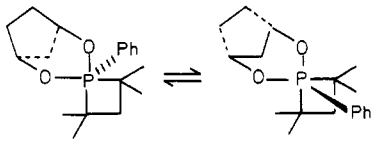
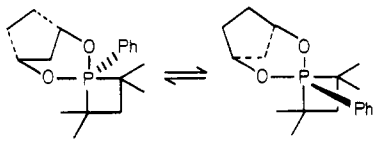
cess which passes through a phosphorane in which the four-membered ring spans the equatorial–equatorial positions of the trigonal bipyramid. The ^{13}C spectral data is only consistent with the population of the trigonal bipyramids **5** and **6** or the square-pyramidal phosphoranes



5 **5′**



6 **6′**

3 and **4**. Heating the reaction mixture to 145 °C resulted in the slow decomposition of the phosphoranes without any indication of the onset of pseudorotation.

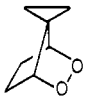
The lower limits for the activation barriers which place the four-membered and bicyclo[3.2.1] rings in the equatorial–equatorial position of a trigonal bipyramid are 19.5 kcal/mol[14] as determined by the use of eq 1 and 2.[15] The

$$k_c = \pi|\delta\nu|/2^{1/2} \quad (1)$$

$$\Delta G^*_{T_c} = 4.57T_c(10.32 + \log T_c/k_c) \quad (2)$$

rate constant at coalescence is determined by eq 1 where $\delta\nu$ is the difference in frequency of peaks which are averaged by the conformational process (e.g., the phenyl rings are averaged by the pseudorotation which forces the four-membered ring equatorial–equatorial and the two methyls in each phosphorane by the conformational process which forces the bicyclo[3.2.1] ring equatorial–equatorial). This represents the first estimation of the barrier necessary to place a bicyclo[3.2.1] ring equatorial–equatorial. The equatorial–equatorial four-membered ring has previously been estimated to be greater than 20 kcal/mol higher in energy than the apical–equatorial conformation,[16] consistent with our results here.

We have also examined the reaction of **2** with the tricyclic peroxide **7** and found very similar results. Two phosphoranes were formed as detected by two ^{31}P NMR peaks at −43.99 and −42.87 ppm in an integrated ratio of 1.0:1.2, respectively.



7

Experimental Section

Materials. The synthesis of bicyclic peroxides **1**[17] and **7**[18] and phosphine **2**[9] were accomplished as reported previously. All compounds gave satisfactory spectral and physical data. Benzene was distilled in a N_2 atmosphere from benzophenone ketyl and then was stirred over the disodium salt of EDTA.

Dioxaphosphoranes 3 and 4. These compounds were synthesized by addition of phosphine **2** via syringe to a serum capped 10-mm NMR tube containing **1** and benzene at −78 °C. The reaction mixture was then allowed to warm to room temperature where the spectral data were collected. ^{13}C NMR (aromatic region only) for **3** δ 127.5 (J_{P-C} = 11.1 Hz), 129.1 (J_{P-C} = 22.1 Hz), 133.3 (J_{P-C} = 9.2 Hz), and 141.7 (J_{P-C} = 97.7 Hz); for **4** δ 126.6 (J_{P-C} = 11.1 Hz), 128.4 (J_{P-C} = 16.6 Hz), 133.9 (J_{P-C} = 9.2 Hz), 139.1 (J_{P-C} = 95.9 Hz); ^1H NMR δ 0.7–2.2 (m, 40 H), 4.28 (d, 2 H, J_{P-H} = 15.4 Hz), 4.39 (d, 2 H, J_{P-H} = 20.5), 7.1–7.4 and 7.8–8.1 (aromatic hydrogens). The ^1H NMR spectra are available as supplementary materials (see the paragraph at the end of the paper for further details).

