Desulfurization of Episulfonium Salts 3a–d with Sodium Iodide.—In a typical procedure, 0.0040 mole of episulfonium salt was dissolved in 20 ml. of dry acetonitrile, and 1.5 g. (0.010 mole of sodium iodide in 30 ml. of acetonitrile was added in one portion. After 5 min. at room temperature, the reaction mixture was titrated with 0.10 *N* sodium thiosulfate. Yields of iodine varied from 80–100%.

The titrated solutions from **3a** and **3c** were poured into 200 ml. of water and extracted with 100 ml. of pentane. Gas chromatographic analysis of the extract (10-ft. column of GE SF-96 silicone oil on Fluoropak at 110°) revealed only two components other than solvent. These corresponded in retention volume to cyclooctene and alkyl disulfide in a molar ratio of 2:1. The product from **3a** that corresponded to cyclooctene was trapped from the exit gases. Its refractive index, $n^{22}D$ 1.4692, and infrared spectrum were identical with those of an authentic sample of cyclooctene.

Desulfurization of 3e with Sodium Iodide.—To 1.2 g. (0.0080 mole) of sodium iodide in 10 ml. of acetone was added 2.0 g. (0.0040 mole) of the episulfonium salt. As the compound dissolved, a second solid phase separated and the characteristic red color of the trinitrobenzenesulfonate–iodide ion complex[25] appeared, but the more intense red color of iodine was not apparent until after the mixture stood overnight. To ensure complete reaction the mixture was heated under reflux for 1 hr. The cold material was then poured into 100 ml. of water and titrated with sodium thiosulfate. The yield of iodine was 70%. The mixture was extracted with 10 ml. of pentane and chromatographed. Cyclooctene and *t*-butyl disulfide were detected in the ratio of 2:1.

Desulfurization of 3a with Lithium Methyl Mercaptide.—Butyl lithium (1.5 ml. of 15% solution in hexane) was added slowly to 0.5 g. of methyl mercaptan in 15 ml. of acetonitrile. The resulting suspension was added to 0.45 g. (0.0010 mole) of **3a** in 10 ml. of acetonitrile. After 20 min. the mixture was poured into 50 ml. of water, and extracted and analyzed as before for products. A 1:1 ratio of cyclooctene–methyl disulfide was detected.

Reaction of Cyclohexene with Ethanesulfenyl 2,4,6-Trinitrobenzenesulfonate.—A solution of 0.076 mole of ethanesulfenyl 2,4,6-trinitrobenzenesulfonate was prepared by adding 4.0 g. of silver 2,4,6-trinitrobenzenesulfonate in 15 ml. of nitromethane to 0.010 mole of ethanesulfenyl bromide in 25 ml. of methylene chloride at −25°. To this was added 0.90 g. (0.011 mole) of cyclohexene in 20 ml. of methylene chloride. The mixture began turning black immediately. After 5 min. the solid was removed by filtration and the filtrate was evaporated to near dryness at reduced pressure. The addition of 100 ml. of ether resulted in the separation of a viscous black oil. Attempts to crystallize the oil failed. Similar observations were made with the methane- and butanesulfenyl salts and cyclohexene.

Acknowledgment.—This investigation was supported in part by Grant GM 8185 from the National Institutes of Health, U. S. Public Health Service.

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[25] When sodium iodide in acetone or acetonitrile was mixed with trinitrobenzenesulfonic acid or its salts, a red solution was formed. The red color was discharged immediately by the addition of water.

The Chlorination of Active Hydrogen Compounds with Sulfuryl Chloride. II. Esters, Nitriles, Nitro Compounds, and Aldehydes

DONALD P. WYMAN, PAUL R. KAUFMAN, AND WILLIAM R. FREEMAN

Mellon Institute, Pittsburgh 13, Pennsylvania

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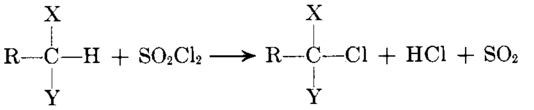
The following compounds were inert to sulfuryl chloride at room temperature: chloroacetonitrile, ethyl phenylacetate, ethyl chloroacetate, methylene chloride, acetonitrile, nitroethane, 1-chloro-1-nitroethane, ethyl acetate, and ethyl propionate. Acetoacetate reacted very vigorously, but only tars were isolated. Aldehydes also reacted very rapidly, but the yields of chlorinated derivatives were low, and polymers formed by acid-catalyzed polymerization were the major products. Ethyl cyanoacetate in a 1:1 molar reaction with sulfuryl chloride yielded predominantly ethyl dichlorocyanoacetate, whereas ethyl acetoacetate and diethyl malonate under the same conditions gave mainly monochloro derivatives, ethyl α-chloroacetoacetate and diethyl chloromalonate, respectively. Competitive chlorinations established that ethyl acetoacetate was more reactive than acetone or diethyl malonate and about as reactive as chloroacetone. Similar competitions showed that acetone also was more reactive than diethyl malonate. Acid-catalyzed ionic mechanisms differing somewhat from those used to explain acid-catalyzed chlorination with chlorine are proposed to explain the experimental results.

