Synthesis of Azirenes from Allenic Esters

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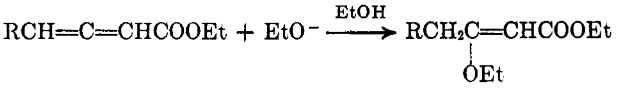
Conjugated vinyl azides are conveniently prepared by the addition of azide ion to conjugated allenic esters. These intermediates are converted on irradiation to azirene esters as major products. 4,4-Disubstituted allenic esters give ill-defined products. Catalytic reduction of the azirene esters involves ring cleavage to generate acyclic enamines. The mechanisms for these transformations are discussed.

The addition of nucleophiles to conjugated allenes constitutes a very facile synthesis of α,β-unsaturated esters,[1] nitriles,[2] and ketones,[3] as shown. The reaction

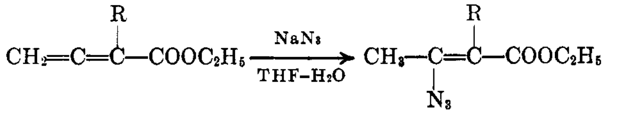


$$RCH{=}C{=}CHCOOEt + EtO^- \xrightarrow{EtOH} RCH_2\underset{\displaystyle OEt}{C}{=}CHCOOEt$$

occurs by Michael addition to the β carbon atom followed by anionic rearrangement.[1] However, the products can usually be obtained by alternate routes, *i.e.*, the addition of the nucleophile to the conjugated acetylene. We have utilized the addition of azide ion to allenic esters to generate β-azidocrotonates. In this case no convenient alternative synthesis is possible. Azide ion undergoes cycloaddition to propargyl esters to give vicinal triazoles[4] and treatment of 2,3-dibromo esters with sodium azide produces mixtures.[5]

The addition of azide to allenic esters is best conducted in aqueous tetrahydrofuran or acetone with an excess of sodium azide.[6] The reaction is outlined in Chart I.

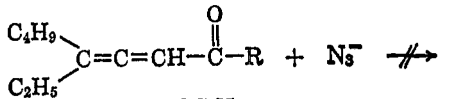
CHART I



$$CH_2{=}C{=}\overset{\displaystyle R}{C}{-}COOC_2H_5 \xrightarrow[THF-H_2O]{NaN_3} CH_3{-}\underset{\displaystyle N_3}{C}{=}\overset{\displaystyle R}{C}{-}COOC_2H_5$$

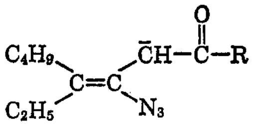
1a, R = H **2a**, R = H
b, R = CH_3 **b**, R = CH_3

Addition of azide ion to a terminally disubstituted allene ester or amide (**3a** or **3b**) does not give a vinyl azide or any definitive products after several hours of heating. At ambient temperatures no reaction occurs. This is probably because the energy barrier to addition precludes formation of a tetrasubstituted olefin (**4**).



$$(C_4H_9)(C_2H_5)C{=}C{=}CH{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R + N_3^- \not\rightarrow$$

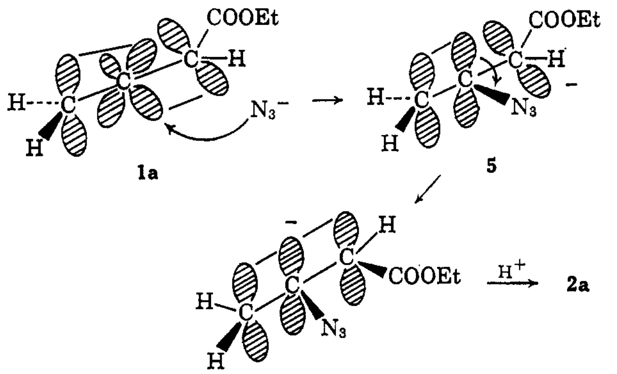
3a, R = OC_2H_5
b, R = $N(C_2H_5)_2$

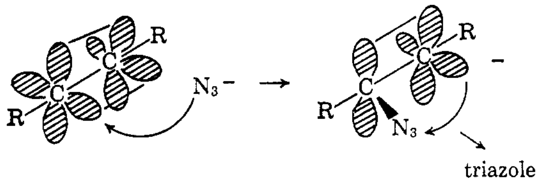


$$(C_4H_9)(C_2H_5)C{=}C(N_3){-}\bar{C}H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R$$

