[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Ketene Acetals. XXXVII. Cyclopropanone Acetals from Ketene Acetals and Carbenes

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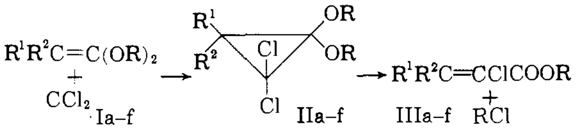
2,2-Dichlorocyclopropanone acetals (II), prepared from ketene acetals and dichlorocarbene, are readily pyrolyzed to α-chloroacrylic esters (III). A mechanism for this transformation is suggested. Benzal chloride yields phenylchlorocarbene, which adds to ketene acetals to give 2-phenyl-2-chlorocyclopropanone acetals. The reductive dehalogenation of these chloroacetals follow different patterns depending upon their structures. All of the cyclopropanone acetals are remarkably stable to hydrolysis, *e.g.*, cyclopropanone diethylacetal may be recovered from its solution in concentrated hydrochloric acid. More strenuous conditions of hydrolysis produces ring fission as does bromination.

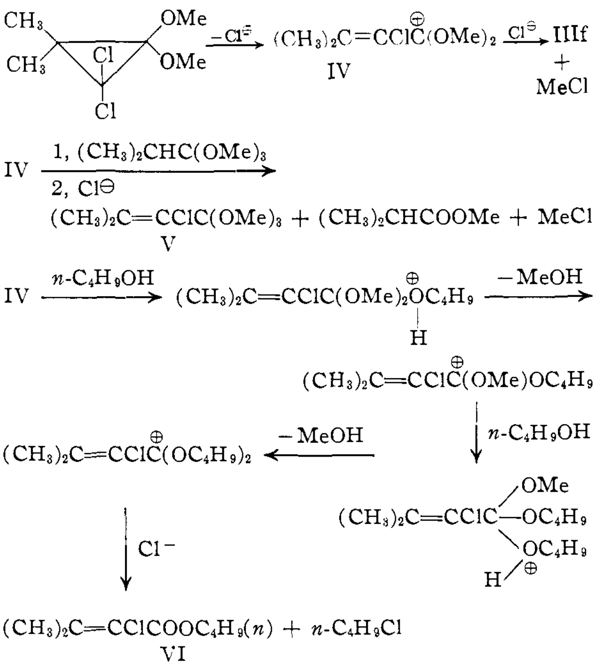
Ketene acetals (I) react with dichlorocarbene, generated by the action of sodium *t*-butoxide on chloroform, to form the 2,2-dichlorocyclopropanone acetals (II). These products (IIa-f), which may be obtained in yields of 40–60%, can be isolated only by distillation under low pressures as they undergo pyrolysis above 100° to the corresponding α-chloroacrylic esters III (a–f) and an alkyl chloride.



a, $R^1 = R^2 = H, R = CH_3$
b, $R^1 = R^2 = H, R = C_2H_5$
c, $R^1 = H, R^2 = R = CH_3$
d, $R^1 = H, R^2 = C_2H_5, R = CH_3$
e, $R^1 = H, R^2 = n\text{-}C_3H_7, R = CH_3$
f, $R^1 = R^2 = R = CH_3$

The pyrolysis of II to III, which occurs quite rapidly at 140–150°, gives the chloroacrylic esters in quantitative yield. The mechanism of this rearrangement appears to involve an allylic carbonium ion (IV) which reacts with the expelled chloride anion to give the products. Evidence for such a reaction course was obtained by the pyrolysis of IIf in solvents that react with the intermediate carbonium ion IV. When IIf was pyrolyzed in a solution of methyl orthoisobutyrate, methyl isobutyrate and methyl ortho-α-chloro-β-methylcrotonate (V) were formed[2] along with the normal pyrolysis product IIIf. Also, when IIf was refluxed in a sevenfold excess of *n*-butyl alcohol, an 82% yield of *n*-butyl α-chloro-β-methylcrotonate (VI) was obtained. The alkyl chloride was *n*-butyl chloride and the methoxyl groups of IIf appeared as methyl alcohol. As the methyl ester IIIf was not affected by refluxing in *n*-butyl alcohol, the carbonium ion IV would seem to be the most likely intermediate to account for the formation of VI and *n*-butyl chloride.

The pyrolysis of the dichlorocyclopropanone acetals (II) to the chloroacrylic esters (III) is analogous to previously reported reactions, *e.g.*, the conversion, *via* halocyclopropane intermediates, of indenes to β-halonaphthalenes,[3] pyrroles to β-substituted pyridines,[4] indoles to β-haloquinolines[5] and more recently of 2,2-dibromobicyclo[3.1.0]hexane to 2-bromo-2-cyclohexen-1-ol.[6]



The reaction of dichlorocarbene with phenylketene dimethylacetal (VII) was more complex than those involving the simpler ketene acetals I. The reaction product distilled over a 50° range. Infrared analysis indicated steadily increasing triple bond character through the fractions, a maximum of ketene acetal double bond character in the intermediate fractions and a shift in the carbonyl peak from 5.76 to 5.84 μ (unconjugated to conjugated ester) in the intermediate fractions with almost complete absence of carbonyl absorption in the highest boiling fractions. The spectra of these latter fractions had characteristic orthoester bands in the 8–10 μ region.[7] These fractions consequently, were hydrolyzed with dilute acid. From this hydrolysis methyl phenylpropiolate was obtained in good yield. This ester was present in the intermediate fractions of the distillate as shown by saponification to phenylpropiolic acid. These fractions also were found to contain unreacted ketene acetal and its hydrolysis product, methyl phenylacetate.

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1956–1958.

[2] *Cf.* the bromination of dimethylketene dimethylacetal in the presence of methyl orthoisobutyrate (S. M. McElvain and W. R. Davie, THIS JOURNAL, **74**, 1816 (1952)).

[3] W. E. Parham, *et al.*, *ibid*, **77**, 1177 (1955); **78**, 1437 (1956); *J. Org. Chem.*, **22**, 730, 1473 (1957).

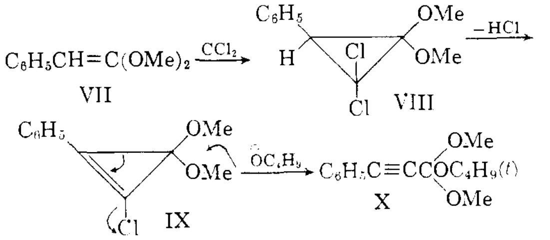
[4] E. R. Alexander, *et al.*, THIS JOURNAL, **72**, 2760 (1950).

[5] G. Magnanini, *Ber.*, **20**, 2608 (1887).

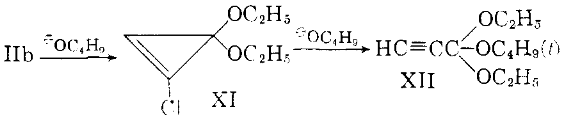
[6] P. S. Skell and S. R. Sandler, THIS JOURNAL, **80**, 2024 (1958).

[7] S. M. McElvain and R. E. Starn, Jr., *ibid.*, **77**, 4571 (1955).

The formation of the orthoester, believed to be dimethyl *t*-butyl orthophenylpropiolate (X), requires the initial formation of 2,2-dichloro-3-phenylcyclopropanone dimethylacetal (VIII). Dehydrochlorination of VIII by the butoxide anion to the cyclopropene IX followed by a concerted elimination of chloride ion, ring opening and attachment of a butoxide anion would produce the orthoester X. The normal esters methyl phenylpropiolate and methyl phenylacetate result from the partial hydrolysis of X and VII, respectively, during the workup of the reaction mixture. Inasmuch as three moles of base are necessary to produce the orthoester X from the ketene acetal VII and chloroform, it would be expected that unreacted VII would remain when only the one mole of base required to form the cyclopropanone acetal VIII was used. The formation of X from VIII means that this acetal effectively competes with the chloroform for the available base.



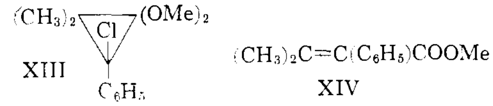
Support for the cyclopropene intermediate IX is furnished by a comparison of the rates of reaction of the cyclopropanone acetals IIb and IIf with potassium *t*-butoxide. The reaction of IIb with two moles of the base is highly exothermic and gives an immediate precipitate of potassium chloride. The reaction product, obtained in 70% yield, is diethyl *t*-butyl orthopropiolate (XII), the structure of which was established by elemental analysis, infrared spectroscopy, and hydrolysis to ethyl propiolate. With one mole of the base a mixture of this orthoester and unreacted IIb was obtained, indicating that the intermediate cyclopropene XI is more reactive toward the base than is IIb. Consequently, it was not possible to isolate the cyclopropene derivative.



