[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Reaction of Ketene with Organic Halogen Compounds[1]

BY A. T. BLOMQUIST, ROBERT W. HOLLEY AND ORVILLE J. SWEETING[2]

Although the chemical behavior of ketene has been studied widely, there is only one recorded example of its reaction with an organic halogen compound to give an acid halide (1).

$$CH_2{=}C{=}O + RX \longrightarrow RCH_2COX \qquad (1)$$

Staudinger and Tuerck[3] described the reaction of chloromethyl methyl ether with ketene in the presence of aluminum chloride. The acid chloride was not isolated but treatment of the reaction mixture with ethyl alcohol afforded ethyl β-methoxypropionate (2).

$$ClCH_2OCH_3 + CH_2{=}C{=}O \xrightarrow[\text{followed by } C_2H_5OH]{AlCl_3} CH_3OCH_2CH_2CO_2C_2H_5 \qquad (2)$$

The addition of organic halides to various other types of carbon–carbon double bonds is well known. Thus, Schmerling[4] has recently reported detailed investigations of the addition of alkyl halides to unsaturated hydrocarbons. McElvain and his students[5] have made extensive studies of the addition of alkyl halides to ketene acetals, while Staudinger, Göhring and Schöller[6] described the addition of acid chlorides to diphenylketene.

It was of interest to study the reaction of ketene with organic halogen compounds as a possible useful method for synthesizing various acid halides. Ketene was found to react with α,β-dichloroethyl ethyl ether, α-chlorobenzyl methyl ether, and triphenylchloromethane but failed to react, under the conditions studied, with benzyl chloride, benzyl bromide, benzotrichloride, benzoyl chloride, chloroacetone and 2-chloro-2-nitropropane.

Of the halides which failed to react, benzyl chloride was investigated most extensively. It was unreactive toward ketene at elevated temperatures and pressures and at lower temperatures in the presence of catalysts.

The reaction of α,β-dichloroethyl ethyl ether with gaseous ketene did not occur at room temperature in the absence of a catalyst. However, in the presence of aluminum chloride, as specified by Staudinger for chloromethyl methyl ether,[3] reaction took place. The reaction product was not isolated but on treatment with absolute alcohol it afforded ethyl γ-chloro-β-ethoxybutyrate in 43% yield, considering the amount of α,β-dichloroethyl ethyl ether recovered (3).

$$ClCH_2CHCl{-}O{-}C_2H_5 + CH_2{=}C{=}O \xrightarrow[\text{followed by } C_2H_5OH]{AlCl_3} ClCH_2CH(OC_2H_5)CH_2CO_2C_2H_5 \qquad (3)$$

α-Chlorobenzyl methyl ether reacted rapidly with gaseous ketene at room temperature in the absence of a catalyst. The distilled β-methoxy-β-phenylpropionyl chloride, obtained in 70% yield, was characterized by conversion to the known β-methoxy-β-phenylpropionic acid[7] and a number of its esters.

The increased reactivity toward ketene of α-chlorobenzyl methyl ether as compared with α,β-dichloroethyl ethyl ether is not unexpected. The former has the reactivity not only of an α-chloroether but, in addition, that of a benzyl chloride.

Triphenylchloromethane in benzene solution required aluminum chloride as a catalyst to effect reaction with gaseous ketene at room temperature. Since the ketene reaction with organic halides probably proceeds by an ionic mechanism the substitution of a solvent of high dipole moment for benzene was indicated for facilitating the reaction. It was observed that triphenylchloromethane in nitrobenzene reacted readily with ketene in the absence of a catalyst (4).

$$\begin{matrix}(C_6H_5)_3C{-}Cl + \\ CH_2{=}C{=}O\end{matrix} \;\begin{matrix}\xrightarrow[\text{with } AlCl_3]{\text{in benzene}} \\ \text{or} \\ \xrightarrow[\text{without catalyst}]{\text{in nitrobenzene}}\end{matrix}\; (C_6H_5)_3C{-}CH_2COCl \qquad (4)$$

The β,β,β-triphenylpropionyl chloride was not purified but was characterized by conversion to the known β,β,β-triphenylpropionic acid,[8,9] and its ethyl[9] and butyl esters. The ethyl ester was obtained in 67% yield from triphenylchloromethane.

The use of nitrobenzene as a solvent did not bring about the reaction of benzyl chloride with ketene and it did not increase the rate of reaction of ketene with α-chlorobenzyl methyl ether. This is not surprising since nitrobenzene replaced benzene as a solvent in the reaction with triphenylchloromethane. The other halogen compounds were liquids and, previously, the pure liquids had been treated with ketene. In these cases, nitrobenzene would act as a diluent and

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[1] This work was done under a research contract between Cornell University and the B. F. Goodrich Company during the period August 1, 1943–July 31, 1944.

