the reaction mixture was hydrolyzed as previously described. Acidification of the alkaline solution precipitated 0.52 g. of **7-methoxy-1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid** in the form of a cream-colored solid. The adduct was not crystallized successfully, but was partially purified by solution in cold acetic acid and reprecipitation with xylene. It then formed a colorless powder which sintered and darkened at 280° and finally melted at 310°, dec. The compound is nearly insoluble in hot xylene or hot chlorobenzene, but is readily soluble in cold acetic acid. Molecular weight (by neutralization) was 300; calculated, 340.

**1-(6′-Methoxy-2′-naphthyl) - 2 - methylcyclopentene - 1 (IX).**—This compound was prepared in the usual manner by dehydrating the carbinol obtained from 6-methoxy-2-naphthylmagnesium bromide and 2-methylcyclopentanone. The crude product was distilled twice in vacuum, and the fraction boiling at 200–205° (0.9 mm.) was crystallized from ethanol. Boiling for one hour with an equivalent weight of maleic anhydride removed the colored impurities and the **1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentene-1** finally crystallized from methanol in clusters of colorless needles; m. p. 74–75°; yield 4.0 g. The compound gives an orange-red color with concentrated sulfuric acid.

*Anal.* Calcd. for $C_{17}H_{18}O$: C, 85.7; H, 7.6. Found: C, 85.6; H, 7.7.

**1-(6′-Methoxy-2′-naphthyl) - 2 - methylcyclopentene - 1 and Maleic Anhydride.**—When a mixture of 0.7 g. of the methoxy derivative and 2.94 g. (ten mols) of maleic anhydride was heated on a steam-bath for twenty hours and the alkaline solution of the hydrolyzed product was acidified with dilute hydrochloric acid, 0.9 g. (92%) of **7 - methoxy - 2 - methyl - 1,2 - cyclopentano - 2,3,4,4a - tetrahydrophenanthrene-3,4-dicarboxylic acid** was obtained in the form of a colorless, granular precipitate. The adduct is practically insoluble in hot xylene but is readily soluble in cold acetic acid. It was partially purified by solution in cold acetic acid, and reprecipitation with xylene: the colorless powder so obtained sintered and darkened at 275° and finally melted at 292°, dec.

## Summary

Maleic anhydride reacts with 1-(α-naphthyl)-cyclopentene-1, 1-(α-naphthyl)-2-methylcyclopentene-1, 1-(β-naphthyl)-cyclopentene-1, 1-(β-naphthyl)-2-methylcyclopentene-1, 1-(6′-methoxy-2′-naphthyl)-cyclopentene-1 and 1-(6′-methoxy-2′-naphthyl)-2-methylcyclopentene-1. In these reactions one of the double bonds of the diene system is part of the aromatic naphthalene ring.

Dry distillation of the calcium salt of 3,4-cyclopentano-1,2,3,10a-tetrahydrophenanthrene-1,2-dicarboxylic acid or 1,2-cyclopentano-2,3,4,4a-tetrahydrophenanthrene-3,4-dicarboxylic acid with a mixture of calcium oxide and zinc dust produces excellent yields of 3,4-cyclopentenephenanthrene or 1,2-cyclopentenophenanthrene, respectively. This reaction offers a convenient route to the synthesis of these two hydrocarbons.

ANN ARBOR, MICHIGAN RECEIVED JULY 14, 1938

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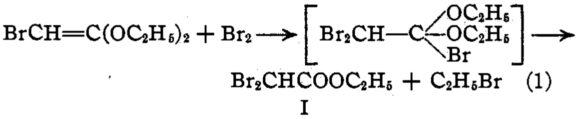
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# Ketene Acetals. III. The Bromination of Bromoketene Diethylacetal. Other Halogenated Ketene Acetals

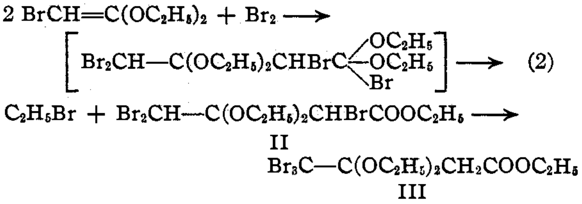
BY ARTHUR MAGNANI[1] AND S. M. MCELVAIN

A continuation of the study of various halogenated ketene acetals led to an investigation of the bromination of bromoketene diethylacetal.[2] Although the bromination did not prove to be of any value from the standpoint of preparing other ketene acetals, it seems to be of sufficient interest to report at this time.

