leum Research Fund, administered by the American Chemical Society. We thank Mr. Donald R. Schifferl for assistance with the mass spectral determinations.

Registry No. 3, 71663-75-7; 4, 72229-72-2; 5, 71404-96-1; 6, 71405-00-0; 7, 72229-73-3; 2 (R, $R^2 = CH_3$), 7486-91-1; 2 (R^1 = BocNH, R^2 = H), 72229-74-4; 8, 495-18-1; 9, 72229-75-5; 10, 3532-25-0; 11, 959-32-0; 12, 16817-96-2; 13, 63820-45-1; 26, 71405-01-1; 27, 72229-74-4; 28, 1482-97-9; 30, 26048-92-0; 31, 72229-80-2; benzamide, 55-21-0; benzaldehyde, 100-52-7; ethyl phenylacetate, 101-97-3; *N*-methylhydroxylamine, 593-77-1; benzyl alcohol, 100-51-6; benzoic acid, 65-85-0; *N*-methylhydroxylamine hydrochloride, 4229-44-1; *N*-methylbenzamide, 613-93-4; benzyl bromide, 28807-97-8; *O*-benzyl-β-chloropivalohydroxamic acid, 72229-76-6; *N*-Boc-L-serine, 3262-72-4; β-chloropivaloyl chloride, 4300-97-4; *O*-benzylhydroxylamine, 622-33-3; *O*-benzylhydroxylamine hydrochloride, 2687-43-6; ethyl β-(benzyloxyamino)pivalate, 72229-77-7; β-(*N*-acetyl-*N*-benzyloxy)pivalic acid, 72229-78-8; 2,2-dimethyl-3-(benzyloxyamino)propanol, 72229-79-9; *N*-methylbenzeneacetamide, 6830-82-6; benzeneacetaldehyde, 122-78-1; β-chloropivalic acid, 13511-38-1.

Static and Flow Nuclear Magnetic Resonance of Dehydrohalogenation of 2-Chloropropanoyl Chloride[1]

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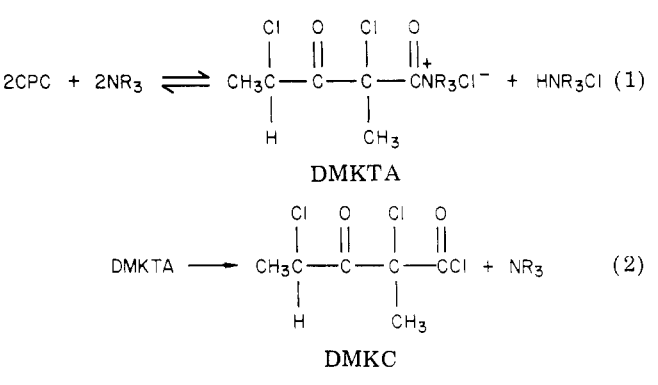
The dehydrohalogenation of 2-chloropropanoyl chloride (CPC) using diazabicyclooctane (Dabco) or triethylamine (TEA) in chloroform has been studied at temperatures ranging from 30 to −30 °C by using ^1H nuclear magnetic resonance spectroscopy under static and flowing conditions. In addition to several minor products, three species that have not been found previously are observed: $CH_3CHClCOCCl(CH_3)CClO$ (DMKC), $CH_3CHClCOCCl(CH_3)CO(NR_3)Cl$ (DMKTA), and 2,4-dichloro-2,4-dimethyl-1,3-cyclobutadione (DDC). For Dabco, the formation of DMKC from DMKTA is fast at 30 °C, and DMKTA cannot be detected above 0 °C. On the other hand, for TEA, DMKTA can be detected at 30 °C, and the formation of DMKC is slow, occurring over a period of several hours (depending on the TEA concentration). This decrease in rate allows the formation of DDC from DMKTA to become competitive. DDC is unstable in the reaction solution. Methylchloroketene appears to be a precursor of DMKTA; however, it is too reactive in the presence of base to be detected even by stopped-flow NMR at −30 °C. The presence of cyclopentadiene in the reaction mixture does not prevent the formation of DMKC when Dabco is used, but DMKC slowly decays with the resultant formation of the ketene–cyclopentadiene adduct. On the other hand, for TEA, this adduct is formed rapidly, and neither DMKTA nor DMKC is detected. Although the results appear different for the two bases, they can be accommodated by a common mechanism in which the rate of certain steps depends on the nature of the base.

The dehydrohalogenation of acyl halides using a base has been studied primarily by product analysis.[2-5] When the reaction is performed with 2-chloropropanoyl chloride (CPC) in the presence of triethylamine (TEA) and cyclopentadiene, *endo*- and *exo*-7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-ones (CMBH) are observed, indicating the presence of transient methylchloroketene. On the other hand, in the absence of cyclopentadiene, the ester, 1,2-dichloropropenyl-2-chloropropanoate (CCCP), is observed when a CPC/TEA concentration ratio of 2 is used in dry hexane.[2-4] In this case, CCCP is believed to form via reaction between the ketene and CPC. The tentative mechanisms suggested for these two reactions are based solely on product analysis. None of the possible intermediates have been detected, and no information concerning the time dependence of these reactions is available.

