spectrum of the separated 4-picoline gave a ratio of (H-2 and H-6)/(H-3 and H-5) = 1. The integration of the methyl group accounted only for 2.25 ± 0.05 H, which reflects the amount of deuterium incorporated into the methyl group (CH_2D).

Registry No. 1, 73853-36-8; 2, 2294-74-8; 3, 20151-01-3; 4, 6580-93-4; 5, 20151-37-5; 6, 20151-33-1; 7, 6312-10-3; 2-picoline, 109-06-8; *p*-methoxybenzaldehyde, 123-11-5; *p*-nitrobenzaldehyde, 555-16-8; 4-picoline, 108-89-4.

Dimethylformamide-Catalyzed Decarboxylation of Alkyl Chloroformates. A Synthesis of Primary Alkyl Chlorides

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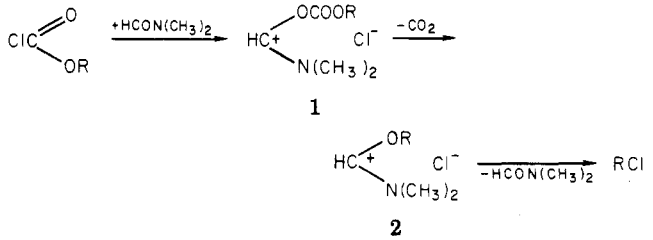
We required an efficient method for the synthesis of a number of primary aliphatic mono- and dichlorides from readily available aliphatic alcohols as starting materials. Most of the methods available for the OH → Cl exchange employ phosphorous halides or oxy halides (PCl_3, PCl_5, $POCl_3$, R_3PCl_2) and thionyl chloride as chlorinating agents, often in conjunction with pyridine or other tertiary amines as bases, which can complicate the workup and lead to undesirable byproducts. The preparation of primary alkyl chlorides from long-chain alcohols and hydrogen chloride requires generally long reaction times, high temperatures, and Lewis acid catalysts in order to obtain good yields. This method also gives poor results with long-chain diols.[1]

We developed a method for the clean and convenient preparation of primary alkyl chlorides by decarboxylating the corresponding alkyl chloroformates in the presence of dimethylformamide (DMF) as catalyst. The reactions are based on the observation by Bredereck et al.[2] that ethyl chloroformate is readily decarboxylated by DMF, presumably via a labile 1:1-adduct of type **1**.



The chloroformates used for these transformations are prepared from the corresponding alcohols and phosgene, preferentially in a solvent, prior to decarboxylation and are not isolated or further purified. The decarboxylations are carried out in solvents such as chloroform or 1,2-dichloroethane (DCE), especially when low-boiling alkyl chlorides are prepared; chloroformates derived from long-chain alcohols do not require a solvent and are either added to DMF, which is used as reaction medium, or heated with catalytic amounts of DMF (for details see Table I). This indicates that the catalyst/substrate ratio is not critical and depends solely on the ease with which decarboxylation takes place. Progress of the reactions can be coveniently followed by IR spectroscopy on monitoring the disappearance of the characteristic carbonyl band of chloroformates at 1760–1780 cm^{-1}. Reaction durations ranged from 2 to 10 h and were never optimized although milder conditions and thus longer durations were always preferred to avoid anticipated side reactions. Formation of olefinic byproducts was never encountered. The overall reactions were found to be surprisingly clean and only occasionally were crude products contaminated by trace amounts of dialkyl carbonates. Yields of distilled products were found to be generally above 90%; lower yields are mainly due to loss of alkyl chlorides during workup (volatility). Where codistillation of product and DMF was anticipated, extraction of the reaction solution with water preceded isolation. The mono- and dichlorides prepared by this method are listed in Table I.

The thermal decomposition of a number of alkyl chloroformates has been studied extensively, especially in connection with the related chlorosulfite decompositions.[3] No attempt has been made, however, to utilize these reactions for the synthesis of alkyl chlorides.[4] The results of these investigations indicate further that uncatalyzed decompositions have indeed only limited synthetic usefulness as mixtures of products are often obtained.

Primary alkyl chloroformates are relatively stable provided the RO bond in ROCOCl is not weakened by additional substituents in R that could enhance the formation of R^+ (as in benzyl or secondary alkyl chloroformates[5,6]). Ethyl chloroformate shows no tendency to decarboxylate on heating neat or in solution but will eventually do so in the gas phase above 150 °C.[7] *n*-Butyl and *n*-pentyl chloroformate are equally resistent to decarboxylation and only on prolonged heating at 150 °C will they yield mixtures of primary as well as secondary alkyl chlorides together with olefinic products.[6] It was therefore unexpected that the DMF-catalyzed decarboxylations of unactivated alkyl chloroformates proceeded smoothly and often at room temperature.

