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THE ADDITION OF ARYL AZIDES TO UNSTRAINED OLEFINS

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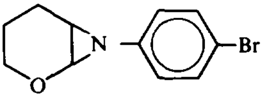
Abstract—Aryl azides have been found to add to unactivated olefins, providing a convenient route to alkyl substituted triazolines. Similarly, conjugated dienes undergo cycloaddition with azides to give 5-vinyltriazoline derivatives. The orientation of the additions accords with previously reported mechanistic considerations, and it appears to be controlled by electronic rather than steric factors.

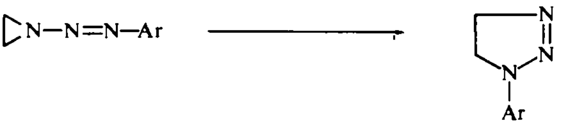
THE photodecomposition of Δ^2-1,2,3-triazolines has been shown to produce aziridines in high yield.[1] In contrast to classical preparative methods, e.g. Wenker and Gabriel procedures,[2] triazoline photolysis is carried out under extremely mild conditions. Any inert, transparent solvent may be employed, and photolysis occurs efficiently at room temperature or below. Thus the method is particularly suitable for the preparation of aziridines that are sensitive to polar reagents and elevated temperatures. Aziridine I, for example, was obtained in 67% yield from the corresponding triazoline.[3] However, for triazoline photolysis to be of general value as a route to aziridines, the triazoline starting materials must themselves be available. The present paper describes the preparation of triazolines from "unactivated" olefins and dienes.

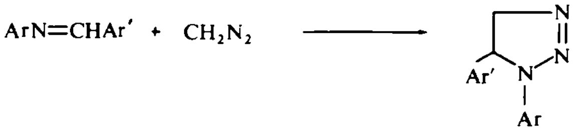


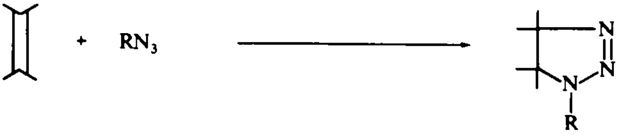
I

Three reactions have been reported to give triazolines. The rearrangement of arylazoaziridines (Eq. 1)[4] is of limited value, due to the inaccessibility and instability of the starting materials. Of greater scope is the cycloaddition of diazomethane, and presumably other diazoalkanes, to Shiff's bases (Eq. 2).[5] Although successful for the preparation of 1,5-diaryltriazolines, it is questionable whether this reaction can be applied to other, less stable, imines. The most promising general route to triazolines involves the addition of azides to olefins (Eq. 3).

First reported in 1912,[6] the reaction of azides with olefinic bonds has subsequently been extended to a variety of substituted[7] and strained olefins.[8] It is notable, however, that linear, unstrained olefins have not been employed. Using cycloalkenes, Alder and Stein[9] observed a dramatic rate-enhancement for angle-strained (winkelgespannte) double bonds, when compared with unstrained cycloalkenes. Thus, while norbornene and, to a lesser degree, cyclopentene added aryl azide rapidly, no adduct

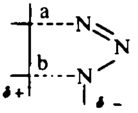

(1)


(2)


(3)

was obtained with cyclohexene. The origin of this phenomenon has not been fully elucidated, but it would appear that Alder's observation of the *relative* sluggishness of unstrained olefins has discouraged further investigation of their reactivity.

Recently, azide-olefin addition has been studied from a mechanistic point of view.[10] The results indicate that the addition of aryl azides to electron-rich olefins* occurs in a concerted manner, proceeding through an electronically unsymmetrical transition state II. In II, bond formation at a has progressed to a greater extent than at b, resulting in the indicated charge imbalance. The polarity of the charge imbalance is reflected by substituent effects in both the azide and olefinic addends, e.g. $\rho = +0{\cdot}84$ for the addition of substituted phenyl azides to norbornene.[10] The high reactivity of enamines[11] and enol ethers[12] is explicable in terms of a resonance interaction of the adjacent heteroatom with the partial positive charge generated in the transition state. Other groups capable of stabilizing the transitional positive charge, hence lowering the activation energy, should also facilitate the reaction. On the other hand, the concerted nature of the addition, evidenced by its stereospecificity[13] and large negative entropy of activation,[10, 8a] suggests a sensitivity to steric factors. However, currently available mechanistic information indicates no *a priori* reason why linear, unactivated olefins should not undergo azide addition.



