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

[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).

ENOL CONTENT OF β-KETO ESTERS, $RCH_2COCHR'COOR''$, IN 0.1 *M* HEXANE SOLUTION AT 25°

No.	R	R′	R″	% enol, range of values found	Detns.
1	H	H	CH_3	55.5–56.3	11
2[a]	H	H	C_2H_5	46.4–47.4	12
3	H	H	*n*-C_3H_7	53.8–55.3	11
4	H	H	*i*-C_3H_7	53.7–54.5	11
5	H	H	*n*-C_4H_9	54.7–55.7	11
6	H	H	*i*-C_4H_9	57.4–59.4	12
7	H	H	*s*-C_4H_9	55.7–56.4	10
8[a]	H	*n*-C_4H_9	C_2H_5	7.1– 7.9	11
9[a]	H	$C_6H_5CH_2$	C_2H_5	7.1– 7.5	12
10	CH_3	CH_3	C_2H_5	9.9–10.2	12
11	C_2H_5	C_2H_5	C_2H_5	7.7– 8.0	11
12	*n*-C_3H_7	*n*-C_3H_7	C_2H_5	5.8– 6.2	10
13[b]	*i*-C_3H_7	*i*-C_3H_7	C_2H_5	2.3– 2.6	7
14[b]	*t*-C_4H_9	*t*-C_4H_9	C_2H_5	1.8– 2.1	11
15	*n*-C_5H_{11}	*n*-C_5H_{11}	C_2H_5	4.1– 4.8	12
16[c]	*n*-C_7H_{15}	*n*-C_7H_{15}	C_2H_5	4.8– 4.9	3
17	*n*-$C_{12}H_{25}$	*n*-$C_{12}H_{25}$	C_2H_5	2.8– 3.0	5

[a] Values for the keto esters nos. 2, 8 and 9 as reported by Conant and Thompson[4] are 48.0–50.0, 9.0–11.0 and 11.0–13.0%, respectively; in alcoholic solution these workers reported 9.0–11.0, 5.7–6.4 and 5.0–5.5% enol content, respectively, for the same esters. [b] In alcoholic solution these esters show no enol content. [c] The sample of this keto ester that was used was not pure in that it contained small amounts of the corresponding ketone.[2]

all of them (as a normal chain) on the α-carbon (*cf.* nos. 8 and 11). An increase in size of the normal α- and γ-alkyl substituents causes a progressive lowering of the enol content of the substituted β-keto ester (nos. 10–12, 15–17). The work of Conant and Thompson shows that an increase in the size of a single normal α-alkyl substituent does not produce the same progressive lowering of the enol content of the β-keto ester.[6] Branching of the carbon chain that substitutes the α- and γ-carbons of the keto ester causes a further lowering of the enol content (*cf.* nos. 13 and 14 with 12 and 15). Conant and Thompson found that a similar effect was produced by branched substituents.[7]

It should be noted that ethyl isovalerylisovalerate (no. 13) contains almost as much of the enol form as does ethyl myristyl-myristate (no. 17). The latter ester may be prepared with sodium ethoxide as the condensing agent but the former ester (as well as no. 14) cannot be so prepared.[3] It must be concluded, therefore, that the failure of these esters that contain branched substituents, to be formed from condensations using sodium ethoxide cannot be attributed to their inability to enolize. It should be pointed out also that these keto esters with branched substituents seem to enolize very slowly as compared to those having *n*-alkyl substituents. In the direct titration of the latter type of keto esters the bromine coloration disappears in less than one minute after the end-point has been reached. With the branched chain substituted keto esters (13 and 14), however, the bromine coloration persisted for several (three to five) minutes before it was finally discharged. That this slow loss of the bromine color was due to a slow rate of enolization rather than to bromine substitution seems likely for the reason that neither of these keto-esters (13 and 14) showed any measurable absorption of bromine when absolute alcohol instead of hexane was used as a solvent. This observation is in line with that of previous investigators[4] who found that β-keto esters in general are enolized to a considerably less extent in alcohol than they are in hexane (*cf.* footnote *a* of the above table).