[2] Present address: University of Colorado, Boulder, Colorado.

[3] Staudinger and Tuerck, British Patent 539,163 (1941); *C. A.*, **36**, 3509 (1942); U. S. Patent 2,316,465 (1943); *C. A.*, **37**, 5734 (1943).

[4] Schmerling, THIS JOURNAL, **67**, 1152 (1945); **68**, 1650, 1655 (1946).

[5] McElvain and Kundiger, *ibid.*, **64**, 254 (1942); McElvain, Kent and Stevens, *ibid.*, **68**, 1922 (1946).

[6] Staudinger, Göhring and Schöller, *Ber.*, **47**, 40 (1914).

[7] Schrauth, Schoeller and Struensee, *ibid.*, **44**, 1432 (1911).

[8] Henderson, *J. Chem. Soc.*, **51**, 224 (1887).

[9] Fosse, *Bull. soc. chim.*, **49**, 159 (1931).

would replace the halogen compound, which probably has a high dipole moment.

The reactivities of the halogen compounds toward ketene parallels their reactivities as measured by other means, *e.g.*, α-chlorobenzyl methyl ether is hydrolyzed quantitatively in five seconds by shaking with ether saturated with water at room temperature[10]; triphenylchloromethane is 75% hydrolyzed in eight hours and benzyl chloride not appreciably hydrolyzed in a week under the same conditions[10]; while α,β-dichloroethyl ethyl ether is hydrolyzed very rapidly by water at room temperature.[11]

Experimental[12]

Starting Materials.—The ketene was prepared in a generator similar to that described by Williams and Hurd.[13] The filament was fabricated from six feet of Chromel "A" wire, B. and S. gage 22. A current of 6.8 to 7.0 amp. was used and about 0.2 mole of ketene was produced per hour. A gas absorption apparatus similar to that described by Bolstad and Dunbar[14] was used in the reactions with gaseous ketene.

Benzyl chloride, benzyl bromide, benzotrichloride, benzoyl chloride, chloroacetone, 2-chloro-2-nitropropane, and α,β-dichloroethyl ethyl ether were commercial products and were redistilled before use. α-Chlorobenzyl methyl ether was prepared according to the method of Straus and Heinze.[10a] Triphenylchloromethane was prepared according to "Organic Syntheses."[15]

Attempted Reactions with Ketene.—(a) **Benzyl chloride** was treated with an excess (4 to 6 equivalents) of gaseous ketene at atmospheric pressure at temperatures as high as 140°. No hydrocinnamoyl chloride could be detected. The recovery of unchanged benzyl chloride was nearly quantitative. Treatment of benzyl chloride with liquid ketene for four days at Dry Ice temperature, and in a bomb heated to 80° for six hours gave none of the desired product. Attempts to catalyze the reaction by the use of one equivalent of pyridine at room temperature, 30% by weight of anhydrous zinc chloride at room temperature, 2% by weight of anhydrous aluminum chloride at −30°, and a trace of acetic acid at 100° were all unsuccessful. The use of Friedel–Crafts type catalysts was limited since benzyl chloride was rapidly polymerized by most of them. A trace of anhydrous aluminum chloride at room temperature, an equivalent amount of aluminum chloride at −30°, or 30% by weight of stannic chloride at −30° caused polymerization. The use of nitrobenzene as a diluent did not bring about any reaction with gaseous ketene at 100°.

(b) Similarly gaseous ketene in excess did not react at all at room temperature with benzyl bromide nor with benzotrichloride, chloroacetone and 2-chloro-2-nitropropane, either alone or in the presence of a catalytic amount of aluminum chloride.

Reaction of α,β-Dichloroethyl Ethyl Ether with Ketene.—Treatment of α,β-dichloroethyl ethyl ether with six equivalents of gaseous ketene at room temperature brought about no reaction. In the presence of aluminum chloride, reaction occurred. A mixture of α,β-dichloroethyl ethyl ether and 10% by weight of anhydrous aluminum chloride was treated with four equivalents of gaseous ketene. An excess of absolute ethanol was added and the mixture was left at room temperature overnight. It was added to 3 *N* hydrochloric acid and the mixture was extracted repeatedly with ether. The ether extracts were washed with water and dried over anhydrous magnesium sulfate. Distillation of the residue obtained from the ether solution gave a 30% recovery of α,β-dichloroethyl ethyl ether and a 30% yield of a chlorine containing ester, presumably ethyl γ-chloro-β-ethoxybutyrate. Saponification of the ester in diethylene glycol[16] gave an alcohol, positively identified as ethanol, and an odoriferous liquid acid. The ethyl γ-chloro-β-ethoxybutyrate was redistilled, with good recovery, for analysis: b. p. 95–98° (17 mm.), n^{20}_{D} 1.4527, d^{20}_{4} 1.105.

