The Intermediacy of Trichloromethyl Anions in the Reaction of Enamines with Bromotrichloromethane

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Reaction of *N*-(cyclohex-1-enyl)pyrrolidine with bromotrichloromethane in dimethyl sulphoxide generates trichloromethyl anions which have been trapped by addition to iminium cations or converted into chloroform in the presence of a hydrogen ion source.

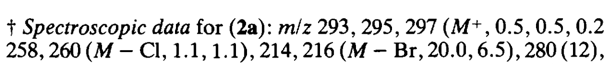
Reactions of enamines with tetrahalogenomethanes (CCl_4, CF_2Br_2, CF_2BrCl) have been reported to give products which are characteristic for radical chain processes.[1—3] It was suggested that the initiation step for these reactions is an electron transfer from the enamine to the halogenomethane, which thereby dissociates into a trihalogenomethyl radical and a halide anion, equation (1).[1]

We have now obtained evidence for the initial formation of halogenoiminium cations and trichloromethyl anions in the reaction of the enamine *N*-(cyclohex-1-enyl)pyrrolidine (**1**) with bromotrichloromethane; a result at variance with equation (1).

In our mechanistic investigations of the novel acid-catalysed halogenation reaction of amidines with tetrahalogenomethanes,[4a] we found that the ketene aminal (enediamine) tautomer is a reactive intermediate.[4b] The ketene aminal reacts with the tetrahalogenomethane, probably by a non-chain one-electron transfer mechanism, with subsequent halogen-atom transfer within the solvent cage. The intermediate halogenoamidinium ion and trihalogenomethyl anion react then to form halogenated amidine and trihalogenomethane. The present report provides results which show that enamines may react by a similar pathway.

A 0.1 M solution of *N*-(cyclohex-1-enyl)pyrrolidine (**1**) in dimethyl sulphoxide was treated with an equimolar amount of bromotrichloromethane at room temperature. A fast reaction consumed the enamine within a few minutes (monitored with ^{1}H n.m.r.). After hydrolysis, a crystalline compound was isolated (5% yield, m.p. 176—177 °C) from the complex product mixture and identified as the amide *N*-(1-chloro-2-bromocyclohexylcarbonyl)pyrrolidine (**2a**).†

G.l.c.–mass spectral analysis tentatively indicated formation of minor amounts of (**2b**) (1%),‡ (**2c**) (3%), and (**2d**)



(1)

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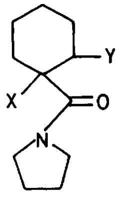
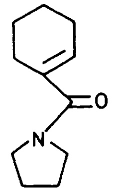
† *Spectroscopic data* for (**2a**): *m/z* 293, 295, 297 (M^+, 0.5, 0.5, 0.2%), 258, 260 (M – Cl, 1.1, 1.1), 214, 216 (M – Br, 20.0, 6.5), 280 (12), 179 (M – BrCl, 16), 178 (28), 109 (27), 98 (M – C_6H_9BrCl, 100); δ_H (100 MHz, $CDCl_3$) 1.7—2.5 (12H, m), 3.5 (3H, br m), 4.1 (1H, br m), and 4.85 (1H, dd, *J* 2.6 and 2.9 Hz); δ_C ($CDCl_3$) 19.6, 20.6, 25.2br, 29.9, 31.5, 47.7br, 52.5 (CHBr), 70.9 (CCl), and 166.5 (CON). The broad signals are most likely caused by a slow rotation of the pyrrolidine ring around its amide linkage, occurring near the coalescence temperature.

‡ Approximate g.l.c. yields.



(2)