In a previous paper[1] in this series the ease with which a variety of ketones possessing α-hydrogen atoms were chlorinated by reaction with sulfuryl chloride was described. As a logical extension of that study, we have investigated the same kind of chlorination with a number of different compounds containing active methyl, methylene, and/or methine protons. The over-all reaction is shown in eq. 1. A large variation



$$\mathrm{R{-}\overset{\overset{\large X}{|}}{\underset{\underset{\large Y}{|}}{C}}{-}H + SO_2Cl_2 \longrightarrow R{-}\overset{\overset{\large X}{|}}{\underset{\underset{\large Y}{|}}{C}}{-}Cl + HCl + SO_2} \quad (1)$$

in the nature of X, Y, and R was investigated with respect to their relative ability to enhance the chlorination.

It was evident from the experimental results that keto groups, $-\overset{\overset{\large O}{\|}}{C}-$, strongly favor the reaction shown in eq. 1 and that chlorinations of this kind are different (in several ways) from similar chlorinations performed with molecular chlorine. The details of this investigation along with tentative explanations of the differences bebetween chlorinations with chlorine and sulfuryl chloride are presented in this paper.

Results

The products obtained from the chlorination of several active hydrogen compounds with sulfuryl chloride are listed in Table I. Ethyl cyanoacetate when treated with sulfuryl chloride (1:1 molar) at about room temperature yielded[2] mainly the dichloro derivative, ethyl dichlorocyanoacetate (67%), along with ethyl chlorocyanoacetate (21%). Ethyl acetoacetate and

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[1] D. P. Wyman and P. R. Kaufman, *J. Org. Chem.*, **29**, 1956 (1964).

[2] In all cases the per cent yields are based on the conversion of sulfuryl chloride to products. Thus, for example, a 1:1 molar reaction of sulfuryl chloride with ethyl cyanoacetate which gave a 67% yield of ethyl dichlorocyanoacetate means that 67% of the available sulfuryl chloride was used in the formation of this product, but, obviously, only 33.5% of the available ethyl cyanoacetate.

TABLE I

CHLORINATION OF VARIOUS ACTIVE METHYLENE COMPOUNDS

Compound	[SO$_2$Cl$_2$]/ [compound]	Products[a-c] (% based on SO$_2$Cl$_2$)
Ethyl cyanoacetate	1	Ethyl chlorocyanoacetate (21) + ethyl dichlorocyanoacetate (67)
Diethyl malonate	1	Diethyl chloromalonate (71) + diethyl dichloromalonate (20)
Diethyl malonate	2	Diethyl chloromalonate (35) + diethyl dichloromalonate (57)
Ethyl acetoacetate	1	Ethyl α-chloroacetoacetate (80) + ethyl α,α-dichloroacetoacetate (5)
Ethyl acetoacetate	2	Ethyl α-chloroacetoacetate (22) + ethyl α,α-dichloroacetoacetate (71)
Acetoacetone	1	Tars obtained
Malononitrile	1	Tars obtained
Chloroacetonitrile	1	d
Ethyl phenylacetate	1	d
Ethyl chloroacetate	1	d
Methylene chloride	1	d
Acetonitrile	1	d
Nitroethane	1	d
1-Chloro-1-nitroethane	1	d
Ethyl propionate	1	d
Ethyl acetate	1	d

[a] All reactions were performed at temperatures under 35°. [b] Only major products are listed. Those which were obtained in <1% yields were ignored. [c] Analyses were by gas chromatography. [d] No reaction.

diethyl malonate under the same conditions yielded mainly the monochloro derivatives, ethyl α-chloroacetoacetate (80%) and diethyl chloromalonate (71%), respectively. Smaller amounts, 5 and 20%, respectively, of the corresponding dichloro derivatives were formed.

Sulfuryl chloride reacted very rapidly with acetoacetone at temperatures ranging from 0–25°. In no cases, however, were simple, chlorinated derivatives isolated, but, rather, tars were invariably obtained. Virtually the same kind of results were obtained during attempts to chlorinate malononitrile.