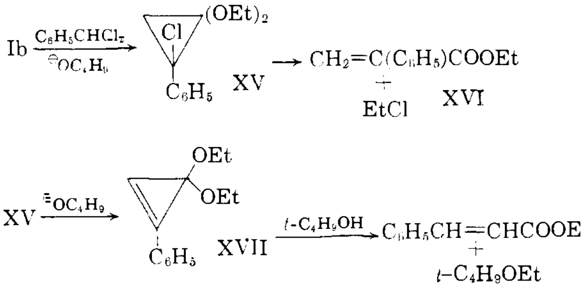
When IIf, which cannot form a cyclopropene, was heated with potassium *t*-butoxide in *t*-butyl alcohol solution there was no immediate reaction and after refluxing for one hour only a faint precipitate of potassium chloride was apparent. After three days of refluxing, a considerable precipitate of potassium chloride had accumulated. The main reaction product was the pyrolysis product IIIf which probably contained some of the corresponding *t*-butyl ester. A small amount of what appeared to be dimethyl *t*-butyl ortho-α-chloro-β-methylcrotonate, resulting from the combination of the *t*-butoxide anion with the allylic carbonium ion IV, comprised the higher boiling fraction.

The fact that the cyclopropanone acetals IIa–f can be successfully prepared while the 2,2-dichloro-3-phenylcyclopropanone acetal (VIII) cannot be isolated indicates that the latter compound undergoes dehydrochlorination more readily than chloroform or IIa–f. This behavior is doubtless due to the activation of the 3-hydrogen of VIII by the 3-phenyl substituent.

Benzal chloride reacts with sodium *t*-butoxide in the presence of the ketene acetal If to yield 2-chloro-2-phenyl-3,3-dimethylcyclopropanone dimethylacetal (XIII) in 77% yield. This reaction, which is noticeably less vigorous than the one involving chloroform (If→IIf), most certainly involves the intermediate phenylchlorocarbene, C_6H_5CCl. The acetal XIII shows no reaction with 2% bromine in carbon tetrachloride solution or with alcoholic silver nitrate solution. Even after two hours of refluxing in methanolic potassium hydroxide solution an aliquot, after acidification, gave only a slight cloudiness with silver nitrate solution. However, XIII was quantitatively pyrolyzed to methyl α-phenyl-β-methylcrotonate (XIV).



When phenylchlorocarbene, as generated from benzal chloride, was allowed to react with ketene diethylacetal (Ib), the resulting cyclopropanone acetal XV could not be distilled without partial pyrolysis. The reaction product, therefore, was completely pyrolyzed before the distillation was continued. When this reaction mixture was fractionated, it was found to contain 53% of the original benzal chloride. The reaction products were ethyl atropate (XVI) and ethyl cinnamate, which were isolated in 41 and 19% yields, respectively, based on unrecovered benzal chloride. After it was found that benzal chloride did not react with Ib in the absence of base and, consequently, that such a reaction could not have been the source of ethyl cinnamate, it appeared that the formation of this ester must have resulted from a base-induced decomposition of XV. If this acetal were dehydrochlorinated to the corresponding cyclopropene XVII, it seems likely that this intermediate could undergo alcoholysis to form cinnamate and ethyl *t*-butyl ether. No effort was made to find this latter product.

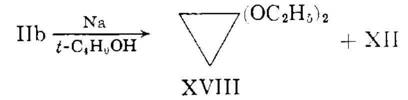


The formation of the cinnamic ester by this process requires two equivalents of the base and explains the large recovery of unreacted benzal chloride. Obviously, this chloride is less readily dehydrochlorinated than is the chlorocyclopropanone acetal XV. Evidence for this reaction course was obtained when ketene dimethylacetal (Ia), benzal chloride and two equivalents of sodium *t*-butoxide were allowed to interact. From this reaction a 58% yield of methyl cinnamate was obtained; no methyl atropate was found.

An attempt was made to generate diphenylcarbene from benzhydryl chloride, but no evidence of such a product was obtained. When benzhydryl chloride was treated with potassium *t*-butoxide in the presence of the ketene acetal If, the only reaction product was benzhydryl *t*-butyl ether.

Dechlorination of the Chlorocyclopropanone Acetals.—It seemed that a cyclopropene might be prepared by the removal of the elements of ethyl hypochlorite from IIb with sodium in the manner that ketene acetals are obtained from α-bromo-orthoesters.[8] It was found, however, that IIb reacted very slowly with sodium sand in pentane. After a week of stirring this mixture, 44% of the acetal IIb was recovered and an intractable red tar remained as the reaction product. Doering[9] has reported that sodium converts *gem*-dibromocyclopropanes to allenes. It is possible that the tar obtained from IIb and sodium was a polymer of the corresponding diethoxyallene.

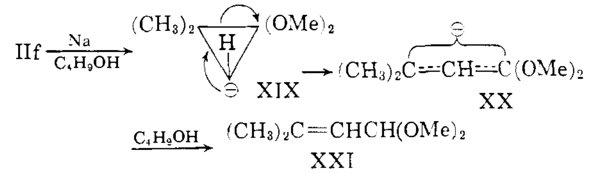
The reaction of sodium with IIb in the presence of *t*-butyl alcohol proved more successful. A 27% yield of cyclopropanone diethylacetal (XVIII) and a small amount of diethyl *t*-butyl orthopropiolate (XII) were obtained.



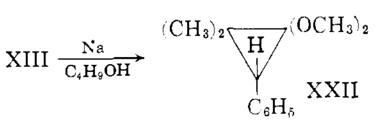
XVIII

The acetal XVIII was also prepared by the procedure of Dull and Abend,[10] which involves the reaction of IIb with diazomethane.

An extension of this reductive dechlorination of IIf did not produce the corresponding cyclopropanone acetal, but instead β-methylcrotonaldehyde dimethylacetal (XXI) was obtained in 26% yield. The formation of this product indicates that the intermediate anion XIX undergoes an E_2 type of elimination involving one of the ring bonds to form the anion XX, which then is protonated to form XXI.

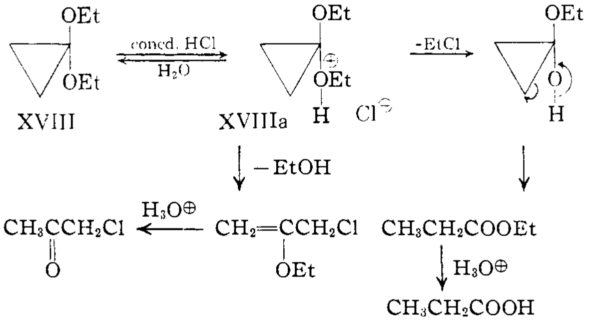


The phenyl chlorocyclopropanone acetal (XIII), in contrast to IIb, reacted exothermically with sodium sand in benzene, but as in the case of IIb the reaction product was a red resin and 35% of unreacted XIII was recovered. When *t*-butyl alcohol was used with the sodium in benzene, XIII was smoothly reduced to the cyclopropanone acetal XXII in 92% yield. In contrast to its precursor XIII, the acetal XXII is stable up to 250°.



The excellent yield of XXII in this reduction is doubtless due to the ability of the phenyl group to stabilize the intermediate carbanion. The lack of such stabilization is probably the reason the dichlorocyclopropanone acetals behaved so differently in the sodium–alcohol reduction.

All of the cyclopropanone acetals are quite resistant to hydrolysis. After heating IIf with concentrated hydrochloric acid at 90–95° for 14 hours, 33% of the acetal was recovered; the remainder was converted by pyrolysis to the ester IIIf and corresponding acid. Cyclopropanone diethylacetal (XVIII) is soluble in concentrated hydrochloric acid and may be recovered unchanged, after standing 0.5 hr. at room temperature, by dilution with water. When this acid solution of XVIII was refluxed, the acetal was converted to a mixture of chloroacetone (34%), ethyl propionate (12%) and propionic acid (30%). Lipp[11] has reported that cyclopropanone hydrate rearranged slowly on standing and more rapidly on heating to propionic acid. The solubility of XVIII in the concentrated acid indicates the formation of the oxonium salt XVIIIa. The cation of this salt is quite stable at room temperature, but at elevated temperatures is converted by the chloride anion to (a) the hemiacetal of cyclopropanone by attack at the oxonium center and (b) the enol ether of chloroacetone by attack at a methylene carbon of the ring. Hydrolysis of the latter compound yields chloroacetone while rearrangement of the hemiacetal gives ethyl propionate, which then is partially hydrolyzed to propionic acid.



Anhydrous hydrogen chloride showed no reaction with XVIII at 30°, but at 95° yielded ethyl propionate as the only product besides unreacted starting material.

Unlike XVIII, the 2-phenylcyclopropanone acetal XXII is not soluble in concentrated hydrochloric acid. When XXII was heated in refluxing hydrochloric acid for two hours, 40% of unreacted XXII was recovered. The remainder of the acetal was converted to a mixture of products boiling over a wide temperature range. Other than an

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(8) P. M. Walters and S. M. McElvain, THIS JOURNAL, **62**, 1482 (1940).

(9) W. von E. Doering, *Tetrahedron*, **2**, 75 (1958).

(10) M. F. Dull and P. G. Abend, personal communication; a report of the work of these authors appears in an accompanying paper.

(11) P. Lipp, *et al.*, *Ann.*, **499**, 1 (1932).

