In the work-up procedure, aliquots (5 ml) were mixed with pentane (5 ml) and 10% aqueous sodium chloride solution (25 ml). The organic layer was separated, and the aqueous layer was washed with two 5-ml portions of pentane. The last two organic layers were combined and mixed with a dilute aqueous sodium bicarbonate solution (2 ml). The pentane was removed from the collected organic layer by evaporation, and the first organic layer was then added to the residue. The resulting solution was analyzed by vpc. Control experiments showed that this procedure provided quantitative isolation of the products.

The product mixture from 3-hexyne was analyzed using column A at 108° with a helium flow at 25 cc/min. Retention times (minutes) were: 3-hexyne, 2; 3-chloro-*trans*-3-hexene, 4; 3-chloro-*cis*-3-hexene, 5.5; 3-hexanone, 13. The conversion of 3-acetoxy-*trans*-3-hexene to 3-hexanone was followed using column A at 110° with a helium flow of 30 cc/min. Retention times were: 3-hexanone, 7.5; 3-acetoxy-*trans*-3-hexene, 10. Reaction mixture compositions were calculated from the peak ratios (taken as equal to mole ratios), measured with a disk integrator attached to the recorder. It was established that this method was valid by calibration with mixtures of known composition.

In a control experiment it was shown that pure 3-chloro-*cis*-3-hexene treated in 1.16 *M* hydrogen chloride solution at 25° underwent no appreciable isomerization. Similarly, neither chloride C nor T, in a solution of 0.8 *M* hydrogen chloride, or in a solution of 0.8 *M* hydrogen chloride and 0.21 *M* TMAC, showed significant isomerization (more than 1%) after 5 hr at 80°. A solution of 3-hexyne in acetic acid containing 0.214 *M* TMAC showed no product formation after 24 hr at 80°. A pseudo-first-order rate constant of 7×10^{-4} sec^{-1} for conversion of 3-acetoxy-*trans*-3-hexene to 3-hexanone was measured at 25° with initial acetate and hydrogen chloride concentrations of 0.057 and 1.16 *M*, respectively.

Acknowledgment. We thank Professor Charles Perrin for many helpful discussions and suggestions concerning this work.

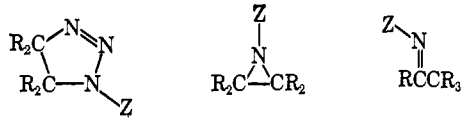
Addition of Electronegatively Substituted Azides to Allenes

R. F. Bleiholder[1a] and H. Shechter[1b]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio. *Received December 11, 1967*

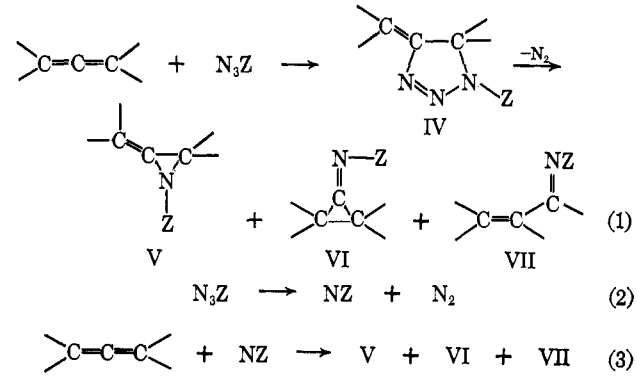
Abstract: Addition of azides to allenes yields alkylidenetriazolines IV and/or isomers of allenimines III. Picryl azide and tetramethylallene (IX) give 4-isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI) which thermolyzes to N-(1,2,3-trimethyl-2-butenylidene)picramide (XII). Reactions of benzenesulfonyl azide and *p*-toluenesulfonyl azide with IX yield N-(1,2,3-trimethyl-2-butenylidene)benzenesulfonamide (XV) and N-(1,2,3-trimethyl-2-butenylidene)*p*-toluenesulfonamide (XVI). The nuclear magnetic resonances of XV and XVI indicate that they suffer severe steric restriction. Thermolysis of ethyl azidoformate in IX results in ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XX) and 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XXI). XXI is formed on photolysis of XX. Irradiation of ethyl azidoformate in 1,1-dimethylallene (XXIV) leads to 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (XXV). The chemistry of the products of reaction of azides and allenes is described.

Olefins react with organic azides to give 1,2,3-Δ^2-triazolines I, aziridines II, and imines III.[2] The aziridines II and the imines III result from decomposition of the 1,2,3-Δ^2-triazolines I or from reaction of the olefins with nitrenes derived from decomposition of the azides.[2]



I II III

The present investigation is concerned with thermal and photochemical reactions of various azides and allenes and studies of the chemistry of the products obtained therein. Objectives of this research include possible (1) addition of azides to allenes (eq 1) to give alkylidenetriazolines IV which can be decomposed to allenimines[3] V, their isomeric cyclopropanonimines[3] VI, or related isomers VII; and (2) capture of nitrenes by



IV

V VI VII

(1)

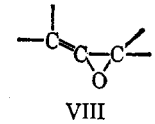
$$N_3Z \longrightarrow NZ + N_2 \quad (2)$$

(3)

(1) (a) Abstracted from the Ph.D. thesis of R. F. Bleiholder, The Ohio State University, Columbus, Ohio, 1966; (b) to whom inquiries should be addressed.

(2) L. Wolff, *Ann.*, **394**, 23, 59, 68 (1912); K. Alder, and G. Stein, *ibid.*, **485**, 211 (1931); **501**, 1 (1933); P. Scheiner and W. R. Vaughan, *J. Org. Chem.*, **26**, 1923 (1961); P. K. Kadaba and J. O. Edwards, *ibid.*, **26**, 2331 (1961); W. Lwowski and T. W. Mattingly, *Tetrahedron Letters*, 277 (1962); W. Lwowski, T. Maricich, and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **85**, 1200 (1963); L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963); F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964); P. Scheiner, J. Schomaker, S. Deming, W. Libbey, and G. Norwack, *ibid.*, **87**, 306 (1965); P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

(3) N-Propylallenimine (A. T. Bottini and R. E. Olsen, *J. Am. Chem. Soc.*, **84**, 195 (1962)) and tetramethylcyclopropanone (N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2775 (1965)) are isolable compounds. Their isomers or structures of type VI and VII are as yet unreported.

