

Acid-Catalyzed α -Halogenation of Amidines by Tetrahalomethanes. Kinetic- and Isotope-Effect Evidence for the Intermediacy of the Ketene Aminal Tautomer

Stefan Löfås and Per Ahlberg*†

Contribution from the Department of Organic Chemistry, University of Uppsala, S-751 21 Uppsala, Sweden, and the Department of Organic Chemistry, University of Göteborg, S-41296 Göteborg, Sweden. Received April 2, 1985

Abstract: The mechanism for the novel reaction of the amidine 2,10-diazabicyclo[4.4.0]dec-1-ene (**1**) with CBrCl_3 in benzene giving the α -brominated amidine **9** and CHCl_3 has been studied. High-performance liquid chromatography (HPLC) conditions suitable for direct analysis of highly basic amidines were developed and used in the kinetics. The consumption of **1** under various reaction conditions was followed by HPLC and was found to be acid-catalyzed with a pseudo-first-order rate dependence on acid. The acid-catalyzed reaction of **1** with CBrCl_3 is not affected by radical chain inhibitors, indicating a nonchain process. In the absence of added acid, a side reaction of radical chain nature produces acid, which causes an autocatalytic behavior of the reaction of **1**. Similar rate constants for the α -bromination of **1** and the α -H/D exchange in **1** at the same concentration of acid indicate a common rate-limiting step for these reactions. Experiments with competing α -bromination and α -deuteration of **1** and deuterium isotope effect studies on the α -bromination suggest the ketene aminal tautomer **8** as a reactive intermediate and that **8** is formed in a rate-limiting step. The reaction of **8** with CBrCl_3 is believed to occur by a one-electron-transfer step followed by a bromine atom transfer within the solvent cage. An accompanying halogen-exchange reaction which forms CCl_4 and CHBrCl_2 during the α -bromination of **1** is also observed, and possible mechanisms for this exchange are discussed.

We recently discovered the reaction of amidines with carbon tetrachloride (CCl_4), giving α -chlorinated amidines and chloroform, Scheme I.¹ The reaction was investigated on the bicyclic amidines 2,10-diazabicyclo[4.4.0]dec-1-ene (**1**), 2-methyl-2,10-diazabicyclo[4.4.0]dec-1-ene (**2**), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,5-diazabicyclo[4.3.0]non-5-ene (DBN). Amidines **1**, **2**, and DBU gave the monochlorinated amidines **3**, **4**, and **5**, while DBN gave a mixture of the mono- and dichlorinated amidines **6** and **7**. We have shown that the α -chlorinated amidines can be used for synthetic purposes. For example, hydrolysis of **3**, **4**, and **5** gave new bicyclic and spiroazalactams which, on further hydrolysis, may be transformed into α -amino acids.²

We found this novel α -chlorination reaction intriguing, and several mechanistic alternatives may be figured out.¹ A reviewer has suggested a free-radical chain reaction initiated by electron transfer,³ a mechanism similar to that of reactions of amines with CCl_4 .⁴⁻⁷ It has also been proposed that amidines form carbanions by proton abstraction from the α -carbon.⁸ These carbanions may react with CCl_4 to give the observed products.

The present paper reports a detailed mechanistic study of the title reaction when using the amidine **1** as the substrate and bromotrichloromethane (CBrCl_3) as the reagent in benzene. This reaction proceeds at rates convenient for detailed kinetic studies.

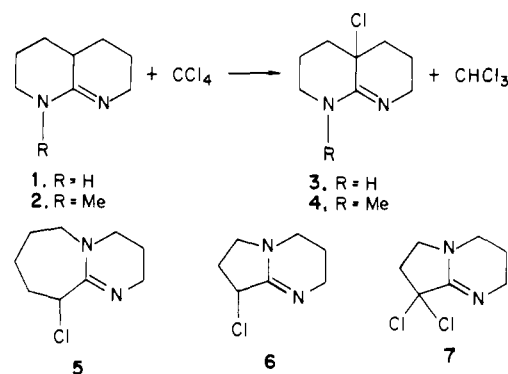
Conditions of high-performance liquid chromatography (HPLC) suitable for direct quantitative measurement of the consumption of **1** were developed. The HPLC method was used to determine the kinetics for the reaction of **1** with CBrCl_3 . Rates of H/D exchange of the α -hydrogen in **1** were measured by using ^2H NMR.

The results obtained from this investigation show that the α -bromination of **1** is acid-catalyzed and of nonchain type, in contrast to the chain reactions of amines with CCl_4 .⁴⁻⁷ The acid which catalyzes the bromination of **1** seems to be formed in a side reaction by a radical chain mechanism. Kinetic results and measured hydrogen isotope effects indicate that the ketene aminal tautomer **8** is an intermediate in the α -bromination. The reaction of **8** with CBrCl_3 probably occurs via a redox reaction within the solvent cage.

Results

Chromatographic Method. The kinetic runs were carried out by following the consumption of **1** by HPLC. We have developed

Scheme I



an HPLC procedure suitable for direct quantitative analysis of highly basic compounds, such as **1**. The high $\text{p}K_a$ values (ca. 13.5) for the corresponding acids of aliphatic amidines⁹ make it difficult to analyze these compounds quantitatively by normal chromatographic methods. In straight-phase HPLC systems, amidines are very strongly adsorbed on the column. Likewise, reversed-phase conditions with water-containing mobile phases have to be avoided in view of the tendency of aliphatic amidines to hydrolyze.

However, in these studies, we used an amino column and a mobile phase of ethanol containing small amounts of added strong base. The best results were attained by adding the amidine base DBN, which has a $\text{p}K_a$ value comparable to that of **1**. DBN probably blocks the residual acidic sites on the amino column, which would otherwise strongly adsorb **1**. However, the high UV

- (1) Löfås, S.; Ahlberg, P. *J. Chem. Soc., Chem. Commun.* **1981**, 998-999.
- (2) Löfås, S.; Ahlberg, P. *J. Heterocycl. Chem.* **1984**, *21*, 583-586.
- (3) "Organic Reaction Mechanisms 1981"; Knappe, A. C., Watts, W. E., Eds.; Wiley: Chichester-New York-Brisbane-Toronto-Singapore, 1982; p 95.
- (4) Smith, J. R. L.; Malik, Z. A. *J. Chem. Soc. B* **1970**, 617-623; **1970**, 920-926.
- (5) Lautenberger, W. J.; Jones, E. N.; Miller, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 1110-1115. Willermet, P. A.; Miller, J. G. *J. Phys. Chem.* **1976**, *80*, 2473-2477.
- (6) Kender, D. *Diss. Abstr. Int. B* **1976**, *37*, 1689-1690.
- (7) Markarian, S. A.; Fischer, H. *J. Chem. Soc., Chem. Commun.* **1979**, 1055-1056. References to earlier studies of this reaction are given in this article and in ref 4-6.
- (8) Barczynski, P.; van der Plas, H. C. *J. Org. Chem.* **1982**, *47*, 1077-1080.
- (9) Barton, D. H. R.; Elliott, J. D.; Géro, S. D. *J. Chem. Soc., Perkin Trans. I* **1982**, 2085-2090.

† Present address: University of Göteborg.

