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FREE RADICAL VS IONIC ADDITIONS OF HALOGEN AZIDES TO OLEFINS[1]

Alfred Hassner and Fred Boerwinkle

Department of Chemistry, University of Colorado, Boulder, Colorado

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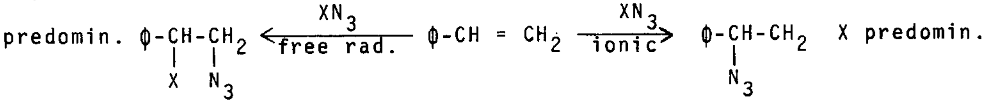
The chemistry of azides is continuing to attract the interest of the organic chemist.[2] Recently it was reported that bromine azide possesses the remarkable attribute of adding to olefins readily and regiospecifically[3] by two different pathways, namely a radical or an ionic process.[4] In an effort to determine if other halogen azides could be induced to behave in a similar fashion and what factors influence this trend we studied the addition of chlorine azide to olefins.

From the electronegativity trend $I<N_3 \approx Br<Cl$, one would expect an increasing amount of homolysis in the halogen azides $IN_3<BrN_3<ClN_3$. Indeed ClN_3 reacts with styrene predominantly as an $N_3\cdot$ radical reagent leading to *2*a, but by adjusting the reaction conditions it can be induced to add via Cl^+ attack on the double bond giving the opposite regioisomer (*1*a).

Iodine azide, which has been reported to react exclusively as an I^+ reagent,[5] can under special conditions (see Table III) be induced to react via an azide radical mechanism.



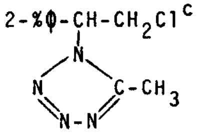
$$\text{predomin.}\ \phi\text{-}\underset{X}{\text{CH}}\text{-}\underset{N_3}{\text{CH}_2} \xleftarrow[\text{free rad.}]{XN_3} \phi\text{-CH} = \text{CH}_2 \xrightarrow[\text{ionic}]{XN_3} \phi\text{-}\underset{N_3}{\text{CH}}\text{-CH}_2\ X\ \text{predomin.}$$

*2*a, R=Cl   *1*a, R=Cl
*2*b, R=Br   *1*b, R=Br
*2*c, R=I   *1*c, R=I

In Tables I, II and III are summarized some data obtained for the addition of ClN_3, BrN_3 and IN_3 to styrene.[6] It is clear that the free radical pathway is enhanced in solvents of low polarity, in the presence of light and in the absence of oxygen (free radical inhibition), while the ionic pathway is prefer-

TABLE I[a]

Effect of Variable Solvent and Reaction Conditions in the Addition of ClN_3 to Styrene at 0°

Conditions	% 2a	% 1a	%ϕ-CH=CH-Cl	%ϕ-$\underset{Cl}{CH}$-$\underset{Cl}{CH_2}$
1. Pentane, air	100	-	-	-
2. CH_2Cl_2, air	100	-	-	-
3. CH_3CN, O_2^b	66	14	2-%ϕ-CH-CH_2Cl^c 	
4. CH_3NO_2, O_2	17	48	23	
5. CH_3NO_2, air, $H_2SO_4\cdot SO_3$ 1 eq.	47	47		
6. CH_3NO_2, O_2, dark, H_2SO_6-SO_3 1 eq.	-	92	8	

a. Percentages given are relative and based on nmr integration; actual yields were 80% or better. b. purged with O_2 at 0 to -15° for 5 min. c. assumed structure from spectral similarity to bromo analog.

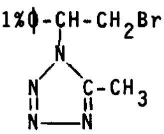
red in polar medium in the presence of O_2. Whereas the character of BrN_3 as an exclusive ionic or a free radical reagent can be adjusted with ease, this can be accomplished only in part under forcing conditions for ClN_3 and IN_3.

The effect of light (reactions 4 and 5 in Table II), although not large, is significant and consistent with a free radical mechanism for the formation of β-azido-α-bromoethylbenzene (2b). The effect of oxygen, under constant light input (reactions 2 and 3, Table II or 1 and 2, Table III), is easily explained by O_2 inhibition of the radical addition.

Both pure β-azido-α-chloro-ethylbenzene (2a) and a 1:1 mixture (by nmr) of 1a and 2a analyzed correctly for $C_8H_8ClN_3$. Furthermore, 2a was treated with KO_t_Bu in ether to give α-chlorostyrene and β-azidostyrene.[7] Evidence that the mixture formed in the addition of iodine azide to styrene (reaction 1, Table III) was as reported, is that elimination of HI with potassium _t_-butylate from the mixture of 39% 2c and 61% 1c gave in 93% yield β-azido and α-azidostyrene

TABLE II

Effect of Variable Solvent and Reaction Conditions in the Addition of BrN_3 to Styrene at 0°

Conditions	% 2b	% 1b	
1. Pentane, N_2	100	-	
2. Ch_2Cl_2,N_2	86	14	
3. CH_2Cl_2,O_2	33	67	
4. CH_2Cl_2, air, light	77	23	
5. CH_2Cl_2, air, dark	50	50	
6. CH_3CN,O_2	9	50	41%  a
7. CH_3CN,N_2	35	40	25% " b
8. CH_3NO_2,N_2	<4	>96	
9. CH_3NO_2,O_2	-	100	

a. crude product; b. pure product

TABLE III

Variable Reaction Conditions in the Addition of IN_3 to Styrene at 0°

Conditions	% *2c*	% *1c*
1. Pentane, N_2	39	61
2. Pentane, O_2	13	87
3. CH_2Cl_2,N_2	12	88
4. CH_3CN	-	100

in a ration of 37:63. Both vinyl azides had previously been synthesized.[4]

Another interesting result is found in the ionic addition of chlorine azide (reactions 4, 5 and 6 in Table I), where fuming sulfuric acid inhibits the formation of the by-products β-chlorostyrene and styrene dichloride. Presumably, this effect arises in part from the inhibition of loss of a proton from the intermediate β-chlorophenethyl cation by the acid, although acid catalyzed HN_3 addition to β-chlorostyrene may also be involved.

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4. A. Hassner and F. Boerwinkle, J. Am. Chem. Soc., *90*, 217 (1968).

5. F. W. Fowler, A. Hassner, L. A. Levy, J. Am. Chem. Soc., *89*, 2077 (1967).

6. Chlorine azide and iodine azide were prepared through the methatetical reactions $Cl_2 + NaN_3 \rightarrow ClN_3 + NaCl$ and $ICl + NaN_3 \rightarrow IN_3 + NaCl$ using similar conditions to those reported for bromine azide,[4] i.e. a heterogeneous mixture of methylene chloride, sodium azide, halogen and a small amount of water. The IN_3 reagent exists only to the extent of approximately 5% in the organic phase, but the reaction can be forced to completion by adding the olefin to the heterogeneous mixture. The organic phase for the addition in pentane or dichloromethane was the respective solvent, for all others, the halogen azide was prepared in dichloromethane (0.05 moles in 100 ml) and added to 0.04 moles of styrene in the reported solvent (300 ml) at 0°.

7. J. H. Boyer, W. E. Krueger, G. J. Mikol, J. Am. Chem. Soc., *89*, 5504 (1967).