as proceeding by a synchronous mechanism. They are discussed in this section.

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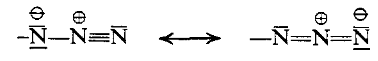
Table I
Stabilization of Intermediate Nitrenes

Nitrenes	*Reaction products*	*Ref*
Alkylnitrenes	Imines	21, 37–41
	Amines	21
	Pyrrolidines	21
	Imidazoles	39, 42, 43
	Indigo	43
Arylnitrenes	Arylamines	44–48
	Azoarylenes	44, 46, 48–50
	Carbazoles	45, 50–54
	Indolines	23, 45–47
	Azepines	55–58
	Carbolines	59, 60
	Thienoindole	59
	Benzimidazoles	61
	Tetrahydroquinoline	47
	Phenanthridine	53
	Phenothiazine dioxide	62
	3-Phenylanthranil	62
	Nitriles	63–66
	Nitrogen imines	67
Sulfonylnitrenes	Sulfonamides	19, 20, 68–80
	Nitrogen imines	77, 78
	Iminosulfuranes and iminooxysulfuranes	81
	Sulfonalkoxyamines	81
	Sultam	23
Carboalkoxynitrenes	Urethans	31, 82–93
	Azodiformates	91, 94
	Nitrogen imines	89
	Aziridines	82, 83, 85–87, 95–97
	Azepines	83, 98–101
	Oxazoles	102, 103
	Oxadiazoles	91, 95, 104
	2-Oxazolidones	23, 88, 90, 91, 105

To compare the reactivity of different classes of organic azides, the region is determined in which the rate constant for the decomposition reaction is of the order 10^{-3} to 10^{-2} min.$^{-1}$ Table II[110–126] shows the results. The decomposition temperature decreases in the order alkyl and aryl azides > azidoformates and sulfonyl azides > acyl azides. The difference in reactivity between acid azides and alkyl or aryl azides can be explained easily in terms of resonance stabilization in the azide molecule. According to the two octet resonance contributors of the azide group (**2** and **3**), the order of the N-N_2 bond which breaks is 1.5. This double-bond character is decreased by introducing an acyl, ester, or sulfonyl group in conjugation with the triazo group (**4** and **5**, respectively). Therefore acyl azides, azidoformates, and sulfonyl azides are less stable than alkyl and aryl azides. There still remains a great difference in reactivity between acyl azides and the two other acid azides which cannot be explained on the basis of the resonance forms. The only explanation, therefore, is that the former decompose

Table II
Decomposition Region of Some Organic Azides

Azides	*Decomposition region, °C*	*Ref*
Benzoyl azide	50–80	110–112
3-X- and 4-X-benzoyl azides	50–80	111–114
2-X-Benzoyl azides	25–45	115, 116
Aliphatic acyl azides	25–45	114, 117, 118
Azidoformates	100–130	89, 90, 119
Sulfonyl azides	120–150	34, 80, 81, 114, 120–122
Phenyl azide	140–170	48, 123, 124
3-X- and 4-X-aryl azides	140–170	114, 124, 125
Alkyl azides	180–200	48, 114, 126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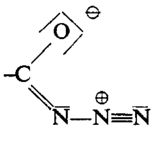
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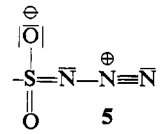
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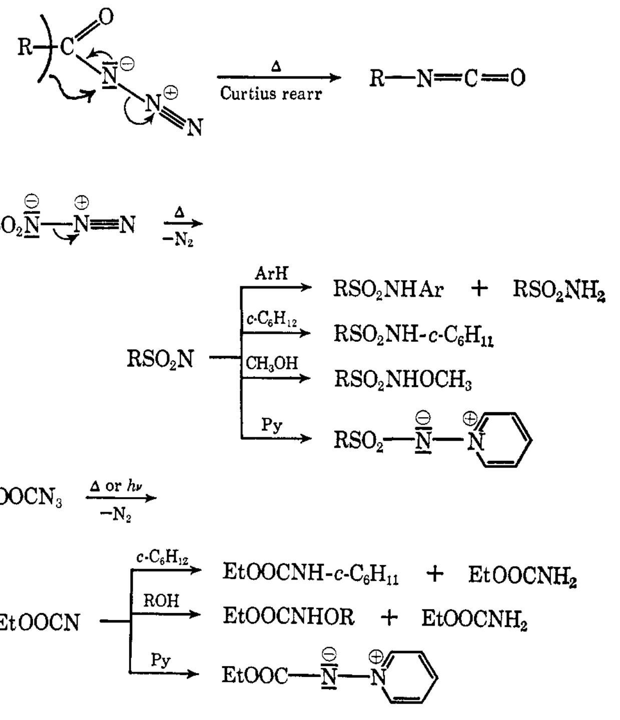
Scheme I



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by a synchronous mechanism and the latter do not (Scheme I). This conclusion is supported by the fact that neither insertion or addition products, nor amides are isolated in the thermal Curtius rearrangement.[127–129]

These reaction products would result if an intermediate nitrene were formed (see Table I). The values of the entropy of activation (Table III) are also in good agreement with a synchronous mechanism. Some values, however, are rather high for such a reaction. If, nevertheless, in these cases the loss of nitrogen would precede the rearrangement, the lifetime of the intermediate nitrene should be so short that it would not have time to react with the solvent.

The photochemical decomposition of acyl azides, on the other hand, proceeds by an intermediate nitrene which, in many cases, leads to typical nitrene reaction products.[33,81,91,130–143] This is not unreasonable since a photochemical reaction provides enough energy to break the N-N_2 bond without alkyl or aryl participation. Horner, for example, has proved the existence of benzoylnitrene as the primary cleavage product of the photolysis of benzoyl azide in the presence of trapping reagents (Scheme II).[137]

Scheme II

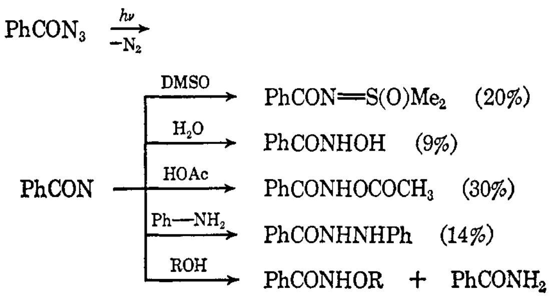

Table III

Energy and Entropy of Activation for the Curtius Rearrangement

Azide	*Solvent*	$\Delta H^{\ddagger}$, *kcal/mol*	$\Delta S^{\ddagger}$, *cal/(°C mol)*[a]
Benzoyl azide[b]	Toluene	27.1	−0.7
	Acetic acid	25.4	−3.2
	Aniline	25.4	−2.9
	Benzene	26.4	−2.5
	Pyridine	26.3	−2.1
	Butanone	27.0	−0.1
	Nitromethane	26.9	+0.6
	Triethylamine	28.3	+1.9
	Ethyl acetate	27.9	+2.2
	Dioxane	28.0	+2.7
	Chlorobenzene	28.9	+4.7
	n-Heptane	31.6	+10.8
o-X-Benzoyl azide[c]			
X = CH_3	Toluene	23.5	−3.2
Cl	Toluene	22.2	−6.6
Br	Toluene	22.0	−6.6
NO_2	Toluene	24.7	−0.4
m-X-Benzoyl azide[b]			
X = CH_3	Toluene	24.5	−8.3
CH_3O	Toluene	27.7	+0.5
Br	Toluene	27.7	+0.3
NO_2	Toluene	29.2	+4.3
	Acetic acid	28.6	+4.6
p-X-Benzoyl azide[b]			
X = *t*-C_4H_9	Toluene	26.2	−3.7
	Acetic acid	25.7	−2.3
OH	Toluene	29.9	+3.8
	Acetic acid	25.6	−2.8
CH_3	Toluene	28.4	+2.6
CH_3O	Toluene	28.6	+2.7
	Acetic acid	25.5	−3.3
C_2H_5O	Toluene	28.6	+2.5
Cl	Toluene	27.7	+0.4
	Acetic acid	26.1	−1.7
Br	Toluene	27.4	−0.3
NO_2	Toluene	28.0	+1.5
	Acetic acid	27.0	+0.6
CON_3	Toluene	28.1	+1.2
Phenylacetyl azide[c]	Toluene	21.5	−10.6
	Acetic acid	15.0	−30.1

[a] The $\Delta S^{\ddagger}$ values are calculated from the data found in the literature[110–113,115,118] using the following equation: $\Delta S^{\ddagger} = 4.57 \log k_1 (\text{sec}^{-1}) - 49.14 - 4.57 \log T + \Delta H^{\ddagger}/T$. [b] Entropy value determined at 65°. [c] Entropy value determined at 30°.

Decomposition of *o*-nitroaryl azides gives furoxans in good yields (**6**, **7**).[51,144–152] The lower decomposition temperature (65–80°) as compared to the other substituted aryl azides (140–170°) is easily rationalized in terms of a concerted mechanism, involving rupture of the N-N_2 bond of the azide with concomitant cyclization. The low entropies of activation support this conclusion (Table IV[153–155]).

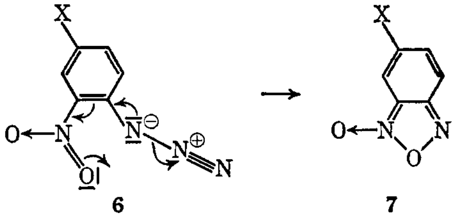

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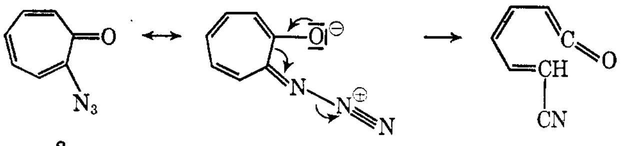
Table IV

Activation Parameters for Decomposition of 4-X-2-Nitrophenyl Azides

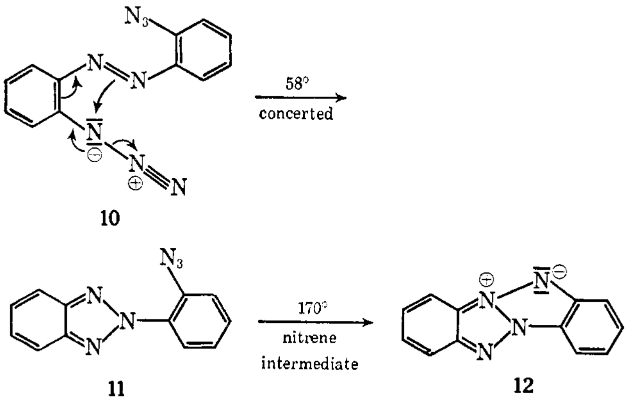
4-X	*Solvent or state*	$\Delta H^{\ddagger}$, *kcal/mol*	$\Delta S^{\ddagger}$, *eu*
CH_3O	Xylene	26.5	−6.7
	Dibutyl phthalate	25.6	−8.1
	Dimethylformamide	25.7	−7.7
	Solid	24.7	−9.8
	Melt	25.4	−8.1
H	Heptane	26.6	−3.5
	Dibutyl phthalate	25.7 (26.3)	−5.9 (−3.8)
	Cyclohexanol	26.3	−3.7
	Dimethylformamide	25.9	−5.1
	Melt	26.6	−2.2 (−2.8)
NO_2	Benzene	22.7	−10.1
	Dibutyl phthalate	27.1	+3.9
	95% EtOH	22.2	−11.0
	Dimethyl phthalate	22.4	−10.2
	Solid	22.8	−7.8
	Melt	22.3	−9.4

Thermal decomposition of 2-azidotropone (**8**) gives a ketene (**9**) as primary product which cyclizes to *o*-salicylonitrile or reacts with protonic solvents to give the corresponding carboxylic acid derivatives.[156,157] The reaction occurs at a quite moderate temperature (60–80°) and is therefore best explained by a concerted mechanism.