NMR Measurements. The ^{31}P NMR measurements were made on a JEOL FX270 instrument at 109.13 MHz. A total of 16 384 points were collected over a spectral width of 50 000 Hz by utilizing a pulse delay of 50 s. All the chemical shifts are reported relative to 85% H_3PO_4 by substitution. A negative chemical shift is indicative of an upfield peak. The proton and ^{13}C NMR data were also collected in benzene-d_6 on a JEOL FX270 instrument and the data referenced to tetramethylsilane by substitution.

Acknowledgment. We thank the University of Wyoming and the Biomedical Research Grant Program, Division of Research Resources, National Institutes of Health (Grant S07 BR07157), for support of this work.

Registry No. **1**, 279-35-6; **2**, 37895-59-3; **3**, 86088-70-2; **4**, 86118-04-9; **7**, 67105-55-9; 2″,2″,4″,4″-tetramethyl-3′-phenyldispiro[cyclopropane-1,8′-[2,4]dioxa[3]phosphabicyclo[3.2.1]octane-3′,1″-phosphetane] (isomer 1), 86088-71-3; 2″,2″,4″,4″-tetramethyl-3′-phenyldispiro[cyclopropane-1,8′-[2,4]dioxa[3]-phosphabicyclo[3.2.1]octane-3′,1″-phosphetane] (isomer 2), 86118-05-0.

Supplementary Material Available: Full NMR data for compounds **3** and **4** (2 pages). Ordering information is given on any current masthead page.

(14) This analysis is not dependent on the geometry of the most stable phosphorane and is correct if the phosphorane is trigonal bipyramid or square pyramidal.

(15) Peccinni-Leopardi, C.; Fabre, O.; Reisse, J. *Org. Magn. Reson.* **1976**, *8*, 233.

(16) (a) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (b) Ruff, R. E.; Oram, R. K.; Trippett, S. *J. Chem. Soc., Chem. Commun.* **1971**, 1011. (c) Denney, D. Z.; White D. W.; Denney, D. B. *J. Am. Chem. Soc.* **1971**, *93*, 2066.

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(18) (a) Adam, W.; Erden, J. *J. Org. Chem.* **1978**, *43*, 2738. (b) Adam, W.; Eggelte, H. J. *Ibid.* **1977**, *42*, 3987.

The Solution Thermolysis of 2-, 3-, and 4-(2-Hydroxy-2-arylethyl)pyridines

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Received December 9, 1982

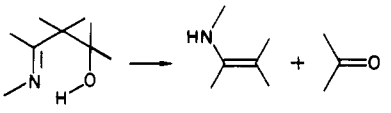
An increasing interest has recently developed in retro-ene reactions[1] of systems containing a carbon–nitrogen double bond and a β-hydroxy group (Scheme I). In a previous study[1] we examined compounds in which the nitrogen atom was part of a pyrazine ring. 2-(2-Hydroxy-2-arylethyl)pyrazines were found to undergo smooth retro-ene type reactions to form the corresponding aldehydes and the 2-methylpyrazines. A concerted mechanism involving a nonpolar six-membered-ring transition state was proposed for this reaction.[1]

The present investigation was aimed at extending this study to (2-hydroxyarylethyl)pyridines and, in particular, at comparing the reactivity of the 2-, 3-, and 4-pyridyl isomers of these substrates. The syntheses of these compounds were carried out by reacting the corresponding

(1) Houminer, Y. *J. Org. Chem.* **1980**, *45*, 999 and references cited therein.

0022-3263/83/1948-2622$01.50/0

Scheme I



Scheme II

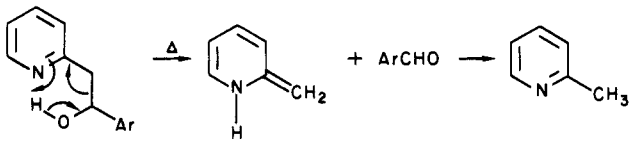
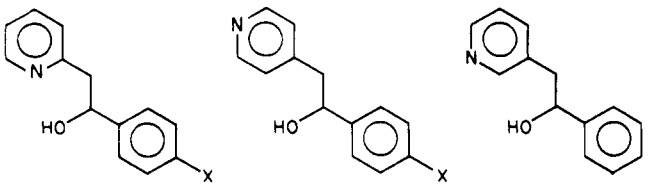


