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THE REACTIONS OF HYPOCHLORITES WITH OLEFINS IN NITROMETHANE

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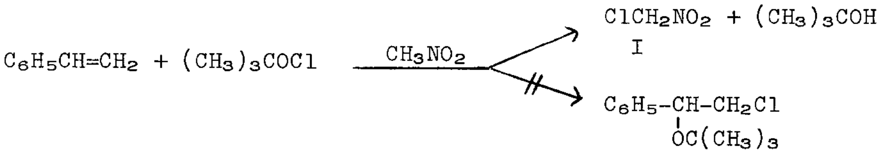
In a recent attempt to add t-butyl hypochlorite to olefins such as styrene and 1-hexene in nitromethane, we were surprised to find that the exclusive products of these rapid reactions are chloronitromethane ($ClCH_2NO_2$,I) and t-butyl alcohol in nearly quantitative yield. This reaction is outlined in the following equation:



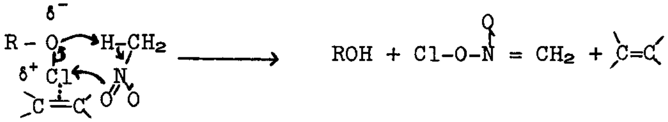
Methyl and ethyl hypochlorite also react with these olefins to give only I. We have shown conclusively that the hypochlorites and nitromethane do not give more than a few per cent of I in the absence of the olefin. For example, when methyl hypochlorite and nitromethane are mixed at 0°C, approximately 4% of I is formed immediately, but there is no further increase in the amount of I for days. Similarly, t-butyl hypochlorite and nitromethane at 0°C react immediately to give 1-2% of I, and the resulting solution was stable indefinitely at 0°C. A slow loss in oxidant was observed at room temperature over several days, but without further increase in I.

The olefins evidently function as catalysts in these reactions since in the reaction of methyl hypochlorite and styrene, the latter was recovered quantitatively. The catalytic role of the olefin is dramatically indicated by the fact that a molar ratio of 1-hexene: t-butyl hypochlorite of 1:14 resulted in complete consumption of the hypochlorite and formation of I in 86% yield. Alcohols do not have a catalytic effect in these reactions.

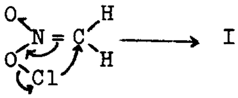
Additional exploratory studies on the reactions of hypochlorites, olefins and nitroalkanes reveal the following facts: (a) we have qualitatively observed that the rate of the reaction increases with an increase in the basicity of the olefin. For example, the reaction rate is extremely rapid with tetramethylethylene, and no reaction occurs with 1,2-dichloroethylene. 1-Hexene gives a rate which is intermediate between these two olefins. (b) Reactions other than formation of I may occur with certain olefins. α-Methylstyrene, methyl hypochlorite, and nitromethane give both formation of I and substitution of chlorine on the double bond in the ratio of 6 to 1. Tetramethylethylene reacts rapidly with t-butyl hypochlorite, as indicated above, but does not give any I. By analogy to the reaction of chlorine and tetramethylethylene, substitution on the double bond probably occurs(1). (c) Active aromatic compounds catalyze the reaction of nitromethane and t-butyl hypochlorite to give I, and/or undergo substitution on the ring, as is indicated by the following data: naphthalene, I(92%); anisole, I(10%) and chloroanisole (75%); m-xylene, I(75%) and chloro-m-xylene (12%); p-xylene, I(50%) and chloro-p-xylene (21%). (d) Chlorine and acetyl hypochlorite react with 1-hexene in nitromethane to give exclusively addition to the double bond. (e) Nitroethane reacts similarly to nitromethane. Styrene and nitroethane reacted with methyl and t-butyl hypochlorite to give chloronitroethane in 67% and 70% yields, respectively.

The reactions described above appear to occur by ionic rather than radical mechanisms. Some evidence for this is summarized below. All of the reactions were carried out at low olefin concentrations to discourage radical formation, and gave identical results under O_2 or N_2. At high styrene concentrations in nitromethane, methyl hypochlorite reacted to form both I and 1-chloro-2-methoxyphenylethane. Under these conditions, the methoxy radical probably formed by molecule-induced homolysis, and added to the double bond of the olefin(2). However, if O_2 is present, only I is formed. The assumption can be made that the methoxy radical is not present with O_2 as an inhibitor, and therefore I is not formed by a radical substitution reaction. Further evidence against a radical mechanism is provided by the reaction of t-butyl hypochlorite and 1-hexene in nitromethane, which leads exclusively to I. If the t-butoxy radical were present, abstraction of the allylic hydrogen should be the predominant reaction(3) producing primarily 1-chloro-2-hexene. This compound was not found in detectable amounts.