The present paper describes the study of the dehydrohalogenation of CPC as a function of time as well as the detection of a few transient species during the course of the reaction under various conditions using both static and flow proton nuclear magnetic resonance (NMR) at temperatures ranging from 30 down to −30 °C. For this purpose the solvent was changed from hexane to chloroform to simplify the NMR spectra and to avoid precipitation.

Scheme I



Two bases have been employed, TEA and diazabicyclooctane (Dabco), and although they differ in their effects on product distribution and on the time scale for the formation of certain products as well as on the lifetime of certain intermediates, it is possible to present a common mechanism that is consistent with the results obtained with either base. The main aspects of this mechanism involve

(1) Preliminary report presented at the 62nd Canadian Chemical Conference, Vancouver, B.C., June 1979.
(2) (a) W. T. Brady and R. Roe, Jr., *Tetrahedron Lett.*, 1977 (1968); (b) W. T. Brady, F. Parry, III, R. Roe, Jr., E. Hoff, and L. Smith, *J. Org. Chem.*, **35**, 1515 (1970); (c) W. T. Brady and R. Roe, Jr., *J. Am. Chem. Soc.*, **92**, 4618 (1970).
(3) R. Giger, M. Rey, and A. S. Dreiding, *Helv. Chim. Acta*, **51**, 1466 (1968).
(4) J. M. Lavanish, *Tetrahedron Lett.*, 6003 (1968).
(5) W. E. Truce and P. S. Bailey, Jr., *J. Org. Chem.*, **34**, 1341 (1969).

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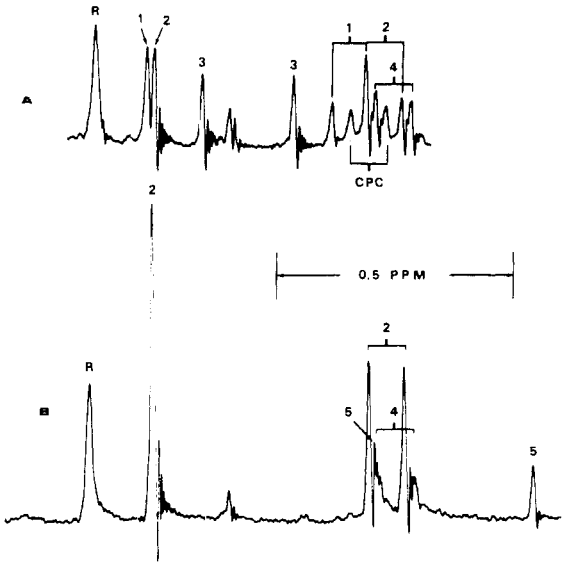
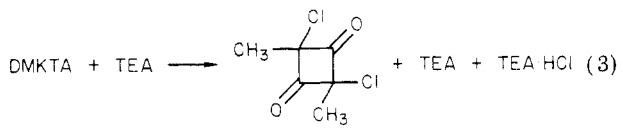


Figure 1. Static 100-MHz proton NMR spectra of the CH_3 resonance region obtained for chloroform solutions at 30 °C with the magnetic field strength increasing from left to right. The resonance labeled R is due to the CH_3 protons of toluene, which is used as an internal reference. (A) Spectrum obtained 12 min after mixing, for a solution containing 0.47 M TEA and 0.21 M CPC initially. (B) Spectrum obtained 1 min after mixing, for a solution containing 0.22 M Dabco, 0.21 M CPC, and 0.83 M cyclopentadiene initially. Resonance assignments are given in Table I.

the formation of two species, which apparently have not been detected previously, according to Scheme I. The equilibrium between 2,4-dichloro-2-methyl-3-keto-*N*,*N*,*N*-trialkylpentanamide (DMKTA) and CPC is rapid for both bases. However, the rate for the subsequent formation of 2,4-dichloro-2-methyl-3-ketopentanoyl chloride (DMKC) depends on the nature of the base, being substantially faster for Dabco than for TEA.

In addition to DMKC and DMKTA, a number of other compounds are detected over a period of a few hours; most are minor products that occur when either Dabco or TEA is used. However, the cyclic dimer of methylchloroketene is produced only when TEA is used. This compound does not appear to be formed directly via dimerization of the ketene. Instead, the mechanism involves cyclization of DMKTA according to eq 3. Thus, (3) is competitive with



(cis and trans)

(2) when TEA is used but not when Dabco is used. This difference in behavior for the two bases occurs because the rate for (2) is appreciably slower for TEA than for Dabco.