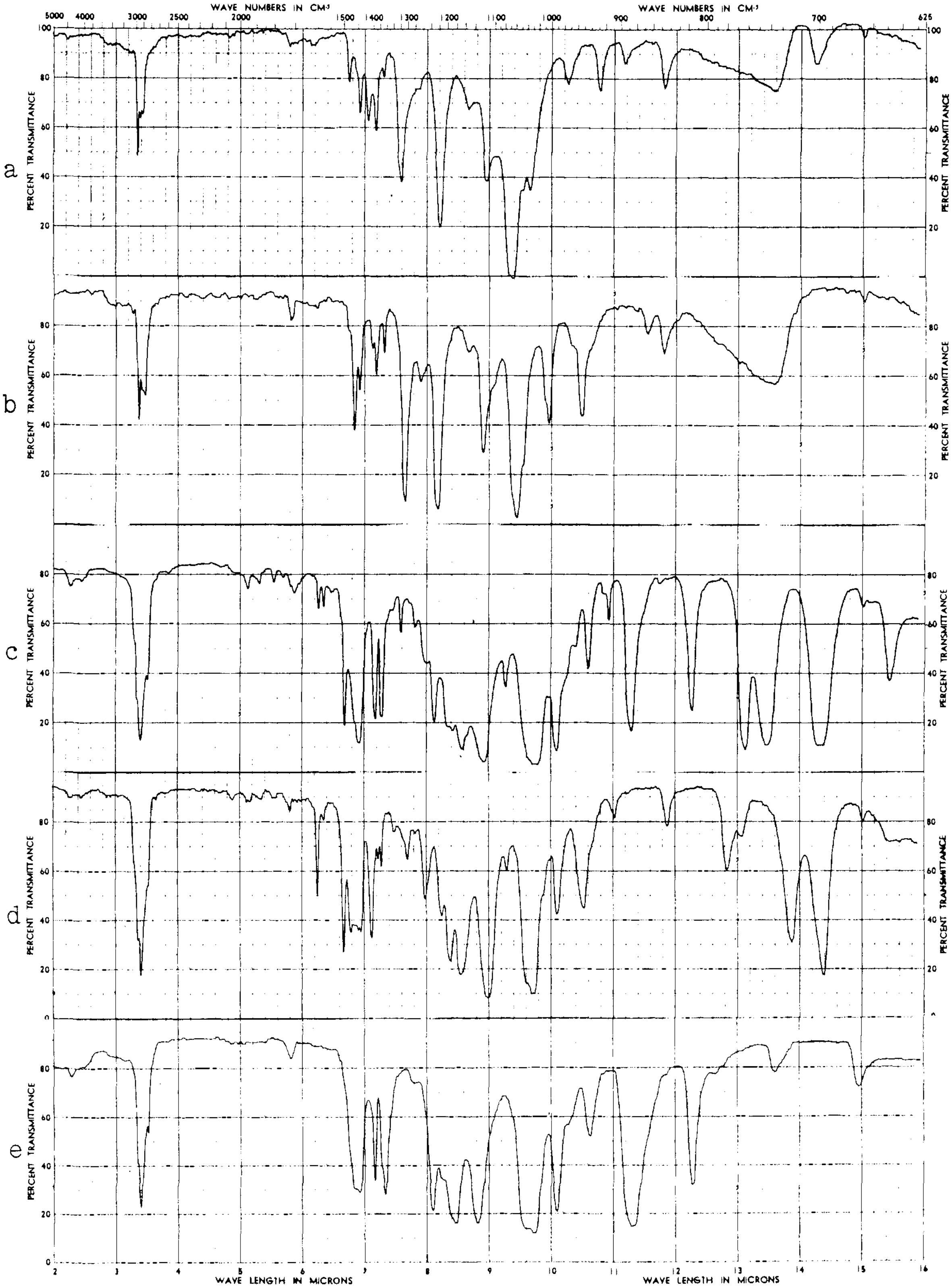

Fig. 1.—Infrared spectra: (a) 2,2-dichlorocyclopropanone diethylacetal (IIb), 0.3 M carbon tetrachloride solution, 0.1-mm. cell; (b) cyclopropanone diethylacetal (XVIII), 0.3 M carbon tetrachloride solution, 0.1-mm. cell; (c) 2-phenyl-2-chloro-3,3-dimethylcyclopropanone dimethylacetal (XIII); (d) 2,2-dimethyl-3-phenylcyclopropanone dimethylacetal (XXII); (e) 2,2-dichloro-3,3-dimethylcyclopropanone dimethylacetal (IIf)

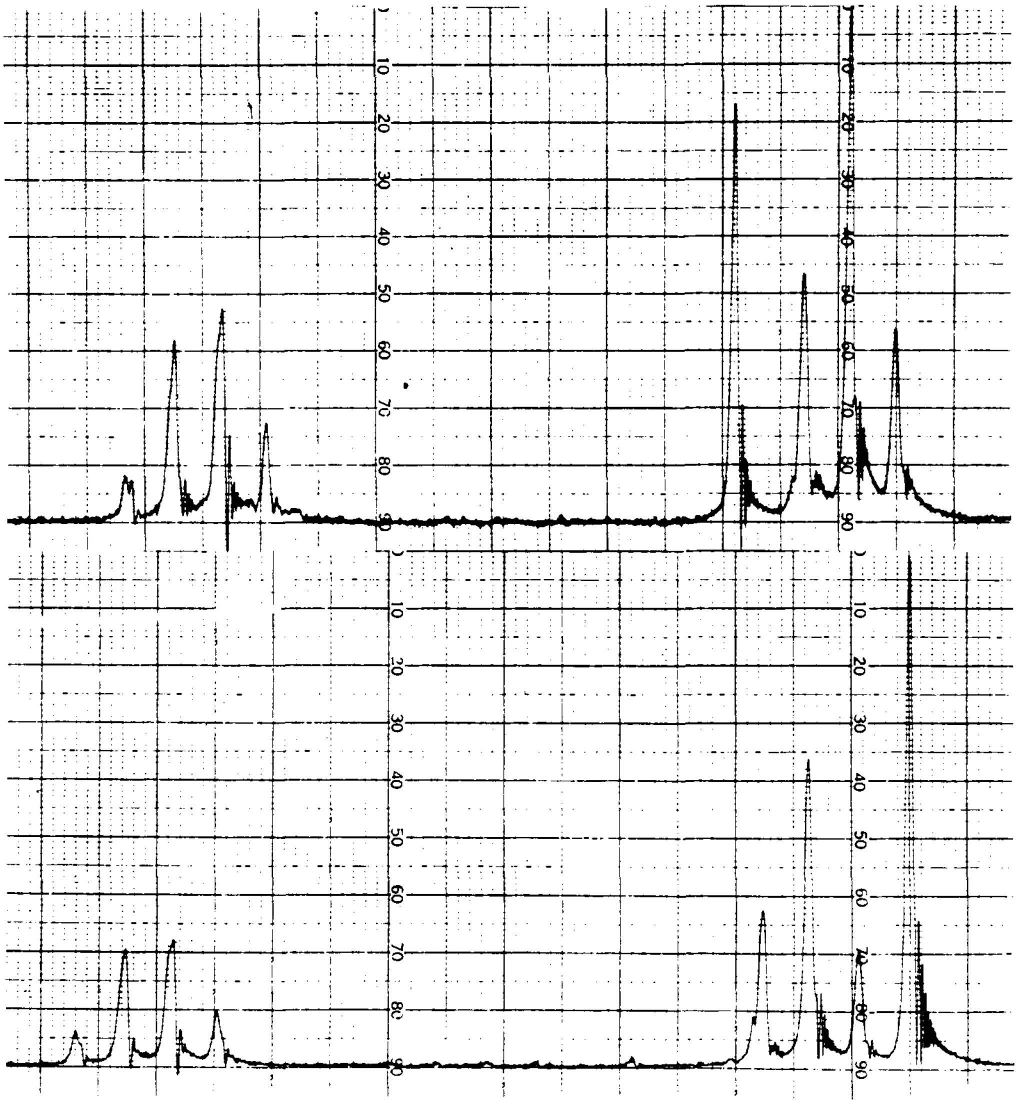

Fig. 2.—Nuclear magnetic resonance spectra: top, 2,2-dichlorocyclopropanone diethylacetal (IIb); bottom, cyclopropanone diethylacetal (XVIII).

examination of the infrared spectrum, which showed the presence of carbonyl and hydroxyl functions, no attempt was made to characterize this mixture.

The cyclopropanone acetal XVIII reacts with bromine at a moderate rate to yield a mixture of ethyl β-bromopropionate and ethyl α,β-dibromopropionate in approximately equal amounts. The formation of these esters doubtless involves the intermediate carbonium ion XVIIIb, which may

$$\text{XVIII} \xrightarrow{Br_2} \underset{\text{XVIIIb}}{CH_2BrCH_2\overset{\oplus}{C}(OEt)_2\,Br^{\ominus}} \xrightarrow{-EtBr} CH_2BrCH_2COOEt$$

$$\downarrow -HBr$$

$$\underset{\text{XVIIIc}}{CH_2BrCH{=}C(OEt)_2} \xrightarrow{Br_2} CH_2BrCHBrCOOEt + EtBr$$

eliminate ethyl bromide to form the monobromoester or lose hydrogen bromide to give the ketene acetal XVIIIc. Further bromination of the latter compound produces the dibromoester. This pattern of bromination is analogous to the bromination of ketene acetals to monobromo and dibromo esters.[12]

The dichlorocyclopropanone acetal IIb reacts with bromine to yield only the monobromoester, ethyl β,β-dichloro-β-bromopropionate (XXIII), which was characterized by dehydrobromination of ethyl β,β-dichloroacrylate.

$$\text{IIb} \xrightarrow{Br_2} \underset{\text{XXIII}}{CCl_2BrCH_2COOEt} \xrightarrow{^{\ominus}OEt} CCl_2{=}CHCOOEt$$

The infrared spectra of some representative cyclopropanone acetals are shown in Fig. 1. These spectra were run as a liquid film between sodium chloride crystals unless otherwise stated. Each of the acetals has medium to strong absorption peaks between 7.05 and 7.19 μ, between 7.98 and 8.20 μ, and, with one exception, *viz.*, 2,2-dichlorocyclopropanone diethylacetal (IIb), between 9.85 and 10.10 μ. Absorption in this latter region is

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(12) S. M. McElvain and W. R. Davie, THIS JOURNAL, **74**, 1816 (1952).

apparently not related to the cyclopropane structure as Allen and co-workers have pointed out that in a random selection of organic compounds 42% contained one or more moderate or strong absorption peaks between 9.7 and 10.05 μ.[13] The same authors noted that absorption in the 3.2 μ region, which previously had been ascribed to the methylene group of the cyclopropane structure, is also unreliable. The spectra of Fig. 1 show no absorption at 3.2 μ, but a shoulder appears consistently at 3.35 μ. It is not likely that absorption at this latter wavelength is related to the cyclopropyl C–H bond as it is apparent in the completely substituted cyclopropane IIf.