The role of the catalyst is based on the readiness of DMF to be *O*-acylated to give adduct **1**. Elimination of carbon dioxide is believed to lead to **2** which is expected to be very labile as DMF is not easily alkylated by alkyl chlorides.[2,8] Stabilization of type **2** compounds with counterions other than Cl^-, such as $CH_3OSO_3^-$ and BF_4^-, has been shown to be possible.[2,9] We were able to ascertain in two cases the formation of formimidate salts **2** as reaction intermediates. On slow addition of the dichloroformate of trans as well as cis/trans mixtures of 1,4-bis(hydroxymethyl)cyclohexane to a large excess of DMF at 3–5 °C, decarboxylation is accompanied by formation of copious amounts of a colorless, water-soluble precipitate of **2a** (R = $CH_2C_6H_{10}CH_2$), which can be stabilized by conversion into the tetrafluoroborate **3** (isolated in 55% yield). Hydrolysis of **2a** suspended in DMF at room temperature gives high yields of the diformate of 1,4-bis(hydroxymethyl)cyclohexane. If, on the other hand, suspensions of **2a** are heated to 75 °C for 2 h, gradual cleavage of the formimidate chloride into *trans*-1,4-bis(chloromethyl)cyclohexane (isolated in 90% yield) and DMF takes place.

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(2) Bredereck, H.; Effenberger, F.; Simchen, G. *Chem. Ber.* **1963**, *96*, 1350.
(3) For a review, see Kevill, D. N. In "The Chemistry of Acyl Halides"; Patai, S., Ed.; Interscience: Wiley, London, 1972; p 381.
(4) Alkyl fluorides have been synthesized via fluoroformate decarboxylation catalyzed by pyridine: Nakanishi, S.; Meyers, T. C.; Jensen, E. V. *J. Am. Chem. Soc.* **1955**, *77*, 3099.
(5) Wiberg, K. B.; Shryne, T. M. *J. Am. Chem. Soc.* **1955**, *77*, 2774.
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(7) Choppin, A. R.; Frediani, H. A.; Kirby, G. F. Jr. *J. Am. Chem. Soc.* **1939**, *61*, 3176.
(8) Hünig, S. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 548.
(9) Ikawa, K.; Takami, F.; Fukui, Y.; Tokuyama, K. *Tetrahedron Lett.* **1969**, 3279.

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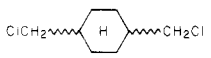
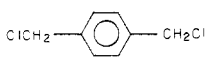
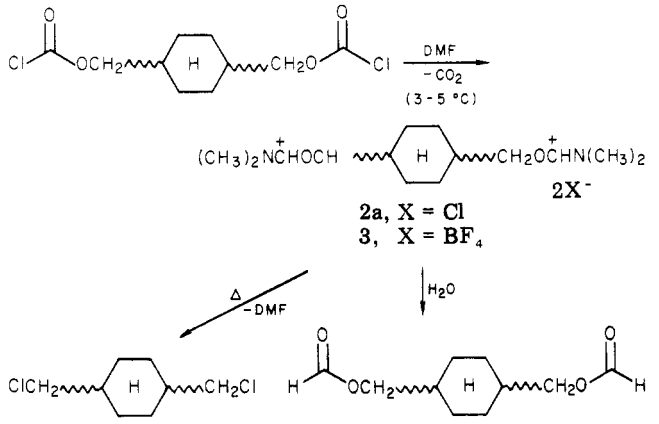
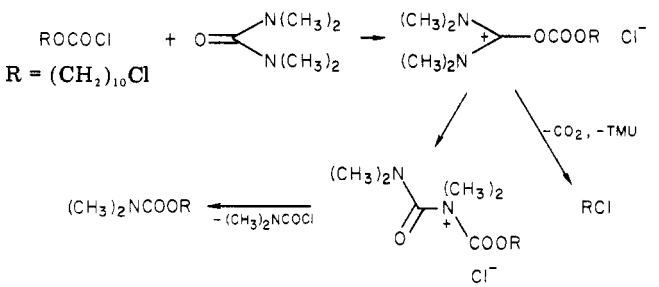
Table I. Alkyl Chlorides from Primary Alcohols