II

RESULTS AND DISCUSSION

To determine the feasibility of the addition of aryl azides to simple olefins, a series of olefins incorporating varying degrees of alkyl substitution was reacted with *p*-

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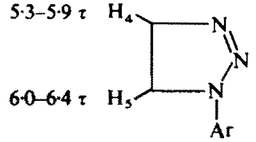
* Simple olefins, and those possessing substituents capable of donating electrons to the double bond. The following discussion does not include electron deficient double bonds, e.g. acrylonitrile.

bromo- and *p*-nitrophenyl azides. The reaction was found to occur quite slowly at room temperature. *p*-Bromophenyl azide in excess 1-hexene, for example, afforded an 89% yield of adduct after 5·5 months at room temperature. At elevated temperatures (>80°), extensive decomposition of the triazoline adducts was observed. This behavior has been noted previously; the thermal instability of triazolines formed from cyanogen azide,[14] picryl azide,[15] and arylsulfonyl azides[16] has thus far precluded their isolation. With aryl azides, however, it was possible to obtain acceptable yields of triazoline, provided that the temperature and time of the reaction were carefully controlled. A generally satisfactory procedure involved treating the azide with excess olefin at temperatures in the range 40–70°, and terminating the reaction after evolution of ca. 20% of the theoretical nitrogen (derived from triazoline decomposition). The data in Table 1 suggest that increased yields are obtained at lower temperatures, but prohibitively long reaction times may be required. Tetramethylethylene failed to undergo addition, either at room temperature or 60°.

The structures assigned to the adducts of unsymmetrical olefins are supported by their NMR spectra. A survey of the chemical shifts for hydrogen adjacent to the azo linkage (H_4) and for hydrogen adjacent to the N-aryl group (H_5) in several symmetrically 4,5-dialkyl substituted triazolines revealed the following ranges: H_4, 5·3–5·9 τ and H_5, 6·0–6·4 τ (cf. Huisgen *et al.*, Ref. 8*b*). Use of these values led to the structures shown in Table 1. (The indicated chemical shifts are not applicable to triazolines possessing substituents other than aryl groups at the 1-position.) The assigned structures accord with reaction *via* transition state II, but they are inconsistent with orientations predicted from steric considerations. As observed with other systems, the orientation of azide addition to electron-rich olefins is controlled by electronic rather than steric factors.[5, 11, 12]



For predictive purposes, the addition may be viewed as occurring in a Markownikoff sense, initiated by electrophilic attack of the terminal azido nitrogen on the olefin. Superficially, that attack which generates the most stable carbonium ion on the olefinic component, predicts the observed orientation in the product. While useful, this predictive rule must be considered only a rough approximation of the operative cycloaddition mechanism. (For a partial exception to the rule, see below.)

Since groups capable of stabilizing the positive charge in transition state II should facilitate the reaction, it was anticipated that conjugated dienes would be reactive with azides.* Thus, while no detectable addition was observed with cyclohexene after 3 months at room temperature, adduct from 1,3-cyclohexadiene and *p*-bromophenylazide began to crystallize in 3 days. A 77% yield of the triazoline was obtained after 18 days at room temperature. Similar rate-enhancement was noted for other dienes (Table 2). The addition of azides to conjugated dienes is of special interest, since, in conjunction with triazoline photolysis, it provides a simple and efficient route to 2-vinylaziridines.[17]

The NMR spectra of the diene adducts showed two vinyl hydrogens in each case.