The nuclear magnetic resonance spectra of 2,2-dichlorocyclopropanone diethylacetal (IIb) and cyclopropanone diethylacetal (XVIII) are shown in Fig. 2. These spectra were obtained at 40 megacycles per second in a magnetic field of approximately 9400 gauss. The compounds were run neat in a 5-mm. spin tube. The zero of reference in each spectrum was taken as the resonance position of pure benzene contained in an inserted sealed capillary tube. The shift values of the main peaks in the spectra were determined by the audio frequency side band method in cycles per second from the benzene reference.

For IIb the shift values for the ethyl group methylene hydrogens (main peak), the cyclopropyl methylene hydrogens and the ethyl group methyl hydrogens (main peak) are 114, 193 and 212 cycles per second, respectively. The areas under the curves are in the ratio of 2:1:3, respectively.

For XVIII the shift values for the ethyl group methylene hydrogens (main peak), for the ethyl group methyl hydrogens (main peak) and for the cyclopropyl methylene hydrogens are 128, 223 and 237 cycles per second, respectively. The areas under the curves are in the ratio 2:3:2, respectively.

Acknowledgment.—The authors are indebted to Professor Paul Bender of this department for the determination and interpretation of the nuclear magnetic resonance spectra of compounds IIb and XVIII. They also are grateful to Professor M. F. Dull, Department of Chemistry, University of Pittsburgh, for the use of his procedure for the preparation of cyclopropanone diethylacetal from ketene acetal and diazomethane.

Experimental

The ketene acetals I used in this work were prepared by methods previously reported.[14]

2,2-Dichlorocyclopropanone Acetals (II).—To a suspension of sodium *t*-butoxide, prepared by addition of 2.4 g. (0.1 mole) of sodium hydride to 100 ml. of *t*-butyl alcohol, was added 0.1 mole of ketene acetal. The flask was fitted with a small pressure-equalizing dropping funnel containing 11.9 g. (0.1 mole) of chloroform. While stirring (magnetic), the contents of the flask were cooled in an ice–water-bath until the *t*-butyl alcohol began to crystallize. Then the chloroform was dropped into the flask at a rapid rate such that the temperature did not rise above 50°. When addition of the chloroform was complete, the ice–water-bath was removed and stirring continued until the contents of the flask warmed to room temperature. The mixture was then treated with water (100 ml.) to dissolve the precipitated salts. Ether was added to aid separation. The organic layer was separated and the aqueous layer extracted twice more with ether. The combined ether fractions were dried (magnesium sulfate) and distilled at reduced pressure to yield the dichlorocyclopropanone acetal. The physical constants, yields and analytical data are listed in Table I.

An alternate method of isolation of the dichlorocyclopropanone acetals involved removal of the *t*-butyl alcohol solvent by distillation at reduced pressure followed by extraction of the residue (salts and product) in a Soxhlet extractor for 2–4 hours. No improvement in yield resulted with this method.

Pyrolysis of 2,2-Dichlorocyclopropanone Acetals. α-Chloroacrylic Esters (III).—A 0.025-mole sample of a 2,2-dichlorocyclopropanone acetal was heated with magnetic stirring in a 50-ml. flask fitted with a 25-cm. Vigreux column connected to a small Dry Ice–acetone trap carrying a calcium chloride drying tube. At 140–150° the reaction became vigorous and the evolved alkyl chloride caused foaming. When foaming ceased the flask was allowed to cool and the column washed with a small amount of ether. Fractionation through a 30-cm. Podbielniak column gave the α-chloroacrylic ester in yields approaching theoretical. The Dry Ice–acetone trap contained about 1 g. of methyl or ethyl chloride (b.p. −24 or 12°, respectively). The physical constants and analyses of these esters are listed in Table II.

To 3.0 g. (0.02 mole) of methyl α-chloro-β-methylcrotonate (IIIf) was added 25 ml. of 10% sodium hydroxide and 25 ml. of ethanol. The mixture was stirred magnetically and refluxed for 2 hours. Acidification with dilute sulfuric acid and extraction yielded 2.1 g. (75%) of α-chloro-β-methylcrotonic acid. The melting point after two recrystallizations from petroleum ether (b.p. 60°) was 85–86° (previously reported[15] m.p. 85–86°); neut. equiv. 135.5, calcd. 134.6. Elemental analysis showed 44.8% carbon, 5.42% hydrogen and 26.4% chlorine (Calcd.: C, 44.6; H, 5.24; Cl, 26.4).

Reaction of Phenylketene Dimethylacetal with Chloroform and Base.—To a suspension of sodium *t*-butoxide, prepared by addition of 4.8 g. (0.20 mole) of sodium hydride to 175 ml. of *t*-butyl alcohol, was added 20.51 g. (0.125 mole) of phenylketene dimethylacetal. While stirring, the contents of the flask were cooled to 0°. Then 15.0 g. (0.125 mole) of chloroform was added in one portion. The reaction was exothermic and cooling was necessary to keep the reaction temperature below 50°. After the reaction subsided the coolant was removed and the contents of the flask were stirred at room temperature for 1 hour. The *t*-butyl alcohol was removed by distillation at reduced pressure. The residue (salts and products) were transferred to a Soxhlet extractor and extracted with ether for 12 hours. The ether was removed and the products fractionally distilled through a 30-cm. Podbielniak column at 18 mm. to give the following fractions: (a) 1.30 g., b.p. 110–118°, n^{25}_{D} 1.5071; (b) 2.35 g., b.p. 118–121°, n^{25}_{D} 1.5021; (c) 1.40 g., b.p. 121–130°, n^{25}_{D} 1.5013; (d) 2.05 g., b.p. 130–135°, n^{25}_{D} 1.5058; (e) 2.00 g., b.p. 135–145°, n^{25}_{D} 1.5168; (f) 2.20 g., b.p. 145–158°, n^{25}_{D} 1.5246; (g) 1.95 g., b.p. 158–161°, n^{26}_{D} 1.5167; (h) 4.30 g., b.p. 161–163°, n^{25}_{D} 1.5108.

Fractions a and b were largely methyl phenylacetate (19.5%) as shown by infrared analysis (carbonyl peak at 5.76 μ) and saponification of fraction b to phenylacetic acid, m.p. 77–78°.

Fractions c, d and e were mixtures of methyl phenylacetate, phenylketene dimethylacetal and methyl phenylpropionate as indicated by infrared analysis of fraction d which showed carbonyl peaks at 5.76 and 5.84 μ, the ketene acetal peak at 6.08 μ and the triple bond peak at 4.49 μ. Estimated recovery of unreacted ketene acetal was 16%.

Fraction f contained the highest proportion of methyl phenylpropiolate. This was shown by saponification of the fraction to phenylpropiolic acid (50%), m.p. 137–138°, mixed melting point with an authentic sample, 137–139°.

The major component of fractions g and h is dimethyl *t*-butyl orthophenylpropiolate (X) (20%). This was substantiated by infrared analysis of fraction h, which showed strong absorption peaks previously attributed to ortho esters[7] in 8–10 μ region in addition to the triple bond peak at 4.49 μ. The spectrum also indicated normal ester impurity (slight carbonyl peak at 5.84 μ). The orthoester could not be further purified by redistillation. To a 2.85-g. sample

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[13] C. F. H. Allen, *et al.*, *J. Org. Chem.*, **22**, 1291 (1957).

[14] S. M. McElvain, *et al.*, This Journal, **74**, 1816 (1952); **77**, 5601 (1955); *Org. Syntheses* **23**, 45 (1943).

[15] B. Prentice, *Ann.*, **292**, 279 (1896).