8 **9**

When O,O′-diazidoazobenzene (**10**) is heated, nitrogen is liberated in two distinct stages: one mole at the surprisingly low temperature of 58° yielding 2-(*o*-azidophenyl)-2H-benzotriazole (**11**) and the second mole at approximately 170° to give dibenzo-1,3a,4,6a-tetraazapentalene (**12**).[158,159] It seems quite reasonable that **11** is formed by a concerted process and **12** by a nitrene intermediate.



10

11 **12**

Triarylmethyl azides (**13**) rearrange thermally (170–190°) or photochemically (room temperature) to benzophenone anils (**14**).[126,160–162] The strong variation of the enthalpy and entropy of activation with the *para* substituent in the thermal decomposition (Table V) cannot only be explained in terms of an inductive effect, but is in agreement with a concerted mechanism involving an electron-deficient α-nitrogen atom in the transition state.[126] Indeed a *para*-electron-repelling substituent will then stabilize the transition state, and a *para*-electron-withdrawing substituent will have the reverse influence. Consistent with a synchronous mechanism for the thermal decomposition is also the fact that electron-repelling substituents aid and electron-withdrawing substituents hinder migration (Table V). The photochemical decomposition, on the other hand, involves discrete nitrene intermediates.[161,162] This is concluded from the observation that the migration aptitude is practically one for all *para*-substituted triphenylmethyl azides as well in the direct photolysis as in the photosensitized rearrangement (Table V[126,161,162]).

Table V

Decomposition of Diphenyl(4-X-phenyl)methyl Azides[126,161,162]

			Migration aptitudes		
				Photochemical	
4-X	$\Delta H^{\ddagger}$, *kcal/mol*[a]	$\Delta S^{\ddagger}$, *cal/(°C mol)*	*Thermal*	*A*[b]	*B*[c]
Nitro	34.3	−4.6	0.20	1.03	1.1
Chloro	33.8	−5.6	0.4	1.3	1.0
Not substituted	32.0	−9.8	1.0	1.0	1.0
Methyl	29.0	−16.1	1.8		0.9
Methoxy	28.9	−16.0	2.5	1.2	1.1
Dimethylamino	25.4	−22.5	6.7		1.1

[a] Thermal, in dibutylcarbinol. [b] Direct photolysis in hexane solution. [c] Photolysis sensitized by triphenylene.

$$\underset{\mathbf{13}}{Ar_3CN_3} \xrightarrow{-N_2} \underset{\mathbf{14}}{Ar_2C{=}NAr} \xrightarrow{H_3O^+} Ar_2C{=}O + Ar\overset{\oplus}{N}H_3$$

C. ACID CATALYSIS

In this section some significant studies about acid-catalyzed decomposition of azides are described.

1. *Acid Catalysis of Curtius Rearrangement*

Yukawa and Tsuno have studied the decomposition of substituted benzoyl azides in various solvents.[112] The decomposition of *para*-substituted benzoyl azides in toluene or in acetic acid solution failed to give a linear Hammett plot. In acetic acid containing 20% sulfuric acid, however, a linear Hammett correlation was observed with a ρ value of −1.1 (electron-releasing groups favor the rate of decomposition). This result was similar to that of the Schmidt reaction of carboxylic acids.[163] It is therefore assumed that the acid-catalyzed Curtius rearrangement and the Schmidt rearrangement of carboxylic acids have the same rate-determining step, namely the decomposition of the conjugate acid of the acyl azide (eq 1).[112,164–166]

$$RCON_3 + H^{\oplus} \rightleftharpoons RCO\overset{-}{N}H - \overset{\oplus}{N}_2 \xrightarrow[\text{slow}]{} R\overset{\oplus}{N}H{=}C{=}O \quad (1)$$

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Coleman, Newman, and Garrett have kinetically investigated the decomposition of benzoyl azide in benzene and nitrobenzene solution with halides as Lewis acids.[167] They grouped the halides into three classes based on the kinetic equation involved:

class 1: $GaCl_3 > AlBr_3 > AlCl_3 > FeCl_3$
class 2: $SbCl_5 > TiCl_4 > SnCl_4 > TeCl_4$
class 3: $SbCl_3 > SbBr_3$

In each class the halides are listed in order of their relative acid strengths.

In the presence of gallium chloride, aluminum bromide, aluminum chloride, and ferric chloride, benzoyl azide is decomposed according to eq 2. Here complex formation is very fast, and the decomposition of the complex is the rate-determining step. The halides do not complex with the phenyl isocyanate formed and, as a consequence, they are not consumed in the reaction. As long as benzoyl azide is in excess, the concentration of the complex is equal to the halide concentration and remains constant. The experimentally determined pseudo-zero-order rate constant depends therefore upon the first power of the initial halide concentration. When, however, the reaction is at a stage where the azide is no longer in excess, the rate of the reaction becomes first order with respect to benzoyl azide and zero order with respect to halide.

$$PhCON_3 + AlBr_3 \xrightarrow[fast]{} PhCON_3{\cdot}AlBr_3 \xrightarrow[slow]{} PhN{=}C{=}O + N_2 + AlBr_3 \quad (2)$$

In the presence of antimony pentachloride, titanium tetrachloride, stannic chloride, and tellurium tetrachloride, the decomposition reaction follows a second-order rate law, first order with respect to each component. Equation 3 is in accordance with these results. With antimony trichloride and antimony tribromide as Lewis acids, the reaction rate depends upon the first power of the azide concentration and half-power of the halide concentration. The kinetics of this reaction can be interpreted by assuming that the catalyst exists essentially in dimeric form in aromatic solvents and that the monomeric form is the active substance.

$$PhCON_3 + SbCl_5 \overset{K}{\rightleftharpoons} PhCON_3{\cdot}SbCl_5 \xrightarrow[slow]{k} PhN{=}C{=}O + N_2 + SbCl_5 \quad (3)$$

$$R = k(\text{complex}) = kK(PhCON_3)(SbCl_5)$$

$$2SbCl_3 \rightleftharpoons Sb_2Cl_6 \qquad K_d = (Sb_2Cl_6)/(SbCl_3)^2$$

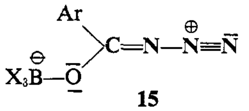
$$R = k(\text{azide})(SbCl_3) = k/K_d^{0.5}(\text{azide})(Sb_2Cl_6)^{0.5}$$

The halides, $GaCl_3$, $AlBr_3$, $AlCl_3$, and $FeCl_3$, very probably also exist in dimeric form. With these halides, however, the complexation reaction with the azide is the fast step so that no square-root term is found in the kinetic equation. Arsenic trichloride, arsenic tribromide, phosphorus trichloride, and phosphorus pentachloride were without effect on the rate of decomposition of benzoyl azide. Finally, the authors have observed that the catalytic influence of boron tribromide was much higher than all the other halides. Its rate constant was estimated to be about 18 times larger than that for gallium chloride.

Some further details about the Curtius reaction with boron halides are given by Fahr and Neumann.[168] They have found that benzoyl azide and substituted derivatives react with boron trifluoride or trichloride in toluene solution at *ca.* −60° to give an adduct which decomposes between −20 and 0°. The adducts could be isolated as crystalline substances from the reaction mixture. Their infrared spectra in dichloromethane indicated that the BX_3 molecules add onto the carbonyl group and not onto the azido group (**15**). Very probably the same phenomenon occurs in the reactions studied by Newman and coworkers.

Table VI
Eyring Parameters for Acid-Catalyzed Decomposition of Benzhydryl Azides and 1,1-Diphenylethyl Azide

Azide	*p-X*	$\Delta H^{\ddagger}$, *kcal/mol*	$\Delta S^{\ddagger}$, *eu*
Benzhydryl	...	21.2	−22.3
	p-Bromo	20.5	−27.0
	p-Chloro	22.8	−19.5
	m-Chloro	20.4	−28.3
	p-Fluoro	21.3	−22.5
	p-Methoxy	19.5	−23.4
	p-Methyl	22.5	−16.0
1,1-Diphenylethyl	...	15.2	−45.1



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2. *Acid Catalysis of Alkyl and Aryl Azides*

The acid catalysis of alkyl and aryl azides has been studied fairly extensively.[169, 170] Gudmundsen and McEwen[171] have studied the acid-catalyzed rearrangement of benzhydryl azides and 1,1-diarylethyl azides in order to furnish additional information to the Schmidt rearrangement of benzhydrols and 1,1-diphenylethylenes.[172–177] Both reactions are assumed to proceed by the same rate-determining step—the decomposition of the conjugate acid of the azide. The large negative entropies of activation (Table VI) suggest that nitrogen elimination occurs synchronously with aryl migration.

In solutions of hydrogen bromide in acetic acid many *o*-azidobiphenyls decompose vigorously at 50–60°.[178] While noncatalytic decomposition reactions (thermal and photochemical) of *o*-azidobiphenyl (**16**) and substituted derivatives result in formation of carbazoles (**17**)[6,51–53] (or furoxans), the hydrogen bromide catalyzed decompositions give rise to amines. Furthermore the *ortho* and *para* positions with respect to the original azido group are brominated when, however, these positions are not blocked by other substituents. Thus 2-azido-5-nitrobiphenyl (**18**) and 2-azido-3-nitrobiphenyl (**20**) are converted into 2-amino-3-bromo-5-nitrobiphenyl (**19**) and 2-amino-5-bromo-3-nitrobiphenyl (**21**), respectively. Decomposition of 2-azido-4′-nitrobiphenyl (**22**) gives a mixture of 2-amino-5-bromo-4′-nitrobiphenyl (**23**) and 2-amino-3,5-di-

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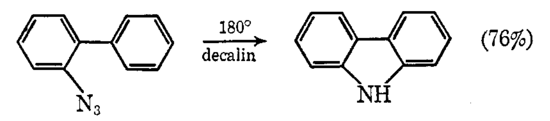
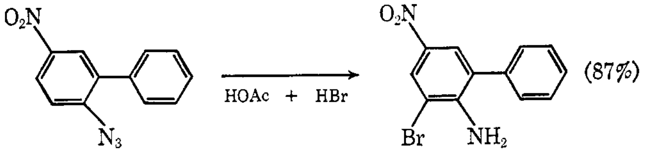


16. **17**



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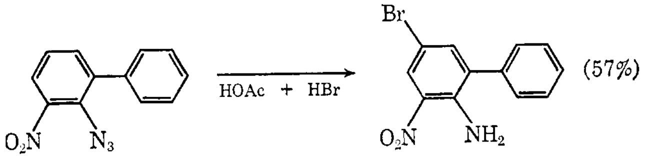