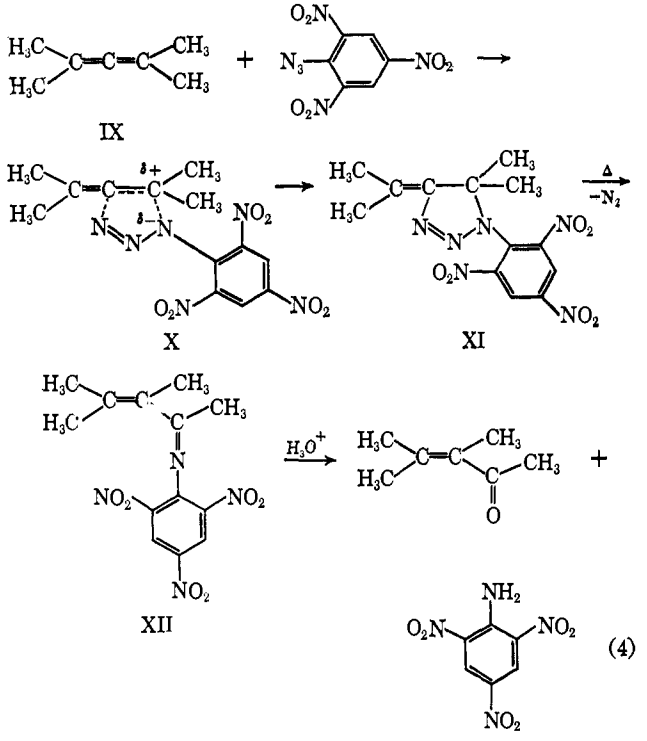


VIII

allenes (eq 2 and 3) to afford a direct synthesis of substituted allenimines[3] V and/or their rearrangement products[3] VI and VII. The systems presently described include reactions of tetramethylallene with the following electronegatively substituted azides: picryl azide, *p*-nitrophenyl azide, phenyl azide, benzenesulfonyl azide, *p*-toluenesulfonyl azide, and ethyl azidoformate. The study also includes determination of the structure of the product of photolysis of ethyl azidoformate and the unsymmetrical allene, 1,1-dimethylallene. The information obtained from this investigation is summarized as follows.

Discussion of Results

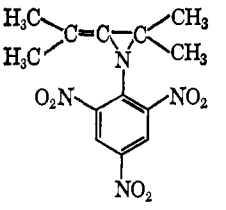
Reactions of Tetramethylallene with Picryl Azide, *p*-Nitrophenyl Azide, and Phenyl Azide. Picryl azide and excess tetramethylallene (IX) react in chloroform at 25° in 6 hr (eq 4) to give 4-isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI, red crystals) in 72% yield. The reaction falls within the type known as "1,3-dipolar additions"[4,5] and probably involves a transition state such as X in which there is stabilization of the partial negative charge on α-nitrogen by the electron-withdrawing 2,4,6-trinitrophenyl group and of the positive charge on the tertiary carbon by the electron-donor effects of the methyl groups. The structure of



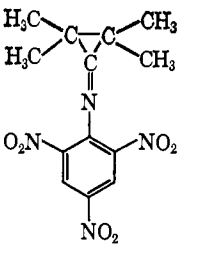
(4)

XI is confirmed by its analysis, spectroscopic properties, nuclear magnetic resonance, and subsequent chemistry.

Thermal decomposition of XI in 95% ethanol gives N-(1,2,3-trimethyl-2-butenylidene)picramide (XII, 65%) as derived by loss of nitrogen and migration of a methyl group. The rearrangement product is also obtained by thermolysis of XI in ethyl acetate.[6] The structure of XII is deduced from its analysis, its spectroscopic and nuclear magnetic properties, and its hydrolysis (eq 4) under acidic conditions to 3,4-dimethyl-3-penten-2-one (isolated as its 2,4-dinitrophenylhydrazone, 66%) and picramide (50%). Photolysis of XI did not yield the allenimine XIII or allow isolation or capture of the possible intermediate XIV when photolyzed in acetone or in furan. The theoretical quantity of nitrogen



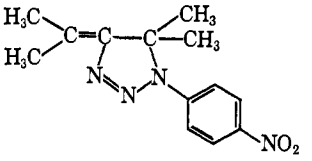
XIII



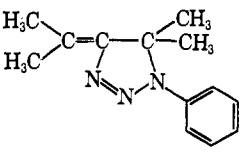
XIV

is evolved; however, the products are as yet not identifiable.

p-Nitrophenyl azide and phenyl azide react slowly with refluxing tetramethylallene (IX) to yield 4-isopropylidene-5,5-dimethyl-1-*p*-nitrophenyl-Δ^2-1,2,3-triazoline (XV, 73%) and 4-isopropylidene-5,5-dimethyl-1-phenyl-Δ^2-1,2,3-triazoline (XVI, 29%), respectively. The structures of XV and XVI are assigned on the basis of analytical, spectroscopic, and nuclear magnetic resonance data, and by analogy with the product



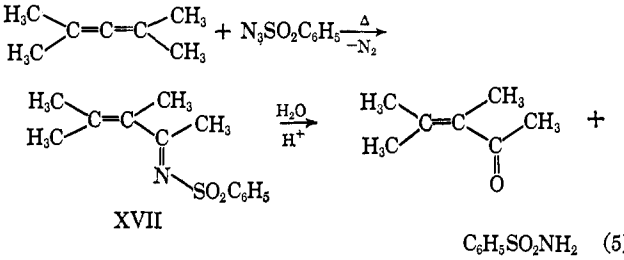
XV



XVI

derived from addition of IX and picryl azide. Adducts XV and XVI are much more stable to heat than is XI; further study of their photolysis and thermolysis products is in progress.