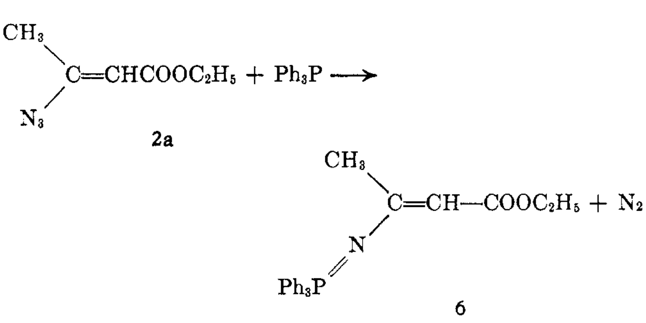
4

The fact that ring closure of the initial adduct **5** does not occur to give *v*-triazole indicates that this intermediate anion has time to rotate 90° about the 2,3 bond in order to achieve full π-orbital overlap. This places the π electrons orthogonal to the azide moiety preventing ring closure. This is illustrated in the following orbital diagrams. When azide adds to an acetylene the rigid vinyl anion is locked in a nonorthogonal position and ring closure to triazole occurs.





The β-azidocrotonates **2a** and **2b** were characterized by their absorption spectra and conversion to a phosphinimine by reaction with triphenylphosphine.[7]



$$(CH_3)(N_3)C{=}CHCOOC_2H_5 + Ph_3P \longrightarrow (CH_3)(Ph_3P{=}N)C{=}CH{-}COOC_2H_5 + N_2$$

2a **6**

Photolysis of **2** led to a 4:1 mixture of azirene **7** and ketenimine **8** in 93% yield.

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[1] (a) G. Eglington, E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3197 (1954); (b) A. R. Pudovik, N. G. Khusainova, and I. M. Aladzheva, *Zh. Obshch. Khim.*, **34**, 2470 (1964).

[2] P. Kurtz, H. Gold, and H. Disselnkotter, *Ann.*, **624**, 1 (1959).

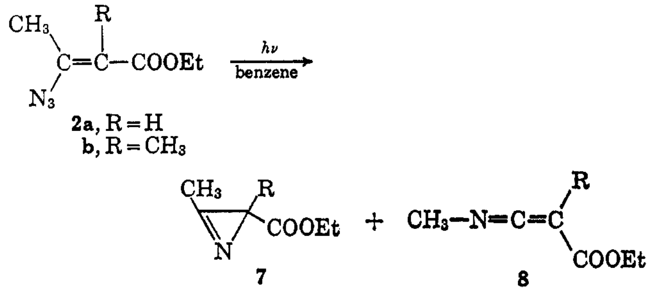
[3] (a) M. Gaudermar, *Ann. Chim.* (Paris), **1**, 161 (1956); (b) M. Bertrans and J. LeGras, *Compt. Rend.*, **260**, 6929 (1965).

[4] (a) J. H. Boyer and F. C. Cantor, *Chem. Rev.*, **54**, 1 (1954); (b) J. H. Boyer, "Heterocyclic Compounds," Vol. VII, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961.

[5] We have found that sodium azide and ethyl 2,3-dibromopropionate gave mixtures of α- and β-azidoacrylates; for similar results on cinnamates, see K. A. N. Rao and P. R. Venkataraman, *J. Indian Chem. Soc.*, **15**, 194 (1938).