Bromoketene diethylacetal absorbs bromine rapidly at 0–5° but the absorption stops abruptly after approximately 0.7 of an equivalent of bromine has reacted. No further absorption of bromine occurs even if the temperature of the reactants is allowed to rise to 25°. The products that were isolated from the resulting reaction mixture can be explained on the basis that slightly less than one-half of the bromoketene acetal reacts according to reaction (1) while somewhat more than one-half of the acetal follows the course shown in reaction (2)



$$BrCH{=}C(OC_2H_5)_2 + Br_2 \longrightarrow \left[ Br_2CH{-}C\begin{matrix} OC_2H_5 \\ OC_2H_5 \\ Br \end{matrix} \right] \longrightarrow \underset{\text{I}}{Br_2CHCOOC_2H_5} + C_2H_5Br \quad (1)$$



$$2\,BrCH{=}C(OC_2H_5)_2 + Br_2 \longrightarrow \left[ Br_2CH{-}C(OC_2H_5)_2CHBrC\begin{matrix} OC_2H_5 \\ OC_2H_5 \\ Br \end{matrix} \right] \longrightarrow \quad (2)$$

$$C_2H_5Br + \underset{\text{II}}{Br_2CH{-}C(OC_2H_5)_2CHBrCOOC_2H_5} \longrightarrow \underset{\text{III}}{Br_3C{-}C(OC_2H_5)_2CH_2COOC_2H_5}$$

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[1] Du Pont Post-doctorate Research Assistant, 1937–1938.

[2] Beyerstedt and McElvain, THIS JOURNAL, 59, 2266 (1937).

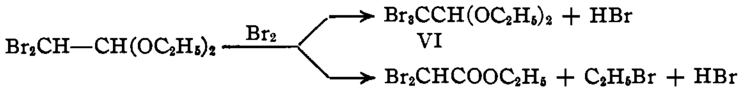
In addition to these main reaction products, small and practically equivalent amounts of ethyl tribromoacetate (IV) and the dibromoacetoacetic ester acetal (V) were found in the reaction mixture. These products appear to have been formed by the interaction of I and II, thus

$$\begin{array}{l} Br_2CHCOOC_2H_5 + Br_2CHC(OC_2H_5)_2CHBrCOOC_2H_5 \longrightarrow \\ \quad \underset{IV}{Br_3CCOOC_2H_5} + \underset{V}{Br_2CHC(OC_2H_5)_2CH_2COOC_2H_5} \quad (3) \end{array}$$

It may be seen that reaction (1) requires one equivalent of bromine per mole of the bromoketene acetal while reaction (2) requires only one-half of this quantity of bromine. These ratios of reactants explain the failure of the ketene acetal to absorb more than about 0.7 of an equivalent of bromine.

The brominated acetic esters (I and IV) were identified as amides; the brominated acetals of acetoacetic ester (III and V) were hydrolyzed to the corresponding brominated acetones which were identified.