Reactions of Tetramethylallene with Benzenesulfonyl Azide and *p*-Toluenesulfonyl Azide. Benzenesulfonyl azide reacts with excess refluxing tetramethylallene (IX, eq 5) to yield N-(1,2,3-trimethyl-2-butenylidene)-benzenesulfonamide (XVII, 26%). The addition process occurs with loss of nitrogen and carbon-skeleton rearrangement, and the product corresponds in type to that (XII) observed from decomposition of the triazoline XI (eq 4). The structure of XVII is consistent



XVII

$C_6H_5SO_2NH_2$ (5)

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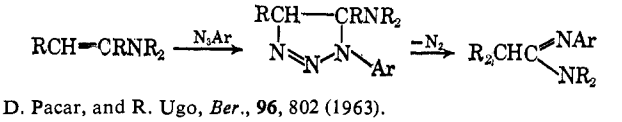
(4) R. Huisgen, *Proc. Chem. Soc.*, 357 (1961).

(5) Picryl azide reacts with strained olefins to form either aziridines or Schiff bases; the possible intermediate triazolines have not been reported: A. S. Bailey, J. J. Merer, and J. E. White, *Chem. Commun.*, 4 (1965).

(6) Migration similar to that found in formation of XII from XI is observed when electronegatively substituted aryl azides or arylsulfonyl azides react with enamines to form amidines: R. Fusco, G. Bianchetti,



D. Pacar, and R. Ugo, *Ber.*, **96**, 802 (1963).

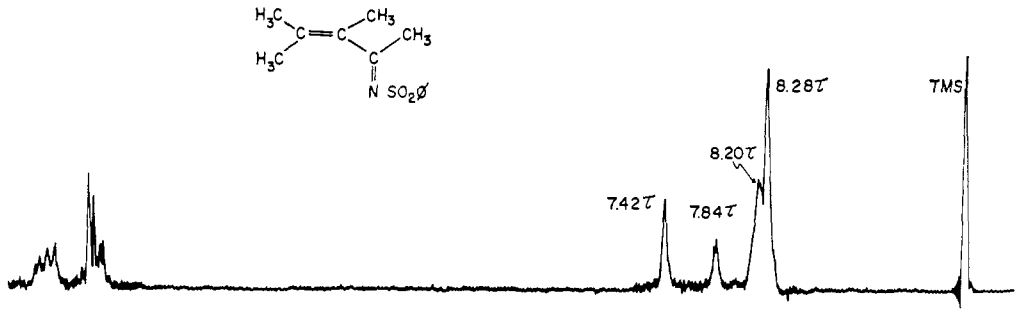


Figure 1. The nuclear magnetic resonance spectrum of XVII at room temperature.

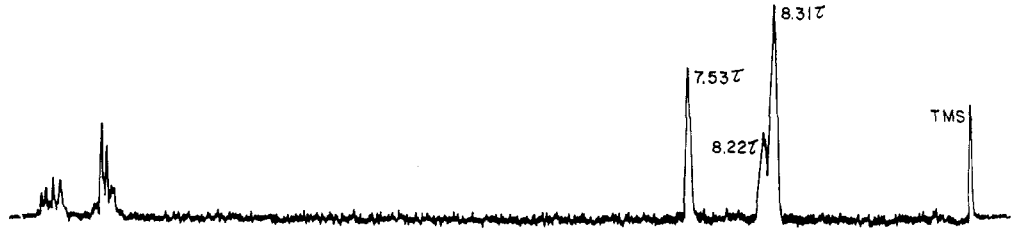
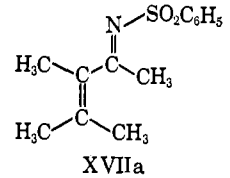


Figure 2. The nuclear magnetic resonance spectrum of XVII at 140°.

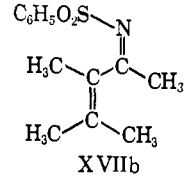
with its infrared (6.10 μ for C=C, 6.22 μ for C=N, and 7.63 and 8.65 μ for $-SO_2-$) and ultraviolet absorption (λ_{max} in 95% ethanol at 209 mμ (ϵ 11,250), 218 mμ (ϵ 12,250), and 277 mμ (ϵ 3880)). Acid-catalyzed hydrolysis of XVII (eq 5) yields 3,4-dimethyl-3-penten-2-one and benzenesulfonamide. The identity of 3,4-dimethyl-3-penten-2-one was established upon comparison (mixture melting point and nuclear magnetic resonance[7]) of its 2,4-dinitrophenylhydrazone with an authentic sample.

Of particular interest are the nuclear magnetic resonance properties of XVII. At room temperature in carbon tetrachloride XVII shows absorptions (Figure 1) for the three methyl groups β and γ to the benzenesulfonimide group at τ 8.29 and 8.20 (nine protons), a singlet at τ 7.84 (one proton), and a doublet at τ 7.42 (two protons) for the methyl group α to the sulfonimide group, and the aromatic multiplets (five protons) at τ 2.52 and 2.12. *It is of note that the ratios of the methyl hydrogens are 9:1:2 at room temperature.* At 140° (Figure 2), the three methyl groups β and γ to the sulfonimide group absorb at τ 8.31 and 8.22 (nine protons); the α-methyl group now absorbs as a singlet at τ 7.53 (three protons); and aromatic multiplets are (five protons) at τ 2.48 and 2.05. *At the elevated temperature the ratios of the methyl hydrogens are 9:3.* Upon cooling the sample to room temperature the original spectrum is obtained.

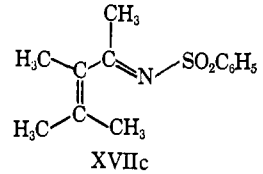
Adduct XVII may exist as two geometric isomers;[8] each isomer can be represented in two principal conformations (XVIIa–d). Of the four, XVIId appears



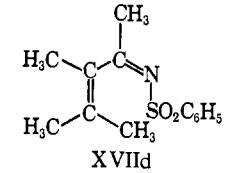
XVIIa



XVIIb



XVIIc



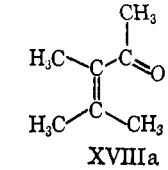
XVIId

to be the most sterically strained and XVIIc the most sterically favored.[9] The observed nuclear magnetic resonance results may possibly be explained by hindered rotation of the α-methyl by the sulfonyl group in XVIIc, the most favored form. If the assumption is correct, the protons on the α-methyl group should be magnetically nonequivalent[10] because of their interaction with the sulfonyl group. The observed *splitting* seems to support this interpretation. The two protons adjacent to the $-SO_2-$ group should be deshielded and

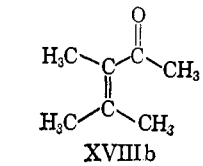
(7) Resonance (in τ values) is displayed for the β- and γ-methyls at 8.20 (nine protons), the α-methyl at 7.82 (three protons, singlet), and the aromatic multiplets at 2.07 (one proton), 1.72 (one proton), and 0.96 (one proton).