[6] (a) The mixture should be kept basic so that hydrazoic acid will not add to the α,β-unsaturated ester; (b) see J. H. Boyer, *J. Am. Chem. Soc.*, **73**, 5248 (1951).

[7] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 841 (1963).

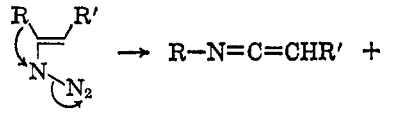


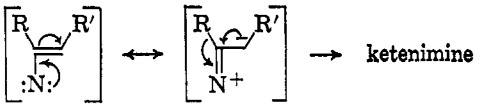
2a, R = H
b, R = CH$_3$

7 8

The pure azirenes (**7**) obtained by fractional distillation of the reaction mixture are quite stable and could be stored at room temperature in a nitrogen atmosphere for several months. In contrast with the strong infrared absorption at 5.7 μ exhibited by simple alkyl or aryl azirenes[8] the spectra of **7** showed only weak stretching intensities in this region. The singlet ring proton at δ 2.20 in **7a** compared with 2.60 in ethyl 3-methyl-2-aziridine carboxylate[9] indicates a substantial azirine ring current.

The ketenimine could be detected by the strong stretching vibration at 4.87 μ[10] and by the position of the N-methyl group at δ 3.08 in the nmr spectrum and comprised 20% of the crude photolysis mixture (nmr and glpc assay). The ketenimine (**8a** or **8b**) was destroyed during distillation of the mixture. The formation of a ketenimine in the photolysis and pyrolysis of vinyl azides gives no indication of the intermediate responsible for this product mixture. Concerted loss of nitrogen with alkyl migration would be similar to other carbon-to-nitrogen rearrangements.[11] The nitrene is equally capable of effecting the same rearrangement.



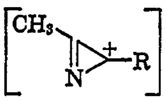


Attempts to trap the vinyl nitrene with 2-methyl-2-butene failed. Similarly, Smolinsky[8] has failed in attempts to effect C–H insertion during vinyl azide pyrolysis. The existing evidence seems to favor concerted loss of nitrogen although the vinyl nitrene still cannot be eliminated as an intermediate since intramolecular insertion would certainly be favored kinetically and by a lower entropy of activation as in vinyl carbene reactions.[12]

The mass spectra of azirenes **7a** and **7b** are almost identical except for their 14 m/e difference (Table I). Both azirenes showed major fragments at M − 73 for loss of a carbethoxy group which corresponds to the azirenyl cation **9** indicating that this species could be generated in solution.[13]

TABLE I
MASS SPECTRA OF AZIRENES **7a** AND **7b**

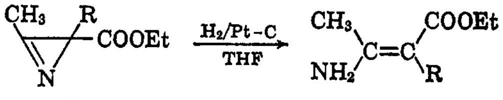
Compd	Relative %					
	M$^+$	M − 28	M − 45	M − 56	M − 73	M − 98
7a	0.67	25	32	50	58	100
7b	0.04	15	5	25	40	100



9

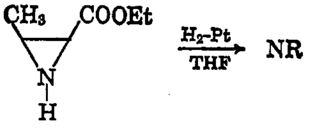
The mass spectra of both azirenes showed only weak molecular ions (Table I) but an array of heavier fragments to m/e 200. The unstable ring is apparently undergoing other reactions in the inlet chamber.[14]

When azirenes **7a** and **7b** were catalytically hydrogenated at atmospheric pressure, 1 equiv of hydrogen was rapidly consumed. The products were not the expected aziridines but β-aminocrotonates (**10**). The rearrangement is not acid catalyzed because it occurs equally well on a palladium–barium carbonate catalyst.[15] The aziridine is not an intermediate because **11** was recovered unchanged after the same treatment.