Table I. Reaction Conditions and Observed Rate Constants (k_{obsd}) for Reaction of 2,10-Diazabicyclo[4.4.0]dec-1-ene (**1**) with Bromotrichloromethane in Benzene at 25.0 °C^a

entry	[1], mM	[CBrCl ₃], mM	[HBr- 1], mM	other added substances	$10^4 k_{\text{obsd}}, ^b \text{ s}^{-1}$	comments ^c
1	14	635			(1.3)	S-shaped
2	29	628			(2.0)	S-shaped
3	41	626			(2.6)	S-shaped
4	28	371			(2.7)	S-shaped, 1 kept in air
5	29	627			(1.4)	S-shaped, freeze-pump-thaw degassed
6	29	638			(2.3)	S-shaped, oxygen atmosphere
7	29	625		41 mM 9,10-dihydroanthracene	(1.0)	S-shaped
8	29	629		11 mM (<i>t</i> -Bu) ₂ NO	(0.8)	S-shaped
9	28	662	0.56		2.4	init value, slightly S-shaped
10	29	631		susp. of 1.8 mmol of anhydr. K ₂ CO ₃	0.07	
11	28	622	0.03		0.4	init value, S-shaped
12	28	632	0.14		1.0	init value, slightly S-shaped
13	28	631	2.2		9.3	
14	30	628	1.1		5.3	oxygen atmosphere
15	26	653	1.2	29 mM 9,10-dihydroanthracene	5.3	
16	29	643	0.56	11 mM (<i>t</i> -Bu) ₂ NO	2.4	
17	36	635	0.60	95 mM CH ₂ Cl ₂	3.1	
18	36	278	0.54		2.0	
19	36	977	0.54		2.6	
20	37	553	0.54	462 mM CDCl ₃	4.0	
21	37	553	0.54	460 mM CHCl ₃	2.0	
22	37	553	0.54	462 mM CDCl ₃ , added 6.5 h before start of kinetics	0.72	

^a Reaction performed under an N₂ atmosphere unless otherwise stated. ^b Values within parentheses refer to the pseudo-first-order rate constants obtained after ca. 75% reaction. ^c The term "S-shaped" refers to the appearance of the [**1**]-time dependence curve.

absorption of the mobile phase, caused by the presence of DBN, ruled out the use of UV detection in the analysis. Accordingly, we used a well-thermostated high-sensitivity refractive index detector for the chromatographic analysis.

Kinetic Studies. The kinetic measurements of the reaction of **1** with CBrCl₃ were performed in the dark in benzene at 25.0 °C. A large excess of CBrCl₃ was used in all experiments. The concentration of CBrCl₃ was typically 22 times the concentration of **1**. The results of the kinetic runs are summarized in Table I.

In an inert atmosphere, the reaction showed autocatalytic behavior with an S-shaped substrate consumption curve (Figure 1). After ca. 75% reaction, a first-order dependence on **1** was obtained, entry 2 in Table I. The initially observed rate constant was estimated to have a value of ca. $0.2 \times 10^{-4} \text{ s}^{-1}$. The rate constant increased approximately 10-fold during the reaction. Some rate dependence on the initial concentration of **1** was observed. Thus, a 14 mM solution of **1** gave a rate constant of $1.3 \times 10^{-4} \text{ s}^{-1}$ toward the end of the reaction, compared with $2.6 \times 10^{-4} \text{ s}^{-1}$ for a reaction mixture with a concentration of **1** that was 3 times higher, entries 1 and 3, respectively.

When substrate **1** had been exposed to air, its reaction with CBrCl₃ showed a more pronounced S-shaped curve. In this case, the rate constant at the later stage of the reaction was $2.7 \times 10^{-4} \text{ s}^{-1}$, entry 4, a somewhat higher value than the rate constants obtained for reactions where freshly sublimed **1** was used. The presence of two additional peaks in the HPLC chromatogram indicated that autoxidation of **1** had taken place, which might be the cause of the different behavior. Accordingly, the freshly prepared reaction mixtures were usually deoxygenated by bubbling nitrogen or argon through the solution. In one experiment, the solution was carefully degassed by the freeze-pump-thaw technique. The S-shaped time dependence of the concentration of **1** remained but was less pronounced, entry 5.

Studies with Inhibitors and Catalysts. The influence of radical scavengers on the reaction rate has also been studied. An effective scavenger for the trichloromethyl radical is 9,10-dihydroanthracene.¹⁰ When present in a concentration comparable to that of **1** (41 and 29 mM, respectively), it caused a retardation in the rate of disappearance of **1**, Figure 1 and entry 7. This retardation persisted throughout the reaction and reduced the rate constant by a factor of 2 at the latter stage of the reaction, compared with the reaction without any inhibitor present.

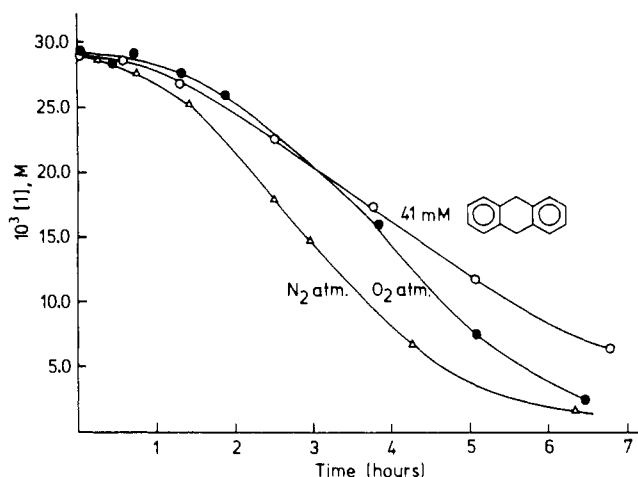


Figure 1. Dependence of [**1**] on time for the reaction of **1** with 0.63 M CBrCl₃ in benzene at 25.0 °C in an N₂ atmosphere (Δ , entry 2), with added 9,10-dihydroanthracene (\circ , entry 7), and in an O₂ atmosphere (\bullet , entry 6).

The stable radical di-*tert*-butyl nitroxide,¹¹ when present in 39 mol % of the initial concentration of **1**, also retarded the reaction of **1** with CBrCl₃, entry 8. Thus, only 50% **1** had reacted after 6 h with di-*tert*-butyl nitroxide in the reaction mixture, compared with 50% reaction of **1** after 3 h in the absence of inhibitor. No significant consumption of 9,10-dihydroanthracene or di-*tert*-butyl nitroxide could be detected by GLC during the reactions.

In an oxygen atmosphere, the reaction of **1** with CBrCl₃ showed a somewhat different course from the reaction in an inert atmosphere, Figure 1 and entry 6. The slow disappearance of **1** in the beginning of the reaction (the induction period) was more pronounced, but the reaction then accelerated in the same way as the reaction in an inert atmosphere. The function of oxygen as a radical scavenger is well-known but, since autoxidation of **1** probably forms peroxidic derivatives which may initiate radical chain reactions, the interpretation of the results in an oxygen atmosphere is ambiguous.

Preliminary experiments using unpurified CBrCl₃ showed a fast first-order disappearance of **1**. A possible impurity in CBrCl₃

(10) Kooyman, E. C. *Disc. Faraday Soc.* **1951**, 10, 163. See also ref 5 and 16.