The other halogenated ketene acetals which have been prepared in this work are monochloro-, dichloro-, and dibromoketene diethylacetal. Each of these ketene acetals was prepared by the procedure which has been used previously in this Laboratory, *viz.*, the elimination of hydrogen halide from the properly halogenated acetaldehyde acetal. Dichloroacetal was prepared by the direct chlorination of acetal. Trichloroacetal was prepared by treating $\alpha,\beta,\beta,\beta$-tetrachlorodiethyl ether ($Cl_3CCHCl\text{-}O\text{-}C_2H_5$) with alcohol; the tetrachloro ether was obtained by the action of phosphorus pentachloride on chloral alcoholate.[3] Tribromoacetal VI could not be prepared successfully by the procedure which was used for the corresponding chloro compound. It was finally prepared by the bromination of dibromoacetal. This reaction gave a very low yield (12–15%) of the desired tribromoacetal, partly because of the fact that the hydrogen attached to the carbon atom carrying the ethoxyl groups was replaced by bromine as easily as was the hydrogen on the carbon carrying the bromine atoms, thus



$$Br_2CH{-}CH(OC_2H_5)_2 \xrightarrow{Br_2} \begin{cases} \underset{VI}{Br_3CCH(OC_2H_5)_2} + HBr \\ Br_2CHCOOC_2H_5 + C_2H_5Br + HBr \end{cases}$$

The yield of ethyl bromide (90%), however, was very much greater than that of ethyl dibromoacetate (17%). This discrepancy in yields, and the fact that a large amount of bromal (45%) was found among the reaction products, indicate that the main reaction that takes place is the splitting of the acetal linkages of tribromoacetal or some of the starting acetal by the hydrogen bromide to yield ethyl bromide and the free aldehyde which, in the case of dibromoacetaldehyde, is brominated further to bromal.

The halogenated acetaldehyde acetals are converted smoothly by potassium in *t*-butyl alcohol into the corresponding halogenated ketene diethylacetals. The yields range from 55 to 85% of the theoretical. These ketene acetals show the same vigorous reaction with water and alcohol that was observed with ketene diethylacetal[4] and bromoketene diethylacetal.[2]

In the second paper of this series[2] it was pointed out that these ketene acetals are ethers of the enolic forms of esters and their boiling points, in general, are considerably higher than those of the corresponding esters.[5] The table below lists the analyses and properties of the halogenated ketene acetals and compares their boiling points with those of the corresponding esters. The monobromoketene diethylacetal is included for comparison.

## Experimental

**Bromination of Bromoketene Diethylacetal.**—In a 1-liter 3-necked flask, fitted with a stirrer, a dropping funnel and a reflux condenser carrying a drying tube, was placed 176 g. (0.90 mole) of bromoketene diethylacetal.[2] The flask was cooled in an ice–salt bath until the contents reached a temperature of 0–5° and then a solution of 145 g. (0.90 mole) of bromine in 150 cc. of carbon tetrachloride was added to the stirred solution at such a rate that the temperature did not rise above 5°. After about one and a half hours, when 0.61 mole of bromine (68% of the theoretical) had been added, the bromine was no longer decolorized.

The contents of the reaction flask were allowed to come to room temperature and the ethyl bromide and carbon tetrachloride were distilled from the slightly yellow solution at atmospheric pressure. The remaining products were then fractionated through a Widmer column (26 cm. spiral) under reduced pressure. The following compounds, in the amounts indicated, were obtained: 64.3 g. (0.59 mole) ethyl bromide, b. p. 37–38°; 81.9 g. (0.33 mole) of ethyl dibromoacetate, b. p. 66–70°

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[3] (a) Paternò and Pisati, *Gazz. chim. ital.*, **2**, 334 (1872); (b) Pergami, *ibid.*, **26**, II, 468 (1896).

[4] Beyerstedt and McElvain, THIS JOURNAL, **58**, 529 (1936).

[5] Due to an oversight a ketene acetal which has been described in the recent literature was omitted from the table of known ketene acetals that appeared in this paper. This ketene acetal is dicarbomethoxylketene dimethylacetal, $C(COOCH_3)_2{=}C(OCH_3)_2$, which was described by Martius and Arndt [*Ann.*, **499**, 268–270 (1932)] as boiling at 142–145° (13 mm.). The corresponding ester, tricarbomethoxymethane ($HC(COOCH_3)_3$), boils at 130° (16 mm.).