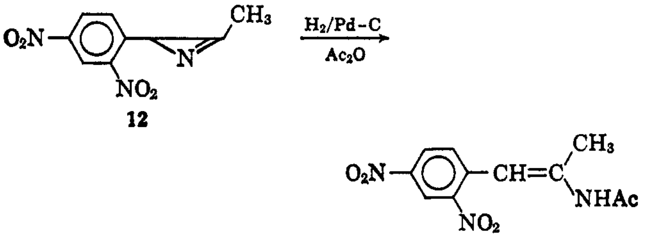
7a, R = H
b, R = CH$_3$

10



11

This same behavior of azirenes was first observed by Cram and Hatch[16] on azirene **12**.



12

13

The enamine was trapped as the enamide by hydrogenating in acetic anhydride. This reduction was explained as preferential reduction of the strained C–N single bond.[16] Leonard[17] has shown that the C–N single bond of azirenyl cations preferentially reacts with unsaturated bonds as a 1,3 dipole. This explanation cannot be excluded for the azirenes **7a** and **7b**. Alternatively, the results can be explained by a two-step hydrogenation with concurrent rearrange-

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[8] G. Smolinsky, *J. Org. Chem.*, **27**, 3557 (1962).

[9] F. Hoffman-LaRoche and Co., British Patent 847205 (1961); *Chem. Abstr.*, **55**, 7433*e* (1961).

[10] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., p 28.

[11] H. O. House and W. F. Berkowitz, *J. Org. Chem.*, **28**, 307 (1963).

[12] G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 2015 (1961).

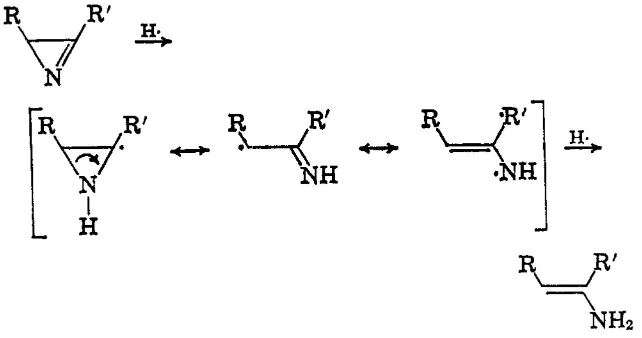
[13] Simple Hückel LCAO–MO calculations indicate a delocalization energy of 1.58β. The η and δ parameters used in this calculation were from A. Streitweiser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

[14] For a recent discussion of this phenomenon, see D. W. Thomas and K. Bieman, *J. Am. Chem. Soc.*, **87**, 5447 (1965).

[15] A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *ibid.*, **87**, 1050 (1965).

[16] D. J. Cram and M. J. Hatch, *ibid.*, **75**, 33 (1953).

[17] R. J. Leonard, Abstracts of First Midwest Regional Meeting of American Chemical Society, Kansas City, Mo., Nov 1965, p 40.



ment.[18] It is interesting to note that diazirene reduction is anomalous also giving only small quantities of amines.[19]

We have demonstrated that conjugated allenes are useful intermediates for the preparation of vinyl azides which can be photolytically transformed into functionalized azirenes. With the availability of simple allenic esters,[1,20-23] ketones,[3] and nitriles[2] a variety of new azirenes may now be prepared *via* these intermediates.[24] This will complement the other syntheses of azirenes using halo azides,[8,25] oxime tosylates,[16] and quaternary methiodides.[26,27]

Experimental Section[28]

Ethyl 2,3-Butadienoate (1a).—This was prepared by the method of Jones, *et al.*:[1a] bp 60° (70 mm); $\tilde{\nu}_{max}$ 1960, 1940 (allene), and 850 cm^{-1} (terminal allene); nmr, δ 5.15 (2 H multiplet) and 5.5 (1 H quartet).

Anal. Calcd for $C_6H_8O_2$: C, 64.25; H, 7.20. Found: C, 64.11; H, 7.21.