(11) Nelsen, S. F.; Bartlett, P. D. *J. Am. Chem. Soc.* **1966**, 88, 143–149. Kornblum, N.; Boyd, S. D.; Ono, N. *Ibid.* **1974**, 96, 2580–2587.

Table II. Reaction Conditions and Observed Rate Constants for α -H/D Exchange and α -Bromination Competition Experiments of **1** in Benzene at 25 °C in N₂ Atmosphere, Measured by ²H NMR

entry	[1], ^a mM	[CBrCl ₃], mM	[HBr- 1], mM	other added substances	10 ⁴ k _{obsd} , s ⁻¹	comments
23	22		0.35	462 mM CDCl ₃	1.8	α -H/D exchange rate
24	22 ^a		0.35	459 mM CHCl ₃	0.36	α -D/H exchange rate
25	37		0.54	462 mM CDCl ₃	2.4	α -H/D exchange rate
26	37	553	0.54	462 mM CDCl ₃	~4.9 ^b	

^a Protium substrate (**1**(HH)) except in entry 24, where the substrate was dideuterated (**1**(DD)). ^b k_{obsd} for the α -bromination rate for reaction in the NMR probe, measured by HPLC.

spectrum of **1** is complex, and the α -H/D exchange is accordingly measured more easily by ²H NMR. Thus, a reaction mixture of **1** and CDCl₃ in C₆H₆ with an acid concentration of 0.35 mM was determined by ²H NMR to have an exchange rate constant of $1.8 \times 10^{-4} \text{ s}^{-1}$ for the α -H/D exchange, entry 23 in Table II. The rate of α -D/H exchange of the α -deuterated **1** with CHCl₃, using the same acid concentration, was also determined. A rate constant of $0.36 \times 10^{-4} \text{ s}^{-1}$ was obtained, entry 24.

The similarity between the rates of exchange of the α -hydrogen in **1** and the bromination of **1** with CBrCl₃ at the same level of acid, entries 9 and 25, is striking. This indicates that both processes have a common rate-limiting step, possibly the formation of the ketene aminal tautomer **8**. The following experiment was designed to study this hypothesis further. Thus, the α -H/D exchange in **1** and the bromination of **1** with CBrCl₃ were studied simultaneously in the same reaction mixture. As described later in the Discussion section, the interdependence on the exchange reaction and the bromination reaction may reveal mechanistic information, for instance, the existence of a common intermediate. Thus, CBrCl₃ and CDCl₃ were simultaneously added to a solution of **1** containing 1.5 mol % HBr-**1** in C₆H₆. The α -D incorporation in **1** was measured by ²H NMR, and the bromination reaction of **1** with CBrCl₃ was followed by taking samples from the NMR tube and analyzing them by HPLC. After the first bromination half-life time (23 min), an α -D incorporation of only ca. 3 mol % of the initial concentration of **1** was detected in the remaining 50 mol % of **1**, entry 26. In contrast, in an experiment without CBrCl₃ in the solution, the α -D incorporation was found to be 26 mol % after the same time and with the same concentration of acid present, entry 25.

The observed rate constant for the acid-catalyzed (1.5 mol %) bromination was $4.0 \times 10^{-4} \text{ s}^{-1}$ when CBrCl₃ and CDCl₃ were added simultaneously, entry 20. For the analogous reaction with CBrCl₃ and CHCl₃, a rate constant of $2.0 \times 10^{-4} \text{ s}^{-1}$ was obtained, entry 21. This value was about the same as the bromination rate when no chloroform was added, entries 18 and 19.

In another experiment, CDCl₃ was added to a solution of **1** and HBr-**1** (1.5 mol %), and the mixture was allowed to react for 6.5 h in order to produce **1**(DD)¹⁴ in situ. Bromination was then performed by the addition of CBrCl₃ to the reaction mixture. A bromination rate constant of $0.72 \times 10^{-4} \text{ s}^{-1}$ was obtained, which is 5.6 times less than the bromination rate constant obtained when CBrCl₃ and CDCl₃ were added simultaneously, entries 20 and 22.

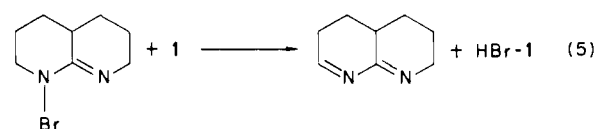
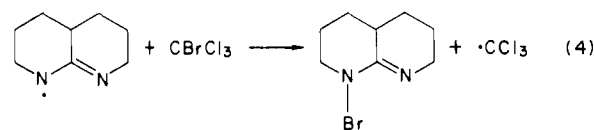
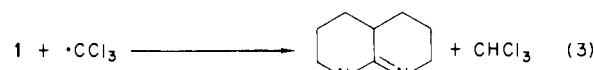
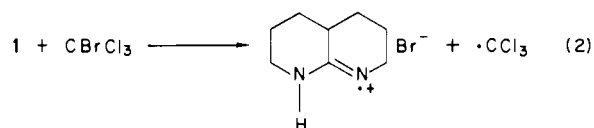
Halogen Exchange in Poly(halomethanes). Observation of the reaction mixture of **1** and CBrCl₃ by ¹H NMR showed that not only CHCl₃ but also CHBrCl₂ was formed. A closer examination of the products by ¹³C NMR showed the α -brominated amidine **3** as the only product from **1**. No evidence for the α -chlorinated **3** was found by ¹³C NMR, with a detection limit of approximately 5 mol %. Furthermore, GLC analysis of the reaction mixture showed that CCl₄ was formed in amounts similar to the amount of the CHBrCl₂ produced. This indicates that a halogen-exchange reaction takes place between the poly(halomethanes) in the presence of **1**. The halogen exchange in the kinetic runs described above was also studied by GLC. The amount of CCl₄ formed was found to be inversely dependent on the acid concentration, thus being greatest in the reactions carried out without any added acid.

For example, with 0.8 mol % HBr-**1** present, the concentration of CCl₄ was estimated to reach 1 mM, and without added acid, [CCl₄] was ca. 5 mM at the end of the reaction of **1** with CBrCl₃. Hexachloroethane, which is a dimerization product of $\cdot\text{CCl}_3$, could not be detected in any of the reaction mixtures.

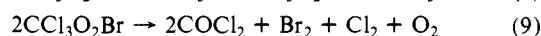
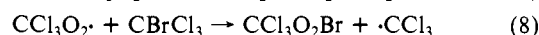
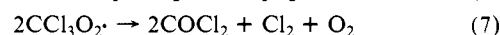
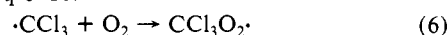
Discussion

The results obtained for the kinetic measurements of the reaction of **1** with CBrCl₃ indicate the occurrence of two processes: (a) a slow reaction which produces traces of acid, and (b) the acid formed then catalyzes the α -bromination of the amidine in another reaction.