Results

Room Temperature. Figure 1 illustrates static 100-MHz proton NMR spectra obtained at 30 °C in chloroform with each base. Figure 1A was obtained 12 min after mixing by using a solution containing 0.47 M TEA and 0.21 M CPC. This spectrum, which shows only part of the CH_3 region and is time dependent, illustrates the presence of a number of compounds in addition to CPC. The CH_3 triplet due to TEA is further upfield and is not illustrated. The broad singlet labeled R is due to the CH_3 protons of toluene and is used as a chemical shift and intensity reference. Assignments of the labeled signals are presented

Table I. Proton NMR Chemical Shifts Relative to Tetramethylsilane for Various Species Observed during the Reaction between 2-Chloropropanoyl Chloride and either Dabco or TEA Obtained at 100 MHz and 30 °C in Chloroform[a,b]

compd	shift, ppm (*J*, Hz) CH_3	CH
$CH_3CHClCClO$ (CPC)	1.73 (7.5)	4.71, q
$CH_3CHClCOCCl(CH_3)CClO$ (DMKC) (2)	1.71 (7.5), 2.20	4.56, q
$(CH_3CHClCO)_2O$ (4)	1.69 (7.5)	4.53, q
cyclic compound[c] (3)	1.90, 2.09	
$CH_3CHClCOCCl(CH_3)CON(Et)_3^+Cl^-$[d] (DMKTA) (1)	1.78 (7.1), 2.21	
$CH_3CHClCOCCl(CH_3)CO$-(Dabco)$^+Cl^-$[e]	1.87 (6.5), 2.18	
$CH_3CHClCOOH$[f]	1.65 (7.5)	
7-chloro-7-methylbicyclo-[3.2.0]hept-2-en-6-one[g] (CMBH) (5)	1.38, endo 1.72, exo	
unknown 1	2.04	
unknown 2	1.66 (7.5), 2.03	

[a] Chemical shifts were obtained in reaction mixtures relative to the CH_3 resonance of toluene whose chemical shift relative to tetramethylsilane is 2.32 ppm (ref 5). [b] CH_3 resonances are either singlets or doublets as indicated. [c] Not observed when Dabco is used, tentatively identified as the cis and trans isomers of 2,4-dichloro-2,4-dimethyl-1,3-cyclobutadione. [d] Observed at 30 °C and at low temperature down to −30 °C. [e] Observed only at low temperatures from −10 to −30 °C. [f] Obtained by mixing a $CHCl_3$ solution of CPC with H_2O for 3 days. Doublet occurs at 1.61 ppm when TEA is present. [g] Obtained when cyclopentadiene is present in the reaction mixture. See text.

in Table I along with chemical shifts relative to tetramethylsilane (Me_4Si) (based on 2.32 ppm for the CH_3 resonance of toluene).[6] Under these conditions, the signals due to CPC continue to decay to zero over a period of about 130 min. In addition, the signals due to DMKTA and the cyclobutadione are transient, with DMKTA disappearing completely after 170 min and the cyclobutadione being reduced to zero after 24 h. DMKC appears stable over this period. The cyclobutadione and DMKC attain maximum concentrations over the same time period (about 170 min), and the decay of the dione does not lead to additional DMKC or any other material whose NMR signals can be detected.

In addition to the dione and DMKC, a number of weaker signals due to minor products are observed; they amount to about 30 and 20% of total observable product for initial TEA concentrations of 0.23 and 0.47 M, respectively (0.21 M CPC in both cases). On the basis of the initial concentration of CPC, the percent conversion of CPC to total observable products is 83 and 88%, respectively. Although it is possible to speculate on the identity of these minor products, we feel that there is insufficient evidence to make assignments except in the case of the anhydride of 2-chloropropanoic acid (Table I).

As indicated above, the rate of decay of CPC increases as the initial concentration of TEA is increased from 0.23 to 0.47 M; i.e., CPC signals cannot be detected after 300 and 130 min, respectively. However, in addition to this slow decay of CPC, there is a rapid initial decay, which is complete before the first scan of the NMR spectrum is made (i.e., about 1 min after mixing). In fact, this initial decay is too rapid to measure by using stopped-flow NMR

(6) N. S. Bhacca, L. Johnson, and J. Shoolery, "High Resolution NMR Catalog", Vol. 1, Varian Associates, Palo Alto, CA, 1962.

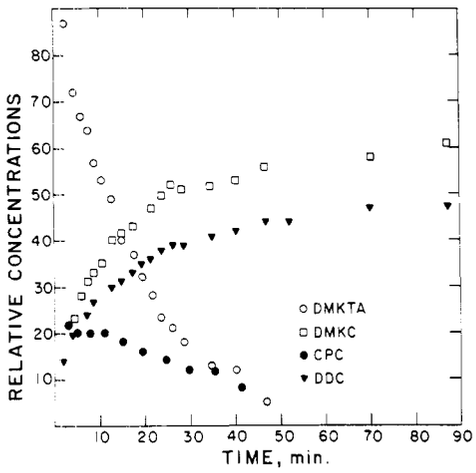


Figure 2. Time dependence for CPC and the major products obtained for a solution containing 0.47 M TEA and 0.21 M CPC initially at 30 °C.

at −30 °C (i.e., complete in less than a few seconds). Concomitant with this decay is the rapid growth of DMKTA to its maximum concentration, which increases as the initial concentration of TEA increases. Thus, for solutions containing 0.12, 0.23, and 0.47 M TEA initially, the DMKTA/CPC NMR intensity ratios are 0.1, 0.6, and 2.6, respectively[7] (0.21 M CPC).