Ethyl 2-Methyl-2,3-butadienoate (1b).—Acetyl chloride (5.4 g, 0.069 mole), carbethoxymethylmethinyltriphenylphosphorane[29] (50 g, 0.138 mole), and 200 ml of benzene were stirred at 50° for 3.25 hr. The mixture was cooled and the phosphonium salt was filtered. The filtrate was concentrated to a slurry and triturated with pentane to precipitate all the triphenylphosphine oxide. The pentane solution was concentrated and distilled to separate 3.0 g (40%) of allene ester, bp 82° (70 mm) [lit.[20] bp 52° (11 mm)]. It exhibited the following spectra: infrared (neat), 1960, 1940 (allene), and 840 cm^{-1} (terminal allene); nmr, δ 5.0 (2 H quartet).

Anal. Calcd for $C_7H_{10}O_2$: C, 66.60; H, 7.94. Found: C, 66.26; H, 8.08.

Ethyl 4-Ethylocta-2,3-dienoate (3a).[30]—To a slurry of 0.5 mole of sodium hydride in 1 l. of tetrahydrofuran was added dropwise 112 g (0.5 mole) of triethyl phosphonoacetate. After stirring for 1 hr, 63.1 g (0.5 mole) of butylethylketene in 300 ml of hexane was added. The solution was heated at 50° for 30 min, cooled, and poured into water. Extraction with pentane and subsequent distillation separated 25 g of the allene, bp 86° (0.4 mm). The product exhibited the following spectra: infrared (neat), 1950 cm^{-1} (allene); nmr, δ 5.42 (1 H triplet).[31]

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.49; H, 10.43. Found: C, 73.30; H, 10.30.

N,N-Diethyl-4-ethyl-2,3-octadienoamide (3b).—N,N-Diethyl diethylcarbamoylmethylphosphonate[32] (64.4 g, 0.27 mole) in 25 ml of tetrahydrofuran was added to 0.28 mole of sodium hydride in 50 ml of the same solvent and sitrred for 1 hr. Butylethylketene (Eastman, 60 g, 0.475 mole) was added dropwise at 10° and allowed to warm to 25° during 8 hr. The solution was heated to boiling and poured into water. Extraction with pentane and washing of the extracts with dilute hydrochloric acid, saturated sodium bicarbonate, and brine furnished, after concentration and distillation, 25.4 g (40%) of the allene amide **3b**, bp 94–97° (0.2 mm). It exhibited the following spectra: infrared, 1953 (allene) and 1626 cm^{-1} (amide); nmr, δ 5.7 (1 H, broad triplet, J^{31} = 3 cps) and 3.35 (4 H quartet, N-ethyl). The remainder of the spectrum is obscured by the broad methylene envelope.

Anal. Calcd for $C_{14}H_{25}NO$: C, 75.40; H, 11.30. Found: C, 75.50; H, 11.51.

Ethyl β-Azidocrotonate (2a).—To 1.88 g (0.168 mole) of ethyl 2,3-butadienoate in 10 ml of tetrahydrofuran was added 1.1 g (0.170 mole) of sodium azide in 10 ml of water. After stirring for 1 hr, the solution was acidified with 8% hydrochloric acid and extracted with ether. The ether was washed with potassium carbonate and brine, and concentrated to 1.83 g (70%) of azide. The oil was purified by passing a petroleum ether (bp 30–60°) solution through 10 g of neutral alumina.[8] The light yellow oil exhibited the following spectra: infrared, 2105, 2083 (azide), 1692 (ester), and 1613 cm^{-1} (conjugated olefin); nmr, δ 2.3 (3 H, methyl doublet, J = 1 cps) and 5.45 (1 H, vinyl proton quartet, J = 1 cps); ultraviolet, λ_{max} 266 mμ (ϵ 17,250). The major fragment in the mass spectrum is at m/e 127 corresponding to loss of nitrogen from the molecular ion at m/e 155.