Acid-Producing Reaction. The autocatalytic behavior of the disappearance of **1** was found to be caused by a side reaction of **1**, producing acid. This was shown by running the reaction in a suspension of potassium carbonate, Figure 2. Under these conditions, the acid produced is neutralized and the autocatalytic behavior consequently disappears. The inhibiting effects of radical scavengers, such as di-*tert*-butyl nitroxide¹¹ and 9,10-dihydroanthracene,¹⁰ on the reaction without added acid indicate that a radical chain process is responsible for the formation of the acid. The initiation of the chain reaction may be similar to that of the reactions of amines with CCl₄.⁴⁻⁷ In the latter reactions, which, among other products, give amine hydrochlorides, imines, and chloroform, the initiation of the radical chain is supposed to be electron transfer from the amine nitrogen to CCl₄, catalyzed by light or metal ions. This step produces trichloromethyl radicals ($\cdot\text{CCl}_3$) and amine radicals, which can propagate the chain. The intermediary chloroamines eliminate hydrochloride in the basic medium, thereby producing the amine hydrochlorides. A similar sequence can account for the acid production in the reaction of **1** with CBrCl₃ (eq 2-5).

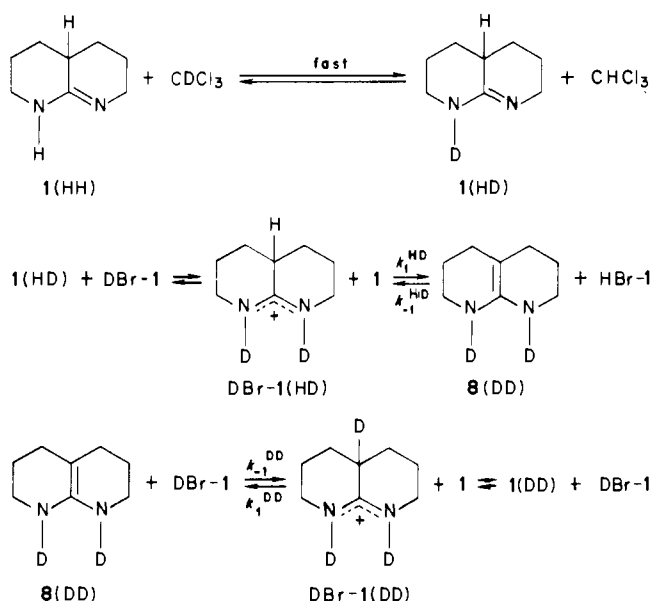


Another possible route for the production of acid is the reaction of $\cdot\text{CCl}_3$ with traces of oxygen in the solution. The following steps have been proposed for this reaction in solutions of diaryl peroxides or arylazotriphenylmethanes in CBrCl₃ in an atmosphere of air or oxygen, eq 6-10.¹⁵



(14) The first letter within the parentheses refers to the hydrogen isotope in the α -position in **1** and the second letter to the hydrogen isotope on the nitrogen in **1**. See also Scheme II.

Scheme II



Nucleophilic attack of **1** on COCl_2 , Cl_2 , and Br_2 will produce acid. This pathway for acid formation is indicated by the slower consumption of **1** in the reaction mixture deoxygenated by the freeze-pump-thaw method, compared with mixtures through which inert gas has been bubbled, which may leave traces of oxygen in the solution.

Thus, added radical scavengers can intervene at various stages of the proposed chain reactions and thereby inhibit acid production.

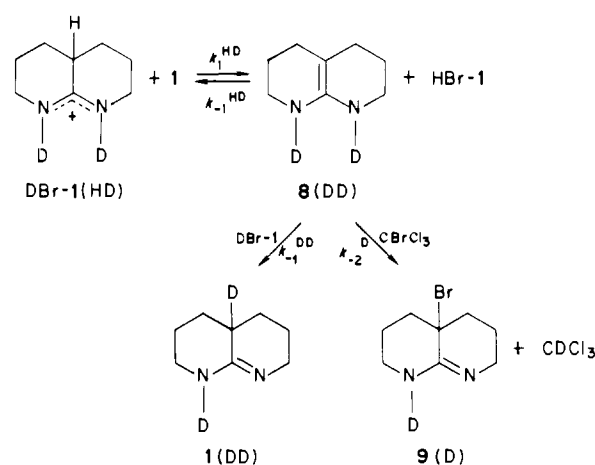
Nonradical pathways are also possible for acid formation. Substitution or HBr-elimination reactions of substrate **1** with **9** may produce acid.

The rate of disappearance of **1** was shown to be pseudo-first-order in acid concentration (Figure 4). From the increase in the observed rate constant in the reaction of **1** with CBrCl_3 without added HBr-1, the amount of acid formed at the end of the reaction can be estimated at 1.5–2.5 mol %. We could not identify any byproducts of acid formation, which would provide further information about this step.

Acid-Catalyzed α -Bromination of 1. Turning our attention to the acid-catalyzed α -bromination of **1**, we observe no effect of the radical-chain inhibitor 9,10-dihydroanthracene. This is in contrast with the great inhibiting effect this compound has on the photochemical reaction of amines with CCl_4 .⁵ In the reaction of 1,4-dihydropyridine derivatives with CBrCl_3 in the dark, the rate of reaction is reduced by 9,10-dihydroanthracene by factors of 25–100.¹⁶ These inhibiting effects were taken as support for radical-chain mechanisms with $\cdot\text{CCl}_3$ at the propagator of the chain.^{5,16}

The stable radical di-*tert*-butyl nitroxide has been used in various reactions as a radical-chain inhibitor.¹¹ The small difference in rate of the acid-catalyzed (2 mol % HBr-1) reaction with and without di-*tert*-butyl nitroxide (entries 9 and 16) merely demonstrates the inhibition of the chain process that produces acid. Thus, the insensitivity of the rate of α -bromination to these chain inhibitors, to oxygen, and to 1,1-dichloroethylene strongly suggests that the reaction is a nonchain process. As shown below, the kinetic results can be explained by simple rate laws. This also supports a nonchain reaction mechanism since radical-chain reactions frequently give kinetics much more complex than those observed.¹⁷

Scheme III



Hydrogen Isotope Effects of α -Bromination. The similarity between the rate constants for the α -H/D exchange in **1** and the α -bromination of **1** indicates a common rate-limiting step for both reactions. A possible mechanism for the α -H/D exchange under acid-catalyzed conditions is outlined in Scheme II. The fast exchange of the N-hydrogen in **1** is assumed to be base-catalyzed by **1**.

The observed rate ratio (isotope effect) of 5 for the α -H/D exchange in **1**(HH) with CDCl_3 and the α -D/H exchange of **1**(DD) with CDCl_3 , respectively, is consistent with the view that the hydron abstraction from the amidinium ion to give **8** is the rate-limiting step. In the determination of the exchange rate using **1**(HH) and CDCl_3 , the ratio $[\text{D}]/[\text{H}]$ of fast exchangeable hydrogens (i.e., CDCl_3 and N-H, respectively) was only 18. The rate of reprotonation of **8**(DD) to yield **1**(HD) must therefore be significant. Consequently, the observed rate constant for exchange must be somewhat smaller than the rate constant k_1^{HD} for the rate-limiting proton-abstraction step. Thus, the primary kinetic isotope effect for this step ($k_1^{\text{HD}}/k_1^{\text{DD}}$) should be larger than 5.

With the assumption that the bromination of **1** follows a similar mechanism when using **8** as an intermediate, the small dependence on the reaction rate of $[\text{CBrCl}_3]$ indicates that the reaction between **8** and CBrCl_3 is substantially faster than protonation of **8**. The measurement of the rate ratio of deuterium incorporation in **1** vs. bromination of **1** with both CDCl_3 and CBrCl_3 present in the reaction mixture yields information about the reaction mechanism. If the exchange and the bromination reaction make use of independent mechanisms, one would expect little or no influence on the rate of formation of **1**(DD) by the CBrCl_3 present. However, with the mechanism given in Scheme III, there is a competition for reaction with **8**(DD) to give **1**(DD) or **9**(D). If $k_2^{\text{D}}[\text{CBrCl}_3] \gg k_{-1}^{\text{DD}}[\text{DBr-1}]$, no α -D incorporation in **1** will be observed.