The subsequent slow decay of CPC corresponds to the same time scale as that for the decay of DMKTA as indicated in Figure 2, which illustrates the time dependences of the intensities of signals due to CPC, DMKTA, DMKC, and the dione for a solution containing 0.21 M CPC and 0.47 M TEA initially. From this figure it is also apparent that the amounts of DMKC and the dione grow with similar time dependences, which correspond to that for the decay of DMKTA.[7] Similar relationships between the time dependences for the various species are observed for 0.12 and 0.23 M TEA although the rates appear slower.

Because the dione forms faster than it decays (Figure 2), a comparison of its concentration with that of DMKC is possible. Thus, the dione/DMKC concentration ratio increases (0.1, 0.4, and 0.8) as the initial concentration of TEA increases (0.12, 0.23, and 0.47 M, respectively) while the CPC concentration is held constant (0.21 M).

The results obtained at 30 °C when Dabco is used as the base are in marked contrast with those found for TEA. First, the formation of DMKC occurs at a substantially faster rate than that observed for TEA. Thus, Figure 1B, which is obtained within 1 min after mixing, indicates that the decay of CPC is complete. Second, the Dabco analogue of DMKTA is not observed. Third, the cyclobutadione DDC is not observed. This spectrum was obtained for a solution containing 0.21 M CPC, 0.22 M Dabco and 0.83 M cyclopentadiene, which was added to illustrate that cyclopentadiene has a minimal effect on the rapid formation of DMKC. As described below, DMKC decays slowly under these conditions to form CMBH, the ketene–cyclopentadiene adduct, and the weak exo and endo CH_3 resonances are observed in Figure 1B. Except for these resonances, the spectrum obtained in the absence of cyclopentadiene is identical with Figure 1B. The formation of DMKC does not depend on the CPC/Dabco concentration ratio. Thus, for solutions containing 0.11, 0.31, and 0.42 M Dabco and a constant concentration of CPC (0.21 M), DMKC is the major product but is unstable in the presence of Dabco and slowly decays to unidentified products with a rate that increases with increasing initial Dabco concentration; the lifetime is less than 24 h for 0.42 M Dabco.

The stability of DMKC in chloroform is increased upon removing Dabco by washing for 1 min with H_2O or D_2O followed by drying over molecular sieves; i.e., little decay is observed over a period of days. This solution was used for the mass spectral analysis, which supports our structure assignment, as described below. Although hydrolysis of DMKC might be expected as a result of this washing procedure, none can be detected in the NMR spectrum. Hydrolysis under these conditions appears slow; i.e., complete hydrolysis of CPC to its corresponding acid in a chloroform–water mixture requires about 3 days.

The intensity of the weak doublet labeled 4 in Figure 1B varies among runs but not in a systematic manner. This doublet has been assigned to the anhydride of 2-chloropropanoic acid. The evidence for this conclusion is that this doublet along with a quartet remains after the chloroform solution has been washed with water to remove Dabco and does not have the same chemical shift as that for 2-chloropropanoic acid (Table I). Varying the water content in the reaction solution could account for the intensity variation.

Low Temperature. For TEA at −10, −20, −25, and −30 °C, the reaction provides the same spectrum as that at 30 °C except that the rates are slower. No new signals are observed even with a flow rate of 30 mL/min. For Dabco, the low-temperature results differ from those at 30 °C both because the rate of formation of DMKC is reduced and because an additional species (doublet at δ 1.87, J = 6.5 Hz, and singlet at δ 2.18 at −30 °C) is observed. This species is believed to be the Dabco analogue of DMKTA because of its spectrum and because it appears to be a precursor of DMKC.

Cyclopentadiene. Figure 1B illustrates that the presence of 0.83 M cyclopentadiene does not prevent the rapid formation of DMKC via reaction between CPC and Dabco. Under these conditions, DMKC is unstable and slowly decays with a concomitant growth of 7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (CMBH), the ketene–cyclopentadiene adduct, over a period of 87 min. The rate of formation of CMBH increases as the initial concentration of Dabco is increased, keeping CPC and cyclopentadiene constant. Thus for solutions containing 0.12, 0.19, and and 0.25 M Dabco, the maximum concentration of CMBH is attained in 113, 87, and 45 min, respectively (for 0.20 M CPC and 0.83 M cyclopentadiene). An accurate determination of the fraction of DMKC converted to CMBH is not possible from the NMR spectrum because precipitation occurs. Qualitatively it appears that a solution containing 0.19 M Dabco and 0.20 M CPC provides the best conversion, approximately 85%.