Anal. Calcd. for $C_8H_{15}O_3Cl$: C, 49.36; H, 7.77; Cl, 18.22. Found: C, 48.85; H, 7.53; Cl, 18.32.

Reaction of α-Chlorobenzyl Methyl Ether with Ketene. Preparation of β-Methoxy-β-phenylpropionyl Chloride.—α-Chlorobenzyl methyl ether was treated with ten equivalents of gaseous ketene. During the passage of ketene the liquid warmed up to 35–40° and then cooled to room temperature. The volume of the mixture increased gradually throughout the run. The product was distilled under reduced pressure. The crude β-methoxy-β-phenylpropionyl chloride, distilling from 91–105° at 3 mm., was used in subsequent reactions and amounted to a 70% yield. The major part of the acid chloride distilled at 100–101° at 3 mm.

β-Methoxy-β-phenylpropionic Acid.—The acid chloride was hydrolyzed by exposing it to moist air or by shaking it with 5% sodium hydroxide solution. The crude acid melted at 97–99°[17] and gave a neutral equivalent of 181 (calcd., 180). The solid acid could be distilled without decomposition; boiling point 140–142° at 2 mm., melting point unchanged. For analysis, a sample was recrystallized once from toluene and once from methanol. The capillary melting point of the analytical sample was 99–100°, with "sintering" at 97°. On a microscope hot stage this "sintering" could be seen to be due to the beginning of sublimation of the solid to a melt at 97°. The micro melting point was 101.5–102.5° (cor.).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.71; neut. equiv., 180. Found: C, 66.64; H, 6.64; neut. equiv., 180.

Esters of β-Methoxy-β-phenylpropionic Acid.—The esters were prepared by treating β-methoxy-β-phenylpropionyl chloride with an equivalent amount of the appropriate anhydrous alcohol. The acid chloride–alcohol mixture was heated gently under reflux until evolution of hydrogen chloride had ceased. The resulting crude esters were purified by distillation. The properties of the various esters are tabulated.

Reaction of Triphenylchloromethane with Ketene. Preparation of β,β,β-Triphenylpropionyl Chloride.—Triphenylchloromethane did not react in benzene solution, in the absence of a catalyst, with three equivalents of gaseous ketene at 50–60°. However, the addition of anhydrous aluminum chloride brought about reaction at room temperature. Treatment of an equimolecular mixture of triphenylchloromethane and aluminum chloride in benzene solution with 1.2 equivalents of gaseous ketene, followed by hydrolysis of the product with 3 *N* hydrochloric acid, gave a 35% yield of β,β,β-triphenylpropionic acid.

Triphenylchloromethane dissolved in nitrobenzene reacted with gaseous ketene at room temperature in the absence of a catalyst. A solution of triphenylchloromethane in an equal weight of nitrobenzene was treated with 1.2 equivalents of gaseous ketene and the material distilling below 80° at 2 mm. removed. The solid residue, presumably a mixture of β,β,β-triphenylpropionyl chloride and unreacted triphenylchloromethane, was not distilled since it seemed to decompose below the boiling point at 2 mm. pressure.

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(10) (a) Straus and Heinze, *Ann.*, **493**, 191 (1932); (b) Straus and Hüssy, *Ber.*, **42**, 2168 (1909).

(11) Mohler and Hartnagel, *Helv. Chim. Acta*, **25**, 859 (1942).

(12) All melting points and boiling points are uncorrected unless otherwise specified.

(13) Williams and Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(14) Bolstad and Dunbar, *Ind. Eng. Chem., Anal. Ed.*, **15**, 498 (1943).

(15) "Organic Syntheses," **23**, 100 (1943).

(16) Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 69.

(17) Schrauth, *et al.*, ref. 7, reported the m. p. as 98°.

TABLE I

ESTERS OF β-METHOXY-β-PHENYLPROPIONIC ACID

Ester	Yield, %	B. p., °C.	n^{20}_D	d^{20}_4	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
Ethyl[a]	75	100–106 (1.5)	1.4975	1.050	69.21	68.97	7.75	8.05
2-Ethylhexyl	65	156–159 (2.5)	1.4868	0.981	73.93	73.73	9.65	9.99
n-Tetradecyl	52	185–190 (2.5)	1.4780	.939	76.55	76.64	10.71	10.30
n-Heptadecyl	60	200–212 (2.0)	1.4818	.941	77.46	77.79	11.08	11.36

[a] Saponification of the ethyl ester in diethylene glycol[16] gave ethanol and cinnamic acid. Apparently methanol is eliminated during the strenuous hydrolysis.