It detonated on contact with sulfuric acid indicating its sensitivity; thus fractional distillation was not attempted.[16b]

Ethyl β-Triphenylphosphiniminocrotonate (6).—To 0.01 mole of ethyl β-azidocrotonate in methylene chloride was added 0.01 mole of triphenylphosphine. After nitrogen evolution ceased (about 1 hr) the solution was diluted with pentane to incipient turbidity and cooled to crystallize 3.8 g (98%) of white solid. After three recrystallizations from methylene chloride–hexane the blades had mp 135–135.5°. The phosphinimine exhibited the following spectra: infrared, 1667 (ester), 1538 (double bond), and 1135 cm^{-1}; ultraviolet, λ_{max} 297 mμ (ϵ 29,200), 275 (25,700), and 268 (23,350); nmr, δ 4.75 (1 H, vinyl quartet, $J \cong 2$ cps).

Anal. Calcd for $C_{24}H_{24}NO_2P$: C, 74.02; H, 6.21; N, 3.60. Found: C, 73.89; H, 6.30; N, 3.63.

Ethyl 2-Methyl-3-azidocrotonate (2b).—To 1.93 g, (15.2 mmoles) of ethyl 2-methyl-2,3-butadienoate in 20 ml of water containing 5 ml of tetrahydrofuran was added 1.04 g (16 mmoles) of sodium azide. The solution was stirred for 24 hr, acidified with dilute hydrochloric acid, and extracted with ether. After washing and drying the ether was removed to leave 1.9 g of the yellow, oily azide. It exhibited the following spectra: infrared 2105 (azide) and 1724 cm^{-1} (ester); nmr, 1.8 (3 H, methyl quartet, J = 1.5 cps) and 2.4 (3 H, methyl quartet, J = 1.5 cps).

This compound detonated with sulfuric acid similarly to **2a**.

Reaction of Sodium Azide with (3b).—Sodium azide (8.0 g, 0.12 mole) and the allenic amide **3b** (22 g, 0.1 mole) were refluxed in 150 ml of aqueous acetone; the reaction was monitored

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(18) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin Co., New York, N. Y., 1965, p 17, and references cited therein.

(19) E. Schmitz and R. Ohme, *Chem. Ber.*, **94**, 2166 (1961).

(20) H. J. Bestmann and H. Hartung, *Angew. Chem. Intern. Ed., Engl.*, **2**, 214 (1963).

(21) E. R. H. Jones, G. H. Whitham, and M. C. Whiting, *J. Chem. Soc.*, 4628 (1957).

(22) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(23) J. H. Wotiz, *ibid.*, **72**, 1639 (1950).

(24) While this work was in progress a report appeared [F. Serratosa, *Tetrahedron Letters*, 895 (1964)] on the reaction of 2 equiv of a Grignard reagent with propargyl bromide to furnish an allenylmagnesium halide. This was said to occur by trapping of a transient allenyl carbene by the organometallic. Attempts to carbonate this proposed intermediate were unsuccessful. Consequently, the reaction mixture containing the hypothetical intermediate allenyl Grignard was hydrolyzed with deuterium oxide. This led to no incorporation of deuterium in the allene hydrocarbon as determined by nmr and mass spectral analysis. Finally, addition of 1 equiv of butylmagnesium bromide to propargyl bromide at −40° and distillation of the anhydrous reaction mixture gave 1,2-heptadiene in 80% yield. Thus, the proposed reaction mechanism is untenable and does not involve an allenyl Grignard reagent.

(25) A. Hassner and L. A. Levy, *J. Am. Chem. Soc.*, **87**, 4203 (1965).

(26) T. F. Parcell, *Chem. Ind.* (London), 1396 (1963).

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

(28) All melting points and boiling points are uncorrected. The infrared spectra were determined in chloroform with a Beckman IR-5A spectrometer. The ultraviolet spectra were determined in absolute ethanol with a Beckman DK-2A recording spectrophotometer. The nmr spectra were determined in deuteriochloroform with a Varian A-60 spectrometer. The data are recorded in ppm downfield from tetramethylsilane. The mass spectra were determined with a CEC-103 mass spectrometer at 70 ev. Microanalysis were performed by Galbraith Laboratories, Knoxville, Tenn. Magnesium sulfate was used as the drying agent throughout this work.