The last nine items of Table I show compounds which gave essentially no reaction with sulfuryl chloride (1:1 molar) at room temperature for 24 hr. In a few instances, *e.g.*, acetonitrile and chloroacetonitrile, small amounts of sulfur dioxide and hydrogen chloride were evolved and the reaction mixtures darkened upon standing. However, analysis (by isolation or gas chromatography) showed that in these cases >95% of starting material could be recovered unchanged and, therefore, it may be concluded that reactions occurred only to a negligible extent with these compounds.

Only major products are listed in Table I. Gas chromatography showed many more to be present, but no one of these amounted to greater than 1% by weight and they were not investigated further.

TABLE II

COMPETITIVE CHLORINATIONS

Reactants[a]	Products[b-d] (% based on SO$_2$Cl$_2$)
Diethyl malonate + ethyl cyanoacetate	Ethyl dichlorocyanoacetate (61) + ethyl chlorocyanoacetate (29) + diethyl chloromalonate (5)
Acetone + diethyl malonate	1,1-Dichloropropane-2 (57) + 1-chloropropanone-2 (31) + diethyl chloromalonate (8)
Ethyl acetoacetate + diethyl malonate	Ethyl α-chloroacetoacetate (89) + ethyl α,α-dichloroacetoacetate (4) + diethyl chloromalonate (2)
Ethyl acetoacetate + acetone	Ethyl α-chloroacetoacetate (51) + ethyl α,α-dichloroacetoacetate (4) + 1,1-dichloropropanone-2 (23) + 1-chloropropanone-2 (12)
Ethyl acetoacetate + 1-chloropropanone-1	Ethyl α-chloroacetoacetate (45) + ethyl α,α-dichloroacetoacetate (5) + 1,1-dichloropropanone-2 (45)

[a] In every case a 1:1:1 ratio of reactants to SO$_2$Cl$_2$ was used. [b] Reactions were conducted essentially at room temperature. [c] Only major products are given (those present to the extent of <1% were ignored). [d] Analyses were by gas chromatography.

The product distributions obtained from several competitive chlorinations are shown in Table II. Ethyl cyanoacetate and ethyl chlorocyanoacetate, *vida infra*, were both more reactive than diethyl malonate. Indeed only about 5% of the available sulfuryl chloride was used in the chlorination of the latter compound. Similarly, acetone (and chloroacetone) and ethyl acetoacetate were also more reactive than diethyl malonate. Ethyl acetoacetate was more reactive than acetone[3] and about as reactive as chloroacetone.

Acetaldehyde, propionaldehyde, and isobutyraldehyde were all treated with sulfuryl chloride under the same conditions used in the chlorination of the other active hydrogen compounds. In all three cases the addition of a few drops of sulfuryl chloride to the aldehyde caused the onset of a very exothermic reaction which required cooling for control. Usually after only a relatively small portion (10–40%) of the theoretical amount (based on a 1:1 molar ratio of sulfuryl chloride–aldehyde) of sulfuryl chloride had been added, no further reaction was evident and sulfuryl chloride was recovered from the reaction mixture. Only low yields of α-chloro derivatives were detected, and the predominant products from these reactions were mixtures of cyclic ether trimers and linear (relatively low molecular weight) polyethers. The structures were assigned on the basis of the molecular weight determinations on the distillable (cyclic trimers) and nondistillable (linear polymers) portions; infrared spectra, which showed very strong ether bands at 9.5 and *no* carbonyl bands at 5.5–6.0 μ; n.m.r. spectra, which showed regions of complex methyl transitions, $\tau \sim 9$, even in the case of acetaldehyde; and elemental analysis which indicated that chlorine was present only in sufficient amounts to be accounted for as an end group and/or impurity.

When isobutyraldehyde or propionaldehyde and sulfuryl chloride were allowed to react in the presence of anhydrous sodium carbonate and then worked up rapidly, it was possible to isolate very low yields of α-chloropropionaldehyde and α-chloroisobutyraldehyde.

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(3) Chloroacetone is converted to 1,1-dichloropropanone-2 faster than acetone is converted to chloroacetone[1,4] (except in the presence of a very large excess of acetone[4]). Consequently it is difficult to ascertain the relative reactivity of a CH$_3$ group in acetone alone in a competitive experiment of this type. It is convenient to consider the total reactivity of acetone as a function of the yield of both the mono- and dichlorinated products.