PROPERTIES AND ANALYSES OF HALOGENATED KETENE ACETALS AND THE BOILING POINTS OF THE CORRESPONDING ESTERS

| Compound | Analyses Calcd. Cl(or Br) | Analyses Calcd. $OC_2H_5$ | Analyses Found Cl(or Br) | Analyses Found OEt | $d^{25}_{25}$ | $n^{25}D$ | B. p., °C. 732–740 (mm.) | °C. Difference |
|---|---|---|---|---|---|---|---|---|
| $ClCH{=}C(OC_2H_5)_2$ | 23.59 | 59.80 | 23.42 | 59.51 | 1.0534 | 1.4375 | 166 | 21 |
| $ClCH_2COOC_2H_5$ | ... | ... | ... | ... | ... | ... | 145 | |
| $Cl_2C{=}C(OC_2H_5)_2$ | 38.38 | 48.65 | 38.05 | 48.46 | 1.1672 | 1.4350 | 177 | 23 |
| $Cl_2CHCOOC_2H_5$ | ... | ... | ... | ... | ... | ... | 154 | |
| $BrCH{=}C(OC_2H_5)_2$ | ... | ... | ... | ... | ... | ... | 180–182 | 24 |
| $BrCH_2COOC_2H_5$ | ... | ... | ... | ... | ... | ... | 158 | |
| $Br_2C{=}C(OC_2H_5)_2$ | 58.39 | 32.84 | 58.34 | 32.18 | 1.5790 | 1.4895 | 206–208 | 20 |
| $Br_2CHCOOC_2H_5$ | ... | ... | ... | ... | ... | ... | 188 | |

(7 mm.); 11.9 g. (0.038 mole) of ethyl tribromoacetate, b. p. 65–69° (2 mm.); 17.4 g. (0.048 mole) of ethyl β,β-diethoxy-γ,γ-dibromobutyrate (V), b. p. 114–117° (3 mm.); and 77.2 g. (0.175 mole) of ethyl β,β-diethoxy-γ,γ,γ-tribromobutyrate (III), b. p. 135–139° (3 mm.).

The ethyl bromide was identified by its boiling point and by its conversion to propionanilide, m. p. 105–106°, through the formation of ethylmagnesium bromide and the reaction of this compound with phenyl isocyanate. Both ethyl dibromoacetate and ethyl tribromoacetate were converted to the corresponding amides, m. p. 154–155°[6] and 119–120°,[7] respectively. These amides were compared with authentic specimens obtained from known esters and found to be identical. The tribromo ester was identified further by hydrolysis with dilute sodium hydroxide into bromoform which was characterized by conversion into carbon tetrabromide, m. p. 91°.[8]

**Ethyl β,β-diethoxy-γ,γ-dibromobutyrate**, as obtained from the reaction, contained 45.50% of bromine (calcd. 44.20) and showed a molecular weight of 356 (calcd. 362) in benzene. Hydrolysis in 40% sulfuric acid for three hours yielded a dibromoacetone, b. p. 90–93° (12 mm.), which contained 75.44% (calcd. 76.23) of bromine. Reduction of this dibromoacetone with zinc and hydrochloric acid yielded acetone, identified as the dibenzilidene derivative, m. p. 110–111°. Both bromine atoms were assumed to be on the same carbon atom of the dibromoacetone and its precursor on account of the report[9] that the symmetrical dibromoacetone is a solid and also because of their analogy to ethyl β,β-diethoxy-γ,γ,γ-tribromobutyrate.

**Ethyl β,β-diethoxy-γ,γ,γ-tribromobutyrate.**—This product showed a bromine content of 57.10% (calcd. 54.42) and a molecular weight in benzene of 482 (calcd. 441). On hydrolysis with 40% sulfuric acid, 13.7 g. of this ester yielded 3.75 g. of tribromoacetone,[10] b. p. 105–108° (8 mm.), which contained 81.07% (calcd. 81.36) of bromine. This tribromoacetone was reduced to acetone as described above and was converted by alkaline hydrolysis into bromoform.