Table I. Thermolysis Rate Data for 1-3 in Diglyme-d_{14} at 170 °C[a,b]

compound	10^5k, s^{-1}
1	1.70 ± 0.04
2	1.37 ± 0.02
3	3.02 ± 0.04

[a] Errors are standard deviations. [b] Repeat kinetic measurements gave reproducibilities of ±3-5%.

methylpyridine with LDA followed by the addition of the appropriate aromatic aldehyde. Compounds 1-6 were



1, X = OCH_3
2, X = H
3, X = NO_2

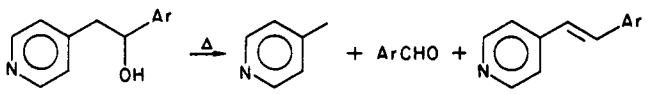
4, X = OCH_3
5, X = H
6, X = NO_2

7

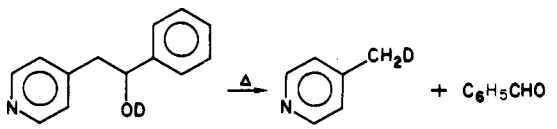
prepared by this procedure, and their thermolysis in diglyme-d_{14} was studied. In addition, we also prepared 3-(2-hydroxy-2-phenylethyl)pyridine (7). However, the latter was found to be unreactive under the thermolysis condition, showing the same degree of stability as 1,2-diphenylethanol.[2] We therefore focused our attention on compounds 1-6, i.e., the 2- and 4-pyridyl isomers. We will divide our results and discussion into two parts, according to two groups of isomers, dealing first with the 2-pyridyl compounds (1-3).

Each of the substrates (1-3) when heated in diglyme at 170 °C underwent cleavage as illustrated in Scheme II. This reaction was found to proceed smoothly, and no side products were observed.[3] At this temperature the cleavage was found to be irreversible; e.g., when an equimolar mixture of both 2-picoline and benzaldehyde was heated in diglyme at 170 °C, no 2 could be detected, even after prolonged reaction periods (>50 h). The kinetics of the thermolyses of 1-3 have been studied by using ^1H NMR spectroscopy to follow the reaction progress.[1] Rate measurements were obtained over a wide reaction range (ca. 10-80%). First-order rate constants were obtained for 1-3 with correlation coefficients >0.998. The results are summarized in Table I. Generally, there is only a small substituent effect in this reaction. Nevertheless, the nitro compound 3 is slightly more reactive. This increase in reactivity may indicate that a small negative charge develops on the benzylic carbon, which could reflect an early proton transfer in the transition state. In a system such

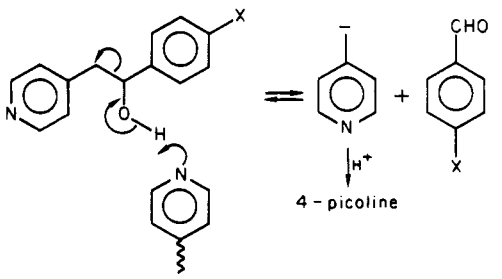
Scheme III



Scheme IV



Scheme V



as 3, where strong intramolecular hydrogen bonding exists between the pyridine nitrogen and the hydroxy group, early proton transfer is not unexpected. The observation of simple first-order kinetics in 1-3, as well as only a small substituent effect, suggests that the thermolyses of these compounds proceed via a concerted mechanism similar to that found for the corresponding pyrazines as shown in Scheme II. Such a mechanism has been previously postulated for other pyridineethanols on the basis of relative reactivities of diastereomers[4] and relative reactivities of 2-(2-pyridyl)ethanol and 2-(4-pyridyl)ethanol.[5]

It is interesting to compare the reactivity of 2 with that of the corresponding pyrazine derivative.[1] The first-order rate constant obtained for 2-(2-hydroxy-2-phenylethyl)-pyrazine under the same experimental conditions is $k = (0.16 \pm 0.02) \times 10^{-5}$ s^{-1}. This is about 1 order of magnitude smaller than that of 2-(2-hydroxy-2-phenylethyl)pyridine (2). This phenomenon may be due to the stronger intramolecular hydrogen bonding that exists in 2 as compared to that in the corresponding pyrazine derivative.[6] It also further supports the suggestion of an early proton transfer in the pyridine substrates 1-3.