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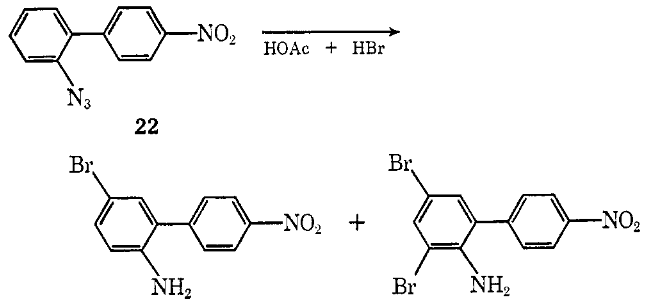


22 **23** **24**

bromo-4′-nitrobiphenyl (**24**) in a ratio of 3:1. The mechanism proposed by Smith and Brown is represented in Scheme III.[178]

Scheme III

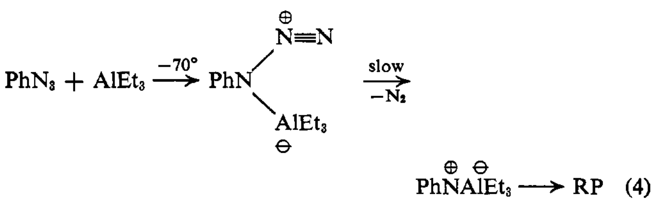
$$ArN_3 + H^{\oplus} \longrightarrow Ar\bar{N}H{-}\overset{\oplus}{N}{\equiv}\bar{N} \xrightarrow[-N_2\ \text{slow}]{Br^{\ominus}} ArNHBr \xrightarrow{H^{\oplus}}$$

$$Ar\overset{\oplus}{N}H_2Br \xrightarrow{Br^{\ominus}} ArNH_2 + Br_2$$

$$ArNH_2 + HBr \rightleftharpoons Ar\overset{\oplus}{N}H_3\,Br^{\ominus}$$

$$ArNH_2 + Br_2 \longrightarrow BrArNH_2{\cdot}HBr$$

Several authors have studied the reaction products in the Lewis acid catalyzed decomposition of phenyl and alkyl azides.[179–185] Hoegerlee and Butler have found that phenyl azide forms a hydrocarbon-soluble complex at −70° with triethylaluminum, diethylchloroaluminum, and ethyldichloroaluminum.[182] Upon warming to room temperature, this complex slowly decomposes into an intermediate phenylimine-aluminum compound (**25**) which then rearranges into a variety of amidoalkylaluminum reaction products (RP) (eq 4).

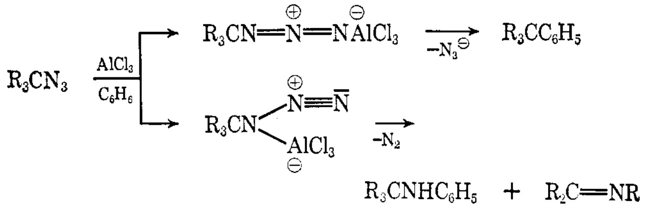


$$PhN_3 + AlEt_3 \xrightarrow{-70^\circ} PhN\begin{matrix}\overset{\oplus}{N}{\equiv}N\\ \underset{\ominus}{AlEt_3}\end{matrix} \xrightarrow[-N_2]{\text{slow}} Ph\overset{\oplus}{N}\overset{\ominus}{Al}Et_3 \longrightarrow RP \quad (4)$$

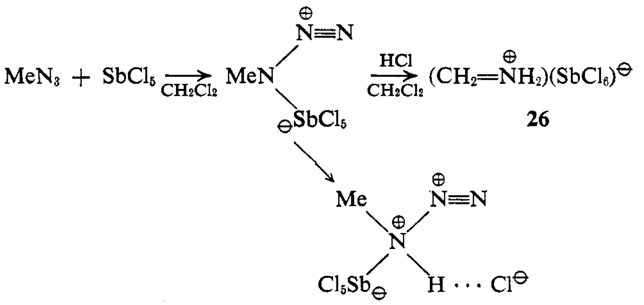
25

Whereas aryl, acyl, and sulfonyl azides decompose in the presence of aluminum trichloride in benzene solution only with evolution of N_2, alkyl azides also split off significant amounts of N_3^-.[183,184] At 50° alkylbenzenes and azomethines are obtained. In order to explain these results, Kreher and Jäger suggested that two intermediate complexes may be formed (Scheme IV). According to Goubeau, Allenstein, and Schmidt, a complex is formed between methyl azide and antimony pentachloride in methylene chloride solution.[181] Under the influence of dry hydrogen chloride, the complex decomposes at room temperature into methylenimmonium hexachloroantimonate (**26**) (Scheme V). By use of deuterium chloride instead of hydrogen chloride, N-monodeuterated methylenimmonium hexachloroantimonate was obtained.

Scheme IV



Scheme V



Halans has studied the aluminum bromide catalyzed decomposition of phenyl azide in toluene solution at 0° in the presence of traces of hydrogen bromide.[186] He has found that an equimolecular complex is formed between the catalyst and phenyl azide and that the catalyst is consumed in the reaction. On the basis of kinetic results, Scheme VI has been proposed for the decomposition mechanism. In connection herewith, Halans observed that whereas an equimolecular mixture of phenyl azide and hydrogen bromide does not decompose at 0°, a mixture of phenyl azide, aluminum bromide, and hydrogen bromide in the ratio 1/1/1 decomposes instantaneously at 0°.

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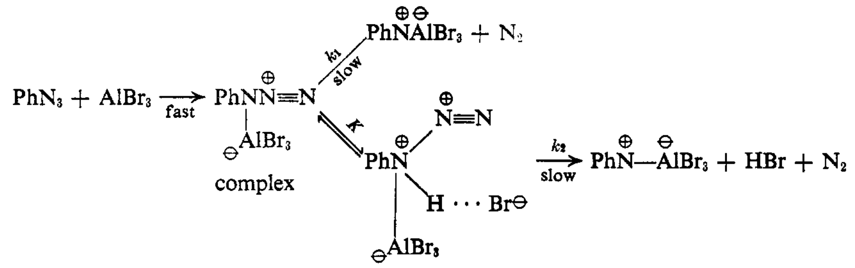
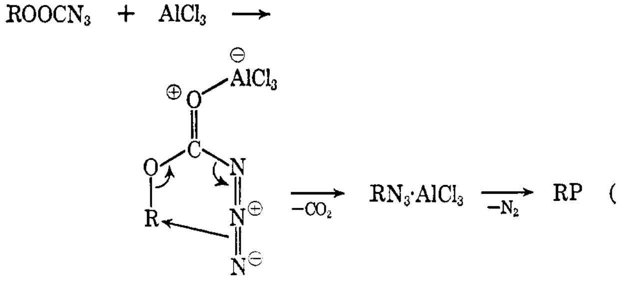
Scheme VI



$$R = \{k_1 + k_2K(\mathrm{HBr})\}(\text{complex})$$

3. Acid Catalysis of Azidoformates

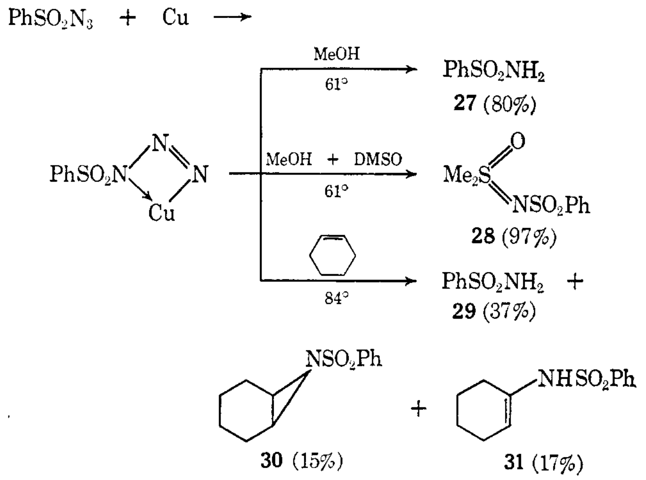
Kreher and Jäger have studied the aluminum chloride catalyzed decomposition of azidoformates in several solvents.[187,188] They reasonably assumed that the decomposition process in *n*-hexane and nitromethane solution proceeds by CO_2 elimination and the formation of alkyl azides which then decompose into imines (eq 5). Furthermore, infrared analysis has shown that the catalyst is fixed at the carbonyl group of the azidoformate.



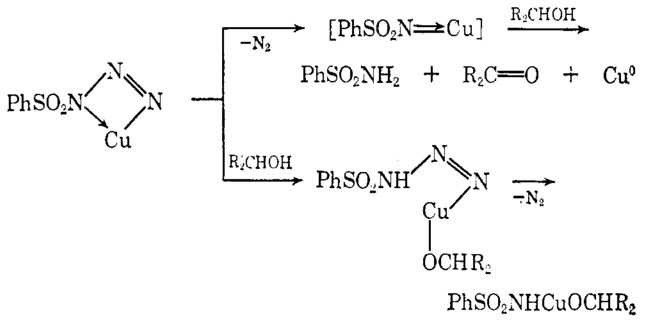
(5)

4. Catalysis of Sulfonyl Azides

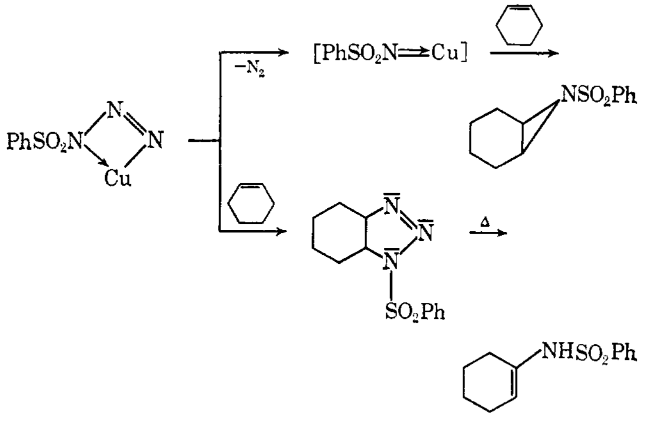
Kwart and Kahn have found that benzenesulfonyl azide forms a complex with freshly reduced copper powder.[189,190] This copper azide complex decomposes at a lower temperature than the pure sulfonyl azide. In refluxing methanol, benzenesulfonamide (27) is isolated as the major product. In the presence of dimethyl sulfoxide, N-benzenesulfonyldimethylsulfoximine (28) is obtained in almost quantitative yield. In cyclohexene solution benzenesulfonamide (29), N-benzenesulfonyl-7-azabicyclo[4.1.0]heptane (30), and 1-cyclohexenylbenzenesulfonamide (31) are isolated as the main reaction products. According to the authors, Schemes VII and VIII represent an acceptable interpretation of the experimental data.[189,190] In pure alcohol, the decomposition should occur by two competitive reactions (Scheme VII) producing benzenesulfonamide together with a ketone and oxidized copper. These last two products have indeed been observed in the reaction mixture. In the presence of DMSO, it seems that a copper–nitrene intermediate is formed which is trapped by DMSO. In cyclohexene solution, the authors have observed that the aziridine (30) disappears from the product composition when DMSO is added. The yield of enamine 31, however, is practically uneffected by DMSO. They proposed therefore to consider the aziridine as resulting from an intermediate copper–nitrene complex and the enamine as resulting from an intermediate unstable triazoline (Scheme VIII).