**Dichloroacetal.**—Into a 3-liter 4-necked flask fitted with a condenser carrying a calcium chloride tube, a thermometer, an efficient stirrer and a 7-mm. inlet tube for chlorine, was placed 745 g. of anhydrous acetal. Chlorine was passed into the acetal at such a rate that a temperature of 34–36° was maintained by the heat of the reaction for about two hours. The acetal was stirred vigorously throughout the entire run. An exit tube from the condenser led to a 1-liter flask in which the characteristic green chlorine color could be seen against a white background.

At the end of two hours the rate of chlorine addition was increased until the temperature of the acetal reached 70° where it was held by the heat of the reaction for about six hours. After this time the temperature began to drop, whereupon heat was supplied from a steam-bath to maintain a temperature of 70° in the flask while chlorine was added slowly over an additional four-hour period. After this chlorination period the acetal was cooled to room temperature. The volume amounted to approximately 1000 cc. It was washed once with water, three times with 300 cc. of a 10% solution of sodium bicarbonate, once with 250 cc. of a 10% solution of sodium thiosulfate, and twice with water. The volume of the reaction product at this point amounted to approximately 800 cc. After drying over anhydrous potassium carbonate the product was fractionated through a 38-cm. Widmer column.

From this fractionation 314 g., b. p. 35–66° (12 mm.), and 440 g., b. p. 66–71° (12 mm.), were obtained. This latter fraction is practically pure dichloroacetal. The yield amounts to 37% of the theoretical. This acetal boils at 178–181° at atmospheric pressure. On standing dichloroacetal appears to decompose to a slight extent to yield hydrogen chloride. Chlorine analyses are generally high on freshly distilled material unless the latter portion of the distillate is taken. Three fractions collected at 69–70, 70–70.5 and 70.5–71° (12 mm.) showed chlorine contents of 46.75, 40.88 and 38.98%, respectively (calcd. 37.94). Each of these fractions, however, gave practically the same yields of chloroketene acetal (see below).

Several attempts to prepare dichloroacetal by the procedure of Fritsch[11] were made. This method involves simply the chlorination of ethyl alcohol. In none of these attempts was an appreciable amount of the dichloroacetal obtained.

**Trichloroacetal (Chloral Diethylacetal).**—This compound was prepared by the procedure of Paternò and Pisati,[3(a)] from chloral, by first preparing the alcoholate, converting this compound into α,β,β,β-tetrachlorodiethyl ether by the action of phosphorus pentachloride, and finally treating the tetrachloro compound with absolute alcohol. The yield of the alcoholate from the chloral is quantitative, of the tetrachlorodiethyl ether from the alcoholate 25–33% of the theoretical, and of the chloral acetal from the tetrachloro ether about 70%. The acetal so obtained boils at 84–85° (10 mm.).

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(6) Steinkopf, *Ber.*, **38**, 2695 (1905).

(7) Broche, *J. prakt. Chem.*, [2] **50**, 100 (1894).

(8) Fuson, Farlow and Stehman, THIS JOURNAL, **53**, 4102 (1931).

(9) Volker, *Ann.*, **192**, 96 (1878).

(10) Étard, *Compt. rend.*, **114**, 754 (1892).

(11) Fritsch, *Ann.*, **279**, 300 (1894).

**Tribromoacetal (Bromal Diethylacetal).**—In a 1-liter 3-necked flask carrying a reflux condenser, a stirrer and a dropping funnel was placed 552 g. (2 moles) of dibromoacetal.[2] The flask was heated on a steam-bath while 320 g. (2 moles) of bromine was added over a period of two hours. After approximately one-half of the bromine had been added, the evolution of hydrogen bromide started and ethyl bromide began to reflux in the condenser. A carbon dioxide snow trap was used to catch any ethyl bromide that was carried from the reaction by the hydrogen bromide. After all of the bromine had been added the reaction mixture was fractionated. The following compounds, in the amounts indicated, were obtained from this fractionation: 1.8 mole of ethyl bromide, b. p. 36–38°; 0.29 mole of dibromoacetaldehyde, b. p. 46–54° (19 mm.); 0.90 mole of bromal, b. p. 69–73° (19 mm.); 0.34 mole of ethyl dibromoacetate, b. p. 88–95° (19 mm.); 0.14 mole of recovered dibromoacetal, b. p. 105–112° (19 mm.); 0.23 mole of tribromoacetal, b. p. 132–135° (19 mm.).