The thermolysis of the 4-pyridyl isomers 4-6 was carried out under the same conditions described for 1-3. Except for 6, these 4-pyridyl isomers were found to undergo both retro-ene type reaction and dehydration. From NMR integration,[1] we have established that 4 undergoes 55% retro-ene reaction and 45% dehydration, whereas 5 gave 70% retro-ene products and 30% dehydration. The overall thermolysis pathway characteristic for the 4-pyridyl isomers is summarized in Scheme III. Compound 6 did not give any dehydration products, thus suggesting that the dehydration process, as expected, is strongly substitutent dependent. None of the 4-pyridyl isomers gives first-order kinetics. The dehydration process complicates the kinetics of substrates 4 and 5, preventing one from focusing on the retro-ene reaction. In the case of 6, where only retro-ene

(2) Kornfeld, R. A.; Houminer, Y. *J. Agric. Food Chem.* **1982**, *30*, 668.
(3) NMR data suggest that 1 undergoes also a very slight dehydration (≲3%).
(4) Hansen, D. W., Jr.; Sinsheimer, J. E.; Burckhalter, J. H. *J. Org. Chem.* **1976**, *41*, 3556.
(5) Goldman, I. M. *J. Org. Chem.* **1963**, *28*, 1921.
(6) Houminer, Y. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Division of Organic Chemistry, Las Vegas, NV March 1982, American Chemical Society: Washington, D.C., 1982; 209. Also some unpulbished results.

Table II. Half-Lives of the Thermolyses of 1–6 at 170 °C in Diglyme-d_{14}

	substrate					
	2-pyridyl			4-pyridyl		
	1	2	3	4[a]	5[a]	6
half-life, h	11.3	14.0	6.4	53.0	91.0	32.4

[a] Because of the dehydration reaction, the accuracies of these numbers are ±10%.

products were obtained, the deviation from first-order kinetics suggests a complex mechanism that does not include a concerted transition state. To further establish and generalize this conclusion for the complete series (4–6), the OD derivative of 5 was prepared by exchanging the hydrogen in the hydroxyl group of 5 with deuterium. 5-OD was thermolyzed, and the 4-picoline obtained from this reaction was analyzed for deuterium distribution. All of the deuterium was found on the methyl group. Not even trace amounts of deuterium were incorporated in the ring (Scheme IV). This experiment establishes that the 4-pyridyl isomers undergo a retro-ene reaction by a different mechanism than the 2-pyridyl substrates. It is most likely that in the 4-pyridyl substrates a base-catalyzed retro-aldol type reaction is operating. The pyridine moiety is sufficiently basic to promote such a reaction at 170 °C (Scheme V). This is further supported by the observation that, for example, in the case of 6, the reaction kinetics appears to be higher than first order in the substrate. It should also be pointed out that the reverse reaction, shown in Scheme V, could not be observed when 4-picoline and benzaldehyde were cothermolyzed at 170 °C in diglyme. It is likely that the protonation step is Scheme V is a very fast reaction, whereas a self-catalyzed deprotonation of 4-picoline may be a very slow reaction.