In contrast with Dabco, TEA generates the ketene–cyclopentadiene adduct very fast with almost 100% conversion, and DMKTA is not observed at any temperature. At −30 °C with flowing at 30 mL/min, the NMR spectrum indicates that adduct formation is about 50% complete. This reaction is too fast to be measured by stopped-flow NMR at this temperature. At −10 or −30 °C, quantitative conversion of CPC to CMBH is attained for a solution containing 0.15 M CPC, 0.25 M TEA, and 0.40 M cyclopentadiene. At 30 °C, a maximum CMBH yield of 84% (based on CPC) was obtained for a solution containing 0.20 M CPC, 0.25 M TEA, and 0.75 M cyclopentadiene. No other products were observed.

(7) The intensities in this figure are directly related to relative concentrations of the various species because the signal intensities have been adjusted for line-width differences; i.e., the ratio of line widths is related to the ratio of peak heights.

Discussion

A common mechanism that can account for both the Dabco and TEA results is presented in eq 1, 2, and 3. According to this scheme, the first step involves rapid equilibration of DMKTA and starting materials. As described below, implicit in this process is the intermediacy of methylchloroketene, which has not been detected. The relative rates for steps 2 and 3 depend on both the nature and concentration of the base.

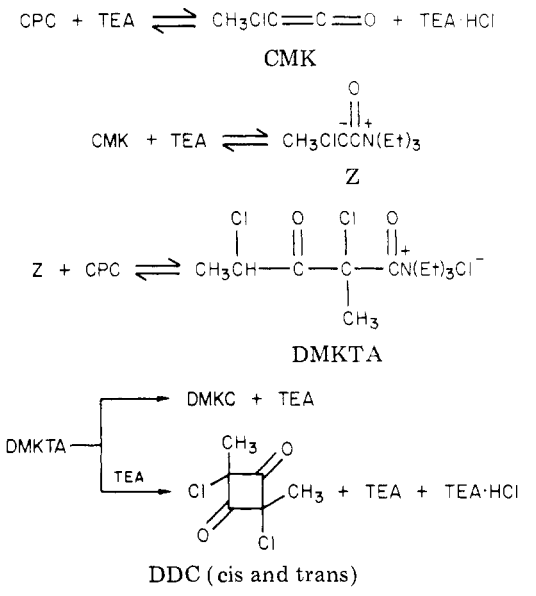
For Dabco, nucleophilic displacement on DMKTA by chloride ion to give DMKC (eq 2) is sufficiently fast at 30 °C so that DMKTA is not detected (Figure 1B). In addition, 2,4-dichloro-2,4-dimethyl-1,3-cyclobutadione (DDC) is not detected in this spectrum, indicating that eq 3 is substantially slower than eq 2 in this case. When the temperature is lowered to −10 °C, reaction 2 is slowed sufficiently to allow the detection of the Dabco analogue of DMKTA.

At these temperatures, reaction 3 is still not competitive with reaction 2 since DDC is not detected during the course of the reaction. The identification of the transient detected at low temperatures is based on its partial spectrum (Table I) and the fact that the time dependence of its signal indicates that it precedes DMKC. Arguments for a rapid equilibrium between DMKTA and CPC will be presented below when the cyclopentadiene results are considered.

The mechanism given by eq 1, 2, and 3 is also consistent with the results for TEA, although the relative rates for the various steps are not the same as those for Dabco. Thus for TEA, steps 2 and 3 are competitive since both DMKC and DDC are formed. Furthermore, these steps appear to be substantially slower than step 2 for the Dabco case for two reasons. First, DMKTA (TEA) is observed at 30 °C and decays slowly over a period of many minutes (depending on initial TEA concentration as discussed below), as indicated in Figure 2. Second, in contrast with the rapid disappearance of CPC in the Dabco case, the complete disappearance of CPC in the presence of TEA requires many minutes (Figure 2). Consequently it appears that changing the base from Dabco to TEA causes a substantial reduction in the rate for step 2, thus allowing the cyclization step (eq 3) to become competitive; i.e., changing from Dabco to TEA probably does not cause a large increase in the rate of cyclization. Two factors may be responsible for the rate difference observed for step 2 when the two bases are compared. First, TEA has bulkier alkyl groups around its nitrogen atom than Dabco. Thus, since step 2 involves chloride ion addition to the acyl carbonyl carbon of DMKTA to subsequently displace the amine to form DMKC, bulky groups on the amine can reduce the rate of this step. In this regard, space-filling models indicate that the acyl carbonyl group of DMKTA is buried in the molecule when TEA is attached whereas one side of this group is accessible when Dabco is attached. Thus, steric hindrance could be partially responsible for the slower rate for TEA compared with that for Dabco. Second, Dabco has a lower pK_a than TEA (9.24[8] vs. 10.65[9]) and, therefore, may be a better leaving group.