Scheme VII



Scheme VIII



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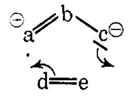
III. Addition Reactions

The addition reactions of organic azides to unsaturated systems can occur by two mechanisms.[191] If the reaction temperature is lower than the decomposition temperature of the azide, a 1,3-dipolar addition is observed. When, however, the reaction is carried out at the wavelength or at the decomposition temperature of the azide, the addition proceeds through an intermediate nitrene.

A. 1,3-DIPOLAR CYCLOADDITIONS

1. General Principles

The characteristics of the 1,3-dipolar cycloaddition mechanism of azides and other 1,3-dipoles (such as diazoalkanes, azomethine imines, nitrones, nitrile imines, nitrile oxides) have been described in detail by Huisgen.[192,193] According to the author, the addition of a 1,3-dipole (a b c) to a dipolarophile (d e) occurs by a concerted mechanism in which the two new σ bonds are formed simultaneously although not necessarily at equal rates (32). As a consequence, a stereoselective *cis* addition is observed. Thus, the addition of *p*-methoxyphenyl azide to dimethyl fumarate (33) yields 1-(*p*-methoxyphenyl)-4,5-*trans*-dicarbomethoxy-Δ^2-triazoline (34),[194] and 4-nitrophenyl azide gives exclusively the respective *cis*-addition products 35 and 36 on addition to *trans*- and *cis*-propenyl propyl ether.[195]



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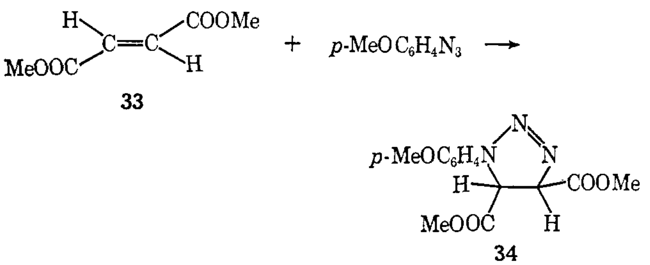

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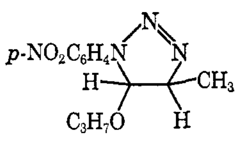

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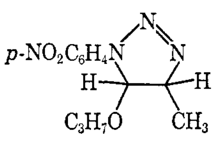

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Concerted cycloaddition reactions of azides are characterized by a large negative entropy of activation, a moderate enthalpy of activation (Table VII), and an almost independence of the rate with respect to solvent polarity.[196–199] The high degree of order in the transition state results from the fact that the 1,3-dipole must necessarily orient itself in such a way as to place the centers a and c in contact with the π bonds of the dipolarophile. The energy of activation accounts partly for the loss of resonance energy when the linear azide chain is bent in the activation process. This bending process does not require much energy (about 5 kcal/mol).[200]

Table VII

Eyring Parameters for 1,3-Dipolar Cycloadditions of Azides

Dipolarophile	*Azide*	*Solvent*	$\Delta H^{\ddagger}$, *kcal/mol*	$\Delta S^{\ddagger}$, *eu*
Norbornene	$C_6H_5N_3$	CCl_4	15.2	−29
	$C_6H_5N_3$	$CHCl_3$	13.9	−33.1
	$C_6H_5N_3$	EtOAc	14.7	−31.0
	p-$CH_3C_6H_4N_2$	EtOAc	15.0	−30.4
	m-$CH_3C_6H_4N_3$	EtOAc	14.9	−30.9
	p-$CH_3OC_6H_4N_3$	EtOAc	14.5	−31.9
	m-$CH_3OC_6H_4N_3$	EtOAc	14.5	−31.6
	p-$BrC_6H_4N_3$	EtOAc	14.7	−29.9
	m-$BrC_6H_4N_3$	EtOAc	14.0	−32.0
	p-$NO_2C_6H_4N_3$	EtOAc	12.5	−34.9
	m-$NO_2C_6H_4N_3$	EtOAc	14.4	−29.4
	Picryl azide	$CHCl_3$	9.8	−33.4
Cyclopentene	Picryl azide	$CHCl_3$	12.3	−35.5
Cyclooctene	Picryl azide	$CHCl_3$	12.7	−34.3
Styrene	Picryl azide	$CHCl_3$	14.0	−34.2
n-Hexadec-1-ene	Picryl azide	$CHCl_3$	15.2	−31.0
Oct-1-ene	Picryl azide	$CHCl_3$	14.2	−35.5
Indene	Picryl azide	$CHCl_3$	14.7	−31.8
1-Morpholino-cyclopentene	$C_6H_5N_3$	C_6H_6	11.7	−36
Vinyl ethyl ether	Picryl azide	$CHCl_3$	11.9	−30.3
Vinyl butyl ether	*p*-$NO_2C_6H_4N_3$	CCl_4	16.0	−32
Dihydropyran	Picryl azide	$CHCl_3$	13.6	−26.8
Dimethyl acetyl-enedicarboxylate	$C_6H_5N_3$	CCl_4	17.4	−26
endo-Bicyclohep-tene-2,3-dicarb-oxylic anhydride	Picryl azide	$CHCl_3$	14.1	−32.3
	Tosyl azide	$CHCl_3$		−29

Azides can add onto asymmetric dipolarophiles in two directions. In the absence of steric effects, the product distribution will be determined by electronic effects occurring in the rate-determining step. With respect to the reactivity centers in the azide molecule, it is known that electrophilic attack (*e.g.*, H^+ $AlCl_3$, R^+) occurs at the α-nitrogen atom and nucleophilic attack (*e.g.*, R^-, PR_3) at the azide terminus.[200a] Many examples of the orientation rule are given in the following sections. Huisgen, Szeimies, and Möbius have clearly established the promoting effect of conjugation on the dipolarophilic activity of double bonds toward azides.[198] Furthermore, they reported that aromatic azides display opposing substituent effects depending on whether they add to electron-rich or electron-poor dipolarophiles. The following Hammett ρ values in benzene at 25° are obtained: maleic anhydride, −1.1; N-phenylmaleimide, −0.8; norbornene, +0.88; cyclopentene, +0.9; and pyrrolidinocyclohexene, +2.5. Thus, electron-deficient double bonds react more easily with azides carrying electron-releasing substituents and *vice versa*. This is attributed to the stabilization of partial negative or positive charge on the α-nitrogen in the transition state (as, *e.g.*, 38). The addition of aryl azides to dipolarophiles thus occurs *via* an essentially concerted process, involving a transition state in which charge is partially developed.

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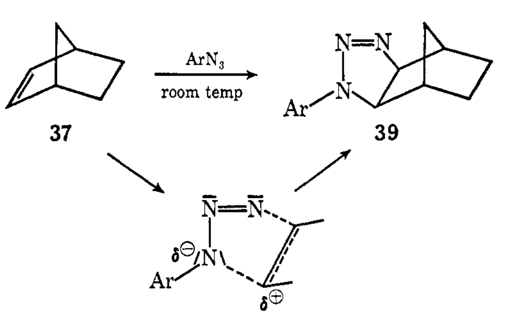
Table VIII

Rates of Addition of Phenyl Azide to Dipolarophiles in CCl_4 at 25°

Dipolarophile	*Heat of hydrogenation, kcal/mol*	*$k_2 \times 10^7$, l./(mol sec)*
Cyclohexene	−27.1	0.033
Bicyclo[2.2.2]octene	−28.3	0.897
Bicyclo[2.2.1]heptene	−33.1	188

2. *Addition of Aryl Azides to Olefins*

Aryl azides react with olefins to give 1,2,3-Δ^2-triazolines.[201-203] Whereas unactivated olefins are sluggish toward aryl azides, strained bicyclic systems, on the contrary, are particularly reactive.[204-208] The rate of phenyl azide addition to a series of olefins parallels the heat of hydrogenation (Table VIII).[197] This thermodynamic parameter is a measure for the degree of strain associated with these molecules.[209] Bicyclo[2.2.1]heptenes, such as norbornene (**37**), react readily at room temperature, and the addition occurs at the less hindered *exo* side (**39**).[196,197,210,211] A striking example of the increased dipolarophilic activity of strained double bonds is the fact that the addition of phenyl azide onto dicyclopentadiene (**40**) occurs exclusively on the double bond of the norbornene nucleus to give **41**.[204,212]



37 **39**

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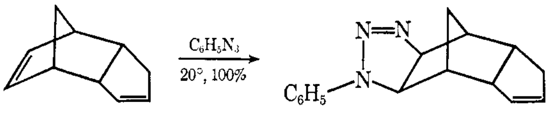
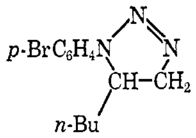


40 **41**

trans-Cyclooctene contains 9.2 kcal/mol more strain energy than *cis*-cyclooctene and adds phenyl azide exothermally.[213] Increasing the ring size of *trans*-cycloolefins diminishes the reactivity toward phenyl azide owing to diminishing ring strain.[214-217] Unactivated olefins react with aryl azides only very slowly at room temperature, and the orientation is controlled by electronic rather than steric factors.[218-221] *p*-Bromophenyl azide in excess 1-hexene, for example, afforded 89% yield of adduct **42** after 5.5 months at room temperature.



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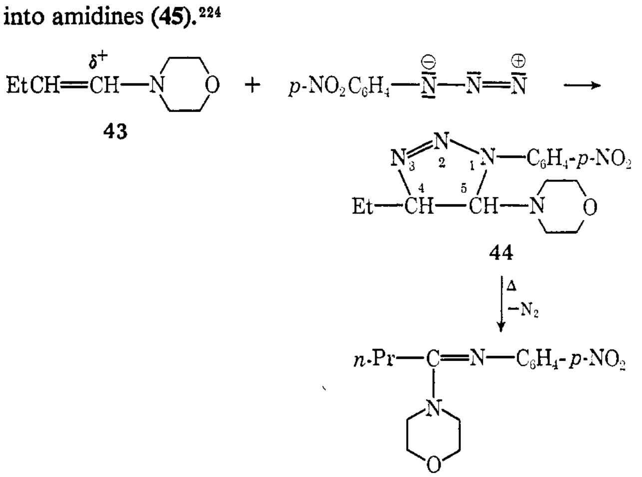
3. *Addition of Aromatic Azides to Enamines, Aldimines, and Ketimines*

Enamines contain electron-rich double bonds and thus react readily with azides (in many cases at room temperature). Only one addition product is formed, namely a 5-amino-Δ^2-triazoline, a result of electronic control.[222-223] Thus 1-(*p*-nitrophenyl)-4-ethyl-5-morpholino-Δ^2-triazoline (**44**) arises from the addition of *p*-nitrophenyl azide to 1-morpholino-1-butene (**43**). The addition products rearrange by heating into amidines (**45**).[224]



45

Ir and nmr analysis of the condensation products of primary amines with aldehydes and ketones are in favor of the Schiff-base structure (**46a**). Nevertheless, these substances react with aryl azides in chloroform solution in the tautomeric enamine form (**46b**) yielding aminotriazolines.[206,225-227] It proves that the dipolarophilic activity of an enamine olefin bond is much greater than that of an azomethine bond.

$$\underset{\textbf{46a}}{RCH_2CH{=}NR'} \rightleftharpoons \underset{\textbf{46b}}{RCH{=}CHNHR'}$$