TABLE I

YIELDS, PROPERTIES AND ANALYSES OF THE 2,2-DICHLOROCYCLOPROPANONE ACETALS (II)

Compound	Formula	Yield, %	$n^{25}\mathrm{D}$	d^{25}_4	B.p. °C.	B.p. Mm.	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
IIa	$C_5H_8Cl_2O_2$	40	1.4477	1.2419	57–59	13	35.1	4.61	41.4	35.60	4.92	40.8
IIb	$C_7H_{12}Cl_2O_2$	68.4	1.4410	1.1373	69–70	9	42.3	6.08	35.6	42.17	6.02	36.2
IIc	$C_6H_{10}Cl_2O_2$	52	1.4504	1.2027	71–72	13	38.9	5.43	38.3	39.15	5.56	38.0
IId	$C_7H_{12}Cl_2O_2$	56	1.4486	1.1473	30	0.1	42.3	6.08	35.6	42.68	6.12	35.4
IIe	$C_8H_{14}Cl_2O_2$	55	1.4520	1.1288	80–82	6	45.1	6.63	33.4	45.23	6.66	32.7
IIf	$C_7H_{12}Cl_2O_2$	61	1.4560	1.1750	30	0.2	42.3	6.08	35.6	42.56	6.13	35.8

TABLE II

α-CHLOROACRYLIC ESTERS (III)

Compound	Formula	$n^{25}\mathrm{D}$	d^{25}_4	B.p. °C.	B.p. Mm.	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
IIIa	$C_4H_5ClO_2$	1.4407	1.1864	139[a]		39.8	4.18	29.4	39.01	4.21	27.9
IIIb	$C_5H_7ClO_2$	1.4378	1.1175	44	15[b]	44.6	5.25	26.4	45.32	5.49	26.8
IIIc	$C_6H_7ClO_2$	1.4551	1.1535	63	17[c]	44.6	5.25	26.4	44.94	5.24	26.4
IIId	$C_6H_9ClO_2$	1.4550	1.1035	75–76	18	48.5	6.10	23.9	48.48	6.17	23.2
IIIe	$C_7H_{11}ClO_2$	1.4572	1.0793	72	8	51.7	6.83	21.9	51.86	6.88	21.8
IIIf	$C_8H_9ClO_2$	1.4628	1.1264	172–173		48.5	6.10	23.9	48.76	6.08	22.7

[a] Previously reported (C. S. Marvel and J. E. Cowan, THIS JOURNAL, **61,** 3156 (1939)), $n^{20}\mathrm{D}$ 1.4400, d^{20}_4 1.189, b.p. 57–59° (55 mm.). [b] Previously reported (C. S. Marvel, *et al.*, *ibid.*, **62,** 3495 (1940)), $n^{20}\mathrm{D}$ 1.4384, b.p. 51–53° (18 mm.). [c] Previously reported (G. Kahlbaum, *Ber.*, **12,** 343 (1879)), $n^{22}\mathrm{D}$ 1.4563, d^{4}_4 1.0933, b.p. 160.8°.

of this orthoester was added a mixture of 14 ml. of water and 1 ml. of concentrated sulfuric acid and refluxed for 2 hours. Ether extraction, drying (magnesium sulfate) and distillation yielded 1.35 g. (79%) of methyl phenylpropiolate, b.p. 138–140° (17 mm.), $n^{25}\mathrm{D}$ 1.5610; previously reported[16] b.p. 132–133° (16 mm.), $n^{25}\mathrm{D}$ 1.5618. Saponification yielded phenylpropiolic acid, m.p. 136–138°, mixed melting point with an authentic sample, 136–138°.

Reaction of 2,2-Dichlorocyclopropanone Diethylacetal (IIb) with Potassium *t*-Butoxide. Diethyl *t*-Butyl Orthopropiolate (XII).—To a solution of potassium *t*-butoxide, prepared by addition of 3.91 g. (0.10 g. atom) of potassium to 100 ml. of *t*-butyl alcohol, was added 10 g. (0.05 mole) of IIb. An immediate precipitation of potassium chloride occurred and the reaction temperature rose rapidly to 70°. After 4 hours stirring, the reaction mixture was poured into a water–ether system. The aqueous layer was separated and extracted twice with ether. The combined ether fractions were dried (magnesium sulfate) and distilled through a 30-cm. Podbielniak column to yield the fractions: (a) 0.25 g., b.p. 168–173°, $n^{25}\mathrm{D}$ 1.4132; (b) 1.25 g., b.p. 173–179°, $n^{25}\mathrm{D}$ 1.4170; (c) 2.15 g., b.p. 179–182°, $n^{25}\mathrm{D}$ 1.4170; (d) 3.15 g., b.p. 182°, $n^{25}\mathrm{D}$ 1.4228.

Redistillation of fractions b, c and d gave an analytical sample of diethyl *t*-butyl orthopropiolate (XII), b.p. 179–180°, $n^{25}\mathrm{D}$ 1.4170, d^{25}_4 0.9100.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 65.9; H, 10.05. Found: C, 66.32; H, 10.30.

To 10 ml. of 1% hydrochloric acid in a separatory funnel was added 2.70 g. of XII. The mixture was shaken for 10 minutes during which an exothermic reaction was evident. Ether was added, the aqueous layer separated and extracted twice with additional ether. The combined ether fractions were dried (magnesium sulfate) and distilled to yield 1.15 g. (87%) of ethyl propiolate, b.p. 115–119°, $n^{25}\mathrm{D}$ 1.4076; C, 60.92; H, 6.55 (Calcd.: C, 61.1; H, 6.17). The infrared spectrum was completely superimposable upon that of a synthetic sample prepared by the method of Perkin and Simonsen.[17]

Reaction of 2,2-Dichloro-3,3-dimethylcyclopropanone Dimethylacetal (IIf) with Potassium *t*-Butoxide.—To a solution of potassium *t*-butoxide prepared by addition of 3.9 g. (0.10 g. atom) of potassium to 100 ml. *t*-butyl alcohol, was added 20 g. (0.1 mole) of IIf. An immediate precipitate did not occur, as it did in the reaction of 2,2-dichlorocyclopropanone diethylacetal, and only a slight cloudiness was evident after 1 hour refluxing. Therefore, the mixture was refluxed for 3 days while the precipitate of potassium chloride became more voluminous. The mixture was transferred to a separatory funnel with the aid of ether and 50 ml. of water. The aqueous layer was separated and extracted twice more with ether. The aqueous layer was then acidified with nitric acid and an aliquot titrated to determine the chloride ion concentration. The results indicated that 74% of one covalent chlorine had become ionic chlorine.

The combined ether fractions were dried (magnesium sulfate) and distilled at 19 mm. to yield the fractions: (a) 1.65 g., b.p. 80–83°, $n^{25}\mathrm{D}$ 1.4528; (b) 1.40 g., b.p. 83–86°, $n^{25}\mathrm{D}$ 1.4538; (c) 2.50 g., b.p. 86–87°, $n^{25}\mathrm{D}$ 1.4547; (d) 2.40 g., b.p. 87–89°, $n^{25}\mathrm{D}$ 1.4536; (e) 2.60 g., b.p. 89–92°, $n^{25}\mathrm{D}$ 1.4530; (f) 1.45 g., b.p. 92–95°, $n^{25}\mathrm{D}$ 1.4521; (g) 1.35 g., b.p. 95–100°, $n^{25}\mathrm{D}$ 1.4512; (h) 2.60 g., b.p. 100–107°, $n^{25}\mathrm{D}$ 1.4503.

Infrared analysis of fractions a, c, e, g and h indicated the absence of any pure product. Unreacted starting material was evident in all fractions except h. There were normal ester peaks (methyl or *t*-butyl α-chloro-β-methylcrotonate) distributed in every fraction.

Fraction h, and the immediately preceding fractions to a lesser extent, showed infrared spectra characteristic of the orthoester function[7] (absorption peaks at 8.12, 8.72, 9.26 and 9.95 μ). This is believed to be due to dimethyl *t*-butyl ortho-α-chloro-β-methylcrotonate. This assignment is supported by chlorine analysis of fraction h: Cl, 14.98; calcd. for $C_{11}H_{21}O_3Cl$, Cl, 14.97. An attempted purification of the orthoester involving pyrolysis, to destroy starting material, and subsequent saponification, to preferentially remove normal ester, failed to produce an analytically pure compound.

Pyrolysis of 2,2-Dichloro-3,3-dimethylcyclopropanone Dimethylacetal (IIf) in Methyl Orthoisobutyrate.—A mixture of 6.7 g. (0.033 mole) of IIf and 32.70 g. (0.22 mole) of methyl orthoisobutyrate was refluxed through a 30-cm. Podbielniak fractionating column surmounted with a total reflux-partial take-off still-head. The material was totally refluxed for 0.5 hour then distillate was slowly withdrawn to yield the fractions: (a) 1.05 g., b.p. 65–70°, $n^{25}\mathrm{D}$ 1.3586; (b) 1.45 g., b.p. 70–102°, $n^{25}\mathrm{D}$ 1.38^{11}; (c) 2.75 g., b.p. 102–130°, $n^{25}\mathrm{D}$ 1.3988; fractions d, e and f, 27.10 g., b.p. 130°, $n^{25}\mathrm{D}$ 1.4010; (g) 0.40 g., b.p. 48–68° (15 mm.), $n^{25}\mathrm{D}$ 1.4166; (h) 0.45 g., b.p. 68–70° (15 mm.), $n^{25}\mathrm{D}$ 1.4400; (i) 3.25 g., b.p. 70–80° (15 mm.), $n^{25}\mathrm{D}$ 1.4559; (j) 1.75 g., b.p. 80° (15 mm.), $n^{25}\mathrm{D}$ 1.4512.

Fraction b contained methyl isobutyrate as shown by infrared analysis and refractionation of the fraction to obtain 0.45 g. of pure methyl isobutyrate, b.p. 91°, $n^{25}\mathrm{D}$ 1.3811.