(8) The *syn* isomer is defined as the configuration in which the α-methyl is *cis* to the sulfonyl group, and the *anti* isomer as that in which the α-methyl is *trans* to the sulfonyl group.

(9) R. Mecke and K. Noack, *Ber.*, **93**, 210 (1960), have shown that because of steric factors, 3,4-dimethyl-3-penten-2-one exists in a fixed *s-cis* (XVIIIa) rather than a *s-trans* (XVIIIb) form.



XVIIIa



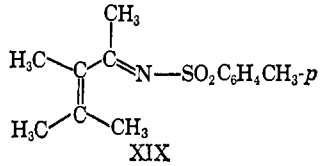
XVIIIb

(10) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

show a signal (τ 7.42) at a lower τ value than the other (τ 7.84). That the signal at τ 7.42 (area 2) is not split may be explained by the nonequivalence (in relation to the oxygen atoms) of the deshielded protons (XVIIc). The deshielded protons may be split by the single proton in such a way that their splittings overlap and only line broadening is observed. At elevated temperatures, sufficient energy can be supplied to the system to allow free rotation of the α-methyl group, thus the singlet at τ 7.53 (area 3). Upon return to room temperature, the initial spectrum is obtained. If the relatively bulky sulfonimide group is replaced by a picrimide or a 2,4-dinitrophenylhydrazone group, the α-methyl appears as a singlet (area 3).

An alternate explanation may be that XVII in solution is a mixture of two geometric isomers. In the *syn* isomer, the α-methyl is deshielded by the $-SO_2-$ group whereas, in the *anti* isomer, deshielding of the α-methyl does not occur. A mixture of two parts *syn* isomer and one part *anti* isomer could give rise to absorptions at τ 7.42 (area 2) and 7.84 (area 1) for the α-methyl group. However, such a mixture does not account for the observed splitting. At higher temperatures, sufficient energy may be added to allow rapid *syn–anti* inversion; thus the methyl is a singlet at τ 7.53 (area 3). Upon cooling to room temperature, the *anti* isomer XVIIc should have the higher population if the structural considerations are correct and thermodynamics finally prevail, and the nuclear magnetic resonance should differ appreciably from the initial spectrum. The observed spectrum is identical however with the initial one at room temperature. Further investigation of the stereochemistry and the nuclear magnetic resonance properties of XVII is in progress.

A study has been made of reaction of *p*-toluenesulfonyl azide and tetramethylallene (IX) to determine if the products and their properties correspond to that obtained from benzenesulfonyl azide and IX. Thermolysis of IX and *p*-toluenesulfonyl azide yields N-(1,2,3-trimethyl-2-butenylidene)-*p*-toluenesulfonamide (XIX) and *p*-toluenesulfonamide (14%). The structure of XIX was deduced from its infrared spectrum (absorptions for C=C at 5.99 μ, C=N at 6.25 μ, and $-SO_2-$ at 7.58 and 8.55 μ), its ultraviolet absorption (λ_{max} in 95% ethanol at 211 mμ (ϵ 11,200), 229 mμ (ϵ 12,900), and 275 mμ (ϵ 3440)), and its hydrolysis to 3,4-

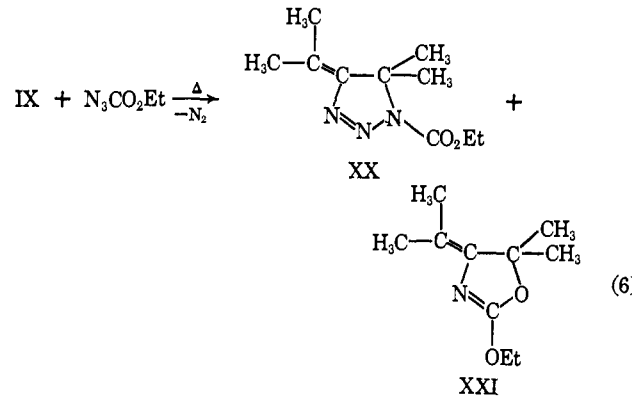


XIX

dimethyl-3-penten-2-one and *p*-toluenesulfonamide. Of particular relevance is that XIX exhibits nuclear magnetic absorptions at τ 8.22 and 8.27 (nine protons) for the methyl groups β and γ to the sulfonimide group, at τ 7.87 (one proton) and 7.43 (two protons) for the α-methyl, a singlet at τ 7.58 (three protons) for the aromatic methyl, and aromatic multiplets at τ 2.73 (two protons) and 2.08 (two protons). The nuclear magnetic resonance of XIX is quite similar to that of XVII, and the reasons for the observed phenomena must be the same in both species.

In reactions of benzenesulfonyl azide and *p*-toluenesulfonyl azide with IX, there is difficulty in determining the over-all mechanisms of formation of XVII and XIX. These products may result from addition of the azides or their derived nitrenes to the allene; the processes differ in whether nitrogen is lost before or after attack on the substrate. The available evidence does not permit elimination of triazolines and N-sulfonylaziridines as intermediates in the formation of XVII and XIX. Transient formation of benzenesulfonylnitrene, $C_6H_5SO_2N$, having the properties of a biradical (the ability to abstract hydrogen), has been reported in decomposition of benzenesulfonyl azide.[11] Isolation of *p*-toluenesulfonamide from reaction of *p*-toluenesulfonyl azide and IX allows supposition of *p*-toluenesulfonylnitrene as an intermediate for at least a portion of the processes involved.