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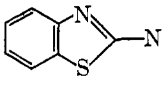
α-Azidoazomethines such as guanyl azide, 2-azidopyridine, 2- and 4-azidopyrimidine, 2- and 6-azidopurine, 2-azidobenzothiazole, and their substituted derivatives are in equilibrium with the corresponding tetrazolo forms.[228–238a] The equilibrium constant depends on the nature of the solvent, temperature, and the nature of substituents. This class of azides also yields Δ^2-triazolines when enamines are added. For example, 2-azidobenzothiazole (**47a**) which exists in equilibrium with tetrazolo[5,1-*b*]benzothiazole (**47b**) reacts with α-cyclohexene-N-morpholine to the corresponding Δ^2-triazoline in 90% yield.[239]



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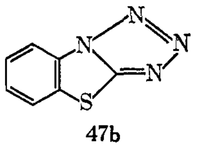
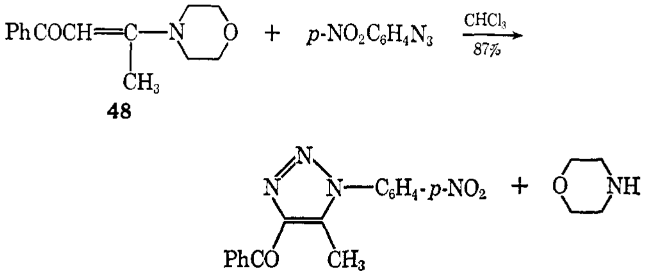


47b

The addition reactions of aryl azides onto enamines bearing a carbonyl, sulfonyl, or nitro group in the β position with respect to the nitrogen atom have been investigated by Italian authors.[240,241] The expected triazoline derivatives could not be isolated but were immediately converted into the corresponding 1,2,3-triazoles (**49**) and secondary amines. The reaction of *p*-nitrophenyl azide with 1-benzoyl-2-morpholino-1-propene (**48**) is given as a typical example.



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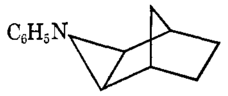
4. *Formation of Unstable Triazolines*

Most of the Δ^2-triazolines obtained from azides and olefins undergo thermal decomposition above 100° and produce aziridines and anils.[197,201,202,205,242–246] The addition product of phenyl azide and norbornene, for instance, decomposes at 160° into 55% aziridine **50** and 27% anil **51**.[197] Aziridines are the main reaction products when the decomposition is carried out photochemically.[197,245,247–249] This does not mean that anils would arise *via* rearrangement of the aziridines in the course of the pyrolysis reaction for aziridines are stable under these conditions.[245]



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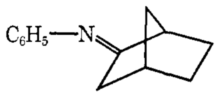

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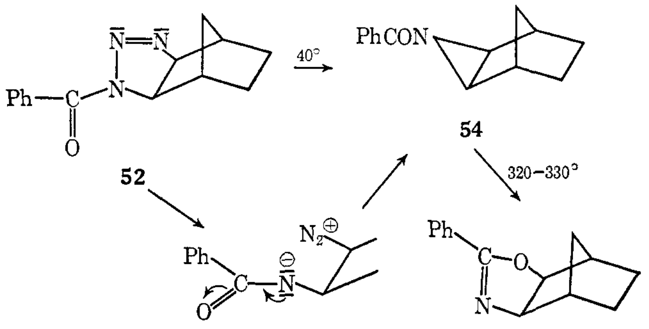
When the triazolinic nucleus carries electron-withdrawing groups at the N_1 position, it is far more labile.[250] This is attributed to the increased stabilization of the betaine intermediate (**53**). Thus, triazoline **52** formed by reaction of benzoyl azide with norbornene already decomposes from 40° into N-benzoylaziridine **54**.[197] This compound isomerizes by distillation under normal pressure quantitatively into an *exo*-oxazoline derivative (**55**).



Analogous methyl azidoformate forms with norbornene a thermal unstable triazoline.[251] The decomposition products are 40% aziridine and 55% imide. Furthermore it has been observed that the rate of nitrogen evolution of the triazoline from methyl azidoformate increases threefold when triglyme and 20-fold when dimethyl sulfoxide are substituted for 1,1-diphenylethane as solvents. This fact supports a betaine intermediate in the thermal decomposition reaction. The triazoline from 2,4-dinitrophenyl azide and norbornene could just be isolated, but from picryl azide only the aziridine was obtained.[252–254] Nevertheless, the high negative value of the activation entropy (−33.4 eu) indicates a similar cyclic transition state for both reactions.

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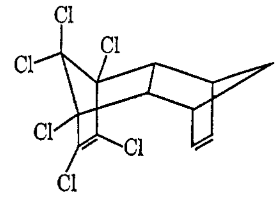
Isodrin (**56**) gives with *t*-butyl azidoformate an isolable triazoline (addition in position C_6C_7) which decomposes into aziridine by chromatography over neutral alumina.[255] With tosyl azide, on the other hand, only the aziridine derivative could be isolated. Both aziridines undergo a series of transformations leading to a so-called bird-cage hydrocarbon **57**.[255]



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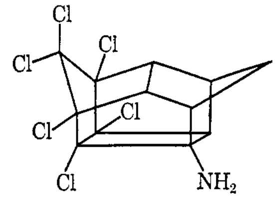

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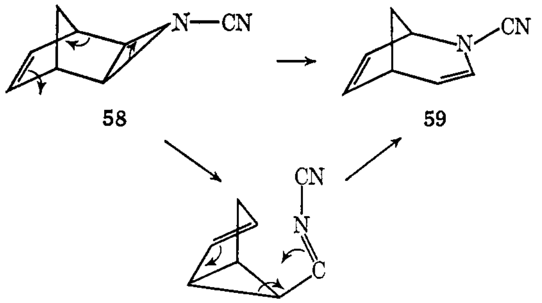
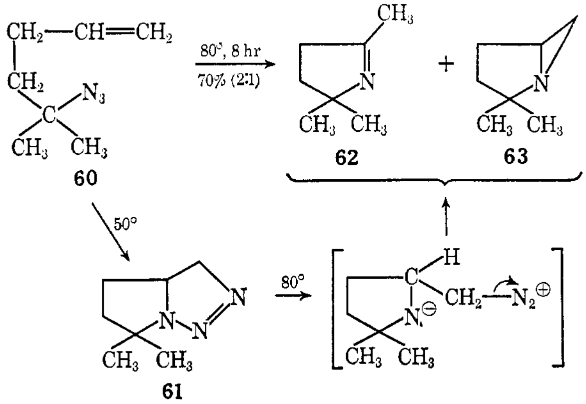
Cyanogen azide reacts with olefins at 0–35° to afford alkylidene cyanamides and/or N-cyanoaziridines arising from decomposition of an intermediate unstable triazoline.[256] With norbornadiene the isolated product is N-cyano-3-azatricyclo-[3.2.1.0$^{2,4-exo}$]oct-6-ene (**58**) which is unstable and rearranges into N-cyano-2-azabicyclo[3.2.1]octa-3,6-diene (**59**).[257]



58 **59**

Olefinic azides (**60**) containing unsaturation at least three carbon atoms away from the azide group decompose in hydrocarbon solution into cyclic imines (**62**) and 1-azabicyclo[3.1.0]-hexanes (**63**).[258] The reaction proceeds through an intermediate triazoline (**61**) which is formed in quantitative yield when the azide is heated at 50° or allowed to stand at 25° for 2 months. Here, too, a dipolar intermediate is formed during the decomposition of triazoline **61** because the rate of nitrogen evolution increases about 10-fold when nitromethane and 20-fold when aqueous diglyme are substituted for toluene as solvents.

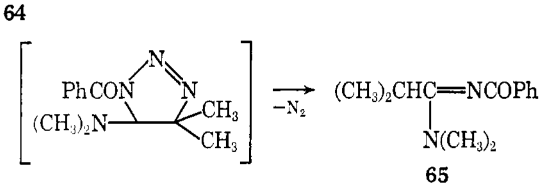


60 **62** **63** **61**

Enamines react with aryl azides to give 5-amino-Δ^2-triazolines which can be thermolyzed to amidines (see preceding section). When, however, enamines or the tautomeric aldimines and ketimines are treated with benzoyl azide at room temperature, amidines are obtained directly.[259] The reaction of benzoyl azide with N,N-dimethyl-2-methylpropenylamine (**64**) in benzene gave a quantitative yield of amidine **65**.

$(CH_3)_2C{=}CHN(CH_3)_2 \ + \ PhCON_3 \ \longrightarrow$

64

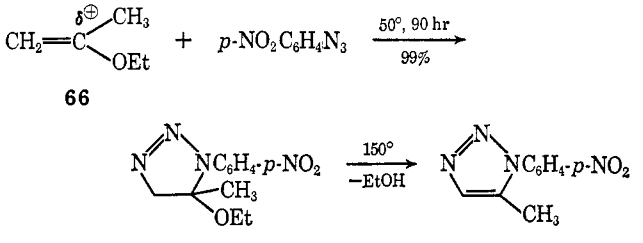


65

5. Triazolines from Vinyl Ethers

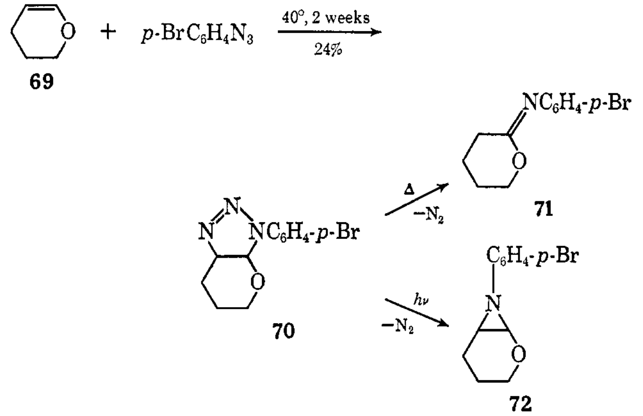
Organic azides combine with open-chain and cyclic enol ethers to give Δ^2-triazolines in high yield. The addition is stereospecific *cis* and the orientation process is determined by electronic effects.[195, 260] The triazolines are unstable above 100° and can decompose in mainly two ways.[260]

Triazolines from the open-chain enol ethers, vinyl butyl ether, β-ethoxypropene, and α- and β-methoxystyrene, eliminate alcohol thermally and are converted into 1,2,3-triazoles. For example, the triazoline **67** from β-ethoxypropene **66** and *p*-nitrophenyl azide decomposes quantitatively at 150° into 1-(*p*-nitrophenyl)-5-methyl-1,2,3-triazole (**68**).