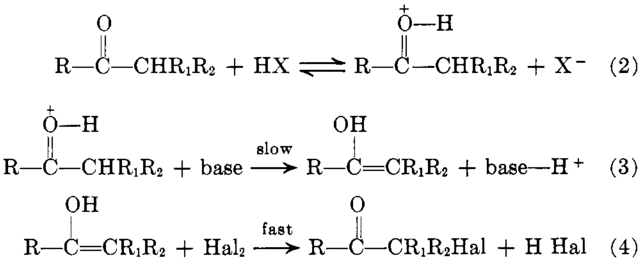
(4) E. R. Buchman and H. Sargent, *J. Am. Chem. Soc.*, **67**, 401 (1945).

However, both chlorinated derivatives were unstable and polymerized on standing, even in the refrigerator.

Finally, from the results given above, it is possible to consider a series of compounds, $X{-}CH_2{-}Y$, and qualitatively, at least, to determine which combinations of groups X and Y lead to rapid reactions with sulfuryl chloride at room temperature and which do not. In the former class are included the following pairs: $[CH_3{-}\overset{O}{\overset{\|}{C}}, CH_3{-}\overset{O}{\overset{\|}{C}}]$; $[CH_3{-}\overset{O}{\overset{\|}{C}}, CO_2Et]$; $[CH_3{-}\overset{O}{\overset{\|}{C}}, Cl]$; $[alkyl{-}\overset{O}{\overset{\|}{C}}, H]$[1]; $[alkyl{-}\overset{O}{\overset{\|}{C}}{-}, aryl]$[1]; $[alkyl{-}\overset{O}{\overset{\|}{C}}, alkyl]$; $[NC, CO_2Et]$; and $[CO_2Et, CO_2Et]$. On the other hand, substituent pairs which were not sufficiently activating to cause a significant reaction with sulfuryl chloride included these: $[Cl, CN]$; $[Ph, CO_2Et]$; $[Cl, CO_2Et]$; $[Cl, Cl]$; $[H, CN]$; $[CH_3, NO_2]$; $[Cl, NO_2]$; $[CH_3, CO_2Et]$; and $[H, CO_2Et]$.

Discussion

In most, but not all,[5,6] cases the acid-catalyzed halogenation of enolizable compounds with halogens is kinetically independent of [halogen] and the rate of reaction is determined by the rate of enolization of the substrate.[7-10] With protic acids this kind of scheme is shown in eq. 2–4. In aqueous solutions the base shown in eq. 3 may be water while in anhydrous (or concentrated aqueous[10]) media considerable evidence points to the fact that halide ions alone are sufficiently basic[10-12] to act as shown. Indeed, the rapidity of the reaction of enols with bromine compared with the rate at which carbonyl compounds enolize forms the basis for quantitative tests of enol contents.[13]



$$R{-}\overset{O}{\overset{\|}{C}}{-}CHR_1R_2 + HX \rightleftharpoons R{-}\overset{\overset{+}{O}{-}H}{\overset{\|}{C}}{-}CHR_1R_2 + X^- \tag{2}$$

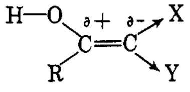
$$R{-}\overset{\overset{+}{O}{-}H}{\overset{\|}{C}}{-}CHR_1R_2 + \text{base} \xrightarrow{\text{slow}} R{-}\overset{OH}{\overset{|}{C}}{=}CR_1R_2 + \text{base}{-}H^+ \tag{3}$$

$$R{-}\overset{OH}{\overset{|}{C}}{=}CR_1R_2 + Hal_2 \xrightarrow{\text{fast}} R{-}\overset{O}{\overset{\|}{C}}{-}CR_1R_2Hal + H\,Hal \tag{4}$$

In those compounds in which enolization can lead to two different structures the one containing the more branched or conjugated olefin is favored as shown by the fact that the order of predominant substitution[14] in ketones during chlorination is methine > methylene > methyl, while compounds such as phenyl acetone chlorinate[1] almost exclusively on the methylene rather than methyl carbon.