(29) H. Saikachi, Y. Tamguchi, and H. Ogawa, *Yakugaku Zasshi*, **82**, 1262 (1962); *Chem. Abstr.*, **58**, 13887*d* (1963).

(30) This procedure is the same as that described in ref 22 for phenylethylketene.

(31) See D. F. Koster and A. Danti, *J. Phys. Chem.*, **69**, 486 (1965), for a discussion of coupling constants in allenic systems.

(32) A. J. Speziale and R. C. Freeman, *J. Org. Chem.*, **23**, 1883 (1958).

by infrared sampling. After 28 hr no allene remained. The solution was poured into dilute hydrochloric acid and extracted with ether. The ether was washed, dried, and concentrated to 25 g of a thick oil. This material had azide and amide absorption at 2105 and 1613 cm^{-1}, respectively, but exhibited a multitude of vinyl protons in the nmr from δ 5.0 to 7.0. The oil showed four spots on thin layer chromatography having similar R_f values and could not be distilled at 300° (0.10 mm). Similar results were obtained with either tetrahydrofuran or dimethylformamide as solvents.

Allene ester **3a** gave the same results when subjected to these conditions.

3-Methyl-2-carbethoxy-2H-azirene (7a).—The azide **2a** (2.60 g, 16.8 mmoles) in 100 ml of benzene was irradiated with a low-pressure mercury lamp (Srinivasan–Griffin Rayonet reactor) at 253 mμ for 18 hr, when nitrogen evolution ceased. The solution was concentrated and distilled at 30° (0.1 mm) to separate 2.0 g (93%) of a light yellow oil. This oil had a strong absorption band in the infrared at 2062 cm^{-1} (ketenimine).[8] This was corroborated in the nmr spectrum which exhibited methyl spikes at δ 2.4 (vinyl methyl) and 3.1 (N-methyl) in the ratio of 3:1. Gas–liquid partition chromatography (SE-30 at 80°) separated two components with the same ratio. Distillation of this oil at 80–90° (70 mm) destroyed the ketenimine and separated 1.4 g of pale yellow azirene. The oil exhibited the following spectra: infrared, 1786 (azirene),[8] 1709 (ester), and 1190 cm^{-1}; nmr, δ 2.2 (1 H singlet, ring) and 2.45 (3 H singlet, vinyl methyl). The mass spectrum is tabulated in Table I.

Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.79; H, 7.30; N, 10.90.

Similar results were obtained with 2-methyl-2-butene as solvent.

2,3-Dimethyl-2-carbethoxy-2H-azirene (7b).—In a similar manner, azide **2b** was irradiated. The crude photolysate before distillation showed ketenimine (25%) as before. Distillation at 95° (32 mm) separated 65% of pure azirene **7b** which exhibited the following spectra: infrared, 1786 (azirene), 1718 (ester) and 1267 cm^{-1}; nmr, δ 1.35 (3 H singlet, saturated methyl) and 2.38 (3 H singlet, vinyl methyl). The mass spectrum is tabulated in Table I.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.60; H, 7.80; N, 9.94; mol wt, 141. Found: C, 59.43; H, 8.01; N, 9.75; mol wt, 143.

Hydrogenation of 3-Methyl-2-carbethoxy-2H-azirene (7a).—The azirene **7a** (1.0 g, 11 mmoles) in 15 ml of tetrahydrofuran was hydrogenated over 100 mg of 5% palladium on charcoal at atmospheric pressure. After 6 hr hydrogen uptake ceased (11 mmoles) and the mixture was filtered and concentrated to 1.0 g of white needles, mp 28–30°. Recrystallization from petane furnished pure ethyl 3-aminocrotonate, mp 30–31° (lit.[33] mp 33°). The nmr spectrum exhibited the vinyl methyl doublet at δ 1.8 ($J \cong 1$ cps) and the vinyl proton quartet at 4.4 ($J \cong 1$ cps).