Comparison of the relative reactivities of the 2- and 4-pyridyl derivatives is not easy since the two series of isomers react by different mechanisms and the order of the reaction is not the same for the two groups. Moreover, no reaction rate constants are available for the 4-pyridyl compounds. Nevertheless, the half-lives of the reactions as measured by the time taken for 50% of each substrate to undergo decomposition is available and are summarized in Table II. It is evident from these results that the 2-pyridyl substrates are about 5 times more reactive than the corresponding 4-pyridyl substrates. It is therefore quite obvious that the proximity of the nitrogen functionality and the hydroxy group is essential for an effective retro-ene reaction. A similar observation was made in the 450 °C pyrolyses of 2 and 5.[2]

Experimental Section

All reactions involving organometallic reagents were carried out under a N_2 atmosphere. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded with a Perkin-Elmer Model 621 spectrophotometer. NMR spectra were recorded with a Brucker Model WP80 spectrometer, and the chemical shifts are given in δ units downfield from internal Me_4Si. Elemental analyses were performed by Galbraith Lab. Inc., Knoxville, TN. Both qualitative and preparative TLC were carried out on silica gel GF plates with hexane containing 15–40% acetone as the eluent. Column chromatography was conducted on silica gel 60 mesh using hexane containing 5–30% acetone as the eluent. The preparation and properties of compounds 2, 5, and 7 were described by us in a previous paper.[2]

2-[2-Hydroxy-2-(*p*-methoxyphenyl)ethyl]pyridine (1). *n*-Butyllithium (55 mmol) in hexane (23.9 mL) was added to a solution of diisopropylamine (5.57 g, 55 mmol) in Et_2O (100 mL) at 0 °C. After the solution was stirred at 0 °C for 20 min, a solution of 2-picoline (4.66 g, 50 mmol) in Et_2O (100 mL) was added dropwise over a 10-min period. The red-brown mixture was stirred for 1 h at about 10 °C and then cooled to 0 °C. A solution of *p*-methoxybenzaldehyde (6.81 g, 50 mmol) in Et_2O (75 mL) was added slowly, and the resulting orange suspension was stirred at room temperature for 1 h. Water was added, and the organic layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure gave an oil (10.0 g). Crystallization from Et_2O gave 2.7 g (24%) of pure 1 as needles. Additional product can be isolated by column chromatography: mp 101–105 °C (lit.[7] mp 107–108 °C); IR (Nujol) 3200, 1610, 1598, 1588, 1569, 1510, 1480, 1465, 1440, 1302, 1262, 1248, 1238, 1175, 1058, 1048, 1030, 830, 812, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.10 (2 H, part of an ABX m, CH_2), 3.78 (3 H, s, OCH_3), 5.11 (1 H, double d, CH), 5.49 (1 H, br s, OH), 6.77–7.72 (7 H, m, aromatic), 8.50 (1 H, m, H-6 pyridine).

2-[2-Hydroxy-2-(*p*-nitrophenyl)ethyl]pyridine (3). The reaction of 2-picoline (4.66 g, 50 mmol) with *p*-nitrobenzaldehyde (7.56 g, 50 mmol) was carried out as described in the case of 1 with the exception that the aldehyde was added in benzene (75 mL). A portion of the crude product was purified by TLC, and recrystallization from CH_2Cl_2 gave pure 3 as yellow needles (total yield 5%): mp 164–166 °C (lit.[8] mp 165–166 °C); IR (Nujol) 3140, 1590, 1508, 1470, 1438, 1345, 1062, 1048, 842, 755, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.15 (2 H, part of an ABX m, CH_2), 5.31 (1 H, double d, CH), 6.28 (1 H, m, OH), 7.06–7.78 (5 H, m, aromatic), 8.21 (2 H, m, aromatic), 8.54 (1 H, m, H-6 pyridine).