The chlorination of active hydrogen compounds with sulfuryl chloride is similar to acid-catalyzed halogenations with halogen in some respects and quite different in others. Thus, the favored position of *initial* substitution[1] is the same in each case (see Discussion, above). On the other hand, substitution of an α-halogen retards[14] further halogenation in acid-catalyzed halogenations with the halogens, but, very often, just the opposite is true in the case of chlorinations with sulfuryl chloride.[1]

From the experimental results obtained in this investigation and the preceding discussion, it is apparent that eq. 2–4 do not offer a completely satisfactory explanation of chlorinations with sulfuryl chloride. For example, if acid-catalyzed enolization was rate determining (eq. 3), one would expect that ethyl acetoacetate[15] would react very much faster than acetone and/or chloroacetone contrary to the results. Furthermore, diethyl malonate[15] might be expected to react faster than acetone and certainly faster than ethyl cyanoacetate, again contrary to the experimental results. It is also apparent, however, that all of the compounds which do react are capable of acid-catalyzed enolization. If it is assumed that this is the case and that eq. 3 is applicable to the sulfuryl chloride system, then the differences which arise must be due to changes in the mechanisms of chloronium abstraction from molecular chlorine and sulfuryl chloride. One possibility is that either eq. 3 or 4 can be rate determining in chlorinations with sulfuryl chloride (and, apparently, in many cases eq. 4 represents the slow step) and the abstraction of a chloronium ion from sulfuryl chloride is more subject to steric and polarization effects. Accordingly, the relative reactivity of an enolic intermediate such as I towards sulfuryl chloride would be enhanced by electronegative groups, *e.g.*, the enols of ethyl cyanoacetate or chloroacetone, which tended to polarize the double bond and localize an electron pair towards the abstracting carbon. Steric effects, however, must be invoked to explain why, for example, 1,1-dichloropropanone-2 does not readily convert to 1,1,1-trichloropropanone-2[1] or why 1,2,3-triphenylpropanone-1 is inert[1] to sulfuryl chloride. These arguments explain, at least in part, why ethylacetoacetate is not much more reactive than chloroacetone (because the steric requirements of the carbethoxy group are greater than those of a chlorine atom) and why ethyl cyanoacetate readily converts to a dichloro derivative (because of the small size and electronegative nature of the linear $-C{\equiv}N$ function). The fact that ethyl acetoacetate and diethyl malonate both could be converted to dichloro derivatives by treatment with an excess of sulfuryl chloride emphasizes that one cannot ignore the contribution of eq. 3 as a driving force for the reaction in very enolizable compounds. It should be pointed out that, in the chlorination of diethyl malonate in aqueous acidic media with molecular chlorine or



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[13] *Cf.* G. Schwarzenbach and C. Wittwer, *Helv. Chim. Acta*, **30**, 657, 669 (1947).

[14] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 383.

[15] Both ethyl acetoacetate and diethyl malonate contain much higher equilibrium enol contents at about room temperature than acetone; *cf.* ref. 14, p. 376.

bromine, it was found that under certain conditions two rate-determining steps similar to those described could be detected.[5,6]

As shown in eq. 1, sulfur dioxide and hydrogen chloride are products of the reaction of active hydrogen compounds with sulfuryl chloride. Thus, the aldehydes suffered extensive acid-catalyzed polymerization, which apparently was a faster reaction than the chlorination. Even by an inverse addition procedure where aldehyde was dropped slowly into an excess of sulfuryl chloride, the predominant reaction was polymerization. Only in the case of isobutyraldehyde and propionaldehyde were very low yields of α-chlorinated products isolable.

Finally, it is worth while emphasizing that the preparation of the α-chloro and α,α-dichloro derivatives of compounds such as ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate by use of sulfuryl chloride can be done in a very simple experimental procedure. The chlorinating agent, sulfuryl chloride, is readily available and inexpensive and the yields of chlorinated products are comparable with or better than those obtained in other procedures, *e.g.*, with molecular chlorine.[16] Consequently, sulfuryl chloride is most likely the reagent of choice in most laboratory-scale chlorinations of active hydrogen compounds such as described here.

Experimental

All starting compounds, except chloroacetone which was synthesized according to literature[1,4] procedures, were reagent grade materials which were commercially available. Gas chromatographic separations were performed with a column composed of 10% APIEZON-L on 80–90-mesh ABS and with helium as the carrier gas. Nuclear magnetic resonance (n.m.r.) spectra were obtained of neat liquids or carbon tetrachloride solutions[17] on a Varian A-60 spectrometer. Tetramethylsilane served as an internal reference throughout. Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Chlorination of Ethyl Cyanoacetate (Preparative Scale).—A 100-ml. round-bottom flask equipped with a magnetic stirrer, thermometer, dropping funnel, and condenser (protected from atmospheric moisture with a calcium chloride drying tube) was charged with ethyl cyanoacetate (22.6 g., 0.2 mole). Sulfuryl chloride (20.2 ml., 0.25 mole) was added all at once. The temperature of the reaction mixture slowly rose from 25 to 35° in about 2 hr. and hydrogen chloride and sulfur dioxide were evolved. After 24 hr. the light yellow solution which was obtained was distilled *in vacuo* through a 14-in. helix-packed column. The first fraction (b.p. to 77° at 30 mm., 12.6 g.) was a mixture of unconverted ethyl cyanoacetate and ethyl chlorocyanoacetate. The latter compound comprised 15% of the mixture (according to gas chromatography), and its structure was assigned according to its n.m.r. spectrum (neat liquid): triplet, τ 8.57; quartet, τ 5.50; and singlet, τ 4.6.