66 **67** **68**

Triazolines from the cyclic enol ethers, dihydrofuran and dihydropyran, decompose at 100–130° into anils and nitrogen. Thus *p*-bromophenyl azide reacts with dihydropyran (**69**) to give triazoline **70** which decomposes thermally into the arylimine of δ-valerolactone (**71**). Photochemical decomposition of **70**, on the contrary, yields 7-*p*-bromophenyl-7-aza-2-oxabicyclo[4.1.0]heptane (**72**) in 67% yield. Scheiner has shown that aziridine **72** is stable at the decomposition temperature of **70**, proving that it is not an intermediate in the thermal conversion of **70** to **71**.[261]



69 **70** **71** **72**

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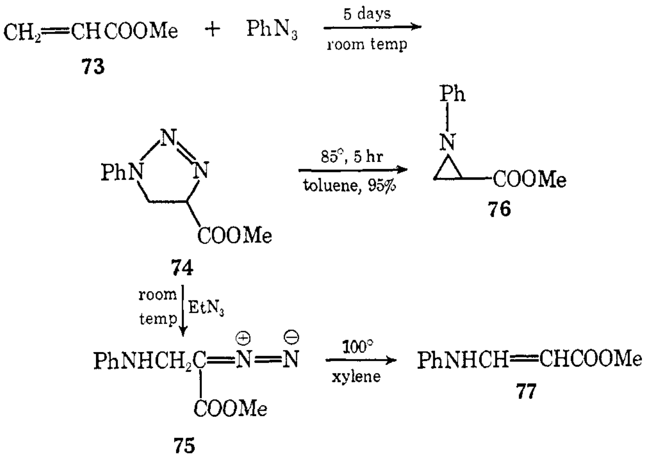
6. Addition of Azides to α,β-Unsaturated Esters and Nitriles

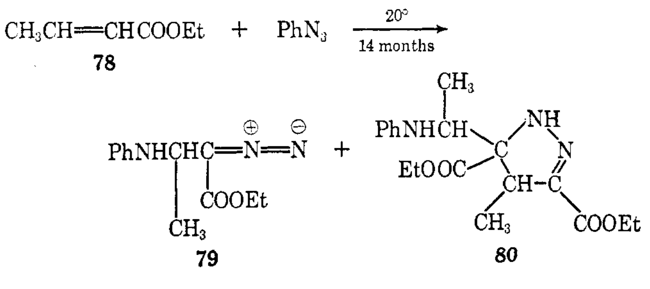
Huisgen, Szeimies, and Möbius have studied the addition reactions of aryl azides to α,β-unsaturated esters and nitriles.[194]

Methyl acrylate (73) reacts with aryl azides to form 1-aryl-4-carbomethoxy-Δ^2-triazolines in agreement with the orientation rule based on electronic effects. These Δ^2-triazolines are completely converted by base catalysis into the ring-opened isomer. Thus 1-phenyl-4-carbomethoxy-Δ^2-triazoline (74) gives, in the presence of triethylamine at room temperature, methyl 3-aniline-2-diazopropionate (75). The Δ^2-triazolines as well as the α-diazoesters are thermolabile. 74 is converted into 1-phenyl-2-carbomethoxyaziridine (76) and 75 gives methyl 3-anilinoacrylate (77) as thermolysis product.[262]

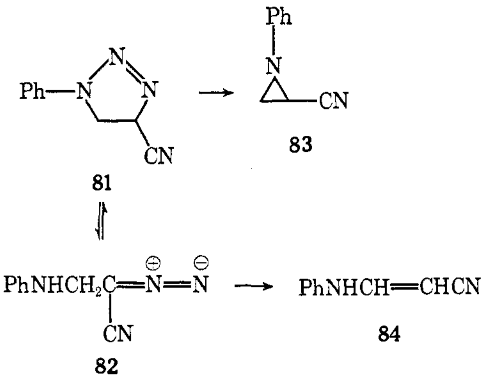


Some α-diazoesters are obtained directly from the addition reaction when a long reaction time is required. Dimethyl fumarate, for example, reacts only very slowly with phenyl azide at 25°. After 60 days the α-diazoester is obtained in 90% yield.

α-Diazoesters are 1,3-dipoles and are thus capable of new cycloadditions to α,β-unsaturated carboxylic esters. This is the reason why the bis-addition product 80 together with ethyl 3-anilino-2-diazobutyrate (79) is obtained in the reaction of phenyl azide with the less reactive ethyl crotonate (78).



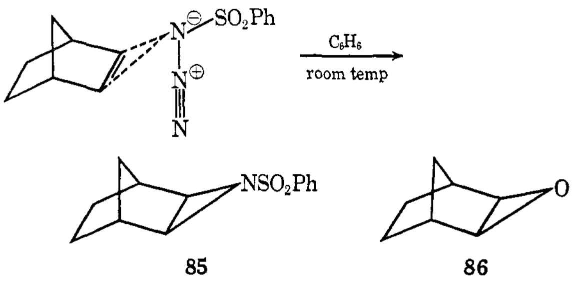
Phenyl azide reacts with acrylonitrile to give 1-phenyl-4-cyano-Δ^2-triazoline (81)[263] which is in equilibrium with 3-anilino-2-diazopropionitrile (82) in the presence of triethylamino (71%/29%).[194] Both isomers decompose thermally in respectively 1-phenyl-2-cyanoaziridine (83) (slowly at room temperature) and 3-anilinoacrylonitrile (84).[262]



7. Addition of Sulfonyl Azides to Double Bonds

Sulfonyl azides react with olefins at a temperature which is much lower than the decomposition temperature of the azides (120–150°). The isolated products are aziridines and anils. The addition can be conceived as a result of two consecutive reactions, namely a 1,3-dipolar cycloaddition of the azide to the olefin immediately followed by decomposition of the formed unstable triazoline. As no triazolines can be detected, these reactions can also be regarded as a concerted addition with concomitant loss of nitrogen.

By treating norbornene with benzenesulfonyl azide in benzene at room temperature, a crystalline product is obtained in quantitative yield.[264,265] On the basis of chemical and nmr evidence, an aziridine structure (85) similar to *exo*-2,3-epoxynorbornene (86) is attributed to the adduct. The addition thus occurs at the least hindered *exo* side of the bicyclic nucleus.



Benzenesulfonyl azide reacts at room temperature with the activated bond of *endo*-dicyclopentadiene yielding an *exo*-aziridine.[266,267] Bicyclo[2.2.2]oct-2-ene is much less strained and thus less reactive than norbornene. The reaction with benzenesulfonyl azide therefore occurs at higher temperature. In refluxing benzene, two products are obtained, an aziridine and an anil.[267] The aziridine obtained at room temperature from norbornadiene and benzenesulfonyl azide is unstable and rearranges spontaneously into a stable azabicyclooctadiene according to the same scheme as the reaction with cyanogen azide (58, 59).[267–269] In none of the preceding examples is a triazoline observed. These would indeed be unstable owing to the electron-withdrawing sulfonyl group so that they eventually decompose faster than they can be formed.

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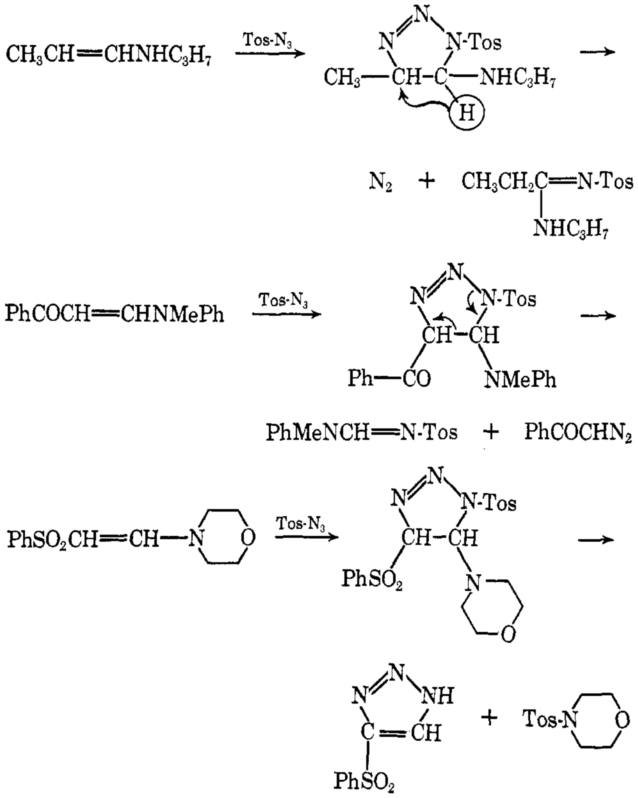
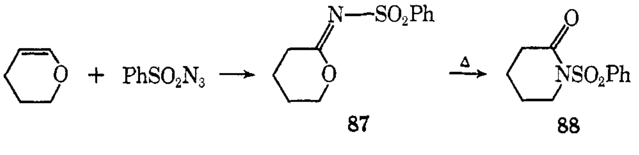
Sulfonyl azides react rapidly (at room temperature) with enamines, and here, too, no triazolines are isolated. The reaction products nevertheless can be easily explained when an intermediate triazoline is postulated. The hypothetic triazoline can then decompose in three different ways leading either to amidines and nitrogen, or to amidines and diazoketones, or to triazoles and sulfonamines.[225,241,270–272] A typical example of each mode of decomposition is given in Scheme IX.

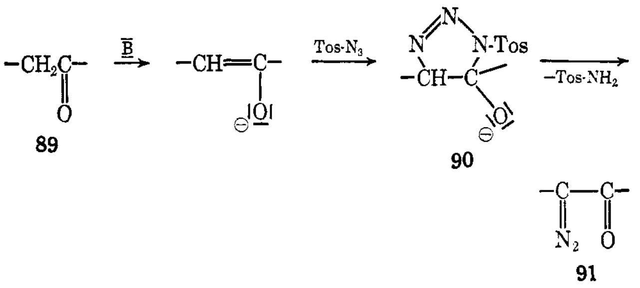
Scheme IX



The reactions of vinyl ethers with sulfonyl azides have been described by several authors.[260,273–275] From dihydropyran the arylsulfonimines of δ-valerolactone (**87**) are obtained. These compounds rearrange at *ca.* 180° into N-arylsulfonyl-2-piperidones (**88**) (Chapman rearrangement).[276]



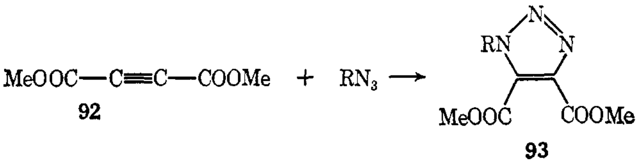
Tosyl azide reacts with enolizable methylene compounds **89** in the presence of bases at room or lower temperature to give α-diazo ketones **91** or related products probably through the unstable triazoline **90**.[277–293] The reaction has been extensively studied and reviewed by Regitz.[294]



8. Addition of Azides to C-C Triple Bonds

Azides have been found to add to acetylenic compounds to give 1,2,3-triazoles.[1, 295–301] Huisgen reported that the dipolarophilic activity of alkynes is similar in magnitude to that of alkenes concluding that the transition state of the cycloaddition does not profit from the aromatic resonance of the products.[193]

Acetylenic esters react with alkyl azides, aryl azides, carboalkoxy azides, and tosyl azide yielding triazoles in all cases studied.[102,302–306] When dimethyl acetylenedicarboxylate (**92**) is the starting material, the 1-substituted 4,5-dicarbomethoxy-1,2,3-triazoles **93** are obtained.