Postulation of an equilibrium for step 1 is based on the time dependence of the TEA analogue of DMKTA as well as on the results obtained in the presence of cyclopentadiene. Thus, when TEA is used, the maximum concentration of DMKTA is obtained quickly at both room and low temperatures and then slowly decreases as CPC decreases (Figure 2). Even with stopped-flow NMR at −30 °C, DMKTA (TEA) reaches its maximum concentration in a time too short to measure. As expected for an equilibrium, the initial concentration ratio DMKTA/CPC increases as the initial concentration of TEA is increased while the initial CPC concentration is constant at 0.21 M, i.e., 0.1, 0.6, and 2.6 for 0.12, 0.23, and 0.47 M TEA, respectively. An attempt to calculate an equilibrium constant based on eq 1 gave values that increase as TEA concentration increases.

Scheme II



On the basis of the discussion and information given above, a more detailed description of eq 1–3 is possible. Scheme II is presented using TEA and will be related to the Dabco results subsequently. According to this scheme, the formation of DMKTA involves dehydrohalogenation of CPC by TEA to form methylchloroketene (CMK) to which TEA subsequently adds to form the zwitterion (Z). The rapid equilibration between CMK and Z in this scheme is consistent with the slow subsequent decay of starting material CPC and the rapid rate at which DMKTA attains its maximum concentration. It is also consistent with the rapid formation of DMKC when Dabco is the base. The equilibrium between Z and DMKTA as well as the two prior equilibria is required because on the one hand, CPC decays slowly in the absence of cyclopentadiene, but on the other hand, it decays rapidly when cyclopentadiene is present in the TEA case. As indicated in Scheme II, TEA is required for the formation of 2,4-dichloro-2,4-dimethylcyclobutadione (DDC) since increasing the initial concentration of TEA causes an increase in the concentration ratio DDC/DMKC. Presumably the rate-determining step for cyclization via DMKTA involves removal of its methine proton. Whether this step is concerted or involves formation of a zwitterionic intermediate cannot be decided on the basis of our results. According to our results, it appears that the alternate route involving reaction between CPC and the anion $(CH_3C(Cl)CClO)^-$ is not competitive, indicating that formation of ketene from this anion is probably rapid.

For TEA, it would appear that this mechanism proceeds up to the formation of DMKTA in the presence of cyclopentadiene even though formation of the bicyclic adduct is fast. This conclusion is based on the fact that DMKC is formed prior to formation of the bicyclic adduct when Dabco is used instead of TEA. Consequently it appears that nucleophilic addition to the ketene CMK by Dabco (and presumably by TEA) is faster than addition of cy-

(8) V. Malatesta and M. Cocivera, *J. Org. Chem.*, **43**, 1737 (1978).
(9) J. Hall, *J. Am. Chem. Soc.*, **79**, 5441 (1957).

clopentadiene to the ketene. As a result, the distinction between Dabco and TEA as reactants occurs in the subsequent reaction of DMKTA; i.e., relative to cyclopentadiene addition to ketene, the reaction between chloride ion and DMKTA to form DMKC is fast for Dabco and slow for TEA. The present data give no indication of the details concerning the formation of the bicyclic adduct (CMBH), i.e., whether the ketene CMK or the zwitterion Z is reacting with cyclopentadiene.

The cyclic compound DDC is a transient species under conditions in which excess base is present. For example, for a solution containing 0.21 M CPC and 0.23 M TEA, the signals due to DDC cannot be detected 24 h after mixing. On the other hand, when the concentration of CPC exceeds that of TEA (0.21 vs. 0.12 M), DDC is stable over this period. Thus, TEA base is required for the decomposition of DDC. The mechanism probably involves nucleophilic addition of TEA to one of the carbonyl carbon atoms of DDC. The identity of the decomposition product(s) cannot be discerned since no new NMR signals were observed.

The mechanisms discussed above are predicated on the identification of the various species in solution as well as on their time dependence. The evidence for the identity of each compound is presented below.