Reaction of Various Allenes and Ethyl Azidoformate. Thermolysis of ethyl azidoformate in refluxing excess tetramethylallene (eq 6) yields ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XX, 38%) and 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XXI, 29%). The triazoline XX appears to be



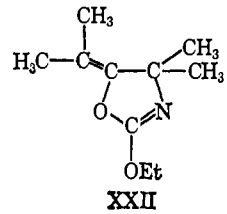
XX

XXI

(6)

formed by 1,3-cycloaddition of ethyl azidoformate to IX. The reaction probably involves a transition state similar to that (X) proposed for addition of picryl azide and IX. The structure of XX is based on mechanistic grounds, its analysis, its infrared absorption, and its nuclear magnetic resonance spectrum. Triazoline XX is not an intermediate leading to XXI; it is recovered quantitatively upon being refluxed in chlorobenzene for 40 hr. Oxazoline XXI is obtained (43%) however by irradiation of XX at 25–30° in hexane.

There are two oxazoline derivatives (XXI and XXII) possible from thermolysis of IX and ethyl azidoformate and by photolysis of XX. That the product is a conjugated alkylideneoxazoline is derivable from its analysis, its infrared absorption (5.91 μ for C=C, 6.10 μ



XXII

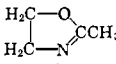
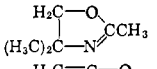
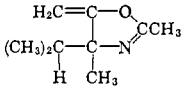
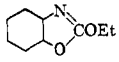
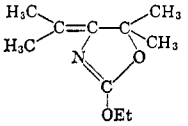
for C=N, and 7.83 μ for C—O stretch), and its ultraviolet properties (λ_{max} in 95% ethanol at 243 mμ (ϵ 13,600)). The nuclear magnetic resonance indicates ring methyls (a singlet at τ 8.48), allylic methyls (singlets

(11) O. C. Dermer and M. T. Edmison, *J. Am. Chem. Soc.*, 77, 70 (1955); J. F. Heacock and M. T. Edmison, *ibid.*, 82, 3460 (1960).

at τ 8.33 and 8.27), and an ethoxyl group (a triplet at τ 8.66 and a two-proton quartet at τ 5.72).

The alkylideneoxazoline is believed to have the structure XXI rather than XXII on the basis of infrared (Table I) and ultraviolet spectral evidence. Alkyl substituents on the 4 and 5 positions and an exocyclic

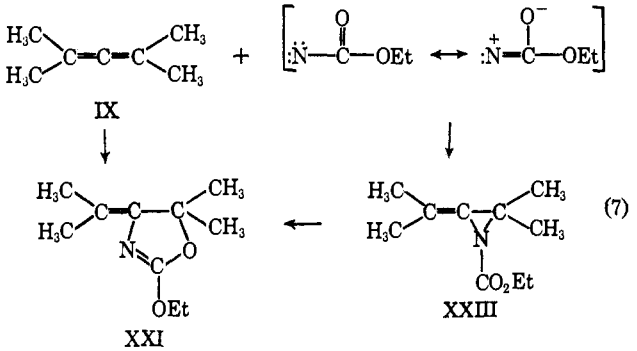
Table I. Infrared Absorption of Substituted 2-Oxazolines

Compound	C=N, cm^{-1} (μ)	C=C, cm^{-1} (μ)
	1678 (5.96)[a]	
	1678 (5.96)[a]	
	1684 (5.94)[b]	1709 (5.85)
	1654 (6.05)[c]	
	1639 (6.10)	1692 (5.91)

[a] P. Bassignana, C. Cogrossi, and M. Gandino, *Spectrochim. Acta*, **19**, 1885 (1963). [b] N. Easton, P. Cassady, and R. Dillard, *J. Org. Chem.*, **30**, 3084 (1965). [c] W. Lwowski and T. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).

double bond on the 5 position of 2-methyl-2-oxazoline have little effect on the C=N frequency of an oxazoline. Substitution of an ethoxyl group on the 2 position lowers the absorption frequency of the C=N bond because of conjugation. The carboethoxynitrene–tetramethylallene adduct is assigned structure XXI in part on the basis of the frequency of its C=N and C=C absorption; the lowering in frequency of absorption for these groups upon comparison with that in oxazolines is attributable to the formal conjugation between the unsaturate centers. *The ultraviolet spectrum of the alkylideneoxazoline in 95% ethanol exhibits a maximum at 234 mμ (ϵ 13,600) which is in agreement with the conjugated structure XXI rather than with XXII.*[12]

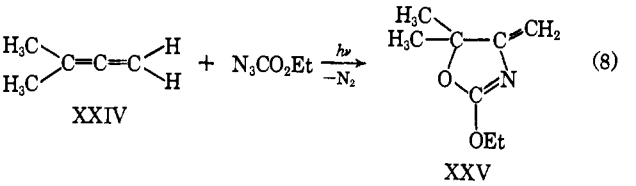
The origin of XXI from thermal reaction of IX and ethyl azidoformate is not established as yet. XXI may result (eq 7) from 1,3-dipolar addition of carbethoxy-



(7)

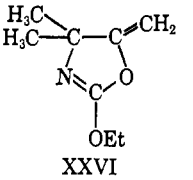
nitrene to IX or by 1,1 addition of the nitrene to yield allenimine XXIII which then rearranges. The mechanism of photolytic conversion of triazoline XX to XXI is also unknown; XXI may be formed directly from XX upon loss of nitrogen, *via* the intermediate allenimine (XXIII) and rearrangement, or by decomposition to IX and carbethoxynitrene and subsequent addition.

An investigation has been made of photolysis of ethyl azidoformate and excess 1,1-dimethylallene (XXIV) in dichloromethane at 0°. Reaction occurs at the more highly substituted double bond of the cumulene to give 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (XXV, 47%, eq 8) by 1,3 cycloaddition of carbethoxynitrene or 1,3 cycloaddition of ethyl azidoformate with loss of nitrogen and rearrangement.