product	rctn cond	bp, °C (mmHg)	% yield (isolated)
$CH_3(CH_2)_5CH_2Cl$	0.4 mol/10 mL of DMF/68 °C	59 (11)	83
$CH_3(CH_2)_8CH_2Cl$	0.225 mol/4 mL of DMF/100-110 °C	65 (0.1)	93
$CH_3(CH_2)_{10}CH_2Cl$	0.1 mol added to 100 mL of DMF/26-32 °C (exotherm)	79 (0.15)	91
$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2Cl$	0.1 mol added to 100 mL of DMF/25-31 °C (exotherm)	110-120 (0.12)	92
$PhOCH_2CH_2Cl$	0.3 mol/100 mL of $CHCl_3$/10 mL of DMF/65-69 °C	99-101 (11)	92
$CH_3(CH_2)_3CH(C_2H_5)CH_2Cl$	0.3 mol/100 mL of $CHCl_3$/10 mL of DMF/72 °C	59-60 (11)	86
$ClCH_2(CH_2)_8CH_2Cl$	0.3 mol/10 mL of DMF/130-140 °C	91-92 (0.1)	97
	0.4 mol/10 mL of DMF/80 °C		
cis + trans		65-70 (0.1)	92
trans		69-70 (0.1)	90
	0.2 mol/100 mL of $CHCl_3$/5 mL of DMF/60-70 °C	mp 98 °C	quant
$ClCH_2C{\equiv}CCH_2Cl$	0.5 mol/250 mL of DCE/10 mL of DMF/80 °C	58-60 (11)	76
	0.3 mol/10 mL of DMF/140-150 °C	106-111 (0.1)	90

Similarly, decyl chloroformate produces with DMF under identical reaction and workup conditions either a mixture of decyl formate and decyl chloride in a ratio of 63:36 (92% combined yield) or, on heating, decyl chloride alone (93%).



The activation of the C–Cl bond in chloroformates is not limited to DMF. *N,N'*-Tetramethylurea (TMU), which, like DMF, is known to react readily with compounds having COCl, SOCl, and POCl groups,[10] can also be used as catalyst, but the decarboxylations require higher temperatures and formation of byproducts is a problem. Thus heating of the bis(chloroformate) derived from 1,10-decanediol with TMU to 130 °C for approximately 10 h leads to 71% of 1,10-dichlorodecane and some 10-chlorodecyl *N,N*-dimethylcarbamate (44%, based on the amount of TMU used), possibly after O → N migration of the ROCO group.



(10) For a review, see Kantlehner, W. In "Iminium Salts in Organic Chemistry"; Böhme, H., Viehe, H. G.; Ed.; Wiley: New York, 1979; p 143.

Experimental Section[11]

General Procedure for the Formation of Alkyl Chlorides from Alkyl Chloroformates. Chloroformates are prepared prior to decarboxylation by standard procedures (reacting the alcohol with excess phosgene in an appropriate solvent, such as CH_2Cl_2, $CHCl_3$, or 1,2-dichloroethane) and are used without purification and are free of phosgene.

Decarboxylations are carried out under conditions as given in Table I. Lower boiling chlorides are prepared in solutions ($CHCl_3$, DCE) containing DMF. Loss of product is prevented by attaching dry-ice condensers to the reaction flasks. Reaction durations range from 1 to 10 h; crude solutions are freed of DMF by extracting several times with small portions of water (efficiency of the extraction can be followed by IR spectroscopy; C=O band at 1665 cm^{-1} has to disappear). Higher boiling alkyl chlorides are best prepared by heating the chloroformates with small amounts DMF or adding the chloroformates dropwise to excess DMF while checking the exotherm of the reaction and the rate of carbon dioxide evolution.

Progress of decarboxylation is monitored in each case by following the disappearance of the C=O band of the chloroformates at ~1765 cm^{-1} in the IR spectra. Products or solutions remain mostly colorless throughout the process; occasionally they turn dark due to formation of small amounts of impurities, which never caused problems during purification. Yields were determined after isolation by distillation.

Decomposition of the Dichloroformate of 1,4-Bis(hydroxymethyl)cyclohexane in the Presence of DMF. A. A sample of the dichloroformate derived from *trans*-1,4-bis(hydroxymethyl)cyclohexane (26.9 g, 0.1 mol) is dissolved in 150 mL of DMF at 3–6 °C. Gas evolution ensues and a thick colorless precipitate is formed. After 3–4 h the mixture is allowed to reach room temperature and a solution of 21.8 g (0.2 mol) of sodium tetrafluoroborate in 100 mL of DMF is added at once. On stirring, the initially very thick suspension becomes very fluid as the imidate **2a** dissolves and sodium chloride precipitates. After 2 h the NaCl is removed (by filtration or decanting) and the filtrate concentrated in vacuo at 55–60 °C, leaving a thick oil that slowly crystallizes. Approximately 50–70 mL of dimethoxyethane (DME) is added to the crystal mass; filtration and washing the residue with DME leaves 23.65 g of **3** (55%), which is dried at 80 °C in vacuo, mp 128–130 °C. A sample of **3** recrystallized for analysis from 1-nitropropane melts unchanged. Anal. Calcd for $C_{14}H_{28}F_8B_2N_2O_2$: C, 39.10; H, 6.59; N, 6.51; F, 35.35. Found: C,

