[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Preparation and Properties of Ketene Diethylacetal

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In 1933 unsuccessful attempts to duplicate Scheibler's preparation of ketene diethylacetal[1] from the product of the reaction between sodium or sodium ethoxide and ethyl acetate were reported[2] from this Laboratory. Scheibler then published[3] a modification of his original procedures and claimed in certain cases to have obtained yields of ketene acetal as high as 34% of the theoretical from the reaction product resulting from the action of a mixture of sodium and sodium ethoxide on ethyl acetate. The present authors have had no better success with this later procedure than was had with the earlier ones. The material which invariably was isolated at the point where ketene acetal should appear consisted of a mixture of ethyl alcohol and ethyl acetate.

It seemed desirable, therefore, to undertake the preparation of ketene acetal by other reactions and to compare the properties of the product so obtained with those reported for this acetal by Scheibler. This paper reports the results obtained from a study of one of the most obvious routes to the structure of ketene acetal (IV), *viz.*, the elimination of the elements of halogen acid from a halogenated acetal (I) by means of alcoholic alkali. In the case of the chloro-acetal the action of an alcoholic solution of potassium hydroxide resulted in a replacement reaction with the formation of the acetal of glycolic aldehyde (II) in 95% yields. This same product was obtained when the bromo-acetal was substituted for the chloro-acetal, but the yield in this case amounted to only 70% of the theoretical even though the halogen had been completely removed as potassium bromide. Evidence of small amounts of ethyl acetate was found in the alcoholic distillate from this reaction. When the iodo-acetal was reacted with alcoholic potassium hydroxide only 30% of the theoretical amount of the hydroxy-acetal was obtained. The remainder of the reaction product consisted of a mixture of ethyl acetate and ethyl orthoacetate (V). The presence of esters of acetic acid in these reaction mixtures suggested that while only a small amount of the elimination reaction had taken place with the bromo-acetal it was the main reaction in the case of the iodoacetal and that the ketene acetal (IV) which resulted from this elimination reaction had added water and ethyl alcohol to form ethyl acetate and ethyl orthoacetate. This supposition was strengthened when it was found that sodium ethoxide in absolute alcohol with the iodo-acetal gave only a 31% yield of the ethoxy-acetal (III) but a 67.5% yield of a mixture of ethyl acetate and ethyl orthoacetate (V).

$XCH_2CH(OC_2H_5)_2$ I	$HOCH_2CH(OC_2H_5)_2$ II
$C_2H_5OCH_2CH(OC_2H_5)_2$ III	$CH_2{=}C(OC_2H_5)_2$ IV
$CH_3C(OC_2H_5)_3$ V	$CH_3CH(OC_2H_5)_2$ VI

It appeared possible, therefore, to stop at the intermediate ketene acetal stage if the elimination of hydrogen iodide from the iodo-acetal could be brought about in a less reactive medium than ethyl alcohol. Tertiary butyl alcohol was found to be quite satisfactory for this purpose. While sodium in tertiary butyl alcohol could be used, it was necessary to carry out the reaction at 125° for several hours in sealed tubes with this reagent. With potassium in tertiary butyl alcohol, however, the reaction was completed in one to two hours at the boiling point of the tertiary butyl alcohol. After removal of the precipitated potassium iodide the ketene acetal was separated from the tertiary butyl alcohol by fractionation. The yield of purified product amounted to 52% of the theoretical.

Ketene diethylacetal prepared in this manner is a colorless liquid which boils at 124–126°[4] at at-

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[1] Scheibler *et al.*, *Ber.*, **55**, 801 (1922); *Ann.*, **458**, 15, 28 (1927).

[2] Snell and McElvain, THIS JOURNAL, **55**, 416 (1933); *cf.* also Scheibler, *ibid.*, **55**, 425 (1933); Snell and McElvain, *ibid.*, **55**, 427 (1933).

[3] Scheibler, *Ber.*, **66**, 428 (1933).

[4] One of the most cogent reasons for doubting the existence of Scheibler's ketene acetal is the boiling point (77–78°) which he reported for the compound. It has seemed to the authors that ketene acetal should boil somewhat higher (perhaps 5–10°) than the corresponding saturated compound, acetal, the boiling point of which is 101–103°. But the value of 124–126° is considerably higher than was expected. Dr. Arthur C. Cope, of Bryn Mawr College, however, has pointed out to the authors that the difference (46°) between the boiling points at atmospheric pressure of ethyl acetate and ketene acetal is comparable to the difference (40°) between the boiling points at 12 mm. of diethyl malonate and carbethoxy-ketene acetal. In this connection it is interesting to note that in a recent paper Adickes and Meister [*Ber.*, **68**, 2198 (1935)] predict that ketene acetal, when it is made, would be found to have a *lower* boiling point than that reported by Scheibler.

mospheric pressure. It *reacts rapidly at room temperature with both water and ethyl alcohol*, with the evolution of considerable heat, to form ethyl acetate and ethyl orthoacetate,[5] respectively. Over Raney nickel it was reduced rapidly at 100° and 2000 lb. pressure. In this experiment, which was kindly carried out by Professor Homer Adkins, only one-half of the theoretical amount of hydrogen was absorbed. The reason for this incomplete reduction was apparent when the bomb was opened. The ether solution of the ketene acetal had set to a jell and the catalyst had been rendered inactive by being covered with the polymerized acetal. However, it was possible to isolate from this jell about 35% of the theoretical amount of acetal (VI) which was hydrolyzed and the resulting acetaldehyde isolated as the 2,4-dinitrophenylhydrazone, m. p. 162–163°.