The tribromoacetal upon refractionating boiled at 85–86° (1 mm.). It contained 68.18% (calcd. 67.61) bromine and 25.29% (calcd. 25.35) ethoxyl; $n^{25}_D$ 1.5158; $d^{25}_{25}$ 1.8721.

**Halogenated Ketene Acetals.**—Chloro-, dichloro- and dibromoketene diethyl acetals were prepared in yields of 85, 76 and 56%, respectively, from the corresponding halogenated acetals by means of potassium in *t*-butyl alcohol.[2] The properties of these compounds are listed in the table in the introductory portion of this paper.

The authors wish to acknowledge their indebtedness to Mr. Donald G. Kundiger for the development of the preparation of dichloroacetal.

## Summary

The bromination of bromoketene diethylacetal has been carried out and the course of the reaction elucidated. The preparation and properties of chloro-, dichloro- and dibromoketene diethyl acetals and of the intermediate halogenated acetaldehyde acetals have been described.

MADISON, WISCONSIN RECEIVED JUNE 16, 1938

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

# The Enol Content of Some β-Keto Esters

BY ARTHUR B. NESS AND S. M. MCELVAIN

Over a period of years a number of β-keto esters have accumulated in this Laboratory from studies of the acetoacetic ester condensation. It seemed worth while to determine the enol content of certain of these esters in the hope that some correlation between this property and the structure of the keto ester might be revealed.

The esters which were studied in this work are of two general types, (a) alkyl acetoacetates[1] and (b) ethyl α,γ-dialkyl acetoacetates.[2] In this latter group are two keto-esters, ethyl α-isovalerylisovalerate and ethyl α,γ-di-*t*-butylacetoacetate, that are of special interest on account of the fact that they cannot be made from the condensation by means of sodium ethoxide,[3] of the substituted acetic ester, $RCH_2COOC_2H_5$, but are readily formed from these esters by the action of mesitylmagnesium bromide.[2c]

The determinations of the enol content were made in 0.1 *M* hexane solution at 25° since the work of Conant and Thompson[4] indicates that this particular solvent has the least solvation effect on the true thermodynamic equilibrium between the keto and enol forms. For the β-keto esters carrying no α-substituent the indirect method[5] of titration was used, while for the α-substituted esters the direct method[5] was employed.

The results that were obtained are summarized in the following table. Data for ethyl acetoacetate, ethyl α-butylacetoacetate, and ethyl α-benzylacetoacetate (nos. 2, 8 and 9) are included for comparison with results obtained by previous workers.

It may be seen from the above table that the alkyl acetoacetates, with the exception of the ethyl ester, have practically the same enol content. The ethyl ester stands out in striking contrast to the other esters of this type by having a decidedly lower enol content.

α-Substitution, as expected, lowers considerably the enol content of the β-keto esters. Distribution of the substituent carbon atoms between the α- and γ-carbon atoms of the keto ester appears to have about the same effect as having

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(1) Fischer and McElvain, THIS JOURNAL, **56**, 1766 (1934).

(2) (a) McElvain, *ibid.*, **51**, 3124 (1929); (b) Briese and McElvain, *ibid.*, **55**, 1697 (1933); (c) Spielman and Schmidt, *ibid.*, **59**, 2009 (1937); *cf.* also Hauser and Renfrow, *ibid.*, **59**, 1823 (1937).

(3) Roberts and McElvain, *ibid.*, **59**, 2007 (1937).

(4) Conant and Thompson, *ibid.*, **54**, 4039 (1932).

(5) Meyer, *Ber.*, **45**, 2843 (1912).