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SOLVENT PARTICIPATION IN ADDITIONS TO OLEFINS[1a]

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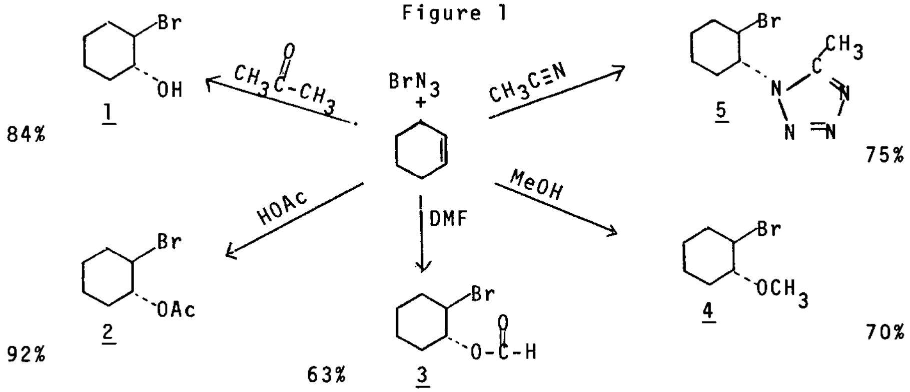
In the course of our study of the addition reactions of bromine azide,[2] we discovered that the solvent can enter into the reaction very readily to give an adduct derived from bromine and solvent.[3] We have been able to adjust reaction conditions so that the incorporation of solvent can occur to the total exclusion of the normal adduct. This provides a synthetically useful procedure for bifunctional compounds. Figure 1 gives the results of some experiments using cyclohexene as the substrate.

Figure 1



The yields are based on isolated pure material except in the case of the reaction in acetic acid, in which case it is based on the nmr analysis of the crude material (quant. yield) which contained 92% bromoacetate and 8% bromoazide adducts. Since bromine azide is prone to free radical addition, care had to be taken to perform the reaction in the dark and to flood the solution with oxygen. Preliminary experiments reveal that chlorine azide exhibits a similar tendency to solvent incorporation though it is more prone to free radical addition than BrN_3.[4a]

The formation of tetrazoles in the addition of BrN_3 in the presence of acetonitrile has received the most attention from us to date and some data are listed in Table 1. These results contrast with IN_3 additions in acetonitrile which proceed entirely without solvent incorporation.[4b]

Since cyclohexene gives only one tetrazole and cis and trans 2-butene give different isomeric tetrazoles, the incorporation of acetonitrile is apparently stereospecific in simple alkenes. The formation of tetrazole can be rationalized as attack of acetonitrile on the incipient three-membered ring bromonium ion to form a Ritter type intermediate, followed by collapse with azide ion and subsequent cyclization[5] of the imino azide to the tetrazole.

The formation of the bromo methoxy derivative arises through attack of methanol on the bromonium ion and subsequent loss of a proton. Methanol has been reported to exhibit a similar tendency but to a lesser degree in bromine additions. The bromoformylation arises as shown below. Indeed, solvolysis reactions in dimethyl formamide have been reported to give formates.[6]

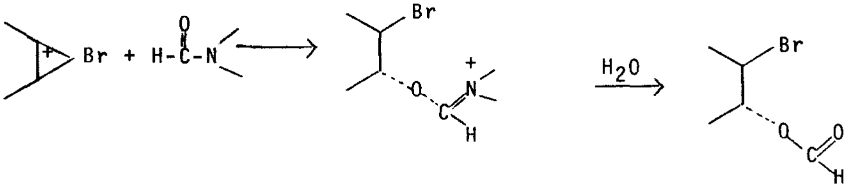
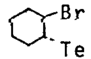
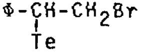
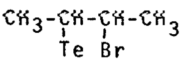
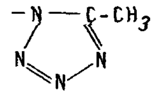


Table 1

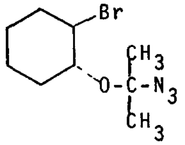
Acetonitrile Incorporation in the Addition of BrN_3 to Olefins

Olefin	Adduct[a]		m.p.	yield
cyclohexene		5	124°	75%
styrene	 $\Phi\text{-}\underset{\text{Te}}{CH}\text{-}CH_2Br$	6	112°	47%
trans 2-butene	 $CH_3\text{-}\underset{\text{Te}}{CH}\text{-}\underset{\text{Br}}{CH}\text{-}CH_3$ erythro	7	91°	22%[b]
cis 2-butene	" threo	8	108°	35%[b]

(a) Te: 

(b) *the remaining product was shown by nmr and ir to be the* BrN_3 adduct.

The addition in acetone to give the bromo alcohol proceeds through the α-azido ether 9 which reacts further with the small amount of water present to give the alcohol. This was proven by the actual isolation of 9, when the addition was performed using carefully dried acetone.[7] Intermediate 9 was obtained



9

in essentially quantitative yield (Calc. for $C_9H_{16}BrON_3$: C 41.23, H 6.15, Found C 41.29, H 6.13, nmr 8.51τ (s, over broad multiplet-14 H), 6.1τ (m broad, 2H); ir 2100 cm^{-1}, 1070 cm^{-1}, no O-H stretch). When 9 was treated with water, acetone and bromo alcohol 7 were formed. The *trans* configuration for 7 was determined by comparison of known derivatives. Alcohols have been isolated from solvolysis reactions with carefully dried solvents when acetone was a co-solvent.[8]

The differences between Br_2 and BrN_3 addition to cyclohexene in acetone, methanol and acetic acid were established (see Table II). Reaction conditions identical to the bromine azide reactions were used and the product ratios were analyzed by integrated intensities of selected non-overlapping proton absorptions in the nmr.

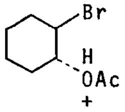
Table II

Addition of Bromine to Cyclohexene in Various Solvents

Solvent	Adduct % Br_2	 % BrOS	Total Yield
1. Acetone	25	75	a
2. Methanol	35	65	96
3. Acetic Acid	74	26	78

a. Principal products were brominated acetones. Percentages given are approx. relative amounts by nmr integrations.

The data from Fig. 1 and Table II clearly indicate that solvent incorporation is much more efficient with BrN_3 than with Br_2. At first this may seem surprising since azide itself is more nucleophilic than bromide,[9] however it is reasonable when one considers the fate of the X portion of BrX in the incorporation reaction. For example, with acetic acid, the intermediate protonated species 10 reacts with X^- to give bromo acetate[3] and HX. When X=Br, hydrobromic



10

acid is formed which is a good source of bromide ion, while when $X=N_3$, hydrazoic acid is formed, which is a relatively poor source of azide ion ($K_a=1.9 \times 10^{-5}$). This view is supported by the findings of van der Linde and Havinga,[10] that in the reaction of Br_2 with phenanthrene in MeOH, dibromide appears only after some HBr is formed from methanol incorporation and by the tendency of N-bromoamides to give solvent incorporation.[11]

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