R = alkyl, tropylium, aryl, carboalkoxy, tosyl

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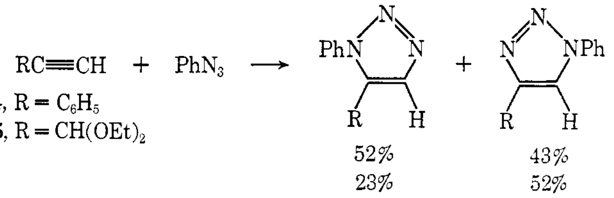
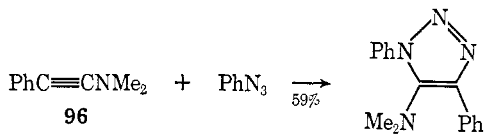
With monosubstituted acetylenes, such as phenylacetylene (**94**) and propiolaldehyde diethyl acetal (**95**), the orientation of phenyl azide is determined both by electronic and steric effects.[307,308]

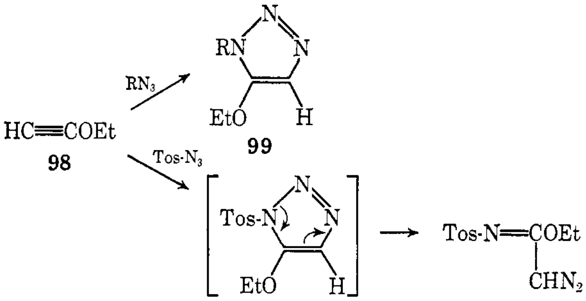


Ynamines (**96**) react with phenyl azide in the same way as enamines and result in formation of amino-substituted triazoles (**97**).[309]



96 **97**

The reaction of azides with ethoxyacetylene (**98**) has been studied by Italian authors. With aliphatic and aromatic azides, the expected 1-substituted 5-ethoxy-1,2,3-triazoles (**99**) are obtained.[310, 311] Sulfonyl azides, on the other hand, react with ethoxyacetylene at room temperature to yield no triazoles but the valence tautomeric diazo compounds (**100**).[312,313]



98 **99** **100**

9. *Addition of Azides to Nitriles*

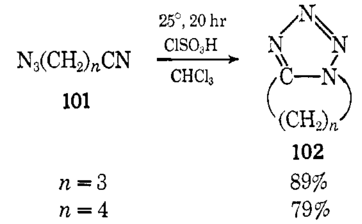
Huisgen has stated that the driving force behind the 1,3-dipolar addition is stronger the more the loss of π-bond energy in the reactants is overcompensated by the energy of the two new σ bonds.[193] Because the order of bond energy is O–N < N–N < C–N, azides do not add at all to aldehydes and ketones and add with more difficulty to nitriles than to olefins. Phenyl azide, for instance, adds preferentially to the C–C double bond of acrylonitrile.[194,263] This is also the reason why the condensation products of aldehydes and primary amines, which essentially exist in the Schiff-base structure **46a**, react in the tautomeric enamine form **46b**.[225,226]

Table IX
Reaction of Activated Nitriles with Azides at 130–150°

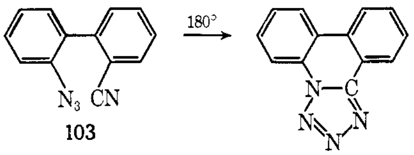
Nitrile	*Azide*	*Tetrazole yield, %*
CF_3CN	n-$C_8H_{17}N_3$	96
C_3F_7CN	$C_6H_5N_3$	22
CCl_3CN	n-$C_8H_{17}N_3$	69
C_3F_7CN	$C_3F_7CH_2N_3$	64

Phenylacetonitrile reacts with azides in the presence of alkoxides to give *vic*-triazoles rather than tetrazoles which would result from addition of the azides onto the nitrile function.[314–316]

Unactivated nitriles only react with azides when the two functions are incorporated into the same molecule. Thus γ-azidobutyronitrile and δ-azidocapronitrile (**101**) undergo an acid-catalyzed cyclization to the corresponding 1,5-disubstituted tetrazoles (**102**)[317] and thermal cyclization of 2-azido-2′-cyanobiphenyl (**103**) yields tetrazolophenanthridine (**104**), a stable compound which decomposes only at 300° into a black glass.[52]



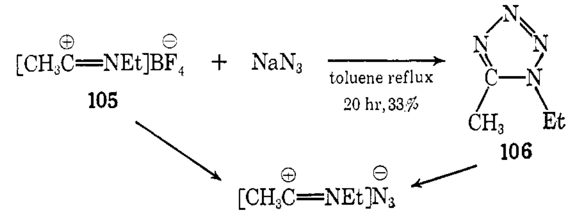
101 **102**



103 **104**

Intermolecular addition can be made to occur if the nitrile is sufficiently activated by electron-withdrawing groups. Table IX gives some results reported by Carpenter.[317]

Nitrilium fluoroborates (**105**) react with sodium azide in boiling toluene to form tetrazoles. By this method 1-ethyl-5-methyltetrazole (**106**) has been obtained in 33% yield.[318]



105 **106**

5-Substituted tetrazoles are formed in good yields by heating hydrazoic acid or ionic azides with nitriles.[319–323]

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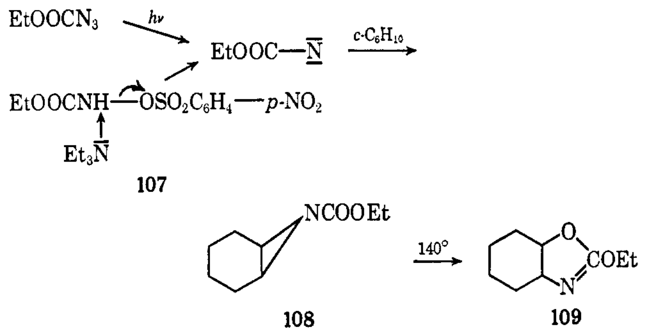
B. NITRENES AS INTERMEDIATES

1. *Addition of Nitrenes to Cyclohexene, Benzene, and Cyclooctatetraene*

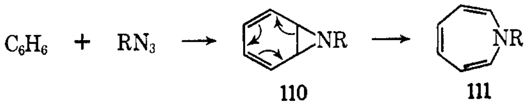
Photochemical decomposition of ethyl azidoformate in cyclohexene gives 7-carbethoxy-7-azabicyclo[4.1.0]heptane (**108**) as main product (56% at 38° and 75% at −75°) together with the three isomeric cyclohexenylurethans.[82,83,85,86] A nitrene mechanism for the reaction is supported by the fact that the same products in almost the same ratio are obtained in the base-induced cleavage of N-*p*-nitrobenzenesulfonoxyurethan (**107**). All evidence indicates that the second reaction yields the carbethoxynitrene by an α-elimination mechanism. The aziridine isomerizes at 140° into 2-ethoxy-4,5-cyclohexano-Δ^2-oxazoline (**109**).



107

108 **109**

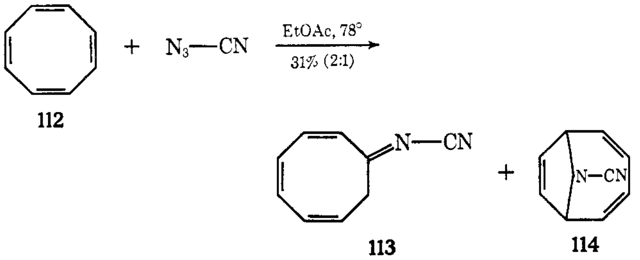
When ethyl azidoformate, cyanogen azide, or $CO(N_3)_2$ is decomposed in benzene solution, no aziridines but azepines **111** are obtained.[83,88,98–101,324,325] The 7-azanorcaradienes (**110**) are most probably formed as unstable intermediates but rearrange immediately into the more stable azepines.



110 **111**

R = COOEt, CN, CON$_3$

Cyanogen azide reacts with cyclooctatetraene (**112**) at room temperature in ethyl acetate to give alkylidenecyanamide.[326] At 78°, a 31% yield of a mixture of the alkylidenecyanamide (**113**) (68%) and the 1,4-adduct **114** (32%) is obtained. Since cyanogen azide decomposes above 40° and since the alkylidenecyanamide does not rearrange to the 1,4 adduct under the reaction conditions, one may believe that the 1,4 adduct forms directly from cyanonitrene and cyclooctatetraene. This is a case of 1,4 addition studied by Anastassiou.[326]

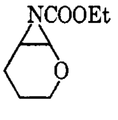


112 **113** **114**

2. *Addition of Carbethoxynitrenes to Enol Ethers and Enol Acetates*

Brown and Edwards have studied the photochemical reaction of ethyl azidoformate with dihydropyran and have isolated in good yield the very reactive aziridine **115**.[96] The thermal reaction between the two compounds, however, takes a completely different course *via* triazoline to imino lactone.

Irradiation of ethyl azidoformate in the presence of enol acetates also leads essentially to the corresponding very reactive N-carbethoxyaziridines.[97] Structures **116** and **117** have been obtained from isopropenyl acetate and 1-acetoxycyclohexene.



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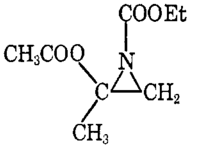

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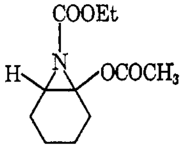


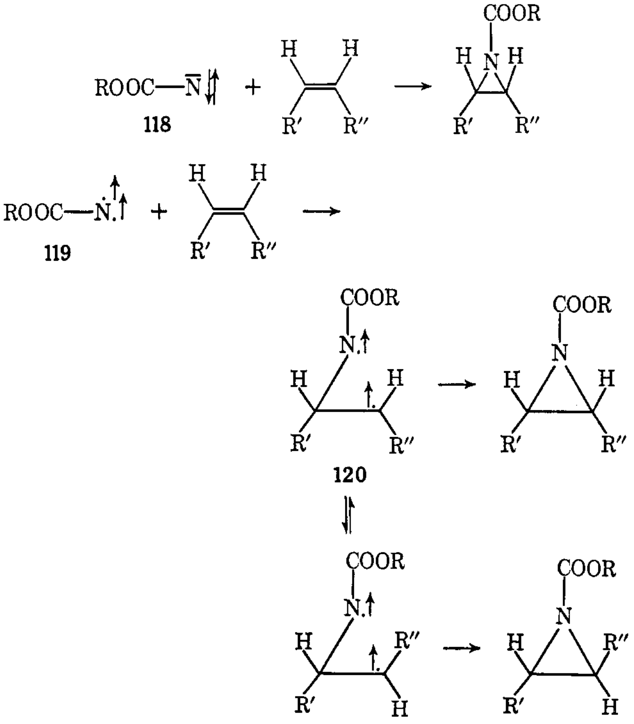
117

3. *Stereospecificity of Addition of Carboalkoxynitrenes*

Some information is available concerning the electronic state of the carboalkoxynitrenes at the moment of their addition to olefins.

Hafner, Kaiser, and Puttner have observed that the addition of carbomethoxynitrene to *cis*- and *trans*-butene-2 at −30° yielding an aziridine proceeds in a stereospecific manner.[327] They concluded that the nitrene reacts preferentially in the singlet state. Indeed, it is generally assumed that singlet nitrenes (**118**) add to double bonds by a one-step, concerted mecha-

Scheme X



118 **119** **120** **121**

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(324) F. D. Marsh and H. E. Simmons, *J. Amer. Chem. Soc.*, **87**, 3529 (1965).

(325) L. E. Chapman and R. F. Robbins, *Chem. Ind.* (London), 1266 (1966).

(326) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **87**, 5512 (1965).

(327) K. Hafner, W. Kaiser, and R. Puttner, *Tetrahedron Lett.*, 3953 1964).