The polymerization of ketene acetal is rapidly accelerated by heat. After each distillation of this acetal, whether under atmospheric or reduced pressure, the interior of the distilling flask is coated with a thin white deposit which is presumably a polymerized form of ketene acetal. When it was first prepared from the iodoacetal and potassium in tertiary butyl alcohol, the reaction mixture was heated several hours longer than was later found to be necessary to complete the reaction. Upon removal of the alcohol from this run by distillation a semi-solid gum remained as the residue. When this gum was heated carefully under diminished pressure, it readily depolymerized into ketene acetal which distilled over. Even at room temperature clear samples of distilled ketene acetal after a few days standing in glass gradually develop a cloudiness from which small particles of a semi-solid gum coalesce and slowly settle out.

Experimental

Halogen-acetals.—Chloro-acetal was prepared by the procedure of Mazzara and Paternò.[6] Bromo-acetal was prepared by the method of Hartung and Adkins.[7] Although iodo-acetal has been reported in the literature[8] as having been prepared by the iodination of acetal, it was prepared in the present work by the following procedure. To 30 g. of bromo-acetal in a Pyrex bomb tube was added a solution of 23 g. of sodium iodide in 110 cc. of dry acetone. The tube was sealed and heated in a bomb furnace for eighteen hours at 110°. Four such tubes were then opened and their contents added to 300 cc. of a saturated solution of sodium chloride. After thorough shaking the upper oily layer was withdrawn and the lower aqueous layer washed twice with 250-cc. portions of ether. These ether extracts were combined with the iodo-acetal layer and the resulting solution washed with 150 cc. of a 10% solution of sodium thiosulfate. This washing was followed by another using 150 cc. of a 10% solution of sodium carbonate. The ether layer was then dried over drierite and distilled. The yield of iodo-acetal boiling at 69–70° (8 mm.) amounted to 115 g. (77%).

Anal. Calcd. for $C_6H_{13}O_2I$: I, 52.2. Found: I, 52.0.

Reaction of the Halogen-acetals with Alcoholic Alkalies

(a) **Chloro-acetal.**—To 38 g. of chloro-acetal was added a 10% excess of potassium hydroxide in the form of a saturated solution in absolute alcohol. This mixture was heated in a sealed tube at 150° for seventy-five hours. The tube was then opened and the sodium chloride filtered off. The amount of salt obtained indicated that the reaction had gone to the extent of 70%. The alcoholic filtrate was then distilled. A yield of 22 g. (95% based on the chloro-acetal not recovered) of glycolic aldehyde acetal (II),[9] b. p. 165–167°, was obtained.

(b) **Bromo-acetal.**—To 29.6 g. of the bromo-acetal was added a 2% excess of potassium hydroxide in a saturated alcoholic solution. This mixture was heated in a sealed tube at 130° for twenty-four hours. After this time 95% of the theoretical amount of potassium bromide was filtered off. Distillation of the alcoholic solution yielded 14.8 g. (70%) of the hydroxy acetal (II). A saponification value of an aliquot of the alcoholic distillate indicated that 3.2 g. (24%) of ethyl acetate had been formed.

(c) **Iodo-acetal.**—In case of this compound 36.5 g. was heated in a sealed tube with a 2% excess of potassium hydroxide in a saturated alcoholic solution at 100° for fifteen hours. From the alcoholic solution 93% of the theoretical amount of potassium iodide was filtered off. Distillation of the alcoholic filtrate gave 10 g. (42%) of ethyl orthoacetate and 6 g. (30%) of the hydroxy acetal. Saponification of an aliquot of the alcohol indicated that 3 g. (23%) of ethyl acetate had distilled over with the alcohol.

When this experiment was repeated using 20 g. of iodo-acetal with a solution of 1.9 g. of sodium in 30 cc. of absolute alcohol instead of the alcoholic potassium hydroxide solution, 6 g. (46%) of ethyl orthoacetate, 4 g. (30%) of the ethoxy-acetal[10] (III), b. p. 65–66° (14 mm.), and 1.5 g. (21%) of ethyl acetate were obtained.