The result obtained of a markedly lower rate of formation of **1**(DD) in the presence of CBrCl_3 is thus strong support for a mechanism in which the two reactions are coupled with a common intermediate (Scheme III). The measured α -D incorporation of 3 mol % in **1** after a half-life time for the bromination of **1** indicates a rate ratio of 50/3 for bromination vs. deuteration with the concentrations used in the experiment. The formation of **8**(DD) from **1**(DD) has been neglected in this determination. The isotope effect of ca. 5 on k_1 indicates that only a minor fraction of the formed **1**(DD) might have reacted to **8**(DD) during the first half-life time of the reaction of **1**(HD).

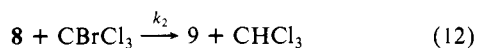
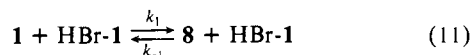
The observed difference in the acid-catalyzed bromination rate when CHCl_3 and CDCl_3 , respectively, are added simultaneously with CBrCl_3 can be explained by the mechanism in Scheme III. The pseudo-first-order rate constant (k_{obsd}) for the disappearance of **1** in the acid-catalyzed bromination (eq 11–12) is described

(15) Cadogan, J. I. G.; Hey, D. H.; Hibbert, P. G. *J. Chem. Soc.* **1965**, 3939–3949.

(16) Kurz, J. L.; Hutton, R.; Westheimer, F. H. *J. Am. Chem. Soc.* **1961**, 83, 584–588.

(17) See cited references in the Discussion section in: Katritzky, A. R.; Kashmiri, M. A.; de Ville, G. Z.; Patel, R. C. *J. Am. Chem. Soc.* **1983**, 105, 90–96.

by eq 13, which has been obtained by using the steady-state approximation applied to **8**.¹⁸



$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{HBr-1}] [\text{CBrCl}_3]}{k_{-1} [\text{HBr-1}] + k_2 [\text{CBrCl}_3]} = \frac{k_1 [\text{HBr-1}]}{\frac{k_{-1} [\text{HBr-1}]}{k_2 [\text{CBrCl}_3]} + 1} \quad (13)$$

Thus, the result of the competition for **8** with acid or CBrCl_3 is that the fraction of bromination becomes larger with DBr-1 than with HBr-1 , due to a primary isotope effect on k_{-1} . For a more detailed interpretation of the rate ratio of 0.5 for bromination in the presence of CHCl_3 and CDCl_3 , respectively, we examine the ratio of rate constants $k_{\text{obsd}}^{\text{H}}/k_{\text{obsd}}^{\text{D}}$ for the two cases (eq 14).¹⁹

$$\frac{k_{\text{obsd}}^{\text{H}}}{k_{\text{obsd}}^{\text{D}}} = \frac{\frac{k_1^{\text{HH}} k_2^{\text{H}} [\text{HBr-1}] [\text{CBrCl}_3]}{k_{-1}^{\text{HH}} [\text{HBr-1}] + k_2^{\text{H}} [\text{CBrCl}_3]}}{\frac{k_1^{\text{HD}} k_2^{\text{D}} [\text{DBr-1}] [\text{CBrCl}_3]}{k_{-1}^{\text{DD}} [\text{DBr-1}] + k_2^{\text{D}} [\text{CBrCl}_3]}} = \frac{k_1^{\text{HH}} [\text{HBr-1}]}{k_1^{\text{HD}} [\text{DBr-1}]} \times \frac{k_2^{\text{H}}}{k_2^{\text{D}}} \times \frac{k_{-1}^{\text{DD}} [\text{DBr-1}] + k_2^{\text{D}} [\text{CBrCl}_3]}{k_{-1}^{\text{HH}} [\text{HBr-1}] + k_2^{\text{H}} [\text{CBrCl}_3]} \quad (14)$$

The minor reaction of **1**(DD) to **8**(DD) has been neglected in the derivation of $k_{\text{obsd}}^{\text{D}}$ in eq 14. This approximation can be made for the same reasons as given above. The reaction of **8**(DD) to **1**(HD) is also omitted due to the low concentration of HBr-1 in the reaction mixture with CDCl_3 and CBrCl_3 .

The first term in eq 14 contains the isotope effect for the α -hydrogen abstraction from the amidinium ion. A proton is abstracted from the α -carbon both in the reaction mixture with CHCl_3 added and in the mixture with CDCl_3 added. Therefore, no primary isotope effect is expected for this reaction. In the reaction mixture with added CDCl_3 , a fast H/D exchange produces N-deuterated substrate (**1**(HD)) and acid (DBr-1). Thus, a secondary isotope effect (sie) on k_1 may be present. In the amidinium ion, the nitrogens are expected to be sp^2 -hybridized. This is not necessarily the case in **8**, in which the nitrogens may have a hybridization in between sp^2 and sp^3 .

According to the theory and experimental results for sie caused by rehybridizations of carbons with attached hydrogens, a change from an sp^2 carbon in the ground state to an sp^3 -like transition state will result in an sie of less than 1. We are not aware of any reported values for sie caused by rehybridizations of nitrogens with attached hydrogens, but one would expect an effect similar to that with carbon. The first term in eq 14 is therefore assumed to be less than 1.

The second term in eq 14 is due to the reaction of **8** with CBrCl_3 . In analogy with the arguments above, a value slightly greater than 1 for this term is tentatively assumed, thereby at least partly compensating for the sie on the first term.

We found that $k_2^{\text{D}} [\text{CBrCl}_3] / k_{-1}^{\text{DD}} [\text{DBr-1}]$ was ca. 50/3 in the competition experiments using mixtures of CDCl_3 and CBrCl_3 . We also found in the α -H/D exchange of **1** that $k_1^{\text{HD}} / k_1^{\text{DD}} > 5$. This implies that $k_{-1}^{\text{HH}} / k_{-1}^{\text{DD}} > 5$. Inserting these ratios in the third term in eq 14 yields a value for this term which is substantially less than 1, thereby contributing most to the ratio of

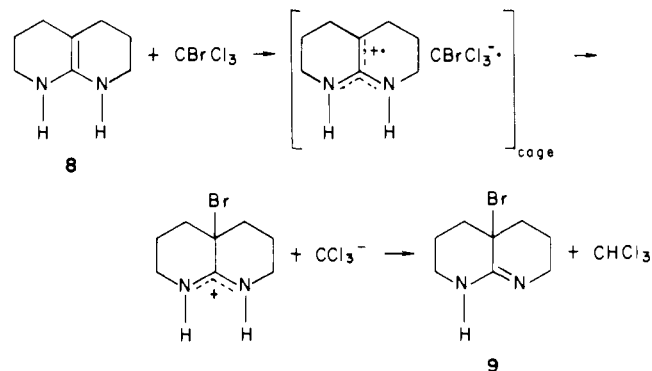
(18) The reaction of **9** with HBr-1 to form **8** and HBr-9 is neglected in the derivation of eq 13. This can be made because of the $\text{p}K_a$ difference between **1** and **9** is ca. 3 $\text{p}K_a$ units, **1** being the stronger base. Lófás, S., unpublished results.