4-[2-Hydroxy-2-(*p*-methoxyphenyl)ethyl]pyridine (4). The reaction of 4-picoline (4.66 g, 50 mmol) with *p*-methoxybenzaldehyde (6.81 g, 50 mmol) was carried out as described in the case of 1. Crystallization of the crude product from CH_2Cl_2 gave 5.74 g (50%) of pure 4 as needles: mp 134–137 °C (lit.[9] mp 138–139 °C); IR (Nujol) 3210, 1610, 1515, 1460, 1250, 1170, 1055, 1025, 1000, 838, 812, 555 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.83 (1 H, br s, OH), 2.97 (2 H, part of an ABX m, CH_2), 3.79 (3 H, s, OCH_3), 4.86 (1 H, double d, CH), 6.79–7.29 (6 H, m, aromatic), 8.38 (2 H, m, H-2 and H-6 pyridine).

4-[2-Hydroxy-2-(*p*-nitrophenyl)ethyl]pyridine (6). The reaction of 4-picoline (4.66 g, 50 mmol) with *p*-nitrobenzaldehyde (7.56 g, 50 mmol) was carried out as described in the case of 3. The crude product was dissolved in hot CH_2Cl_2 and cooled. The resulting precipitate was filtered off and recrystallized from acetone to give pure 6 as yellow needles (5%). Additional product can be isolated by TLC: mp 162–164 °C (lit.[8] mp 171–172 °C); IR (Nujol) 3180, 1608, 1598, 1512, 1460, 1420, 1348, 1058, 998, 848, 750, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.60 (1 H, br s, OH), 3.04 (2 H, d, J = 6 Hz, CH_2), 5.11 (1 H, t, J = 6 Hz, CH), 7.13 (2 H, part of an AB q, J = 6 Hz, H-3 and H-5 pyridine), 7.53 (2 H, part of an AB q, J = 8 Hz, aromatic), 8.23 (2 H, part of an AB q, J = 8 Hz, aromatic), 8.48 (2 H, part of an AB q, J = 6 Hz, H-2 and H-6 pyridine).

Preparation of 5-OD. A sample of 5 (100 mg) was dissolved in CD_3OD (5 mL), and the solvent was evaporated under reduced pressure. The process was repeated twice, and the resulting solid was dried (50 °C, 0.02 mmHg) for 1 h. Integration of the NMR spectrum of 5-OD indicated 69% OD.

Kinetic Experiments. Reactions were carried out in diglyme-d_{14} (Merck Sharp & Dohme, Canada, Ltd.) that was dried over molecular sieves. A 0.2 M solution of each of the substrates (0.5 mL) was placed in a thick-walled NMR tube, and the tubes were sealed. Kinetic runs of all the samples were carried out simultaneously in a constant-temperature oil bath preheated to the desired temperature (170 ± 0.8 °C). The progress of the reaction in each case was followed by NMR spectroscopy using the method described by us in an earlier study.[1]

Thermolysis of 5-OD. A sample of 5-OD (about 20 mg) was heated neat in a sealed tube at 300 °C for 5 min. TLC indicated the presence of benzaldehyde, 4-picoline, dehydration product, and a small amount of unreacted 5-OD. The 4-picoline was separated by GC (80 °C, isothermal). Integration of the NMR

(7) Profft, E.; Linke, H.-W. *Chem. Ber.* **1960**, *93*, 2591.
(8) Al-Tai, F. A.; Sarkis, G. Y.; Al-Najjar, F. A. *Bull. Coll. Sci., Univ. Baghdad* **1967**, *10*, 81; *Chem. Abstr.* **1970**, *72*, 43377*g*.
(9) Brust, B.; Fryer, R. I.; Sternbach, L. H. Belg. Pat. 668701, 1966; *Chem. Abstr.*, *55*, 5446*e*.

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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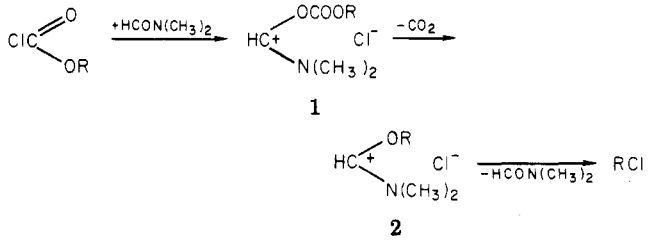
Received December 6, 1982

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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