Preparation of Ketene Diethylacetal.—To 250 g. of tertiary butyl alcohol, m. p. 23–25°, was added in small pieces 16.1 g. (0.41 atom) of potassium. When the metal had dissolved (after four hours at the boiling point of the alcohol) 104 g. (0.426 mole) of the iodoacetal was added from a dropping funnel over a period of twenty minutes. The alcohol was refluxed with stirring for two hours. After this time the reaction mixture was centrifuged and the supernatant liquid decanted from the salt. The salt was washed twice with anhydrous ether and after each

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[5] It should be noted that in all of Scheibler's procedures ketene acetal is in contact with both water and alcohol for long periods of time in the process of its purification.

[6] Mazzara and Paternò, *Gazz. chim. ital.*, **3**, 254 (1873).

[7] Hartung and Adkins, THIS JOURNAL, **49**, 2520 (1927).

[8] Hesse, *Ber.*, **30**, 1442 (1897).

[9] Pinner, *ibid.*, **5**, 150 (1872).

[10] Späth, *Monatsh.*, **36**, 4 (1915).

washing, centrifuged, and the ether decanted. The amount of potassium iodide obtained was practically the theoretical. After removal of the ether from these washings by distillation the residue was added to the alcoholic solution and the latter fractionated carefully through a 35-cm. Widmer column under 200 mm. pressure. The alcohol distilled over at this pressure at 51–52° and, after a few drops of an intermediate fraction, 11.7 g. of ketene acetal (b. p. 85–87° 200 mm.) distilled. There remained 8.3 g. of a higher boiling fraction which on fractionation yielded 5 g. of a compound boiling at 55–57° (8 mm.) and 2.7 g. of unchanged iodo-acetal. The nature of the compound boiling at 55–57° (8 mm.) has not been determined as yet. The tertiary butyl alcohol fraction was refractionated at 200 (mm.) and an additional 9 g. of ketene acetal was obtained. The residue after this fractionation amounted to less than 1 g. A second refractionation of the tertiary butyl alcohol fraction yielded 4 g. more of ketene acetal. The total yield of this product was, therefore, 24.7 g. (52%). After the third fractionation the teritary butyl alcohol still gave a slight test for unsaturation with potassium permanganate solution.

The ketene acetal upon redistillation at atmospheric pressure boiled at 124–126°. The material obtained by distillation at atmospheric pressure was a clear water-white liquid which on standing slowly became turbid. However, samples of ketene acetal which were distilled at lower pressures (200 mm.) remained clear for a much longer period. Other physical properties of ketene acetal are: d^{25}_4 0.87760; n^{25}_D 1.4101; M_D calcd.: 32.69. Found: 32.77. Mol. wt. (freezing point of benzene), calcd., 116. Found: mol. wt. 117.6.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.02; H, 10.41. Found: C, 62.05: H, 10.44.

Some Reactions of Ketene Diethylacetal.—To 2 g. of ketene acetal was added 0.5 g. of water. The mixture became quite warm immediately and the odor of ethyl acetate appeared. After drying the resulting reaction mixture with drierite the product boiled at 75–82°. When this experiment was repeated using absolute alcohol instead of water a decided evolution of heat was noticed and resulting product was ethyl orthoacetate, b. p. 140–145°. The yield of ester in each of these cases was practically quantitative.

A solution of 5.8 g. of ketene acetal in 5 cc. of absolute ether was reduced over Raney nickel at 2000 lb. pressure of hydrogen in the quantitative reduction bomb previously described by Adkins.[11] At 100° about one-half the theoretical quantity of hydrogen was absorbed rapidly and then the reduction stopped. Upon opening the bomb after cooling, the contents had set to quite a stiff jell. This jell was stirred with two 10-cc. portions of absolute ether and filtered. The nickel catalyst which was filtered off was no longer black but was covered with a white substance, presumably polymerized ketene acetal. On fractionation of the ethereal filtrate 2 g. of acetal (VI), b. p. 97–102°, was obtained. This acetal, although insoluble in water, was rapidly hydrolyzed by water containing a trace of hydrochloric acid and the resulting acetaldehyde was isolated as the 2,4-dinitrophenylhydrazone, m. p. 162–163°.

Ketene acetal seems to polymerize to some extent whenever it is heated. The interior of flasks from which it has been distilled are coated invariably with a thin white deposit. In one of the earlier runs with the iodo-acetal and potassium in tertiary butyl alcohol the reaction mixture was heated for twelve hours at the boiling point of the alcohol. When this run was worked up a semi-solid gum remained after the alcohol had been distilled off. This gum, when heated under diminished pressure, yielded ketene acetal as the distillate. An experiment in which ketene acetal alone was heated showed that the acetal refluxed vigorously in an oil-bath kept at 130°. However, after a few minutes this refluxing stopped and raising the temperature of the oil-bath to 155° was not sufficient to cause further refluxing. The resulting material did not solidify, however, but did yield ketene acetal when it was heated under diminished pressure.

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Summary

The preparation and properties of ketene diethylacetal are described. The properties which this compound was found to possess indicate that it has not been described previously.

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[11] Adkins, THIS JOURNAL, 55, 4272 (1933).