(8)

The product of addition of ethyl azidoformate to XXIV is a methyleneoxazoline. Its nuclear magnetic resonance reveals vinyl protons (at τ 6.05 and 5.50), ring methyls (a singlet at τ 8.58), and an ethoxyl group (a triplet at τ 8.63 and a quartet at τ 5.68). On the basis of its infrared characteristics (6.0 μ for C=C, 6.20 μ for C=N, and 7.18 μ for C—O stretch) and its ultraviolet absorption (λ_{max} in 95% ethanol at 232 mμ (ϵ 11,100)), the adduct is believed to be the conjugated methyleneoxazoline (XXV) rather than XXVI (see Table I). In XXV, C=C and C=N absorptions occur at lower



frequencies than in XXI. This may result from steric strain due to *cis* interaction of an allylic methyl with the methyl groups in the 5 position of XXI resulting in twisting of the double bond. In XXV steric strain is minimal, thus allowing fuller interaction between the conjugated centers and absorptions at lower frequencies.

Experimental Section

Reaction of Picryl Azide with Tetramethylallene (IX). Picryl azide[13] (2.54 g, 0.01 mol) in chloroform (30 ml) was added to a stirred solution of tetramethylallene (IX, 9.60 g, 0.10 mol) in chloroform (20 ml) at room temperature. After 5 hr, the solution turned from yellow to red. The stirring was continued for 2 days. No nitrogen was evolved. The mixture on evaporation *in vacuo* yielded 4-isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI, 2.5 g, 72%), mp 124–125°, as red crystals from 95% ethanol. The infrared spectrum of XI exhibits absorptions at 6.02 μ (C=C) and at 6.49 and 7.05 μ (asymmetric and symmetric stretching of nitro groups). The nuclear magnetic resonance shows ring methyls at τ 8.49 (six protons), allylic methyls at τ 7.99 (three protons) and 7.70 (three protons), and aromatic protons at τ 2.66 (two protons).

Anal. Calcd for $C_{13}H_{14}N_6O_6$: C, 44.60; H, 4.00; N, 24.00. Found: C, 44.74; H, 4.07; N, 23.87.

Thermolysis of 4-Isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI). 4-Isopropylidene-5,5-dimethyl-1-picryl-Δ^2-1,2,3-triazoline (XI, 1.0 g, 0.00286 mol) was refluxed in 95% ethanol (50 ml) for 0.5 hr and then evaporated *in vacuo* to yield N-(1,2,3-trimethyl-2-butenylidene)picramide (XII, 0.60 g, 65%), mp 121–123°, yellow crystals from 95% ethanol–water. XII displays infrared absorption for C=C at 5.99 μ and for C=N at 6.17 μ. Its nuclear magnetic resonance indicates absorptions at τ 8.19 and 8.12 (nine

(12) E. A. Braude, *Ann. Rept. Progr. Chem.*, **41**, 105 (1945), reported ultraviolet maxima for the C=CC=N group at 219 mμ (ϵ 25,000) and for the C=CC=NOH group with two substituents at 235 mμ.

(13) B. Schrader, *Ber.*, **50**, 777 (1917).

protons) for the three methyl groups β and γ to the picrimide group and at τ 7.71 (three protons) for the methyl group α to the picrimide group.

Anal. Calcd for $C_{13}H_{14}N_4O_6$: C, 48.45; H, 4.38; N, 17.39. Found: C, 48.56; H, 4.38; N, 17.09.

Hydrolysis of N-(1,2,3-Trimethyl-2-butenylidene)picramide (XII). N-(1,2,3-Trimethyl-2-butenylidene)picramide (XII, 0.032 g, 0.0001 mol) in a 50:50 mixture of 95% ethanol–water (5 ml) and concentratcd hydrochloric acid (six drops) was heated with steam for 1 hr and then cooled. Filtration yielded picramide (0.01 g, 50%), mp 185–186° (lit.[14] mp 187–188°); its melting point on admixture with an authentic sample gave no depression. To the filtrate was added 2,4-dinitrophenylhydrazine (0.10 g, 0.005 mol). After the mixture had been stored overnight, the red 2,4-dinitrophenylhydrazone of 3,4-dimethyl-3-penten-2-one was filtered. Recrystallization from 95% ethanol gave the derivative (0.019 g, 66%) having mp 127–128° (lit.[15] mp 129°). Its melting point is not depressed by an authentic sample.

Reaction of *p*-Nitrophenyl Azide with Tetramethylallene (IX). *p*-Nitrophenyl azide[16] (4.92 g, 0.03 mol) and tetramethylallene (IX, 20.0 g, 0.21 mol) were refluxed in a 50:50 mixture (60 ml) of ethyl acetate–petroleum ether (bp 65–110°) until the infrared absorption for the azide had disappeared. 4-Isopropylidene-5,5-dimethyl-1-*p*-nitrophenyl-Δ^2-1,2,3-triazoline (XV, 5.7 g, 73%) precipitated from solution, and upon crystallization from chloroform and petroleum ether (bp 30–60°) gave yellow needles, mp 187–188°; infrared absorption for C=C at 6.01 μ.

Anal. Calcd for $C_{13}H_{16}N_4O_2$: C, 60.00; H, 6.15; N, 21.50. Found: C, 59.82; H, 6.15; N, 21.36.

Reaction of Phenyl Azide with Tetramethylallene (IX). Phenyl azide[17] (3.57 g, 0.03 mol) and tetramethylallene (IX, 15.0 g, 0.16 mol) were refluxed for 4 days. Evaporation of the mixture *in vacuo* gave a brown residue which upon chromatography on silica gel, elution with 50:50 ethyl ether–petroleum ether (bp 30–60°), and recrystallization at −80° from petroleum ether yielded 4-isopropylidene-5,5-dimethyl-1-phenyl-Δ^2-1,2,3-triazoline (XVI, 1.60 g, 29%), mp 66–67°. The adduct exhibits C=C absorption at 6.0 μ; its nuclear magnetic resonance spectrum shows ring methyls as a singlet at τ 8.43 (six protons), allylic methyls as singlets at τ 8.08 (three protons) and at 7.85 (three protons), and an aromatic multiplet at τ 2.47 (five protons).