(19) For reaction mechanism investigations on branching reactions employing hydrogen isotope effects, see: Thibblin, A.; Ahlberg, P. *J. Am. Chem. Soc.* **1979**, *101*, 7311–7318 and references therein. See also: Melander, L.; Saunders, W. H. In "Reaction Rates of Isotopic Molecules"; Wiley: New York–Chichester–Brisbane–Toronto, 1980; pp 293–297. Bell, R. P. "The Tunnel Effect in Chemistry"; Chapman and Hall: London–New York, 1980; pp 129–135.

Table III. Half-Wave Potentials for Reductions of Halomethanes

compound	$E_{1/2}$, V vs. SCE	solvent	ref
CBr_4	-0.3	dioxane/ H_2O 3:1	28
	-0.22	$\text{Me}_2\text{SO}/\text{C}_6\text{H}_6$ 3:2 v/v	29
CBrCl_3	-0.23	$\text{Me}_2\text{SO}/\text{C}_6\text{H}_6$ 3:2 v/v	29
CCl_4	-0.73	$\text{Me}_2\text{SO}/\text{C}_6\text{H}_6$ 3:2 v/v	29
	-0.73	$\text{Me}_2\text{SO}/\text{C}_6\text{H}_6$ 3:2 v/v	29
CH_2I_2	-0.78	dioxane/ H_2O 3:1	28
	-1.12	dioxane/ H_2O 3:1	28

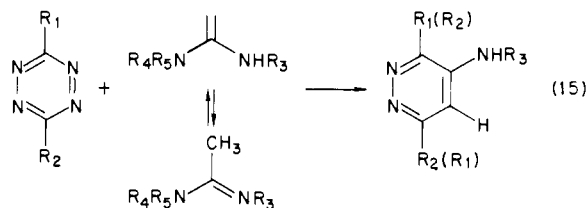
Scheme IV



eq 14. Thus, qualitative agreement with the observed isotope effect of 0.5 is obtained.

The increase in bromination rate of 30% when $[\text{CBrCl}_3]$ is increased from 0.28 to 0.98 M is also in accordance with the mechanism in eq 11 and 12. The experimental values for $k_2^{\text{D}} [\text{CBrCl}_3] / k_{-1}^{\text{DD}} [\text{DBr-1}]$ of 50/3 ($[\text{CBrCl}_3] = 0.55 \text{ M}$, $[\text{DBr-1}] = 0.5 \times 10^{-3} \text{ M}$) and $k_{-1}^{\text{HH}} / k_{-1}^{\text{DD}} \geq 5$ give an approximate value for $k_{-1}^{\text{HH}} / k_2^{\text{H}}$ of 330. Inserting this value and the concentrations from entries 18 and 19 in eq 13, k_{obsd} is calculated to be $3.2 k_1 \times 10^{-4} \text{ M}$ and $4.3 k_1 \times 10^{-4} \text{ M}$ for $[\text{CBrCl}_3] = 0.28$ and 0.98 M , respectively. Thus, the difference of 34% between these two values agrees with the experimentally obtained 30% change in k_{obsd} .

The results presented are thus in favor of the mechanism of eq 11 and 12 for the acid-catalyzed α -bromination of **1** and represent the first mechanistic evidence for the intermediacy of the ketene aminal form. The results also show that tautomer **8** is apparently much more reactive than **1** toward CBrCl_3 . From reported product studies, the ketene aminal form has been suggested as a reactive species in reactions of amidines with electron-deficient aromatics.^{8,20–22} In the Diels–Alder reaction of substituted acetamidines with *S*-tetrazines, the resultant products were taken as evidence for the ketene aminal being the reactive form (eq 15).²³



α -Bromination Step. For the mechanism proposed in eq 11 and 12, the reaction of **8** with CBrCl_3 , giving **9** and CHCl_3 , can formally be regarded as a nucleophilic substitution by **8** on bromine in CBrCl_3 with CCl_3^- as the leaving group. However, as discussed below, the reaction is more likely to be viewed as a redox process involving an initial one-electron transfer.

(20) Bard, R. R.; Strauss, M. J. *J. Am. Chem. Soc.* **1975**, *97*, 3789–3798. *J. Org. Chem.* **1976**, *41*, 2421–2428; **1978**, *43*, 3600–3602.

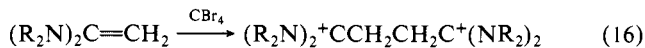
(21) Charushin, V. N.; van der Plas, H. C. *J. Org. Chem.* **1983**, *48*, 2667–2671.

(22) Granik, V. G. *Russ. Chem. Rev.* **1983**, *52*, 377–393 and references therein.

(23) Figeys, H. P.; Mathy, A.; Dralants, A. *Synth. Commun.* **1981**, *11*, 655–662.

Olefins activated by dialkylamino groups are very easily oxidized.²⁴ Tetrakis(dimethylamino)ethylene is exceptional with an oxidation potential of -0.77 V vs. the saturated calomel electrode (SCE) in CH_3CN .²⁵ The ketene aminal $(\text{MeN})_2\text{C}=\text{C}(\text{Me})_2$, which is structurally related to **8**, oxidizes at $+0.05$ V in CH_3CN .²⁵ Ketene aminals have also been oxidized chemically, e.g., by silver nitrate, to give coupling or disproportionation products via intermediate radical cations.²⁶

Furthermore, perhalomethanes, such as carbon tetrabromide, have been used as chemical reagents in the oxidative dimerizations of ketene aminals, eq 16.²⁷ Even methylene iodide is believed



to react partly in an oxidative manner with ketene aminals on prolonged reflux in CH_3CN .²⁸ This demonstrates the readiness with which poly(haloalkanes) are reduced, cf., the reduction potentials in Table III.

The ability of tetrahalomethanes to act as halogenating agents in reactions with carbanions via a one-electron transfer mechanism rather than a nucleophilic substitution mechanism has been proposed by Meyers and co-workers.^{30,31} However, it is difficult to interpret the bromination of **8** as either a nucleophilic substitution mechanism or a one-electron-transfer mechanism when both mechanisms give identical products. On the basis of the electron-donating and -accepting properties of **8** and CBrCl_3 , respectively, we favor the view that the bromination of **8** is a one-electron-transfer process rather than a nucleophilic substitution. A detailed reaction mechanism is shown in Scheme IV.