2,4-Dichloro-2-methyl-3-ketopentanoyl chloride (DMKC) was assigned the spectrum indicated in Table I. Other structures were ruled out for the following reasons. First, washing the reaction mixture with H_2O or D_2O for 1 min (followed by drying over molecular sieves for 1 h) removes Dabco and Dabco·HCl from the $CHCl_3$ solution, leaving almost predominantly the species having the spectrum assigned to this compound.[10] Additional support for the DMKC structure is obtained from the mass spectrum of this compound. Although DMKC could not be isolated from the washed and dried $CHCl_3$ solution without decomposition, its mass spectrum could be obtained by using the solution.[11] In agreement with the molecular weight of DMKC and various isotopic weights for chlorine, three parent ion peaks are observed at m/e 215.8 (M^+), 217.8 ($M^+ + 2$), and 219.8 ($M^+ + 4$) and have relative intensities 3, 3, and 1, respectively. These relative intensities are identical with those expected for a compound containing three chlorine atoms.[12] The ($M^+ + 6$) peak is not observed, presumably because its intensity is expected to be one-tenth the value for the ($M^+ + 4$) peak. Another series of three peaks at m/e 126, 128, and 130 with relative intensities 1.00, 0.63, and 0.10 correspond to the fragment $(CH_3CClCClO)^+$·. These results are consistent only with the DMKC structure and not with 2,4-dichloro-2-methyl-3-ketopentanoic acid or its anhydride. From these results it is clear that washing the $CHCl_3$ solution with water does not result in rapid hydrolysis of the acyl chloride. That this hydrolysis is slow is confirmed by the fact that no hydrolysis (on the basis of the NMR spectrum) was observed when CPC in $CHCl_3$ was mixed with water for $^1/_2$ h. Complete hydrolysis of CPC to its corresponding acid as determined by NMR required about 3 days. The spectrum reported in Table I for 2-chloropropanoic acid was obtained after drying the chloroform solution over molecular sieves for $^1/_2$ h. The fact that DMKC is stable even in the presence of cyclopentadiene over a period of days after Dabco has been washed from the solution indicates that its decomposition requires base.

Other major products are identified solely on the basis of their NMR spectra and their time dependence as described above. Of these NMR assignments, the one for 2,4-dichloro-2,4-dimethyl-1,3-cyclobutadione (DDC) must be considered tentative since the β-lactone structure, which can be formed from DMKTA via ring closure at oxygen after proton removal by TEA, is also consistent with the relative chemical shifts listed in Table I. The butadione structure is chosen because previous data indicate that dimerization of ketoketenes to β-lactones requires the presence of a Lewis acid such as $AlCl_3$.[13] Consequently, since removal of a proton from DMKTA prior to cyclization would result in a zwitterion identical with that which may be envisioned for TEA-catalyzed dimerization of ketoketenes, we tend to prefer the cyclobutadione structure for the species observed in Figure 1A.

Minor products of which three are detected when either base is used amount to 30% or less of the total product as described above. Their growth appears to occur over the same time scale as that for DMKC. Of these three, there is sufficient evidence for the tentative assignment of only one, the anhydride of 2-chloropropanoic acid (Table I and Figure 1). This assignment is based on a process of elimination. Thus, this species is not the quaternized amide of 2-chloropropanoic acid since its resonance remains after Dabco has been removed by washing with water. It cannot be the propanoic acid because its CH_3 proton resonance has a different chemical shift (Table I). In addition, during the period employed for this study, reaction between TEA and $CHCl_3$ (or any possible impurities) could not be detected.

7-Chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one (CMBH) is formed when cyclopentadiene is present although the mechanism depends upon the nature of the base employed; i.e., DMKC is an intermediate for Dabco but not for TEA. In the case of Dabco, the mechanism probably involves removal of the methine proton of DMKC by base to form two molecules of ketene, which subsequently react with cyclopentadiene; i.e., the rate of CMBH formation increases with an increase in initial Dabco concentration. The *exo*- and *endo*-CH_3 isomers of CMBH are observed with CH_3 resonance chemical shifts (Table I) close to those found previously.[2c,14] The exo/endo ratio of about 1.5 appears to be independent of the nature and concentration of base as well as the temperature. On the other hand, solvent affects this ratio (4.3 and 0.59 for hexane and acetonitrile, respectively).[2c]

Experimental Section

NMR. The static proton NMR spectra at 100 MHz were measured at 30 ± 0.2 °C by using a Varian HA-100, and the stopped-flow spectra were measured at −30, −25, −20, and −10 °C by using a Varian HA-100-15 equipped with a flow system described previously.[15]

Chemicals and Solutions. Dabco, triethylamine, and 2-chloropropanoyl chloride were obtained from commercial sources and were purified by literature methods such that their melting points and spectroscopic properties agree with those reported previously. Cyclopentadiene was prepared from the thermal decomposition of the dimer.[16] Solutions were prepared in eth-

(10) Occasionally the CH_3 proton resonance assigned to the anhydride of 2-chloropropanoic acid (Table I) is also observed (Figure 1) with an intensity that varies, presumably because the water content of the solution varies. The reasons for this assignment are given below.

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anol-free chloroform[17] by mixing equal volumes of reactant solutions.

Product Analysis. In a typical run, 2 mL of Dabco, 0.3 M in $CDCl_3$, and 2 mL of chloropropanoyl chloride, 0.15 M in $CDCl_3$, were mixed at room temperature for 30 s; the chloroform solution was immediately washed with water to extract Dabco and dried over molecular sieves. The product, when analyzed by NMR (Table I) and mass spectra as described in the text, agrees with the structure $CH_3CHClCOC(CH_3)(Cl)COCl$.