Table X

Thermal Reaction of Ethyl Azidoformate with Alkyne

Alkyne	*Temp, °C*	*Triazole, %*	*Oxazole, %*
PhC≡CPh	130	0	33
PhC≡CCOOEt	130	0	32
PhC≡CH	130	16	16
MeOOCC≡CCOOMe	130	23	3
HC≡CCOOMe	100	50	3

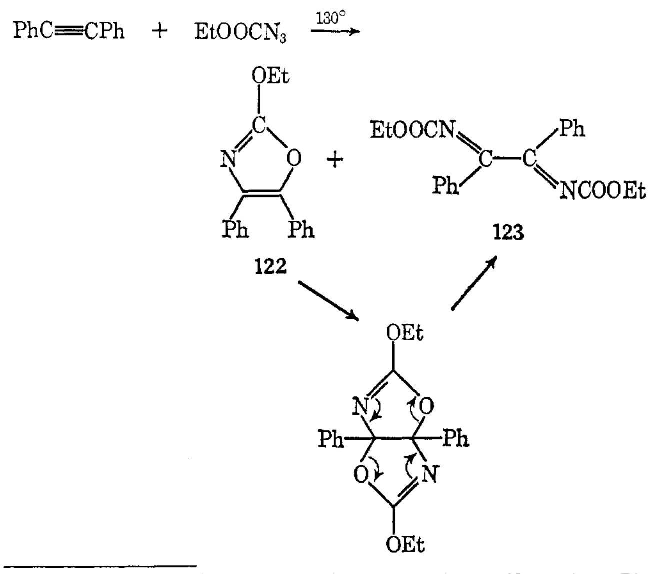
nism, while triplet nitrenes (**119**) first form an open-chain triplet diradical (**120**) followed by a spin inversion process prior to cyclization. The spin inversion process is considered as a slow step so that the open-chain diradical intermediate has an appreciable lifetime permitting rotation about the single bond (giving **121**) to compete with ring closure and thus accounting for a nonstereospecific addition (Scheme X). This theory has first been developed by Skell for carbenes.[328, 329]

Lwowski and McConaghy have investigated the addition of carbethoxynitrene to *cis*- and *trans*-4-methylpentene-2 (MeCH=CH-*i*-Pr).[330–332] Their findings agree with those of Hafner but, in addition, they found that the degree of stereospecificity decreases with decreasing olefin concentration (dilution with dichloromethane). They concluded that (1) all the thermally generated nitrene molecules and two-thirds of the photochemically generated nitrenes are in the singlet state; (2) the stereospecific addition of singlet nitrenes to the olefin competes with intersystem crossing to triplet nitrenes, a unimolecular process which is favored by dilution.

Recently Beckwith and Redmond stated that intersystem crossing in carbethoxynitrene is temperature dependent and has an apparent activation energy greater than that for reaction of the singlet form with olefin.[333]

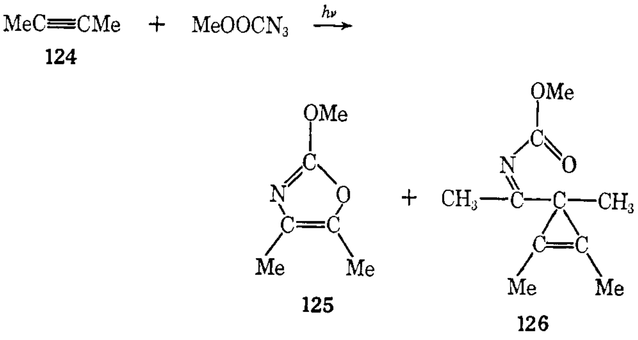
4. *1,3-Dipolar Cycloaddition of Carboalkoxynitrenes*

When ethyl azidoformate is warmed with an alkyne, carbethoxy-1,2,3-triazoles and 2-ethoxyoxazoles can be obtained (Table X).[102] They result from 1,3-dipolar addition respectively of the azide and the nitrene to the triple bond. The triazoles cannot be intermediates of the formation of oxazoles because they are stable under the reaction conditions (130°).

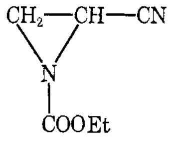


The oxazoles (**122**) are capable of adding a second molecule of nitrene to give a bisethoxycarbonyliminoethane (**123**).

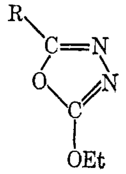
Meinwald and Aue have studied the photochemically induced reaction of methyl azidoformate with 2-butyne (**124**) and have isolated oxazole **125** along with a larger amount of product **126** composed of two molecules of alkyne and one molecule of nitrene.[103]



Carbethoxynitrene adds to unsaturated nitriles (such as acrylonitrile), preferentially onto the double bond, to give an aziridine (**127**).[95] With saturated nitriles, on the other hand, 1,3,4-oxadiazoles (**128**) are obtained.[91,95,104] These are stable heterocyclic compounds which only decompose at *ca.* 500°.[334]



127



128

R = C_6H_5, CH_3, $CHMe_2$, CH_2CH_2OEt, CH_2CO_2Me, CH=CH_2

5. *Syntheses of Azacyclopropenes from Vinyl Azides*

Azacyclopropenes (azirines) are postulated as intermediates in the Neber rearrangement[335–337] and have been prepared from oxime tosylates,[338] quaternary hydrazones,[339–341] and nitrile oxides.[342,343] Smolinsky first reported that pyrolysis of suitable constituted vinyl azides (**129**) represents a useful method for preparing azirines (**130**).[344, 345] Consequently these

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(328) P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, **78**, 4496 (1956).

(329) R. S. Woodworth and P. S. Skell, *ibid.*, **81**, 3383 (1959).

(330) W. Lwowski and J. S. McConaghy, *ibid.*, **87**, 5490 (1965).

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(337) C. O'Brien, *Chem. Rev.*, **64**, 81 (1964).

(338) D. J. Cram and M. J. Hatch, *J. Amer. Chem. Soc.*, **75**, 33 (1953).

(339) R. F. Parcell, *Chem. Ind.* (London), 1396 (1963).

(340) D. F. Morrow, M. E. Butler, and E. C. Y. Huang, *J. Org. Chem.*, **30**, 579 (1965).

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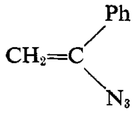
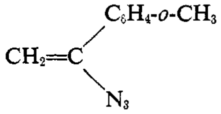
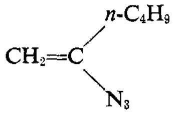
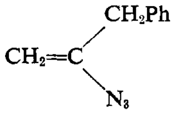
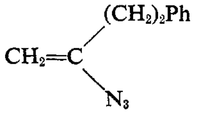
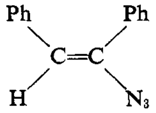
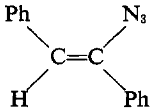
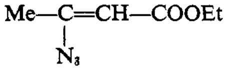
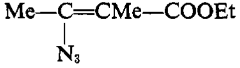
(342) H. J. Bestmann and R. Kunstmann, *Angew. Chem.*, **78**, 1059 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 1039 (1966).

(343) R. Huisgen and J. Wulff, *Tetrahedron Lett.*, 917 (1967).

(344) G. Smolinsky, *J. Amer. Chem. Soc.*, **83**, 4483 (1961).

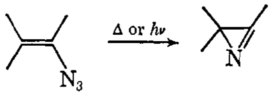
(345) G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

Table XI
Decomposition of Vinyl Azides

Vinyl azide	*Reaction conditions*	*Azirine yield, %*	*Other reaction products*	*Ref*
 $\mathrm{CH_2{=}C(Ph)N_3}$	Δ	80	. . .	345
	hν	58	. . .	49
	hν	85	Azabicyclo[2.1.0]pentane (10%)	346
	hν	94	. . .	347, 348
 $\mathrm{CH_2{=}C(C_6H_4\text{-}\mathit{o}\text{-}CH_3)N_3}$	Δ	78	. . .	345
 $\mathrm{CH_2{=}C(\mathit{n}\text{-}C_4H_9)N_3}$	Δ	29	. . .	345
	hν	81	. . .	347, 348
 $\mathrm{CH_2{=}C(CH_2Ph)N_3}$	*hν*	100	. . .	347, 348
 $\mathrm{CH_2{=}C((CH_2)_2Ph)N_3}$	*hν*	93	. . .	347, 348
$\mathrm{PhCH{=}CHN_3}$	Δ	. . .	Phenylacetonitrile (74%)	349
	100–105°	. . .[a]	. . .	350
	hν	. . .	Polymer (74%)	349
	hν	. . .[a]	. . .	350
$\mathrm{PhCH{=}CMeN_3}$	100–105°	100	. . .	350
	hν	100	. . .	350
 $\mathrm{(Ph)(H)C{=}C(Ph)(N_3)}$	Δ	94	. . .	351
 $\mathrm{(Ph)(H)C{=}C(N_3)(Ph)}$	*hν*	. . .	Pyrazine (40%)	352
$\mathrm{MeCH{=}CPhN_3}$	*hν*	94	. . .	347, 348
$\mathrm{EtCH{=}CEtN_3}$	*hν*	55	. . .	347, 348
$\mathrm{\mathit{t}\text{-}BuCH{=}CHN_3}$	*hν*	. . .	Polymer and pyrazine	348
 $\mathrm{Me{-}C(N_3){=}CH{-}COOEt}$	*hν*	70	Ketenimine 23%	353
 $\mathrm{Me{-}C(N_3){=}CMe{-}COOEt}$	*hν*	65	Ketenimine 25%	353
$\mathrm{CF_3CF{=}CFN_3}$	20°	(36)	. . .	354
$\mathrm{(CN)_2C{=}CRN_3}$	20°	. . .	Ketenimine primary product	355
$\mathrm{ArCOCH{=}CHN_3}$	Δ	. . .	Triazoles and isoxazoles	351, 356–361
$\mathrm{TosCH{=}CHN_3}$	Base	. . .	Triazole	362
Azidocycloalkenes	*hν*	Various	. . .	347, 348

[a] Yield not reported.

substances have been obtained by thermal or photochemical decomposition of several vinyl azides (Table XI[346–362]).



129 130

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(346) F. P. Woerner, H. Reimlinger, and D. R. Arnold, *Angew. Chem.*, **80,** 119 (1968); *Angew. Chem. Int. Ed. Engl.*, **7,** 130 (1968).

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(348) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, **90,** 2869 (1968).

349) J. H. Boyer, W. E. Krueger, and G. J. Mikol, *ibid.*, **89,** 5504 (1967).

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The question as to whether the thermal azirine formation proceeds through a vinyl nitrene intermediate or by a concerted mechanism is not as yet resolved. A nitrene intermediate seems most probable on the basis of its similarity with cyclopropene formation from alkenylcarbenes[363, 364] and because either thermal or photochemical decomposition of vinyl azides yields the azirines (Table XI).

Acknowledgments. The author thanks the "Nationaal Fonds voor Wetenschappelijk Onderzoek" (Belgium) and the "A. von Humboldt-Stiftung" (Germany) for a Postdoctoral Fellowship. He is also grateful to the Department of Organic Chemistry, University of Erlangen (Germany), for its generous hospitality.

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(358) A. N. Nesmeyanov and M. I. Rybinskaya, *Dokl. Akad. Nauk SSSR*, **167**, 109 (1966); *Chem. Abstr.*, **64**, 17578*g* (1966).

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