a; X = Cl, Y = Br
b; X = Cl, Y = Cl
c; X = Cl, Y = H
d; X = Br, Y = H



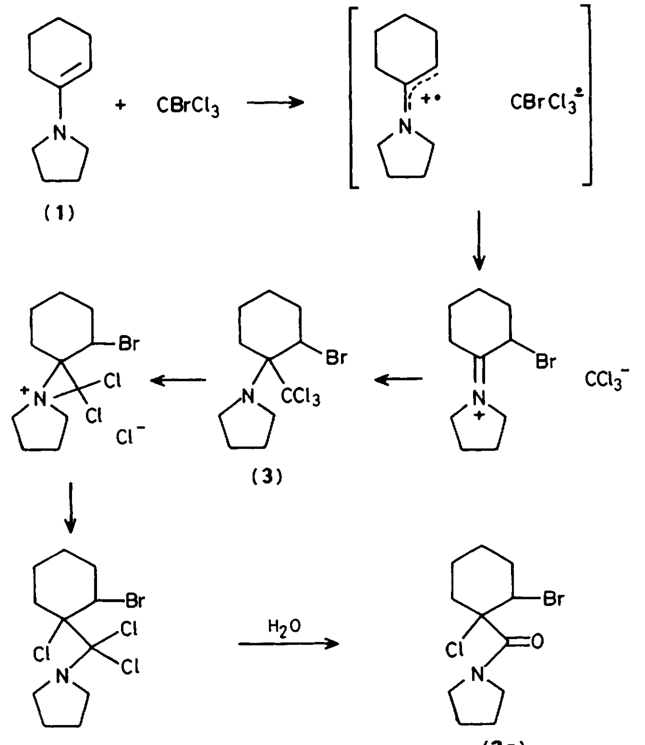
(2e)

(1%). These compounds were not isolated and characterized further, but showed mass spectral fragmentation patterns similar to (**2a**). Also, (**2e**) (15%) was isolated and characterized by ^{1}H and ^{13}C n.m.r. and mass spectral analysis. In addition, cyclohexanone (13%), 2-chlorocyclohexanone (20%), 2-bromocyclohexanone (1.5%), carbon tetrachloride (8%), chloroform (3%), and bromodichloromethane (2%) were identified in the organic phase. The remaining material in the organic phase (*ca.* 15%) was unidentified. The rest of the products are assumed to be in the aqueous phase.

The reaction was also performed in the presence of diethylamine hydrochloride (0.4 M), which may act as a hydrogen-ion donor. In this case the yield of chloroform increased to 70%. This difference in behaviour indicates that trichloromethyl anions are intermediates in the reaction of (**1**) with bromotrichloromethane, and that the anions are trapped predominantly to yield chloroform in the presence of diethylamine hydrochloride.

Moreover, the formation of (**2a**), which is rationalized in Scheme 1, also constitutes evidence for the formation of trichloromethyl anions. The reaction of (**1**) with bromotrichloromethane thus generates bromoiminium cations and trichloromethyl anions. Parts of these species combine to give (**3**) which, *via* (**4**), yields (**2a**) on hydrolysis. This sequence is analogous to the reaction of enamines with trichloroacetic acid in benzene to give chloroamides.[5,6] They were interpreted to occur by initial protonation of the enamine and decarboxylation of the trichloromethyl acetate. Addition of the trichloromethyl anion to iminium cation and subsequent transformations similar to those in Scheme 1 yield the products. Studies of the decomposition of trichloroacetic acid in dimethyl sulphoxide to trichloromethyl anions, and their subsequent reactions have recently been reported.[7] Amides (**2b**—**d**) are probably formed by similar additions of trichloromethyl anions to α-chloroiminium and iminium cations. Dehydrohalogenation of (**2c**) and (**2d**) or base-catalysed ring-opening of intermediate aziridinium ions should account for (**2e**). The α-chloroiminium cations may be the result of a substitution reaction on the initially formed α-bromoiminium cation by chloride ion, which is a powerful nucleophile in dimethyl sulphoxide. Decomposition of trichloromethyl anions to dichlorocarbene and chloride ion may serve as a chloride ion source.

We showed earlier that the rates of reaction of ketene aminals with tetrahalogenomethanes are largely governed by the redox properties of the reactants, and that rates are sharply increased when the solvent polarity is increased.[4b,c] This should also be true for corresponding reactions of enamines. The reported condensation reactions of enamines with tetrahalogenomethanes were performed in nonpolar solvents,[1—3] which disfavours the sequence shown in Scheme 1, and a radical chain reaction may consequently predominate.§



Scheme 1

The results presented here indicate that, in polar solvents, chain propagating radicals are not formed in the initial reduction of tetrahalogenomethane by enamine. Although this appears to be the case in nonpolar solvents, equation (1), trihalogenomethyl radicals may also be produced according to the proposed reaction of trihalogenomethyl anions with tetrahalogenomethanes, equation (2).[8]

$$CX_3^- + CX_4 \rightarrow 2{\cdot}CX_3 + X^- \qquad (2)$$

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§ However, in the reaction of *N*-(cyclohex-1-enyl)piperidine with CCl_4, a by-product was detected which was most likely formed by reaction of dichlorocarbene with the enamine.[2]