At this stage in the investigation, we are inclined to accept a mechanism which involves π-complex formation between the olefin and the hypochlorite, resulting in a polarized halogen-oxygen bond. The polarized Cl-O-bond can then react with nitromethane as shown below:



A facile rearrangement pathway such as shown below, should exist for the conversion of the product of the above reaction to I:



Another mechanism for formation of I from an olefin and nitromethane could involve formation of a chloronium ion, alkoxide ion ion-pair, from which nitromethide ion ($CH_2NO_2^-$) could be formed by reaction of the alkoxide with nitromethane. The nitromethide ion could now remove chlorine from the chloronium ion to produce I. If this were the mechanism cis-stilbene should be isomerized to trans-stilbene during the catalysis process(4). When either methyl or t-butyl hypochlorite was added to cis-stilbene in nitromethane, the olefin was recovered unchanged.

We have also examined the possibility that the alkyl hypochlorites react with nitromethane to produce an unknown compound which is subsequently converted to I by the olefin. At least in the case of t-butyl hypochlorite there does not seem to be a detectable reaction since an infrared spectrum of a 10% solution of this hypochlorite in nitromethane showed only the hypochlorite(5).

In the following paragraph we have summarized some of the more pertinent experimental details of the reactions described above. The reactions were carried out in the following molar ratio of olefin: nitroalkane: hypochlorite, 0.0087: 0.53: 0.0024. The quantity of hypochlorite was greatly increased in several experiments in order to establish that this is a reaction of major significance, and not merely a reaction of a minor component, such as the aci-form of nitromethane. In all cases, large quantities of nitromethane were converted to I. The hypochlorite (in CH_2Cl_2 or CCl_4) was added to the mixture of olefin and nitroalkane at 0°C. With reactive olefins and aromatics, the reactions were complete within 1-2 minutes. The progress of the reaction was followed by iodometric titration. The yields were determined directly from the reaction products using vpc analysis. I was isolated from reaction products by distillation and preparative vpc. The molecular structure of I and its presence in the reaction product was confirmed by its boiling point, ir analyses, and unambiguous synthesis(6). The structure of chloronitroethane was established similarly.

ACKNOWLEDGEMENT

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REFERENCES

1. M. L. Poutsma, J. Am. Chem. Soc., 87, 4285 (1965).

2. Radical addition of CH_3OCl to styrene should give this product since Walling, *et al*. [J. Am. Chem. Soc., 87, 1715 (1965)] have shown that t-butyl hypochlorite undergoes molecule-induced homolysis in styrene to give 2-t-butoxy-1-chloro-phenylethane.

3. C. Walling and W. Thaler, J. Am. Chem. Soc., 83, 3877 (1961).

4. Buckles, *et al*. [J. Org. Chem., 27, 4523 (1967)] have shown that the addition of bromine to *cis*-stilbene in nitromethane occurs by a non-stereospecific pathway. Loss of stereospecificity results from the unsymmetrical bonding in the intermediate bromonium ion, which permits rotation around the ethylenic carbon atoms. In our case, the intermediate chloronium ion should possess less symmetrical bonding than the bromine system and isomerism of *cis*-stilbene would be anticipated.

   It is also possible that the nitromethide ion could react with the alkyl hypochlorite to produce I and alkoxide ion. The alkoxide ion could then form the nitromethide ion, and thereby establish a chain reaction. We attempted to confirm catalysis by the alkoxide ion by adding sodium methoxide and potassium t-butoxide to a solution of nitromethane and the appropriate alkyl hypochlorite. This experiment was unsuccessful, however, because the alkoxides (or the nitromethide salts) were insoluble in nitromethane. We are continuing to explore the possibility of alkoxide ion catalysis.

5. We have not eliminated the possibility that an equilibrium is established between nitromethane, the hypochlorite and a trace amount of an intermediate which is rapidly converted to I when olefin is added. Also the possibility exists that a by-product is formed which functions as a catalyst in the conversion of the reactants to I.

6. Physical data establishing the structure of I is summarized below. Boiling point data: reported, 122-123°; from the reaction product, 122-123°, synthesized, 122-124°. Ir data: the ir spectrum for I from the reaction product was identical with the spectrum reported by Slovetskii, *et al*. [Izv. AN SSSR, Otd. Khim. N, 683 (1960)]. The ir spectrum of the synthesized I was essentially identical with I from the reaction product except the ir of the synthesized compound contained some additional peaks which were probably caused by contamination by Cl_2CHNO_2. Vpc data: the retention times for synthesized I, and I from the reaction product were identical.