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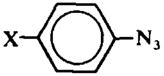
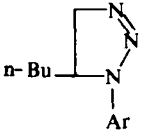
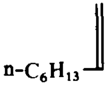
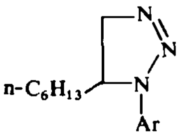
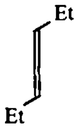
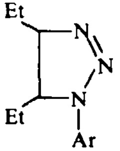
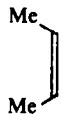
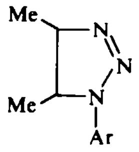
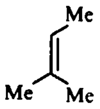
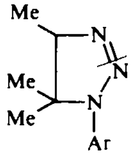
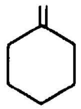
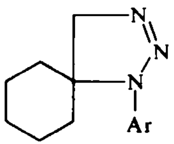
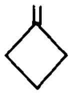
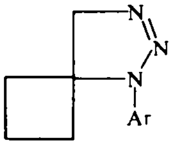
* Alder has described the reaction of isoprene with phenyl azide.[9] No structure was given for the adduct.

TABLE 1. ADDITION OF ARYL AZIDES TO UNSTAINED OLEFINS

Olefin	 X	Triazoline	Yield %[a]	M.P.°	Recryst.[b] Solvent	Analytical Data Calcd./Found C	H	N	Conditions
	Br		43	51–52	A	51·07 50·79	5·72 5·61	14·89 15·0	3 days, 64°
	Cl		89	43	A	60·62 60·34	6·79 6·90	17·68 17·5	5·5 months, room temp
	NO₂		66	105·5–106·5	A	58·05 58·05	6·50 6·57	22·57 22·44	1·5 months, room temp
	Br		79	54–55	A	54·20 54·35	6·50 6·65	13·54 13·66	2 months, room temp
	Br		30	34–35	B	51·07 51·05	5·72 5·75	14·89 14·86	7 days, 55°
	NO₂		53	84–85	A/C	58·05 58·17	6·50 6·47	22·57 22·6	12 hr, 67°

	NO_2		—[c]	109 dec	A/D	54·53 54·48	5·49 5·27	25·44 25·1	4 months, ether soln, room temp
	Br		13	64–65	A	49·27 49·11	5·26 5·32	15·67 15·75	20 days, 38°
	NO_2		30	133–135 dec	A	56·40 56·49	6·02 6·10	23·92 23·8	6 days, 38°
	Br		24	103–104	A	53·07 53·26	5·48 5·52	14·28 14·38	3 days, 69°, n-hexane solvent
	NO_2		23	204–205 dec	E	59·98 60·03	6·20 6·12	21·53 21·59	8 days, 56°, acetone solvent
	Br		13	86–87	B	49·64 49·80	4·55 4·56	15·79 15·69	16 days, 50°, sealed tube
	NO_2		43	158–159 dec	E	56·89 56·73	5·21 5·36	24·13 24·22	6 weeks, room temp

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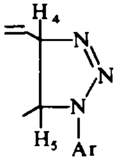
[a] After one recrystallization.

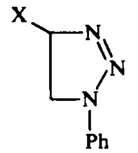
[b] Solvents: A, n-hexane; B, methanol; C, diethyl ether; D, ethyl acetate; E, acetone.

[c] Undetermined.

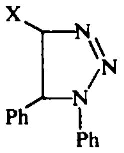
With isoprene and *trans*-piperylene addition therefore occurred at the monosubstituted double bond. The chemical shifts for H_4 and H_5 were again used to determine the orientation of addition. As noted above, hydrogen at position 4 of the triazoline nucleus displays a signal at lower field than hydrogen at the 5-position. The diene adducts, however, showed only complex multiplets (3 H's) from 5·3–5·9 τ, the region of H_4 resonance. The orientations are therefore as depicted in Table 2; the H_5 peaks have been displaced downfield to the H_4 region, due to the presence of the adjacent vinyl group. Had addition occurred in the reverse sense (III), the positions of H_4 and H_5 would have shown a larger than normal separation. The latter effect is apparent in the spectra of the acrylonitrile and methyl acrylate–phenyl azide adducts (IV),[7b] while the styrene and β-methylstyrene–phenyl azide adducts (V)[13b] reveal a downfield displacement of the H_5 signal, similar to that observed for the diene adducts in this study.