Anal. Calcd for $C_{13}H_{17}N$: C, 72.52; H, 7.96; N, 19.52. Found: C, 72.45; H, 7.91; N, 19.46.

Reaction of Benzenesulfonyl Azide with Tetramethylallene (IX). A stirred solution of tetramethylallene (IX, 13.0 g, 0.135 mol) and benzenesulfonyl azide[11] (4.60 g, 0.025 mol) was refluxed until the theoretical nitrogen had been evolved. The mixture was evaporated. Ligroin (100 ml, bp 30–60°) was added to the brown residue and the solution stored at 5° until white crystals (1.60 g, 26%) were formed. Recrystallization of the solid from 95% ethanol gave N-(1,2,3-trimethyl-2-butenylidene)benzenesulfonamide (XVII, 1.40 g, 22%), mp 72–73°.

Anal. Calcd for $C_{13}H_{17}O_2NS$: C, 62.15; H, 6.77; N, 5.58. Found: C, 62.14; H, 6.91; N, 5.59.

Hydrolysis of N-(1,2,3-Trimethyl-2-butenylidene)benzenesulfonamide (XVII). N-(1,2,3-Trimethyl-2-butenylidene)benzenesulfonamide (XVII, 0.50 g, 0.002 mol) in a 50:50 mixture of 95% ethanol–water (5 ml) and concentrated hydrochloric acid (five drops) was heated with steam for 1 hr and then cooled. The precipitate was identified as benzenesulfonamide (0.23 g, 73%) by its infrared absorption and its undepressed mixture melting point.

2,4-Dinitrophenylhydrazine (0.40 g, 0.002 mol) was added to the filtrate. The red derivative was recrystallized from 95% ethanol and identified as 3,4-dimethyl-3-penten-2-one 2,4-dinitrophenylhydrazone (0.4 g, 69%) by its analysis, melting point (127–128°; lit.[15] mp 129°), and undepressed melting point on admixture with an authentic sample.

Reaction of *p*-Toluenesulfonyl Azide with Tetramethylallene (IX). A stirred solution of tetramethylallene (IX, 48.0 g, 0.50 mol) and *p*-toluenesulfonyl azide[18] (19.7 g, 0.10 mol) was refluxed. After the theoretical amount of nitrogen had been evolved, the mixture was concentrated, and the residue dissolved in carbon tetrachloride. A white solid (2.2 g, 14%) precipitated which was recrystallized from an ether–carbon tetrachloride mixture to give *p*-toluenesulfonamide (2.0 g), mp 135–136°. The product is identical in its infrared absorption with *p*-toluenesulfonamide, and a mixture melting point, 135–136°, gives no depression.

Evaporation of the filtrate and storage of the residue in ligroin (100 ml, bp 30–60°) yielded a white solid (9.4 g, 36%) which on crystallization from 95% ethanol gave N-(1,2,3-trimethyl-2-butenylidene)-*p*-toluenesulfonamide (XIX), mp 75–76°.

Anal. Calcd for $C_{14}H_{19}O_2NS$: C, 63.40; H, 7.18; N, 5.78; mol wt, 265. Found: C, 63.46; H, 7.34; N, 5.06; mol wt (in chloroform), 250.

Hydrolysis of N-(1,2,3-Trimethyl-2-butenylidene)-*p*-toluenesulfonamide (XIX). N-(1,2,3-Trimethyl-2-butenylidene)-*p*-toluenesulfonamide (XIX, 0.10 g, 0.00038 mol) in a 50:50 mixture of 95% ethanol–water (5 ml) and concentrated hydrochloric acid (three drops) was heated at 100° for 1 hr. The solution was cooled and *p*-toluenesulfonamide (0.04 g, 61%) separated. The product is identical with an authentic sample in its infrared absorption, and a mixture melting point, mp 135–136°, shows no depression.

Addition of 2,4-dinitrophenylhydrazine (0.10 g, 0.0005 mol) to the filtrate yielded a red derivative which upon recrystallization from 95% ethanol was identified as 3,4-dimethyl-3-penten-2-one 2,4-dinitrophenylhydrazone (0.06 g, 55%), mp 127–128°. A mixture melting point with an authentic sample of the 2,4-dinitrophenylhydrazone is undepressed.

Reaction of Ethyl Azidoformate with Tetramethylallene (IX). A stirred solution of tetramethylallene (IX, 96.0 g, 1.0 mol) and ethyl azidoformate[19] (41.4 g, 0.36 mol) was heated at 130°. When no further evolution of nitrogen was observed, the product was distilled in two fractions: (1) 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XX, 19.3 g, 29%), 46° (1 mm), and (2) ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI, 28.6 g, 38%), 91° (1 mm). The residue was an orange viscous liquid which could not be distilled.

Ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI) upon standing at 5° solidified and crystallized from 95% ethanol as white crystals, mp 36°. Its infrared spectrum reveals no N–H absorption, but carbonyl and olefinic absorptions occur at 5.82 and 5.98 μ, respectively. The nuclear magnetic resonance shows ring methyls at τ 8.42, allylic methyls at τ 8.05 and 7.84, and an ethoxyl group as a triplet at τ 8.67 and a quartet at τ 5.75 (two protons).

Anal. Calcd for $C_{10}H_{17}O_2N_3$: C, 56.85; H, 8.11; N, 19.87. Found: C, 56.93; H, 8.19; N, 20.11.

Analytical and spectral samples of 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XX) were collected from a chromatography column of Carbowax 20M on Chromsorb P45/60 at 170°.

Anal. Calcd for $C_{10}H_{17}O_2N$: C, 65.57; H, 9.29; N, 7.65. Found: C, 65.33; H, 9.00; N, 7.82.

Thermolysis of Ethyl 4-Isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI). Ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI, 1.06 g, 0.005 mol) was refluxed in chlorobenzene (20 ml) for 40 hr. There was no nitrogen evolved. The starting triazoline was quantitatively recovered; its infrared absorption is identical with that of the initial material.