Fractions c, d, e and f were methyl orthoisobutyrate (91%) as determined by refractive index and infrared analysis.

Fractions g, h and i were mixtures of methyl orthoisobutyrate and methyl α-chloro-β-methylcrotonate (IIIf).

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(16) C. Moureu, *et al.*, *Ann. chim.*, [9] **2**, 276 (1914).

(17) W. Perkin and J. Simonsen, *J. Chem. Soc.*, **91**, 833 (1907).

Fraction j was a mixture of IIIf with methyl ortho-α-chloro-β-methylcrotonate (V) the latter being present to the extent of 80%, as shown by chlorine analysis of fraction j to give a value of 19.3%; IIIf contains 23.9% chlorine, while V contains 18.2% chlorine. Infrared analysis indicated a mixture of about 90% orthoester and 10% normal ester.

Fraction j when treated with anhydrous hydrogen chloride gave pure methyl α-chloro-β-methylcrotonate (IIIf) whose infrared spectrum was superimposable upon that of the authentic material.

Pyrolysis of IIf in *n*-Butyl Alcohol. *n*-Butyl α-Chloro-β-methylcrotonate (VI).—A solution of 10 g. (0.05 mole) of IIf in 22.2 g. (0.3 mole) of *n*-butyl alcohol was stirred magnetically and refluxed for 1 hour. The flask then was fitted with a 30-cm. Podbielniak column and a still-head and the following fractions taken: (a) 2.57 g., b.p. 56–64°, n^{25}_D 1.3692; (b) 0.35 g., b.p. 64°, n^{25}_D 1.3650; (c) 0.50 g., b.p. 64–78°, n^{25}_D 1.3682; (d) 0.65 g., b.p. 78–80°, n^{25}_D 1.3750; (e) 1.30 g., b.p. 80–115°, n^{25}_D 1.3882; (f) 11.4 g., b.p. 115°, n^{25}_D 1.3970; (g) 0.70 g., b.p. 39–48° (15 mm.), n^{25}_D 1.3997; (h) 1.25 g., b.p. 48–75° (15 mm.), n^{25}_D 1.4352; (i) 1.15 g., b.p. 75–108° (15 mm.), n^{25}_D 1.4556; (j) 7.89 g., b.p. 108–112° (15 mm.), n^{25}_D 1.4592.

Fractions a through d were mixtures of methyl alcohol and *n*-butyl chloride. On the basis of refractive indices 2.03 g. (63.5% yield) of methyl alcohol and 3.37 g. (73.3% yield) of *n*-butyl chloride were present in these fractions. This distribution was confirmed by quantitative preparation of the 3,5-dinitrobenzoate from the methyl alcohol, 1 g. of fraction a yielding 1.60 g. of methyl 3,5-dinitrobenzoate.

Fraction d was washed with concentrated sulfuric acid and the insoluble top layer isolated as pure *n*-butyl chloride, b.p. 79°, n^{25}_D 1.4015. Fractions e and f contain unreacted *n*-butyl alcohol. Fraction i is mostly the normal pyrolysis product, methyl α-chloro-β-methylcrotonate (IIIf) (15.6%) as determined by comparison of the infrared spectrum with that of an authentic sample. Fraction j is pure *n*-butyl α-chloro-β-methylcrotonate VI and represented an 82% yield.

Anal. Calcd. for $C_9H_{15}ClO_2$: C, 56.8; H, 7.84; Cl, 18.6. Found: C, 56.41; H, 7.93; Cl, 19.4.

Fraction j was saponified with 20% sodium hydroxide solution to yield α-chloro-β-methylcrotonic acid, m.p. 83–85°. Refluxing methyl α-chloro-β-methylcrotonate with 1-butanol for one hour produced none of the butyl ester VI.

2-Phenyl-2-chloro-3,3-dimethylcyclopropanone Dimethylacetal (XIII).—To a solution of potassium *t*-butoxide, prepared by addition of 20 g. (0.5 g. atom) of potassium to 300 ml. of *t*-butyl alcohol, was added 38.7 g. (0.33 mole) of dimethylketene dimethylacetal followed by 59.4 g. (0.37 mole) of benzal chloride. The mixture was stirred magnetically and heated to 60–70° for 3 hours. Potassium chloride precipitated gradually and the mixture turned a light green. The temperature was reduced to 50° while *t*-butyl alcohol was removed at reduced pressure. The semi-solid residue was treated with sufficient water to dissolve the salts and ether was added. The aqueous layer was separated and extracted twice with additional ether. The combined ether layers were dried (magnesium sulfate) and distilled (30-cm. Podbielniak column) to yield 61.6 g. (77%) 2-phenyl-2-chloro-3,3-dimethylcyclopropanone dimethylacetal (XIII), b.p. 87° (0.25 mm.), m.p. 37–38° after refractionation.

Anal. Calcd. for $C_{13}H_{17}ClO_2$: C, 64.9; H, 7.12; Cl, 14.73. Found: C, 64.76; H, 6.95; Cl, 14.52.

Pyrolysis of XIII. Methyl α-Phenyl-β-methylcrotonate (XIV).—A 3.10-g. sample of XIII was heated to 195° with stirring for 2 hours. Methyl chloride, b.p. −24°, was evolved and collected in a Dry Ice–acetone trap. Upon distillation of the residue 2.25 g. (92%) of methyl α-phenyl-β-methylcrotonate (XIV), b.p. 66° (0.06 mm.), n^{25}_D 1.5265, d^{25}_4 1.0380, was obtained. It was found to contain 75.48% carbon and 7.52% hydrogen; sapn. equiv. 186.3, 193.5 (calcd. for $C_{12}H_{14}O_2$: C, 75.8; H, 7.43; sapn. equiv., 190.23); previously reported[18] b.p. 142° (26 mm.). The ultraviolet spectrum had an inflection at 225 mμ, log ϵ 3.86 (95% ethanol), with strong end absorption.

The α-phenyl-β-methylcrotonic acid recovered (92%) from the saponification equivalent determination had m.p. 152.5–153° after one recrystallization from petroleum ether (90°); previously reported[18] m.p. 151°.

Reaction of Ketene Diethylacetal (Ib), Benzal Chloride and Sodium *t*-Butoxide.—To a suspension of sodium *t*-butoxide in *t*-butyl alcohol, prepared by addition of 5.3 g. (0.22 mole) of sodium hydride to 200 ml. of *t*-butyl alcohol, was added 23.2 g. (0.20 mole) of ketene diethylacetal and 32.2 g. (0.20 mole) of benzal chloride. The mixture was stirred magnetically and heated to 70° for 4 hours. The mixture was then cooled and poured into water to dissolve the salts. Ether was added, the aqueous layer separated and extracted twice more with ether. The combined ether fractions were dried (magnesium sulfate) and distilled at 0.20 mm. to yield 17.00 g. (53%) of unreacted benzal chloride. When the distillation was continued the low pressure could not be maintained with the high oil bath temperature (105°). It was evident that pyrolysis of the 2-phenyl-2-chlorocyclopropanone diethylacetal (XV) was occurring. Therefore the distillation was stopped and the contents of the distilling flask were pyrolyzed at 155–160° and atmospheric pressure for 0.5 hour. A Dry Ice–acetone trap attached to the system collected about 2 g. of ethyl chloride, b.p. 12°, during this process. Subsequent distillation yielded 6.70 g. of ethyl atropate (XVI), b.p. 133–138° (18 mm.), and 3.10 g. of ethyl cinnamate, b.p. 148–152° (18 mm.) (41 and 19%, respectively), based on unrecovered benzal chloride.

The redistilled ethyl atropate had n^{25}_D 1.5240, d^{25}_4 1.0419, and a saponification equivalent of 174.4 (calcd. 176.2). The ultraviolet spectrum had λ_{max} 253 mμ, log ϵ 3.81 (95% ethanol); previously reported[19] for ethyl atropate: b.p. 120.2–120.4° (14 mm.), n^{16}_D 1.5260 and $d^{16.1}_4$ 1.0508.

The redistilled ethyl cinnamate had n^{25}_D 1.5358 and a saponification equivalent of 183 (calcd. 176.2). The infrared spectrum was indistinguishable from that of the authentic material. The ultraviolet spectrum, λ_{max} 277 mμ, log ϵ 4.19 (95% ethanol), compared favorably with that of the authentic material, λ_{max} 277 mμ, log ϵ 4.34. The cinnamic acid recovered (80%) from the saponification equivalent determination had m.p. 133–134°, after one recrystallization from water.

This reaction was repeated with ketene dimethylacetal (Ia), benzal chloride and two equivalents of base as follows. To a solution of potassium *t*-butoxide prepared from 15.64 g. (0.4 g. atom) of potassium and 400 ml. of *t*-butyl alcohol, was added 17.62 g. (0.2 mole) of Ia and 32.2 g. (0.2 mole) of benzal chloride. The mixture was heated at 65° for 4 hours, while being stirred magnetically. After cooling, the mixture was transferred to a separatory funnel with the aid of ether and 200 ml. of water. The aqueous layer was separated and extracted twice more with ether. The combined ether extractions were dried (magnesium sulfate) and distilled to yield 5.75 g. (18.5%) of benzal chloride and 15.45 g. (58% based on unrecovered benzal chloride) of impure (low refractive index) methyl cinnamate. There was no material suggestive (infrared and boiling point) of methyl atropate. However, there was 4.35 g. of a higher boiling material that distilled over a wide temperature range (147–160°, 20 mm.) and was not investigated further. The distillate intermediate between benzal chloride and methyl cinnamate showed a carbonyl peak in the infrared at 5.83 μ but no double bond peak. Since it boiled over a wide range (6.0 g., b.p. 106–138°, 20 mm.) it was not investigated further.

