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ADDITION OF HALOGEN AZIDES TO NON-CYCLIC CONJUGATED DIENES

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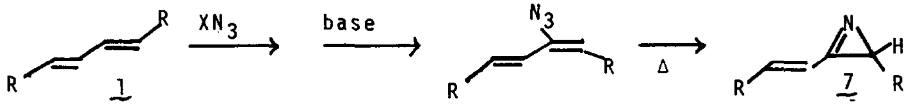
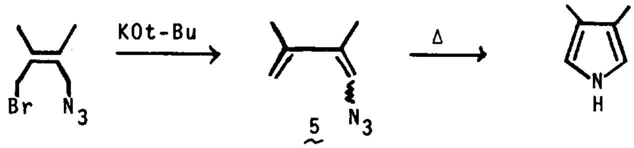
Following the initial discovery[2] of XN_3 additions to multiple bonds, our group[2] and others[3] have investigated the addition of halogen azides to a variety of conjugated and non-conjugated cyclic diene systems. Attempts to add IN_3 to such systems have previously led almost exclusively to unstable diazides, which have not been further utilized. No studies have been reported on the interaction of halogen azides with noncyclic conjugated dienes. These reactions are of interest from the mechanistic point of view, as well as for their potential as a route to novel azirines. For instance XN_3 addition to dienes 1 followed by HX elimination and pyrolysis should provide the as yet unknown[4] 2-vinyl azirines 7 which could act both as a heterodiene or as an azirine in cycloadditions leading to new heterocycles.



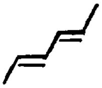
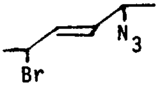
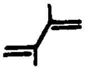
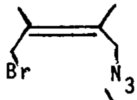
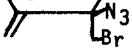
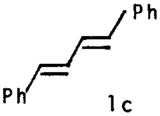
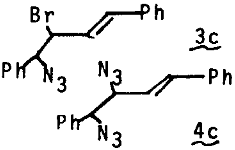
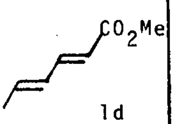
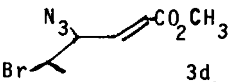
The results of halogen azide additions (chiefly BrN_3) to several non-cyclic diene systems are shown in Table I.[5] Treatment of 1a and 1b with bromine azide[6] at 25°C in pentane affords the 1,4 adducts 2a and 2b respectively. However, low temperature (-70°C) addition of BrN_3 to 1b gives a mixture of 1,4- and 1,2-adducts 2b and 3b, which equilibrates at 25°C to give exclusively the 1,4 adduct 2b. Treatment of 2b with KOt-Bu produces 5 which upon pyrolysis leads to pyrrole 6[7] in 15%. Reaction of diphenylbutadiene 1c with IN_3 gives the stable diazide 4c, mp 68-70°, which is converted by HN_3 elimination and pyrolysis to the vinyl azirine 7, (mp 67-68°). The conjugated azirine structure 7 is in

2b  5 6 + tars

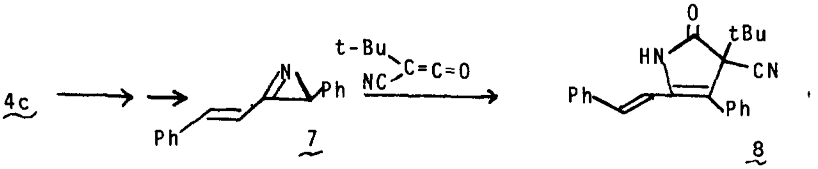
agreememt with its uv (ν_{max} 293 nm) and nmr spectra (singlet at τ6.86).[8] The diazide 4c apparently results from allylic displacement by azide ions on the initially formed IN_3 adduct. Indeed bromoazide 3c is converted to 4c with sodium azide. The overall results suggest that both ionic and free radical addition of XN_3 occur in a 1,2-manner and that the initially formed allylic azides rearrange[9] to the more stable isomer (i.e. 3b ⟶ 2b, but 3c does not rearrange).

Table I

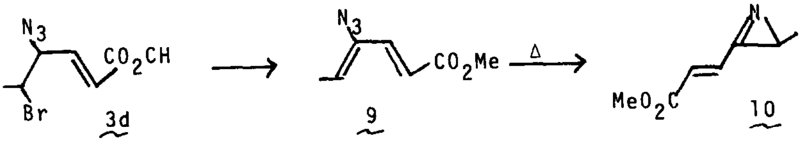
XN_3 Additions to Acylic Dienes 1

Diene	Solvent	Temp.	XN_3	Yield	Product
 1a	Pentane	25°C or -70°C	BrN_3	70%	 2a
	CH_3NO_2 CH_2Cl_2	25°C	BrN_3	65%	
 1b	Pentane	25°	BrN_3	75%	 2b
	Pentane	-70°	BrN_3	75%	 3b
 1c	Pentane	25°	BrN_3	80%	 3c
	CH_3CN	25°	IN_3	60%	4c
 1d	Pentane	25°	BrN_3	—	no reaction
	CH_3NO_2 CH_2Cl_2	25°	BrN_3	80%	 3d

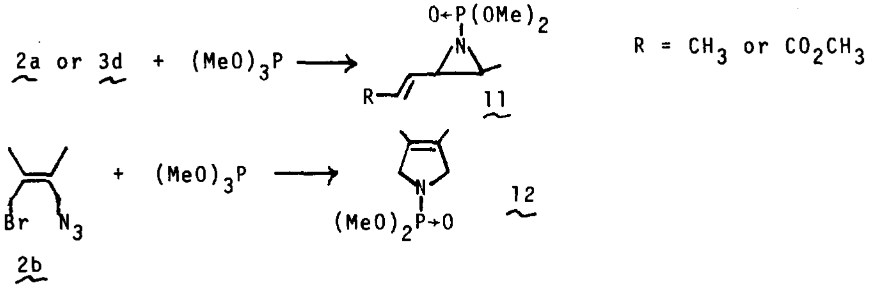
Vinyl azirine 7 proved unreactive toward the dienophiles maleic anhydride, TCNS and dimethyl acetylenedicarboxylate, however, upon reaction with t-butylcyanoketene[10] the pyrrolinone 8, mp 227-230°, was formed.



Methyl sorbade 1d reacts slowly (3 days) with BrN_3 under ionic conditions to give the 1,2 adduct 3d which was subsequently converted to 9 by means of KOt-Bu. Heating of 9 in toluene with a catalytic amount of DABCO[11] resulted in formation of vinyl azirine 10,[5] albeit in low yield.



Furthermore, we succeeded in converting azides 3d as well as 2a to vinyl aziridines 11[5] upon treatment with trimethylphosphite.[12] On the other hand, 2b was transformed to the 3-pyrroline 12.[5]



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3. T. Sasaki, K. Kanematsu and Y. Yukimoto, J. Chem. Soc. Perkin I, 375 (1973); J. Org. Chem., 37, 890 (1972).
4. The only other known 2-vinylazirine, 9-azabicyclo[6.1.0]nona-1(9),2-diene (ref. 2b), is restricted in its reactivity due to steric requirements.
5. Most allylic halides and azides were unstable liquids that slowly decompose at room temperature and were purified by chromatography on alumina. The solids reported here gave correct elemental analyses and all new compounds showed consistent nmr, ir and mass spectra.
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