Thus, the one-electron transfer from **8** to CBrCl_3 yields the radical-ion pair. A fast bromine atom transfer within the solvent cage followed by a proton transfer inside or outside the cage may give the products. From reports on the stability of similar radical ions, it is probable that the pair of radical ions in Scheme IV may be an intermediate. Thus, the radical cation of $(\text{Me}_2\text{N})_2\text{C}=\text{CMe}_2$ has a half-life time of 0.025 s in CH_3CN as measured by cyclic voltammetry.²⁵ Furthermore, γ -irradiation of a sample of CBr_4 revealed an ESR spectrum indicative of the radical anion $\text{CBr}_4^{\cdot-}$.³²

Halogen Exchange. The observed halogen-exchange reactions which gave CHBrCl_2 and CCl_4 indicate the presence of trichloromethyl species in the reaction mixture. Either of the possible species $\cdot\text{CCl}_3$ or CCl_3^- may react with CBrCl_3 to form the observed products. The identity reaction (eq 17) probably occurs most frequently, but CCl_4 is occasionally formed, eq 18. It was pro-



posed that in free-radical chain reactions in mixtures of diaryl peroxides and CBrCl_3 , a reaction between $\cdot\text{CCl}_3$ and CBrCl_3 formed CCl_4 .¹⁵ The yield of CCl_4 increased in an atmosphere of oxygen, which was explained by eq 6–10. Hexachloroethane was also formed in considerable amounts. However, in photoinitiated radical-chain reactions of toluenes with CBrCl_3 , no formation of CCl_4 was observed.¹² The reaction mixtures were there degassed and kept in sealed tubes, ensuring no interference by oxygen. Base-catalyzed halogen-exchange reactions in *N*-

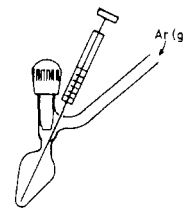


Figure 5. Reaction flask with Rotaflo PTFE valve for sampling with a syringe under an inert atmosphere.

methylpyrrolidinone have also been reported. A radical-chain reaction, initiated by electron transfer, was proposed as the mechanism.³³

The trichloromethyl anion has also been reported to react in halogen-exchange reactions. In the oxidation of tetrakis(dimethylamino)ethylene with CBrCl_3 , CCl_4 and CHBrCl_2 were produced.³⁴ When the reaction was performed in cyclohexene, the formation of dichloronorcarane constituted evidence for the presence of the trichloromethyl anion.³⁴ It has also been shown that trichloromethyl anions generated from trichloromethyl-carboxylates are capable of abstracting halogen from alkyl halides.³⁵

Our present work indicates the possibility of occurrence of both the trichloromethyl radical and the anion in the reaction mixtures of **1** and CBrCl_3 . The smaller amounts of CCl_4 and CHBrCl_2 formed in the presence of acid indicate the predominance of halogen exchange via the anion produced in the reaction shown in Scheme IV. When the acid concentration is increased, the anion is trapped faster, and the halogen-exchange rate consequently decreases.

Experimental Section

General Methods. The NMR spectra were recorded with a JEOL JNM-FX 100 Fourier Transform spectrometer, equipped with a 5-mm $^1\text{H}/^{13}\text{C}$ dual probe. A 10-mm multinuclear probe was used for the ^2H NMR spectra. In the kinetic NMR experiments, the spectra were stored on a floppy disc data-storage device. The temperature in the NMR probe was measured with a copper-constantan thermocouple with an accuracy of ± 0.1 °C.

The kinetics of the bromination reaction was studied by using a HPLC system consisting of an Optilab HSR1 931 chromatograph equipped with an interference refractive index detector and a Hewlett-Packard 20 cm, $5 \mu\text{m}$ NH_2 column or a Brownlee 10 cm, $5 \mu\text{m}$ amino column. A mixture of absolute ethanol/benzene/DBN (85:14:0.8 v/v) was used as the mobile phase. The flow rate was 1.2 mL/min, eluting DBU after 5 min and compound **1** after 7 min. The chromatograms were integrated by using a Hewlett-Packard 3990 A integrator connected to the detector.

Analytical gas chromatography (GLC) was performed with a Hewlett-Packard 5880 A instrument equipped with a FID detector. A glass column with 10% Carbowax 20 M on Chromosorb W-AW DMCS operated at 60 °C with a gas flow rate of 10 mL/min was used in the perhalomethane analysis.

The reaction kinetics was carried out in a HETO 02 PT 623 thermostat at 25.00 ± 0.02 °C. The reaction mixtures were kept either in vials with Mininert valves or in flasks of the type shown in Figure 5. The latter flask enables sampling with a syringe while flushing with an inert gas. The Rotaflo PTFE valve provides an efficient seal for the flask.

The glassware used in the kinetic measurements—volumetric flasks, reaction vials and flasks, NMR tubes, etc.—were kept in concentrated alkali solution for at least 24 h. They were then rinsed successively with distilled water, 1 M hydrochloric acid, distilled water and 1 M ammonia, and finally with at least 10 portions of distilled water. Syringes, needles, and valves were treated in a similar way, but the first alkaline treatment was replaced by ethanol rinsing. The drying of the equipment, except for volumetric flasks, valves, and syringes, was carried out at 150 °C for at least 8 h. A final drying of all equipment was performed in a Leybold-Heraeus vacuum oven operated at 50 °C/0.02 mmHg. The vacuum

(24) Nelsen, S. F. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York-London-Sydney-Toronto, 1973; Vol. II, p 577.

(25) Fritsch, J. M.; Weingarten, H.; Wilson, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 4038–4046.

(26) Weingarten, H.; Wager, J. S. *J. Org. Chem.* **1970**, *35*, 1750–1753.

(27) Effenberger, F.; Gerlach, O. *Tetrahedron Lett.* **1970**, 1669–1672.

(28) Hobbs, C. F.; Weingarten, H. *J. Org. Chem.* **1974**, *39*, 918–921.

(29) von Stackelberg, M.; Stracke, W. *Z. Electrochem.* **1949**, *53*, 118. See also: Casanova, J.; Ebersson, L. "The Chemistry of the Carbon-Halogen Bond"; Patai, S., Ed.; Wiley: London-New York-Sydney-Toronto, 1973; Part 2, pp 979–1047.

(30) Meyers, C. Y.; Matthews, W. S.; Ho, L. L.; Kolb, V. M.; Parady, T. E. "Catalysis in Organic Synthesis"; Smith, G. V., Ed.; Academic Press: New York-San Francisco-London, 1977; pp 197–278.

(31) Meyers, C. Y.; Kolb, V. M. *J. Org. Chem.* **1978**, *43*, 1985–1990.

(32) Mishra, S. P.; Symons, M. C. R. *J. Chem. Soc., Chem. Commun.* **1973**, 577–578.

(33) Orvik, J. A. "Abstracts of Lectures"; Seventh IUPAC Conference on Physical Organic Chemistry, New Zealand, Aug 1984.

(34) Carpenter, W. *J. Org. Chem.* **1965**, *30*, 3082–3084. On the oxidation of tetrakis(dimethylamino)ethylene, see also: Wiberg, N. *Angew. Chem.* **1968**, *80*, 809–822. Hoffmann, R. W. *Ibid.* **1968**, *80*, 823–835.

(35) Wagner, W. M.; Kloosterziel, H.; van der Ven, S.; Bichel, A. F. *Recl. Trav. Chim. Pays-Bas* **1962**, *81*, 947–957. Krapcho, A. P.; Huyffer, P. S. *J. Org. Chem.* **1963**, *28*, 2904–2905.

oven was connected to a Mecaplex glovebox, to which the dried equipment can be transferred directly, without exposure to air. The nitrogen atmosphere in the glovebox was recirculated through molecular sieves (5 Å).

Preparations of solutions and transfers to reaction flasks were carried out in the glovebox, which also was used for storage of air- and moisture-sensitive compounds. Boiling and melting points are uncorrected.