III

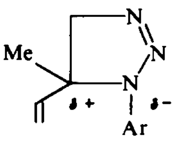


IV, X = CN, CO_2Me

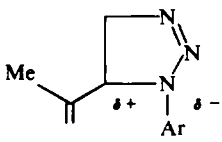


V, X = H, Me

In terms of transition state II, the partial positive charge on the hydrocarbon may be stabilized by delocalization through the conjugated double bond; hence the observed orientation. The additions to isoprene, however, do not strictly follow the predictive rule cited above. Greater stabilization of the positive charge would be anticipated for transition state VI (3°, allylic) than for transition state VII (2°, allylic).



VI

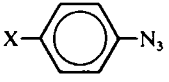
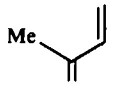
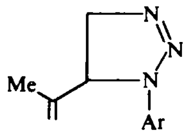
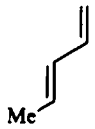
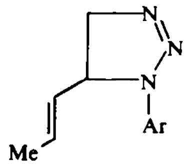
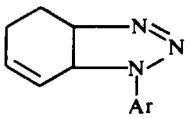


VII

Reaction *via* VII (and not VI) probably results from the increased steric hindrance associated with VI. Stabilization energy gained by the 3°-methyl is apparently more than offset by the steric hindrance of this group; the alternative orientation VII is therefore preferred.

The sensitivity of azide addition to steric hindrance, first noted by Alder[9] and supported by kinetic results,[15] is also reflected by the data in Table 1. Despite longer reaction periods, lower yields were obtained with increased alkyl substitution on the olefin. Steric hindrance to addition and the thermal instability of triazolines thus appear to be the main barriers to triazoline formation. Nevertheless, the results indicate that linear, unstrained olefins and conjugated dienes may be successfully employed in this reaction.

TABLE 2. ADDITION OF ARYL AZIDES TO CONJUGATED DIENES

Diene	 X	Triazoline	Yield %[a]	M.p.°	Recryst.[b] Solvent	Analytical Data Calcd./Found C	H	N	Conditions
	Br		54	115–115·5	A	49·64 49·64	4·55 4·56	15·79 15·79	13 days, 34°
	NO₂		32	142 dec	A/B	56·89 56·75	5·21 5·19	24·13 24·3	7 days, room temp
	Br		42	60·5–61·5	A	[c]			8 days, 43°
	NO₂		22	139–140 dec	A/B	56·89 56·67	5·21 5·02	24·13 24·3	3 days, room temp
	Br		77[d]	113–114 dec	A/B	51·81 51·84	4·35 4·48	15·11 15·1	18 days, room temp
	Cl		74[e]	98–99	C	61·67 61·32	5·18 5·38	17·98 17·8	1 month, room temp

[a] After one recrystallization.
[b] Solvents: A, n-hexane; B, ethyl acetate; C, petroleum ether-diethyl ether.
[c] Adduct too unstable for satisfactory analysis.
[d] 12% after 3 hours at 80°.
[e] Crude yield; 23% after alumina chromatography.

EXPERIMENTAL

NMR spectra were determined in $CDCl_3$ with a Varian A-60 instrument, using TMS as an internal standard. M.ps, uncorrected, were determined with a Fisher–Johns m.p. apparatus.

p-Bromophenyl azide and *p*-nitrophenyl azide were prepared by the method of Smith and Boyer.[18] The olefins were used, without purification, as obtained from commercial suppliers.

The heated reactions described in Tables 1 and 2 were carried out using 0·05 mole of azide and a 3–5 molar excess of olefin; the room temp reactions employed equimolar amounts of azide and olefin. A gas buret was used to measure N_2 evolution in the heated reactions, and heating was discontinued after ca. 20% of the theoretical N_2 was observed. Solvent was then removed under reduced press, and the residue crystallized from an appropriate solvent at −20°.

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