β,β,β-Triphenylpropionic Acid.—The crude acid chloride was hydrolyzed with 10% sodium hydroxide solution. The aqueous solution was washed with ether and acidified. The over-all yield, from triphenylchloromethane, of crude, yellow β,β,β-triphenylpropionic acid was 55%. For analysis, the crude acid was dissolved in hot absolute ethanol, treated with Darco, and then recrystallized twice from absolute ethanol. The recovery was 43%. This material had a capillary melting point of 177–178° with preliminary "sintering." On a microscope hot stage the acid began subliming slightly to a melt at 165° and was subliming rapidly at 179.5°. It melted at 180–181.5° (cor.).[18]

Anal. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00; neut. equiv., 302. Found: C, 83.55; H, 6.41; neut. equiv., 299.

Ethyl β,β,β-Triphenylpropionate.—Crude β,β,β-triphenylpropionyl chloride was dissolved in twice its weight of absolute ethanol and the solution was refluxed for twenty hours. Water was added and the ester was extracted into ether. Distillation of the residue from the ether, at 203–208° at 3 mm., gave a 67% yield of the ethyl ester. The product soon crystallized in the receiver; m. p. 65–77°. Recrystallized once from 95% ethanol, it had a capillary melting point of 79–80°. For analysis, a sample was recrystallized again from 95% ethanol. The recovery from the two recrystallizations was 72%. The analytical sample melted on a microscope hot stage at 81–82°[19] (cor.). The crystals of ethyl β,β,β-triphenylpropionate were optically anisotropic and showed parallel extinction in all views observed.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.71. Found: C, 83.86; H, 6.85.

Butyl β,β,β-Triphenylpropionate.—β,β,β-Triphenylpropionyl chloride was dissolved in an equal weight of *n*-butanol and the solution was refluxed two hours. The product was distilled: b. p. 160–165° at 0.15 mm. A sample was redistilled for analysis: n^{20}_D 1.5875; d^{20}_4 1.097.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.76; H, 7.31. Found: C, 84.31; H, 7.48.

Summary

1. α,β-Dichloroethyl ethyl ether, α-chlorobenzyl methyl ether, and triphenylchloromethane react with ketene to give the corresponding substituted acetyl chlorides. No catalyst is required to effect the reaction with α-chlorobenzyl methyl ether or with triphenylchloromethane in nitrobenzene. The reaction with α,β-dichloroethyl ethyl ether and with triphenylchloromethane in benzene takes place only in the presence of a catalyst such as aluminum chloride.

2. Benzyl chloride, benzyl bromide, benzotrichloride, benzoyl chloride, chloroacetone, and 2-chloro-2-nitropropane failed to react with ketene under the conditions used.

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[18] Henderson, ref. 8, and Fosse, ref. 9, reported the m. p. as 177° and 178–179°, respectively.

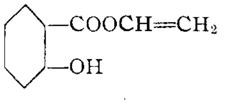
[19] Henderson, ref. 8, reported the m. p. as 81°.

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT OF THE MONSANTO CHEMICAL COMPANY]

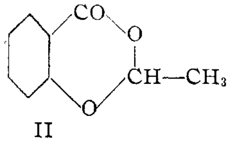
2-Methyl-4-keto-1,3-benzodioxanes from Salicylic Acids and Vinyl Acetate

BY DAVID T. MOWRY, WILLIAM H. YANKO AND EUGENE L. RINGWALD

The preparation of vinyl salicylate (I) was attempted by the mercuric acetate catalyzed ester-interchange method of Hermann and Haehnel[1] using salicylic acid and vinyl acetate as the reagents. The product, obtained in 53% yield, boiled in the expected range, but solidified after long standing and melted at 33° after recrystallization from alcohol. This behavior seemed anomalous since vinyl esters ordinarily melt lower than the corresponding methyl esters and methyl salicylate is reported to melt at −8°.



I



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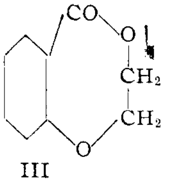

III

Further investigation showed that the compound did not rapidly decolorize bromine water, give a color with ferric chloride solution, or generate methane when dropped into an ether solution of methylmagnesium iodide. An examination of the infrared spectrum revealed the absence of the

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[1] Hermann and Haehnel, U. S. Patent, 2,245,131 (1941), *C. A.*, **35**, 5908 (1941).