Although the methyl cinnamate fractions crystallized when seeded with authentic methyl cinnamate and cooled, the infrared absorption spectrum contained some foreign peaks in addition to all the peaks of the spectrum of the authentic material. Its ultraviolet absorption spectrum showed λ_{max} 277 mμ, log ϵ 4.19. Authentic methyl cinnamate showed λ_{max} 277 mμ, log ϵ 4.33. The saponification equivalent was 189.0 and 189.5 (calcd. 162.78), indicating a purity of 85%, if the impurities are non-saponifiable. The acid isolated from the saponification equivalent in good yield had m.p. 134–135° after one recrystallization from water and melted at 133–135° on admixture with authentic cinnamic acid.

To demonstrate that the cinnamic ester was not formed from the direct reaction of Ia with benzal chloride, equimolecular quantities of these compounds were refluxed together and the infrared spectrum determined after 1 hour and after 4 hours refluxing; no new absorption peaks were apparent. The spectrum was identical to that of a freshly

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(18) E. Blaise and A. Courtot, *Bull. soc. chim.*, [3] **35**, 593 (1906).

(19) K. Auwers and F. Eisenlohr, *J. prakt. Chem.*, **84**, 89 (1911).

prepared equimolar mixture of ketene dimethylacetal and benzal chloride. The spectrum of the composite was equivalent, in turn, to the spectrum obtained by superimposition of the spectrum of ketene dimethylacetal upon that of benzal chloride.

Similar results were obtained when 0.02 molar quantities of ketene dimethylacetal and benzal chloride were heated at 65° for 4 hours with 5 ml. of *t*-butyl alcohol.

Attempts to Form a Carbene from Benzhydryl Chloride. Benzhydryl *t*-Butyl Ether.—To a solution of potassium *t*-butoxide, prepared from 6 g. (0.15 g. atom) of potassium and 180 ml. of *t*-butyl alcohol, was added 17.4 g. (0.15 mole) of dimethylketene dimethylacetal followed by 30.2 g. (0.15 mole) of benzhydryl chloride. The mixture was heated for 2 hours at 60–70° while being stirred magnetically. After several minutes potassium chloride began to precipitate. The mixture was poured into a water–ether system to dissolve the salts. The aqueous layer was separated and extracted twice more with ether. The combined organic fractions were dried (magnesium sulfate) and distilled to yield 28.8 g. (80%) of benzhydryl *t*-butyl ether, b.p. 105–106° (0.2 mm.), m.p. 54–55°, after three recrystallizations from petroleum ether (b.p. 35°).

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.0; H, 8.39. Found: C, 85.38; H, 8.64.

Cyclopropanone Diethylacetal (XVIII).—To a solution of 160 ml. of *t*-butyl alcohol in 800 ml. of benzene was added 34.5 g. (1.5 g. atom) of sodium sand and 40 g. (0.2 mole) of 2,2-dichlorocyclopropanone diethylacetal (IIb). The mixture was stirred for 0.5 hour before an exothermic reaction began and cooling was necessary. Additional benzene (600 ml.) was added to facilitate stirring. After 24 hours, water was added cautiously to dissolve the salts and to react with any unchanged sodium. The aqueous layer was separated immediately and extracted twice with ether. The combined organic fractions were dried (magnesium sulfate) and fractionally distilled through a 30-cm. Podbielniak column over a period of several days with a high reflux to take-off ratio in order to separate the large amount of benzene from the product. This distillation yielded 7.10 g. (27%) of cyclopropanone diethylacetal (XVIII). An analytical sample had b.p. 120–121°, $n^{25}D$ 1.3980, d^{25}_4 0.8663.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.83. Found: C, 64.10; H, 10.50.

Varying amounts (0–10%) of diethyl *t*-butyl orthopropiolate (XII), b.p. 169–175°, were obtained from this and repetitions of this experiment.

The cyclopropanone acetal XVIII was also prepared by the following procedure of Dull and Abend.[10] To 23.2 g. (0.2 mole) of ketene diethylacetal and 0.75 g. of cuprous iodide in 50 ml. of petroleum ether (b.p. 65–68°) was added dropwise a solution of 9.3 g. (0.22 mole) of diazomethane in 500 ml. of petroleum ether. The mixture was stirred magnetically. The reaction flask was connected to a Dry Ice–acetone condenser and a calcium chloride drying tube. The reaction was exothermic but did not cause refluxing. When all the diazomethane solution had been added, the mixture was filtered to remove the catalyst and the polymethylene by-product. The filtrate was distilled to remove the solvent and reduce the volume to about 100 ml. This residue was treated with 5% sulfuric acid to decompose the unreacted ketene diethylacetal and ether added. The organic layer was separated and extracted twice with 30-ml. portions of 10% sodium carbonate. After drying (magnesium sulfate) the organic fraction was distilled to yield 7.40 g. (28%) of cyclopropanone diethylacetal (XVIII).

Sodium–Alcohol Reduction of IIf to β-Methylcrotonaldehyde Dimethylacetal (XXI).—To a solution of 200 ml. of *t*-butyl alcohol in 1 liter of benzene was added 46 g. (2 g. atoms) of sodium sand and 50 g. (0.25 mole) of 2,2-dichloro-3,3-dimethylcyclopropanone dimethylacetal (XV). The mixture became moderately warm and it was necessary to add benzene (750 ml. additional) periodically to permit efficient stirring (Hershberg). When all the sodium had reacted, water was added to dissolve the precipitated salts. The aqueous layer was removed and extracted twice with ether. The combined organic fractions were dried (magnesium sulfate) and fractionally distilled through a 30-cm. Podbielniak column over a period of several days with a high reflux ratio in order to separate the large amount of benzene from the product. This distillation yielded 8.80 g. (26.5%) of β-methylcrotonaldehyde dimethylacetal (XXI), b.p. 107–109°, $n^{25}D$ 1.4058. The infrared spectrum had the absorption peaks: 5.97(s), 6.92(s), 8.2–8.8(s), 9.6(s), 10.1(s), 11.42(s).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.85. Found: C, 65.12; H, 10.34.

This compound gave a red 2,4-dinitrophenylhydrazone derivative, m.p. 182–182.5° (from 95% ethanol). The 2,4-dinitrophenylhydrazone derivative of authentic β-methylcrotonaldehyde had m.p. 180.5–182°.[20] The mixed melting point was 181–182°. The infrared spectra of these two 2,4-dinitrophenylhydrazones are identical.

Reduction of 2-Phenyl-2-chloro-3,3-dimethylcyclopropanone Dimethylacetal (XIII). 2,2-Dimethyl-3-phenylcyclopropanone Dimethylacetal (XXII).—To 125 ml. of benzene containing 3.45 g. (0.15 g. atom) of sodium sand was added 12.05 g. (0.05 mole) of XIII. The mixture was heated to 60° where an exothermic reaction began to take place. Immediately 25 ml. of *t*-butyl alcohol was added and stirring continued (Hershberg). The reaction mixture refluxed from the heat of reaction for 2 hours; it then was heated to maintain reflux for an additional hour. After cooling, water was added slowly to destroy small amounts of unreacted sodium and to dissolve the precipitated salts. The aqueous layer was separated and extracted with ether. The combined organic fractions were dried (magnesium sulfate) and distilled to yield 9.45 g. (92%) of XXII, b.p. 60–62° (0.20 mm.), $n^{25}D$ 1.5008, d^{25}_4 0.9883.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.79. Found: C, 75.72; H, 8.59.

A 1-g. sample of XXII was heated at 250° for one hour to determine its stability toward heat. Distillation yielded quantitative recovery of XXII, b.p. 51° (0.05 mm.), $n^{25}D$ 1.5008.

The above reduction was repeated without the *t*-butyl alcohol. To 50 ml. of benzene containing 2.3 g. (0.1 mole) of sodium sand was added 12.05 g. (0.05 mole) of XIII. There was no immediate reaction, but as the temperature of the mixture was raised and vigorous stirring (Hershberg) continued an exothermic reaction sufficient to cause refluxing began. When the initial reaction subsided the mixture was refluxed for an additional 2 hours. Then water was added, slowly at first, to destroy the small amount of unreacted sodium and dissolve the precipitated salts. The aqueous layer was removed and extracted three times with ether. The combined organic fractions were dried (magnesium sulfate) and the ether and benzene removed at reduced pressure. The residue was distilled yielding 4.25 g. (35.2%) of starting material. The distillation flask contained 4.15 g. of an orange-red tar which was soluble in organic solvents but could not be crystallized or distilled without further decomposition. The aqueous layer contained 64.4% of the chlorine from the starting material as chloride ion.

Attempted Acid Hydrolysis of Cyclopropanone Acetals.—(a) When 5 g. of IIf was treated with 0.91 g. (0.025 mole) of anhydrous hydrogen chloride in a small amount of ether there was no apparent reaction. The material was distilled (0.2 mm.) to yield 4.65 g. (93%) of starting material.