A second colorless liquid fraction (10.4 g., 57%), b.p. 97–98° at 30 mm., was distilled. This compound was ethyl dichlorocyanoacetate (n.m.r.: triplet, τ 8.57; and quartet, τ 5.52).

Anal. Calcd. for $C_5H_5Cl_2NO$: C, 32.8; H, 2.73; Cl, 38.8. Found: C, 32.92; H, 2.75; Cl, 39.00.

Approximately 3.5 g. of residue remained after distillation.

Chlorination of Ethyl Acetoacetate (Preparative Scale).—The apparatus was the same as described above for the chlorination of ethyl cyanoacetate. Sulfuryl chloride (0.1 mole) was added dropwise to ethylacetoacetate (0.1 mole) over a period of 0.5 hr. at such a rate that the temperature did not exceed 35°. After addition was complete the reaction mixture was allowed to stir overnight at room temperature and then was distilled *in vacuo* through a 14-in. helix-packed column. After removal of the unconverted ethyl acetoacetate, three fractions were obtained: (1) b.p. 78–94° at 30 mm. (0.5 g.); (2) b.p. 94–96° at 30 mm. (2.0 g.); and (3) b.p. 96–108° at 30 mm. (1.6 g.). A large residue remained after distillation. Fraction 1, according to gas chromatography, was a mixture (~50:50) of unconverted ethylacetoacetate and ethyl α-chloroacetoacetate. Fraction 3 was a mixture (75:25, respectively) of ethyl α-chloroacetoacetate and ethyl α,α-dichloroacetoacetate. Fraction 2 was pure ethyl α-chloroacetoacetate (n.m.r: triplet, τ 8.70; singlet, τ 7.65; quartet, τ 5.70; and singlet, τ 5.05), n^{26}D 1.4346.

Anal. Calcd. for $C_6H_9ClO_3$: C, 43.75; H, 5.46; Cl, 21.60. Found: C, 43.59; H, 5.28; Cl, 21.21.

The above experiment was repeated with 0.1 mole of ethyl acetoacetate and 0.2 mole of sulfuryl chloride. Two product fractions were obtained: (1) b.p. 90–106° at 30 mm. (5 g.); and (2) b.p. 106–108° at 30 mm. (11 g., 55%). Fraction 1 was a mixture (40:60, respectively, according to gas chromatography) of ethyl α-chloroacetoacetate and ethyl α,α-dichloroacetoacetate. Fraction 2 was pure ethyl α,α-dichloroacetoacetate. The n.m.r. spectrum (neat liquid) of this compound consisted of a triplet, τ 8.65; singlet τ 7.50; and quartet, τ 5.60.

Anal. Calcd. for $C_6H_8Cl_2O_3$: C, 36.18; H, 4.02; Cl, 35.63. Found: C, 35.91; H, 3.92; Cl, 35.55.

Chlorination of Diethyl Malonate (Preparative Scale).—The procedure was the same as used above for the chlorination of ethyl acetoacetate. From 0.1 mole of diethyl malonate and 0.1 mole of sulfuryl chloride there was obtained 7.5 g. (38%) of diethyl chloromalonate: b.p. 127–128° at 20 mm., n^{26}D 1.4360; lit.[18] b.p. 115–116° at 14 mm., n^{24}D 1.4375. A similar reaction conducted with 0.1 mole of diethyl malonate and 0.2 mole sulfuryl chloride yielded 35% of the monochlorinated product and 30% (7 g.) of diethyl dichloromalonate: b.p. 131–133° at 15 mm., n^{26}D 1.4545; lit.[16] b.p. 130–132° at 15 mm., n^{24}D 1.4554.

Competitive and Small-Scale Reactions.—Several small-scale reactions were performed on a 0.01–0.05-mole scale and analyses were performed by gas chromatography (Table I). The standards for gas chromatography were compounds prepared above or by previously described[1,4] procedures. Often in the preparative scale runs extensive decomposition occurred during isolation of the various compounds. This did not occur during the gas chromatographic analysis (performed without flash evaporation); therefore, the yields obtained by the latter method of analysis are different (and more accurate) from those obtained by isolation.