Hydrogenation of 2,3-Dimethyl-2-carbethoxy-2H-azirene (7b).—In a similar manner 1.6 g (11.4 mmoles) of azirene **7b** was hydrogenated in 1.25 hr. The mixture was filtered and concentrated to a solid mass which on recrystallization from pentane furnished 1.0 g of ethyl 2-methyl-3-aminocrotonate, mp 46–47°. A small sample was sublimed to furnish the analytical sample, mp 47–48° (lit.[33] mp 49–59°). The infrared spectrum exhibited principal bans at 3448 (NH_2), 1639 (ester), and 1605 cm^{-1} (conjugated olefin). The nmr spectrum showed the two vinyl methyl spikes at δ 1.70 and 1.85.

Anal. Calcd for $C_7H_{13}NO_2$: C, 58.70; H, 9.16. Found: C, 58.89; H, 9.11.

Identical results were obtained when 5% palladium or platinum on barium carbonate was used as the catalyst.

Attempted Rearrangement of 3-Methyl-2-carbethoxyaziridine (11).—The aziridine[9] **9** (1.0 g) in 20 ml of tetrahydrofuran containing 200 mg of 5% palladium on charcoal was stirred in a hydrogen atmosphere for 1.25 hr. There was no hydrogen uptake. Filtration and concentration furnished 1 g of the same aziridine having an infrared spectrum superimposable with that of starting material.

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[33] F. C. Meyer, *et al.*, *Ann.*, **314**, 202 (1900).

Haloalkyldihydrotriazines[1]

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Dihydrotriazines have been prepared in yields of up to 46% from the reaction of trihaloacetonitriles or tris-(trihalomethyl)-*s*-triazines with organometallic compounds. These products are high-boiling, viscous liquids. Infrared and nuclear magnetic resonance spectra are discussed as they relate to these novel structures, and, from the products, by-products, and reaction characteristics, a reaction scheme is proposed. Mammalian toxicity of these dihydrotriazines is very high, particularly by skin penetration.

Dihydrotriazines of three general types have been known for several years. These are described in reviews by Smolin and Rapoport[2] and by Modest.[3] In addition, recent work by Bader, *et al.*, demonstrated the formation of dihydro-*s*-triazines as low-yield by-products in the reaction of alkyl Grignard reagents with chloro and alkoxy triazines,[4] and the synthesis of these products by condensation of imidates with O-methylisourea salts and ketones.[5] The reaction is of limited value, however, since yields are moderate and neither the aliphatic methyl ketones nor O-methylisourea could be replaced by other related compounds in the reaction. Newman and Moon[6] prepared two trifluoromethyl substituted dihydrotriazones from dicyandiamide and a Schiff base of trifluoroacetaldehyde.

In studying the action of organometallic reagents on various halogen-substituted materials, it was found that the yields of ketones and ketimines from trihaloacetonitriles were very low and work-up of the reaction yielded high-boiling, viscous oils. These have been identified as dihydrotriazines.

The products were identified by their elemental analyses, molecular weights, infrared spectra, and nmr spectra. The elemental analyses and molecular weights indicated that the structures included three trihaloacetonitrile groups for each hydrocarbon group derived from the organometallic reagent. The infrared spectra of these compounds have bands at 3390 cm^{-1} for an

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[1] Presented before the Third International Symposium on Fluorine Chemistry, Munich, Germany, Aug 1965.

[2] E. M. Smolin and L. Rapoport "*s*-Triazines and Derivatives," Interscience Publishers, Inc., New York, N. Y., 1959.

[3] E. J. Modest in "Heterocyclic Compounds," Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1961, pp 627–719.

[4] H. Bader, E. R. Ruckel, F. X. Markley, C. G. Santangelo, and P. Schickedantz, *J. Org. Chem.*, **30**, 702 (1965).

[5] H. Bader, *ibid*, **30**, 930 (1965).

[6] H. Newman and E. L. Moon, *ibid.*, **29**, 2061 (1964).