Materials. **2,10-Diazabicyclo[4.4.0]dec-1-ene (1)** was synthesized according to our recently published method² and was sublimed directly before use in the kinetic experiments. On standing in dry air, some autoxidation of **1** occurs, probably forming the α -hydroperoxide of **1**.³⁶ Moreover, since **1** is sensitive to moisture, it was stored and handled in the glovebox.

2,10-Diazabicyclo[4.4.0]dec-1-ene hydrobromide (HBr-1) was obtained by shaking a solution of 0.7 mmol of **1** in 15 mL of CH_2Cl_2 with 1 mL of 3 M hydrobromic acid. The organic phase was dried with molecular sieves (4 Å), and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 , and Et_2O was added dropwise until the solution became opalescent. Crystals were formed when the solution was kept in the freezer. Filtration and drying afforded HBr-1 (20%): mp 148–149 °C; $^1\text{H NMR}$ (CD_2Cl_2) δ 1.7 (m, 8 H), 2.4 (m, 1 H), 3.4 (m, 4 H), 9.6 (br s, 2 H). A 0.3 M solution of HBr-1 in CH_2Cl_2 was prepared and used in the kinetic experiments.

Benzene (Merck, spectroscopic grade) was predried over molecular sieves (4 Å) and refluxed over and distilled from CaH_2 in a nitrogen atmosphere. The benzene was stored in the glovebox. Bromotrichloromethane (Fluka, purum) was shaken with 5 M NaOH solution and four portions of distilled water and dried with molecular sieves (4 Å). It was distilled in the dark in a nitrogen atmosphere, bp 104.9–105.0 °C (>99% purity from GLC, the content of CCl_4 was 0.7%). The distilled CBrCl_3 was stored in N_2 in the freezer in a flask which was placed in a larger jar filled with dry N_2 and silica gel. 9,10-Dihydroanthracene (EGA-Chemie, purum) was recrystallized from EtOH , mp 112–113 °C. Di-*tert*-butyl nitroxide (Polyscience) was used without further purification. 1,1-Dichloroethylene (Fluka, puriss.) was distilled directly before use, bp 32 °C. CHCl_3 (Fluka, p.a.) and CDCl_3 (Ciba-Geigy, > 99.5% D, from a newly opened ampule) were used directly or purified by distillation from anhydrous K_2CO_3 . The distilled chloroform gave rates identical with those given by the chloroform used directly in the kinetic experiments.

Kinetics. General Procedure. A 30 mM solution of **1** in benzene was deoxygenated by bubbling N_2 or Ar through the solution for ca. 7 min. A 2.5-mL portion of the solution was transferred in the glovebox by means of a syringe to the reaction flask. The flask was wrapped in Al foil and thermostated at 25.0 °C. The reaction was initiated by adding CBrCl_3 with a syringe. The added amount of CBrCl_3 was determined by weighing the syringe before and after the addition. The syringe was filled in the glovebox and wrapped in Al foil. Six to nine aliquots (100

μL each) of the reaction mixture were withdrawn at different times with a 100- μL syringe under a flow of Ar. The kinetic runs were usually followed to 75% reaction of **1** and in the reactions with autocatalytic behavior up to 95% reaction of **1**.

Each aliquot was added to 600 μL of a mixture of EtOH containing 0.8 vol % DBN plus DBU (3.8 mM), which was used as an internal standard. The solution was immediately analyzed by HPLC. This method gave an accuracy of ± 2.0 absolute % in the concentration determinations of **1**.

The rate constants were calculated by a linear least-squares analysis of the $\ln [1]$ vs. time plots using a programable Texas 59. Correlation coefficients typically better than 0.998 were obtained for the acid-catalyzed reactions.

Kinetic measurements in the presence of inhibitors and catalysts were performed by using the general procedure presented above except that the inhibitor or catalyst was added to the solution of **1**, which was then thermostated. 9,10-Dihydroanthracene was weighed and transferred to the reaction flask as a solid. Appropriate amounts of (*t*-Bu) $_2\text{NO}$, $\text{CH}_2=\text{CCl}_2$, and 0.3 M HBr-1 in CH_2Cl_2 were added by using a syringe.

Kinetics in Oxygen Atmosphere. In these experiments, the reaction flask was filled with oxygen before thermostating.

Hydrogen Isotope Exchange Measured by $^2\text{H NMR}$. A solution of **1** (HH) (57 μmol) and HBr-1 (0.8 μmol) in C_6H_6 (2.5 mL) in a 10-mm NMR tube equipped with septum and screw cap was thermostated at 25.0 °C in the NMR probe. CDCl_3 (102 μL , 1.3 mmol) was added with a syringe, and the α -D incorporation in **1** was measured at intervals by integration of the α -D signal by using the N-D signal as reference. The $^2\text{H NMR}$ experiments were performed with a spectral width of 250 or 500 Hz. The α -D/H-exchange rate for the reaction of **1**(DD) with CHCl_3 to **1**(HH) was measured as follows. C_6H_6 and chloroform in the above-mentioned solution of **1**(DD) was evaporated, and 2.5 mL of C_6H_6 was added to the solid residue. CHCl_3 (100 μL) was added to the solution, and the exchange rate was determined as above. The decrease of the α -D signal was measured relative to the growing signal from CDCl_3 .

Kinetic Competition Experiments. To a thermostated solution of **1**-(HH) (100 μmol) and HBr-1 (1.5 μmol) in C_6H_6 (2.5 mL) in an NMR tube equipped with septum and screw cap were simultaneously added 100 μL (1.2 mmol) of CDCl_3 and 150 μL (1.5 mmol) of CBrCl_3 . $^2\text{H NMR}$ spectra were recorded as described above, and aliquots were withdrawn with a 100- μL syringe and analyzed by HPLC following the general procedure above.

These competition experiments were also performed in reaction flasks in the thermostat at 25.0 °C in order to obtain a more accurate determination of the dependence of the bromination rate on addition of CHCl_3 and CDCl_3 . The experiments were carried out as in the general procedure except that CHCl_3 (CDCl_3) and CBrCl_3 were added simultaneously.

Acknowledgment. We thank the Swedish Natural Science Research Council for support.

Registry No. **1**, 60832-40-8; **9**, 98821-50-2; deuterium, 7782-39-0.

(36) Investigations of the autoxidations of structurally related imines have been performed: Schumann, D.; Naumann, A.; Wirtz, K.-P. *Chem. Ber.* **1979**, *112*, 734–742.

Superacid-Catalyzed Alkylation of Adamantane with Olefins^{1a}

George A. Olah,* Omar Farooq, V. V. Krishnamurthy, G. K. Surya Prakash, and Khosrow Laali^{1b}

Contribution from the Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661. Received May 31, 1985

Abstract: The superacid catalyzed alkylation of adamantane with lower olefins (ethene, propene, and butenes) was investigated. Alkyladamantanes obtained show that the reaction occurs by two pathways: (a) adamantylation of olefins by adamantyl cation formed through hydride abstraction from adamantane by alkyl cations (generated by the protonation of the olefins) and (b) direct σ -alkylation of adamantane by the alkyl cations via insertion into the bridgehead C–H bond of adamantane through a pentacoordinate carbonium ion.

Studies of protonation and acid-catalyzed alkylation (by olefins) of saturated hydrocarbons are of importance both in terms of their

usefulness in hydrocarbon conversion processes as well as mechanistic aspects involving carbocationic intermediates. The first