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Registry No. CPC, 7623-09-8; DMKC, 20320-72-3; 2-chloropropanoic anhydride, 39060-20-3; *cis*-DDC, 72206-86-1; *trans*-DDC, 72206-87-2; DMKTA, 72206-88-3; 1-(2,4-dichloro-2-methyl-3-oxopentanoyl)-1,4-diazabicyclo[2.2.2]octane·HCl, 72206-89-4; 2-chloropentanoic acid, 598-78-7; *endo*-7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one, 13363-88-7; *exo*-7-chloro-7-methylbicyclo[3.2.0]hept-2-en-6-one, 13363-87-6; Dabco, 280-57-9; TEA, 121-44-8.

Stereochemistry and Mechanism of a Radical-Induced (E_H) Elimination Reaction. Reaction of Trichloromethyl Radicals with 2-(Trimethylstannyl)butane and 3-Deuterio-2-(trimethylstannyl)butane

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threo- and *erythro*-3-deuterio-2-(trimethylstannyl)butanes (**1**-*d*) were prepared with high purity by the reaction of trimethyltinsodium with *erythro*- or *threo*-3-deuterio-2-[(4-methylphenyl)sulfonoxy]butane. Reaction of these and (trimethylstannyl)butane (**1**) with trichloromethyl radical generated by thermal decomposition of benzoyl peroxide in bromotrichloromethane resulted in the formation of 1-butene plus *cis*- and *trans*-2-butene along with bromobenzene, chloroform, 2-bromo-2-(trimethylstannyl)butane (**2**), trimethyltin bromide, and other products. Analysis of the olefin distributions shows a primary/secondary preference of 15:1 for the hydrogen abstraction and a 75–77% preference for antiperiplanar elimination is calculated by using the experimentally determined primary deuterium isotope effect $k_H/k_D = 5.1 \pm 0.3$. The results are discussed in terms of two proposed elimination mechanisms: (1) a concerted E_H2 reaction with anti and syn elimination pathways, (2) a two-step E2ir reaction in which initial anti proton abstraction to a 3-(trimethylstannyl)-2-butyl radical occurs with subsequent competition between collapse to an olefin and rotation about the C-2,C-3 bond followed by olefin formation.

Solution-phase radical-induced β eliminations have been proposed to rationalize the results of a number of investigations,[1] and anchimeric assistance of hydrogen abstraction, with or without bridging, has been recognized in various systems.[2] Kampmeier and co-workers demonstrated the formation of olefins in the nonchain decomposition of *tert*-butyl sulfide, phenyl *tert*-butyl sulfide, and phenyl amyl sulfides.[3,4] The conclusions were that the reaction occurs by unassisted hydrogen abstraction, giving an intermediate radical, followed by collapse to an olefin and a thiyl radical as the most likely reaction path. It was suggested that a less reactive, more selective radical along with a weaker carbon leaving group bond might result in a concerted E_H2 reaction.

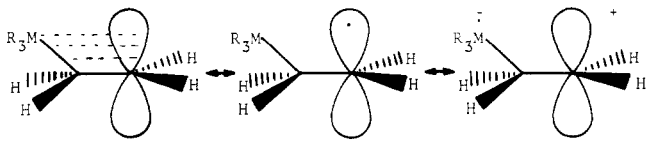
Another way in which a concerted E_H2 reaction might result is if the compound contained a leaving group with demonstrated ability to stabilize a radical center β to it. Kuivila et al.[5] found that tri-*n*-butyltin hydride dehalogenates vicinal dihalides according to the stoichiometry in eq 1. When *dl*- and *meso*-2,3-dibromobutanes were

$$\text{X—C—C—X} + 2(\text{Bu})_3\text{Sn—H} \rightarrow \text{C=C} + 2(\text{Bu})_3\text{SnX} + \text{H}_2 \quad (1)$$

treated independently with 2 mol of tri-*n*-butyltin hydride, mainly *cis*- and *trans*-2-butene, respectively, were produced, indicating preferential anti elimination. Various controls indicated a free-radical chain reaction, and stereospecificity increased with increasing tin hydride concentration. A stepwise pathway was proposed in which an initially formed bridged β-bromoalkyl radical undergoes rotation with concomitant loss of stereospecificity.

It is entirely possible that the stereospecificity originated not from a completely bridged structure but simply from a conformational preference in which the C–Br bond aligns itself with the p orbital of the lone electron to achieve maximum overlap. Evidence for this type of phenomenon will be discussed below.

Kochi and co-workers[6] have shown that compounds of the type $R_3MCH_2CH_2\cdot$ (M = Si, Ge, Sn) are considerably stabilized relative to $CH_3CH_2\cdot$ or $RCH_2CH_2\cdot$ (R = alkyl), and the most stable conformation of the molecule is with the metal–carbon bond lying in the plane described by the carbon–carbon bond axis and the p orbital occupied by the unpaired electron. The β-hydrogen hyperfine splitting and the anisotropic *g* factor were interpreted as indicative of both p–σ hyperconjugation and p–d homoconjugation in the radical–metal interaction.[7] In the case of M = Sn the stabilization was estimated to be approximately 2 kcal/mol.[6b]



p–σ hyperconjugation p–d homoconjugation

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