(11) All prepared alkyl chlorides are known compounds; they were, when possible, compared with authentic samples, using a Beckman Acculab 4 spectrophotometer (IR, $CHCl_3$) and Varian T-60 (H-NMR) and Varian CFT-20 (C-13 NMR) spectrometers with $CDCl_3$ as solvent and Me_4Si as internal standard for spectral identification; melting points are uncorrected. Purity of products was checked routinely by GC analysis (Hewlett-Packard Model 5730A instrument).

38.96; H, 6.44; N, 6.59; F, 35.12.

Solutions of **3** in Me_2SO-d_6 decompose within minutes due to the presence of traces of water; **3** is also readily hydrolyzed in aqueous solution to give the diformate.

B. A suspension of the cis/trans mixture of **2a** in DMF, prepared as described under A, is diluted with 500 mL of water and the resulting milky suspension is extracted with methylene chloride. The extracts are again shaken with water to remove DMF, dried, and concentrated. Vacuum distillation gives 31.4 g (79%) of the diformate of 1,4-bis(hydroxymethyl)cyclohexane, bp 94 °C (0.1 mm); spectroscopic data (IR, ^1H and ^{13}C NMR) confirm the structure of the compound.

C. A suspension, prepared as described under B, is heated for 2 h at 60–70 °C whereby the solid **2a** dissolves and a cis/trans mixture of 1,4-bis(chloromethyl)cyclohexane is formed. After removal of DMF by distillation at reduced pressure (10–12 mm), the product is distilled in vacuo, bp 65–70 °C (0.1 mm), yield 32.7 g (90%); IR and ^1H NMR spectroscopic data confirm the structure of the compound.

Registry No. *cis*-**2a**, 86217-95-0; *trans*-**2a**, 86217-96-1; **3**, 86217-98-3; $CH_3(CH_2)_5CH_2Cl$, 629-06-1; $CH_3(CH_2)_8CH_2Cl$, 1002-69-3; $CH_3(CH_2)_{10}CH_2Cl$, 112-52-7; $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2Cl$, 59485-81-3; $PhOCH_2CH_2Cl$, 622-86-6; $CH_3(CH_2)_3CH(C_2H_5)CH_2Cl$, 123-04-6; $ClCH_2(CH_2)_8CH_2Cl$, 2162-98-3; $ClCH_2C{\equiv}CCH_2Cl$, 821-10-3; $CH_3(CH_2)_5CH_2OCOCl$, 33758-34-8; $CH_3(CH_2)_8CH_2OCOCl$, 55488-51-2; $CH_3(CH_2)_{10}CH_2OCOCl$, 24460-74-0; $CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OCOCl$, 86217-99-4; $PhOCH_2CH_2OCOCl$, 34743-87-8; $CH_3(CH_2)_3CH(C_2H_5)CH_2OCOCl$, 24468-13-1; $ClCOOCH_2(CH_2)_8CH_2OCOCl$, 56757-75-6; $ClCOOCH_2C{\equiv}CCH_2OCOCl$, 16669-40-2; DMF, 68-12-2; *cis*-1,4-bis(chloromethyl)cyclohexane, 53188-14-0; *trans*-1,4-bis(chloromethyl)cyclohexane, 86218-00-0; 1,4-bis(chloromethyl)benzene, 623-25-6; decahydro-2,5-bis(chloromethyl)-4,7-methanoindene, 86218-01-1; *cis*-1,4-cyclohexanediyldimethylene bis(chloroformate), 86218-02-2; *trans*-1,4-cyclohexanediyldimethylene bis(chloroformate), 46744-84-7; 1,4-phenylenedimethylene bis(chloroformate), 10362-03-5; decahydro-2,5-bis[(chlorocarbonyloxy)methyl]-4,7-methanoindene, 86218-03-3; *cis*-1,4-bis(hydroxymethyl)cyclohexanediformate, 86218-04-4; *trans*-1,4-bis(hydroxymethyl)-cyclohexanediformate, 86218-05-5.

