

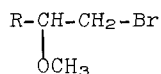
THE REACTIONS OF METHYL HYPOBROMITE AND ACETYL HYPOBROMITE WITH OLEFINS¹

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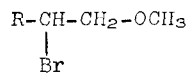
It has recently been shown that certain electrophiles can add to olefins by both molecule-induced radical mechanisms and ionic mechanisms, depending on the conditions. Electrophiles of this type are Cl₂(2), BrN₃(3), and Br₂(4). We wished to determine whether alkyl and acyl hypobromites could add to olefins by both mechanistic pathways. The induced radical addition of t-butyl hypobromite to styrene has already been reported, but an ionic addition reaction for this compound was not observed(5). We decided to investigate the reactions of methyl hypobromite with 1-hexene and styrene, and acetyl hypobromite with 1-hexene under ionic conditions (low concentrations of olefins in the presence of inhibitors such as O₂, or 2,6-di-t-butyl-4-methylphenol, DBMP) and radical conditions (high concentrations of olefins in the absence of inhibitors, under N₂).

The percentages of the methoxybromides formed in the addition of methyl hypobromite to 1-hexene and styrene are listed in Table I, and their structures are shown below:



I, R=C₄H₉

III, R=C₆H₅

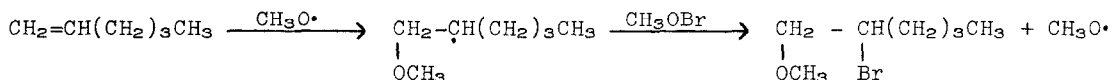


II, R=C₄H₉

IV, R=C₆H₅

The results in Table I suggest that methyl hypobromite adds to 1-hexene by an ionic mechanism under ionic conditions and by a radical mechanism under radical conditions. This is indicated by a large change in product composition with a change in reaction conditions; 1-bromo-2-methoxyhexane (I) is the principal product under ionic conditions (entries 2, 3 and 5), and primarily 2-bromo-1-methoxyhexane (II) is formed under radical conditions (entries 1, 4, and 6).

Formation of I would be expected under ionic conditions by analogy to the bromination of 1-hexene in methanol (ionic conditions) where I is the principal methoxybromide (I, 82%, II, 18%). As outlined in the following equation, II should be formed in a radical reaction (see ref. 3):



The radical mechanism for the reaction at high mole fraction (entries 1 and 4) was further substantiated by the observation that the addition of cyclohexane to the reaction mixture resulted in the formation of large amounts of cyclohexyl bromide. No cyclohexyl bromide was detected under ionic conditions.

TABLE I. REACTION OF METHYL HYPOBROMITE WITH 1-HEXENE AND STYRENE.

Entry	Olefin	Conc. ^a	Conditions ^b	Methoxybromides (%) ^c		Yield (%) ^d
				I and III	II and IV	
1	1-Hexene	0.8	N ₂ , -30°	29	71	
2	1-Hexene	0.02	O ₂ , -30°	71	29	9
3	1-Hexene	0.02	N ₂ , DBMP, -30°	71	29	36
4	1-Hexene	0.8	N ₂ , 0°	15	85	20 ^e
5	1-Hexene	0.02	O ₂ , 0°	71	29	
6	1-Hexene	0.8	N ₂ , light	13	87	
7	Styrene	0.8	N ₂ , -30°	0	100	66
8	Styrene	0.8	N ₂ , -30°	31	69	
9	Styrene	0.02	O ₂ , -30°	95	5	38
10	Styrene	0.02	N ₂ , DBMP, -30°	95	5	50
11	Styrene	0.02	N ₂ , 0°	19	81	
12	Styrene	0.02	O ₂ , 0°	79	21	

^a Expressed as the mole fraction of olefin. ^b All reactions were conducted in the dark except for entry 6. The solvent is dichloromethane. ^c Refers to the percentage composition of the methoxybromide product. ^d Refers to the total yield of methoxybromides based on the CH₃OBr that reacted. ^e The principal products in this reaction are 3-bromo-1-hexene (13%) and 1-bromo-2-hexene (38%).

The results from the addition of methyl hypobromite to styrene dramatically confirm the fact that the mechanism of addition for this reagent can be changed by altering the reaction conditions. 2-Bromo-1-methoxyphenylethane (III) would be anticipated as the predominate product under ionic conditions because of the

stability of the intermediate benzylic carbonium ion (entries 9, 10, and 12). Again, as mentioned for 1-hexene, 1-bromo-2-methoxyphenylethane(IV) would be expected from a radical reaction (entry 7). Entries 8, 11, and 12 suggest that styrene reacts with methyl hypobromite by a radical mechanism more readily than 1-hexene.

Detailed studies on the addition of acetyl hypobromite to 1-hexene indicate that this electrophile reacts with 1-hexene exclusively by an ionic mechanism. For example, a radical reaction could not be detected at high mole fraction of olefin (0.8) and under illumination and the inhibitor, DBMP, had no effect on the product ratio(6). The absence of a radical reaction was established by the fact that the ratio of the acetoxybromides was not changed under any of the conditions that were studied. Also, addition of acetyl hypobromite to 1-hexene at high mole fraction (and with illumination) in the presence of cyclohexane did not produce cyclohexyl bromide. The percentages of 1-bromo-2-acetoxyhexane and 1-acetoxy-2-bromohexane are, respectively: 60% and 40%.

The difference in the reactivities of acetyl and methyl hypobromite toward identical olefins is noteworthy. The fact that acetyl hypobromite reacts only by an ionic pathway could be due to an extremely rapid ionic addition or to a very slow radical reaction. The acetate ion which is involved in an ionic addition of acetyl hypobromite is considerably less basic than the methoxide ion from methyl hypobromite, and consequently an ionic addition for acetyl hypobromite would be favored. On the other hand, anion formation can not be the sole explanation for this difference since bromide ion (from Br_2) and chloride ion (from Cl_2) are very weak bases, whereas the azide ion (from BrN_3) is a very strong base, and still molecule-induced radical additions occur in all these cases. We are currently investigating this problem.

Under ionic conditions methyl hypobromite reacts with 1-hexene and styrene to produce some 1,2-dibromohexane and styrene dibromide(7). We have not established the source of the dibromides, but have confirmed that they do not arise from residual bromine in the methyl hypobromite. We are investigating the source of the dibromides.

Methyl hypobromite was prepared by adding methanol in CH_2Cl_2 to aqueous hypobromous acid from which bromine had been removed. The exclusive presence of methyl hypobromite in solution was established by the following analyses:

nmr (singlet, 6.15τ); ir ($\text{CH}_3\text{O}-$, 2820 cm^{-1}); uv ($280\text{ m}\mu$, $\epsilon = 61$); gravimetric bromide and iodometric titration. Methyl hypobromite was found to be stable for at least 24 hours in the dark at ice-alcohol temperatures. It was unequivocally established that the methoxybromides do not result from a rapid decomposition of methyl hypobromite to bromine and methanol, followed by addition of the latter to the olefins(8). The synthesis of acetyl hypobromite has already been reported(9). The isomeric bromomethoxyhexanes (I and II) were prepared as previously described(10). All other products were synthesized unambiguously, and their structures established by ir, and in some cases nmr. Their presences in the reaction products were confirmed by the peak enhancement method. All analyses were performed by vpc.

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8. Bromination of 1-hexene in CH_2Cl_2 which contained an amount of methanol equal to that which would be expected from decomposition of methyl hypobromite gave 96% dibromide and 4% methoxybromide. Under ionic conditions the ratio of dibromide to methoxybromide from methyl hypobromite was approximately 1:1.
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