Attempted Chlorination of Acetoacetone.—Acetoacetone (10 g., 0.1 mole) was placed in the apparatus described above and then cooled in an ice bath. Sulfuryl chloride (13.5 g., 0.1 mole) was added over a period of 20 min. at such a rate that the temperature of the reaction mixture did not exceed 25°. The reaction was very fast and hydrogen chloride and sulfur dioxide were rapidly evolved. After about half of the sulfuryl chloride had been added, a yellow viscous precipitate separated. After 0.5 hr. the reaction mixture had become black and very viscous. It was insoluble in carbon tetrachloride. These results were entirely reproducible and no "clean" compounds were isolable by distillation or attempted crystallization.

Attempted Chlorination of Malononitrile.—The subject compound (6.6 g., 0.1 mole) was dissolved in 10 ml. of ethylacetate and treated with 0.1 mole of sulfuryl chloride as described above for acetoacetone. The black solution which resulted was allowed to stir overnight. Approximately 0.8 g. of white crystals were deposited and collected. These had m.p. 267–270° dec. and were not investigated further. Removal of the ethyl acetate *in vacuo* left a black gum which proved to be intractable.

Attempted Chlorination of Miscellaneous Compounds.—The procedure used was the same in each case, *viz.*, 0.1 mole of active methylene compound plus 0.1 mole sulfuryl chloride were stirred at room temperature for 24 hr., and then the reaction mixture was analyzed by gas chromatography and/or isolation. The following compounds were studied and under the conditions described above were found to be essentially unchanged by sulfuryl chloride: chloroacetonitrile, ethyl phenylacetate, ethyl chloroacetate, methylene chloride, acetonitrile, nitroethane, 1-chloro-1-nitroethane, and ethyl propionate.

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[16] M. A. King, *Bull. soc. chim. France*, [3]**33**, 324 (1905).

[17] The chemical shifts of α-chloro ketones are noticeably solvent dependent (private communication from Dr. B. L. Shapiro). It is expected, *a priori*, that the same situation would prevail in the cases of α-chloronitriles and α-chloro esters; therefore, chemical shifts of the neat liquids are tentatively assumed to be approximate.

[18] N. P. Buu-Hoï and P. Desmerseman, *J. Org. Chem.*, **18**, 659 (1953).

Attempted Chlorination of Acetaldehyde.—Sulfuryl chloride (27 g., 0.2 mole) was added slowly to acetaldehyde (8.8 g., 0.2 mole) which was cooled in an ice bath. The first few drops of sulfuryl chloride caused the reaction temperature to rise from 5 to 25°. After cooling the reaction mixture again to 5°, the addition of the rest of the sulfuryl chloride did not cause an increase in temperature of the reaction mixture. The viscous light yellow liquid was allowed to stand overnight at room temperature, and then it was distilled. Sulfuryl chloride (18 g.) was recovered. A fraction with b.p. 121–124° (2 g., 23%) was recovered. Its infrared spectrum showed no carbonyl absorptions at 5.5–6.0, but had an intense ether band at 9.5 μ. The n.m.r. spectrum of this compound had a complex series of methyl transitions at $\tau \sim 9$. This material was identical with authentic paraldehyde (b.p. 124°). The viscous residue (mol. wt. 570, Mechrolab vapor pressure osmometer) which remained had infrared and n.m.r. spectra which were similar to the above and, on this basis and elemental analysis, was assigned the structure of a low molecular weight linear polymer.

Anal. Calcd. for $(C_2H_4O)_n$: C, 54.6; H, 9.1. Found: C, 53.9; H, 8.7; Cl, 1.31.

Chlorination of Propionaldehyde.—Sulfuryl chloride (1.9 mole) and anhydrous sodium carbonate (1 mole) were placed in the usual apparatus and well stirred while propionaldehyde (2 moles) was slowly added over a period of $\sim$40 min. Occasional cooling with an ice bath was necessary to moderate the reaction. As soon as the addition was complete, ice–water was added in sufficient quantity ($\sim$500 ml.) to rapidly dissolve all of the salts. The organic layer was separated and washed with 500 ml. of 5% aqueous sodium carbonate and then water. After drying over anhydrous calcium chloride the viscous residue was subjected to distillation using a water bath as heat source. After removal of a small amount of forerun there was obtained 4.0 g. of a colorless liquid, b.p. 84° at atmospheric pressure. The n.m.r.[19] spectrum (neat liquid) consisted of a doublet, τ 8.4, and a multiplet, τ 5.75, which, as a first approximation, was a quartet split by coupling with another proton. The elemental analysis was correct for α-chloropropionaldehyde.