Photolysis of Ethyl 4-Isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI). Ethyl 4-isopropylidene-5,5-dimethyl-Δ^2-1,2,3-triazoline-1-carboxylate (XXI, 1.06 g, 0.005 mol) in hexane (500 ml) was irradiated at room temperature with a Hanovia 450-W mercury immersion lamp (Type L; 679 A-36) until the theoretical amount of nitrogen was evolved (12 hr). The hexane was distilled. The residue (0.84 g) yielded 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XX, 0.39 g, 43%) and four other components[20] upon preparative gas chromatography on a column of Carbowax 20M on Chromsorb P45/60 at 150°.

The 2-ethoxy-4-isopropylidene-5,5-dimethyl-2-oxazoline (XX) was identified by having the same infrared absorption and the same retention time on a Carbowax 29M on Chromsorb P45/60

(14) R. LeFevre, D. Moir, and E. Turner, *J. Chem. Soc.*, 2337 (1927).

(15) R. Heilmann, G. de Gaudemaris, and K. Noack, *Bull. Soc. Chim. France*, **21**, 993 (1954).

(16) Prepared by adaptation of the procedure of P. A. S. Smith and J. H. Boyer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 75.

(17) R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 710.

(18) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

(19) M. O. Forster and H. E. Fiez, *J. Chem. Soc.*, **93**, 81 (1908).

(20) The four components could not be collected in sufficient yield to determine their identities. Their infrared spectra exhibited N—H and C=O absorptions.

gas chromatography column as the oxazoline obtained by thermolysis of ethyl azidoformate in tetramethylallene.

Photolysis of Ethyl Azidoformate in 1,1-Dimethylallene (XXIV). A stirred solution of 1,1-dimethylallene (XXIV, 34.0 g, 0.50 mol) and ethyl azidoformate (5.60 g, 0.05 mol) in dichloromethane (500 ml) was irradiated at 0°. After the dichloromethane and 1,1-dimethylallene had been removed, the residue was distilled to yield 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (XXV, 3.7 g, 47%), bp 46–47° (2 mm). Analytical and spectral samples were collected from a Carbowax 20M on Chromsorb P45/60 preparative gas chromatography column at 170.

Anal. Calcd for $C_8H_{13}O_2N$: C, 61.91; H, 8.44; N, 9.03. Found: C, 61.83; H, 8.49; N, 9.03.

Acknowledgment. Support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. The authors wish to thank Don T. Dix of The Ohio State University and Thomas Page of the Battelle Memorial Institute for their help in the various nmr problems of this research.

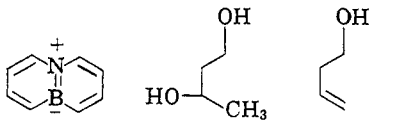
New Heteroaromatic Compounds. XXVIII.[1] Preparation and Properties of 10,9-Borazaronaphthalene[2]

Michael J. S. Dewar and Richard Jones[3]

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received November 2, 1967*

Abstract: The synthesis of 10,9-borazaronaphthalene (I) has been greatly improved and the intermediates have been characterized. The proton nmr spectrum of I has been completely analyzed and its other properties have been studied; I is isomorphous with the isoelectronic naphthalene. Deuteration and bromination of I lead to preferential attack in the 4(5) position as expected theoretically.

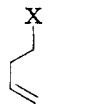
Previous papers of this series[1,4] have described the preparation and properties of a novel series of heteroaromatic compounds, isoelectronic with normal aromatic systems and derived from them by replacement of pairs of adjacent carbon atoms by boron and nitrogen. A comparison of such related aromatic systems present san amusing theoretical problem; however, the comparison is usually complicated by the presence of substituents, since the parent boron-containing compounds would contain the reactive grouping >BH.[5] For this reason 10,9-borazaronaphthalene (I)[6] is of especial interest since the boron atom in it is linked to three atoms other than hydrogen, being at the bridgehead of two fused aromatic rings.



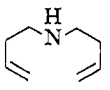
I

II

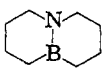
III



IVa, X = Cl
b, X = Br



V



VI

Recently I was prepared[6] in our laboratories by dehydration of 1,3-dihydroxybutane (II) to 4-hydroxy-1-butene (III), conversion of this *via* the chloride (IVa) into di-3-butenylamine (V), hydroboration to 9-aza-10-boradecalin (VI), and dehydrogenation. However, although sufficient material was obtained in this way for its physical properties to be determined and its nmr spectrum measured, the synthesis in its original form was impracticable as a method for preparing I in any quantity. Not only was the over-all yield extremely low but it was not even reproducible, the two final steps being particularly unsatisfactory in this respect. We have now reexamined this route in some detail and effected major improvements in it. While the over-all yield of I from II is still low (0.2%), it is now reproducible, and, in view of the ready availability of II, this now constitutes a practicable procedure for making I in reasonable amounts.

Synthesis of 10,9-Borazaronaphthalene (I)

It soon becomes apparent that much of the trouble lay in the presence of gross impurities in the amine V. These arise partly in the dehydration of II to III, and partly in the conversion of III to V *via* IVa which proceeds in poor over-all yield. We found that a much better yield of amine could be obtained *via* the bromide IVb than *via* IVa, and that most of the impurities in it could be removed by careful fractional distillation through a Teflon spinning-band column.

None of the intermediates in these stages has ever been properly characterized, and glpc showed them to be complex mixtures; even the structure of the key intermediate V had never been established.[7] We there-

(1) Part XXVII: F. A. Davis, M. J. S. Dewar, and R. Jones, *J. Am. Chem. Soc.*, 90, 706 (1968).

(2) This work was supported by a grant from the Robert A. Welch Foundation.

(3) Robert A. Welch Postdoctoral Fellow.

(4) See M. J. S. Dewar, *Progr. Boron Chem.*, 1, 235 (1964).

(5) It is true that the parent borazaro compounds are much less reactive than normal boron hydrides; we have for example found that they do not reduce carbonyl derivatives. However, they are easily oxidized by air and react readily with acids or bases.

(6) M. J. S. Dewar, G. J. Gleicher, and B. P. Robinson, *J. Am. Chem. Soc.*, **86**, 5098 (1964).

(7) W. Reppe, *Ann.*, **596**, 80 (1955), claimed the preparation of V as a by-product from the reaction of 1,4-butenediol with ammonia over