(b) When anhydrous hydrogen chloride was bubbled through 5 g. of IIf for several hours at room temperature and the saturated material allowed to stand stoppered overnight there was no apparent reaction. Distillation (0.2 mm.) yielded 4.35 g. (87%) of unreacted starting material.

(c) A 6.60-g. sample of IIf was treated with anhydrous hydrogen chloride *via* a bubbling tube for 2 hours at 95°. Distillation (0.15 mm.) gave 5.65 g. (85.6%) of unreacted starting material. There was no evidence of any pyrolysis product, methyl α-chloro-β-methylcrotonate (IIIf).

(d) To 10 ml. of concentrated hydrochloric acid was added 3.45 g. of IIf. The heterogeneous mixture was stirred magnetically at 95° for 14 hours. The mixture was extracted several times with ether, the combined ether extractions washed with distilled water, dried (magnesium sulfate) and the ether removed by distillation. The residue was distilled (0.3 mm.) to yield fractions: (a) 0.30 g., b.p. 31.5°, $n^{25}D$ 1.4602; (b) 0.95 g., b.p. 31.5–32°, $n^{25}D$ 1.4596; (c) 0.10 g., b.p. 32–42°, $n^{25}D$ 1.4581; (d) 1.10 g., b.p. 42°, $n^{25}D$ 1.4568.

These fractions contained varying amounts of unreacted starting material IIf, and of methyl α-chloro-β-methylcrotonate (IIIf). Fraction a was almost pure IIIf; fraction d was almost pure IIf. On the basis of the refractive indices

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[20] S. M. McElvain, *et al.*, This Journal, **64**, 1966 (1942).

of the fractions it was calculated that they contain 1.6 g. (33%) of unreacted starting material and 0.86 g. (24%) of IIIf.

The distillation pot, from which these fractions were distilled, contained 0.75 g. (23%) of α-chloro-β-methylcrotonic acid.

(e) To a mixture of 15 ml. of 10% hydrochloric acid and 75 ml. of methanol was added 5.95 g. of IIf. The homogeneous mixture was stirred magnetically at room temperature for 24 hours then refluxed for 1 hour. Methanol was removed by vacuum distillation at room temperature. The residue in the flask separated into two layers. Water and ether were added, the aqueous layer separated and extracted twice with ether and the combined ether fractions dried (magnesium sulfate). Distillation yielded 3.5 g. (60%) of starting material contaminated with traces of the pyrolysis product IIIf. Distillation of the water layer from the separation yielded no organic material.

(f) To 1 g. of cyclopropanone diethylacetal (XVIII) was added 6 ml. of concentrated hydrochloric acid. The homogeneous solution was allowed to stand at room temperature for 0.5 hour and then diluted with 6 ml. of water which caused a second layer to separate. The mixture was extracted with ether and the ether extractions dried (magnesium sulfate). Distillation recovered 0.7 g. (70%) of unchanged XVIII.

(g) To 2 g. of XVIII was added 12 ml. of concentrated hydrochloric acid and the resulting solution heated on the steam-bath for 20 minutes. The mixture was then distilled under reduced pressure; no residue remained. The distillate was neutralized with solid sodium carbonate and extracted with ether. The ether fraction was dried (magnesium sulfate) and distilled to yield 0.185 g. (12%) of ethyl propionate and 0.476 g. (34%) of chloroacetone. The ethyl propionate was characterized by its infrared spectrum which was identical with that of an authentic sample. The chloroacetone was characterized by its infrared spectrum which was identical to that of an authentic sample, and by its 2,4-dinitrophenylhydrazone derivative, m.p. 124–125.5°, which on admixture with an authentic sample melted at 122–123°.

The aqueous fraction was acidified with sulfuric acid and continually extracted with ether for 24 hours. This extracted fraction was titrated with 0.1 *N* sodium hydroxide indicating 4.58 milliequivalents of an acid (30% from the cyclopropanone diethylacetal). The sodium salt was then isolated and converted to the *p*-toluide, m.p. 125–126°, which on admixture with the *p*-toluide of propionic acid melted at 125°.

(h) When XVIII was treated with anhydrous hydrogen chloride at room temperature for 1.5 hours, 0.3 of an equivalent was absorbed but infrared analysis disclosed no new product. Treatment of 1.15 g. of the acetal with hydrogen chloride at 95° produced a 38% yield of ethyl propionate, but no chloroacetone. Unchanged cyclopropanone acetal (21%) was recovered.

(i) To 20 ml. of concentrated hydrochloric acid was added 5 g. of 2,2-dimethyl-3-phenylcyclopropanone dimethylacetal (XXII). The heterogeneous mixture was refluxed for 2 hours and extracted with benzene. Distillation at 0.05 mm. yielded 1.85 g. (40%) of XXII, b.p. 54–58°, n^{25}D 1.5080, and 1.80 g. of a mixture, b.p. 58–76°, n^{25}D 1.5159. The latter fraction gave an infrared spectrum containing carbonyl and hydroxyl absorption peaks and was not investigated further.

Bromination of Cyclopropanone Diethylacetal (XVIII).—To 1.3 g. (0.01 mole) of cyclopropanone diethylacetal in 15 ml. of carbon tetrachloride was added a solution of 1.6 g. (0.01 mole) of bromine in 10 ml. of carbon tetrachloride *via* a dropping funnel over a period of 0.5 hour. The bromine color was dissipated immediately and the resulting solution was light yellow. The solvent was removed by distillation during which hydrogen bromide and some ethyl bromide were evident. Vacuum distillation (7 mm.) of the residue through a 30-cm. Podbielniak column gave the fractions: (a) 0.10 g., b.p. 66–75°, n^{25}D 1.4527; (b) 0.35 g., b.p. 75–85°, n^{25}b 1.4677; (c) 0.50 g., b.p. 85–87°, n^{25}D 1.4774; (d) 0.60 g., b.p. 87–88°, n^{25}D 1.4866; (e) 0.20 g., b.p. 89°, n^{25}D 1.4952.

Fraction a was mostly ethyl β-bromopropionate, characterized by its infrared spectrum.

Fractions d and e were mostly ethyl α,β-dibromopropionate. The infrared spectra of these fractions were superimposable upon that of authentic material prepared by action of bromine on ethyl acrylate.

Infrared analysis of fractions b and c indicated that they were mixtures of the monobromo and the dibromo esters. On the basis of the refractive indices of the fractions it was found that the monobromo ester was produced in 41% yield, the dibromo ester in 39% yield.

Bromination of 2,2-Dichlorocyclopropanone Diethylacetal (IIb).—To 10 g. (0.05 mole) of IIb was added a solution of 8 g. (0.05 mole) of bromine in 7 ml. of carbon tetrachloride *via* a dropping funnel. An ice–water-bath was necessary to cool the exothermic reaction which developed after approximately one-quarter of the bromine had been added. The bromine color was not dissipated completely until the mixture was stirred extensively after each addition of bromine solution. Removal of solvent and distillation yielded 9.65 g. (77.3%) of ethyl β,β-dichloro-β-bromopropionate (XXIII), b.p. 40–46° (0.07 mm.). A middle fraction boiling at 43–44° (0.07 mm.), n^{25}D 1.4857, d^{25}_4 1.6138 was analyzed.

Anal. Calcd. for $C_5H_7BrCl_2O_2$: C, 24.03; H, 2.83; total halogen, 60.35. Found: C, 24.51; H, 3.04; total halogen, 60.6.

A 6.65-g. sample of the ester XXIII was added to a solution of 0.027 mole of sodium ethoxide in absolute ethanol. An immediate precipitation occurred and an exothermic reaction was evident. The mixture was stirred for 3 hours at room temperature and then refluxed for 0.25 hour. Ether (20 ml.) was added, the mixture filtered and distilled to yield 0.80 g. (17.5%) of ethyl β,β-dichloroacrylate, b.p. 173–177°, n^{25}D 1.4621; chlorine content: 41.8% (calcd. 40.7); previously reported[13] b.p. 173–175°.

This ester was saponified by shaking with 5% sodium hydroxide in a separatory funnel until homogeneous (about 5 minutes). Isolation of the acid yielded β,β-dichloroacrylic acid, m.p. 75–76° after two recrystallizations from petroleum ether; previously reported[21] m.p. 76–77°.

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[21] O. Wallach, *Ann.*, **193**, 20 (1878).

[Contribution #1032 from the Department of Chemistry, University of Pittsburgh]

The Reaction of Some Methylene Derivatives with Ketene Diethylacetal[1]

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The reaction of diazomethane with ketene diethylacetal (III) and phenylketene diethylacetal (V) has been found to give cyclopropanone diethylacetal (II) and phenylcyclopropanone diethylacetal (IV), respectively, the latter also being obtained by the reaction of phenyldiazomethane with III. Ethyl diazoacetate and III gave only carbethoxymethylketene diethylacetal (VI), while ethyl α-bromoacrylate was obtained from the reaction of bromoform and potassium *t*-butoxide with III. The formation of unstable 2,2-dibromocyclopropanone diethylacetal as a precursor is postulated.

McElvain and Weyna[2] have shown that when chloroform and benzal chloride are treated with sodium *t*-butoxide in the presence of a variety of ketene acetals the resulting dichloro- and phenylchlorocarbene adds to the ketene acetals to form

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[1] Taken from the thesis of Phillip G. Abend submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Pittsburgh, 1958.

[2] S. M. McElvain and Philip L. Weyna, This Journal, **81**, 2579 (1959).