Anal. Calcd. for C_3H_5ClO: C, 38.9; H, 5.4; Cl, 38.4. Found: C, 38.2; H, 5.4; Cl, 38.3.

Upon standing in the dark in the refrigerator overnight the liquid solidified to colorless crystals, which in 2 days began to darken. After 1 week in the refrigerator the solid had been completely converted to a brownish oil (mol. wt. 265, Mechrolab vapor pressure osmometer). The molecular weight was approximately correct for cyclic trimer (theoretical mol. wt. 277). Most of the product from the attempted chlorination was a low molecular weight, viscous polymer which could not be distilled.

Chlorination of Isobutyraldehyde.—The procedure used was identical with that described above for the chlorination of propionaldehyde. From 1 mole each of isobutyraldehyde and sulfuryl chloride reacted in the presence of 0.75 mole of anhydrous sodium carbonate, there was obtained 5 g. of α-chloroisobutyraldehyde, b.p. 36° at 240 mm. The n.m.r. spectrum consisted of a singlet, τ 8.35. The colorless liquid crystallized when stored overnight in the refrigerator, but the crystals were soon converted into a brown liquid (mol. wt. 800, Mechrolab vapor pressure osmometer). Interestingly, the result which indicates a number average degree of polymerization of 8, implies that α-chloroisobutyraldehyde, unlike α-chloropropionaldehyde (see above), prefers to polymerize linearly rather than trimerize into a cyclic compound.

Most of the product from the reaction of isobutyraldehyde with sulfuryl chloride was a low molecular weight polyether. Neither the polyether or the volatile product described above showed carbonyl bands (5.5–6.0 μ) in their infrared spectra.

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[19] The chemical shift of the proton in the CHO group (a doublet) occurred at $\tau \approx 0.1$ (*cf.* L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 62).

The Action of Alumina on α- and β-Amyrin Sulfonate Esters[1]

Fortüne Kohen, B. K. Patnaik, and Robert Stevenson

Department of Chemistry, Brandeis University, Waltham, Massachusetts

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Filtration of α-amyrin sulfonate ester solutions through neutral alumina results in elimination of the sulfonic acid and formation of a product $C_{30}H_{48}$, "α-amyradiene-IV," previously reported, by the action of boiling pyridine on α-amyrin methanesulfonate. It is shown that "α-amyradiene-IV" is a mixture of ursa-2,12-diene and 3ξ-methyl-24-norursa-4(23),12-diene. Under the same conditions of alumina or tertiary base treatment, β-amyrin sulfonate esters behave in analogous fashion.

Dehydration of the pentacyclic triterpenoid alcohols, α-amyrin (urs-12-en-3β-ol) (**1**, R = H) and β-amyrin (olean-12-en-3β-ol) (**2**, R = H), and related elimination reactions of their ester derivatives have given rise to a variety of diene structural isomers.[2,3] By brief treatment with phosphorus pentachloride, α-amyrin and β-amyrin give, respectively, A-neoursa-3,12-diene (α-**3**)[4–7] and A-neooleana-3,12-diene (β-**3**)[4,6,8,9] which, on prolonged exposure to phosphorus pentachloride or isomerization with trichloroacetic acid, are converted to the corresponding isomers, A-neoursa-3(5),12-diene (α-**4**)[7] and A-neooleana-3(5),12-diene (β-**4**).[9] The benzoate esters (**1**, R = Bz) and (**2**, R = Bz) on pyrolysis behave similarly to yield ursa-2,12-diene (α-**5**)[8] and oleana-2,12-diene (β-**5**).[8,10] These transformations, a retropinacolic dehydration and a thermal *cis* elimination, have been rationalized in terms of conformation theory[11] and are amply documented in related systems.

In view of the close structural relationship of **1** and **2** (differing only in methyl substitution in ring E), it is at first sight surprising that there should be noteworthy differences in their elimination behavior under identical conditions; two such reports, however, exist. By treat-

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[2] Apart from trivial names assigned to these isomers prior to their structure elucidation, the nomenclature used in this paper is that proposed by S. Allard and G. Ourisson [*Tetrahedron*, **1**, 277 (1957)] after consultation with authorities in this field.

[3] To conserve space in the structure formulations, the prefixes α- and β- before formula numbers refer to α-amyrin (ursane) and β-amyrin (oleanane) derivatives, respectively.

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