Vinyl Ether Hydrolysis. 16. 2-Cyclohexylidene-3,3-dimethyloxetane

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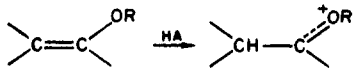
The acid-catalyzed hydrolysis of simple vinyl ethers is a process whose reaction mechanism is well characterized: the first step is known to be rate determining and to consist of proton transfer from the catalyst to the β-carbon atom of the carbon–carbon double bond system (eq 1).[1]



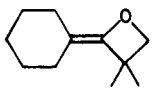
(1)

Table I. Rates of Hydrolysis of 2-Cyclohexylidene-3,3-dimethyloxetane in Aqueous Hydrochloric Acid Solution at 25 °C[a,b]

10^2[HCl], M	$10^2 k_{obsd}$, s^{-1}
0.60	1.47, 1.43, 1.47, 1.45
1.00	2.39, 2.34, 2.41
1.50	3.53, 3.61, 3.58, 3.71
2.00	4.72, 4.47, 4.85, 4.47
2.50	6.06, 5.93, 5.88, 6.08
3.00	7.09, 7.34, 7.10
4.00	9.10, 9.14, 9.18

[a] Ionic strength maintained at 0.10 M by adding NaCl. [b] $k_{obsd} = (1.21 \pm 0.62) \times 10^{-3} + (2.30 \pm 0.03)$[HCl].

This process is therefore especially well suited to investigating the effect of structure on chemical reactivity. A particular example which is perhaps of more than usual interest is the hydrolysis of 2-cyclohexylidene-3,3-dimethyloxetane (1) inasmuch as the vinyl ether functional



1

group in this substance is a part of two separate rings of different size. The hydrolysis reaction converts an sp^2-hybridized carbon atom of the six-membered ring into an sp^3-hybridized atom, which is a process known to be favored over the corresponding change in an acyclic system,[2] but it also introduces a partial double bond into a four-membered ring, and, since small unsaturated rings are highly strained,[3] this change would be disfavored over the corresponding transformation in a similar acyclic system.

It is of interest to determine which of these two opposing effects dominates, i.e., whether 1 is more or less reactive than an analogous acyclic vinyl ether. We have therefore measured the rate of hydrolysis of 1 and report our results herein.

Experimental Section

Materials. 2-Cyclohexylidene-3,3-dimethyloxetane was prepared as described before.[4] Hydrochloric acid solutions were made from deionized water purified further by distillation from alkaline permanganate.

Kinetics. Rates of hydrolysis were measured spectroscopically by following the decrease in absorbance of the vinyl ether functional group at λ = 210 nm. Measurements were made by using a Cary 118 C spectrometer with cell compartment thermostated at 25.0 ± 0.05 °C. The data conformed well to the first-order rate law, and first-order rate constants were evaluated as slopes of plots of ln $(A - A_\infty)$ vs. time.

Results and Discussion

Rates of hydrolysis of 2-cyclohexylidene-3,3-dimethyloxetane were measured in dilute HCl solutions over the concentration range 0.006–0.04 M. The observed first-order rate constants so obtained are accurately proportional to acid concentration, and least-squares analysis of the data (Table I) give the hydrogen ion catalytic coefficient $k_{H^+} = 2.30 \pm 0.03$ M^{-1} s^{-1}.

An appropriate simple acyclic analogue of 2-cyclohexylidene-3,3-dimethyloxetane (1) might be ethyl α-me-

(1) (a) Salomaa, P.; Kankaanpera, A.; Lajunen, M. *Acta Chem. Scand.* **1966**, *20*, 1970. Kresge, A. J.; Chiang, Y. *J. Chem. Soc. B.* **1967**, 53, 58. Kresge, A. J.; Chen, H. L.; Chiang, Y.; Murrill, E.; Payne, M. A.; Sagatys, D. S. *J. Am. Chem. Soc.* **1971**, *93*, 413. (b) Kresge, A. J.; Sagatys, D. S.; Chen, H. L. *Ibid.* **1977**, *99*, 7228. (c) Okuyama, T.; Fueno, T.; Nakatsuji, H.; Fujimoto, T. *Ibid.* **1967**, *89*, 5876. Kreevoy, M. M.; Eliason, R. E. *J. Phys. Chem.* **1968**, *72*, 1313.

(2) Brown, H. C. *Rec. Chem. Prog.* **1953**, *14*, 83; *J. Chem. Soc.* **1956**, 1248. Sicher, J. In "Progress in Stereochemistry"; de la Mare, P. B. D., Klyne, W., Eds.; Butterworths: London, 1962; pp 227–229

(3) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; p 94.

(4) Marschall, H.; Muhlenkamp, W. B. *Chem. Ber.* **1976**, *109*, 2785.

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