The present work has demonstrated that ferric chloride cannot be depended upon as an indicator when the enol content of a β-keto ester is low. At some point between an enol content of 7–8 and 4–5% it fails. Ethyl α-butyrylbutyrate (no. 11) gives a satisfactory ferric chloride test in aqueous suspension or alcoholic solution. The keto esters, nos. 12 to 16, inclusive, in the above table, give no coloration with ferric chloride under these conditions, nor do they show any coloration at the interface when their solutions in hexane, which have stood for several days, are treated with an aqueous or aqueous-alcoholic solution of ferric chloride.

Experimental

The β-keto esters that were used in this work were freshly distilled from samples that had been prepared[2] previously in this Laboratory. Two hundred and fifty cc. of a 0.1 *M* solution of each of these esters in hexane was made and allowed to stand for at least seventy-two hours to attain equilibrium. A 20-cc. sample of this hexane solution was transferred to a 125-cc. Erlenmeyer flask and placed in a thermostat at 25° for several hours. For both the direct and indirect method of titration 50 cc. of 95% alcohol, cooled to −7 to −10°, was added to the hexane solution before titration to freeze the equilibrium.

In the direct method of titration this cold alcoholic solution was titrated immediately with an approximately 0.1 *N* solution of bromine in absolute, aldehyde-free alcohol to a faint yellow color that remained for ten seconds. Exactly the same amount of this bromine solution was run

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(6) For example, Conant and Thompson[4] reported 10.3–12.9, 14–15, 14.3–14.5 and 9–11% enol for α-methyl-, α-ethyl-, α-*n*-propyl- and α-*n*-butylacetoacetic ester, respectively, in 0.1 *M* hexane solution.

(7) The α-isopropylacetoacetic ester and α-*s*-butylacetoacetic ester showed enol contents of 5.85–6.1 and 8.6–9.9%, respectively, in 0.1 *M* hexane (*cf.* values for the *n*-propyl and *n*-butyl compounds in footnote 6).

into a flask containing 50 cc. of water and 10 cc. of a 10% aqueous solution of potassium iodide. The liberated iodine then was titrated with 0.1 *N* sodium thiosulfate.

For the indirect method of titration an excess of the 0.1 *N* bromine solution in alcohol, which had been cooled to −7 to −10°, was added to the cold alcohol–hexane solution of the keto ester. The excess bromine was decolorized immediately by titration with a 10% solution of β-naphthol in absolute alcohol. To this point approximately fifteen seconds were required from the time the equilibrium was frozen by the cold alcohol. Then 15 cc. of a 10% solution of potassium iodide was added and the resulting solution warmed to 25–30° for five minutes, after which time the liberated iodine was titrated with 0.1 *N* sodium thiosulfate.

Summary

The enol contents of a number of alkyl acetoacetates and of some α,γ-dialkyl substituted ethyl acetoacetates are reported.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

The Precipitation of Phenylmagnesium Bromide by Pyridine and by Dioxane

BY ARTHUR C. COPE

The accuracy of the Schlenk dioxane precipitation method[1] for determining the position of Grignard equilibria ($2RMgX \rightleftharpoons R_2Mg + MgX_2$) is still open to question. The method depends upon precipitation of insoluble dioxanates of the RMgX and MgX_2 components, and this precipitation must be rapid compared to the rate of equilibration in order to avoid shifting the equilibrium in the direction of the less soluble dioxanate during precipitation. Recent work has shown that the compositions of the solution and the precipitate change if the two remain in contact,[2] presumably because of the reaction: $2RMgX \cdot$ dioxane (insoluble) $\rightleftharpoons R_2Mg$ (soluble) $+ MgX_2 \cdot$ dioxane (insoluble). If the precipitation is used as an analytical method for determining the position of the original Grignard equilibrium, the latter reaction must be minimized by rapid removal of the precipitate.

In this investigation a number of ethers, sulfides and tertiary amines were added to ether solutions of phenylmagnesium bromide in an effort to find other precipitants for the halomagnesium components, thus making it possible to compare analyses obtained with two or more precipitants. Phenylmagnesium bromide was chosen because in this Laboratory arylmagnesium halides have given consistent analyses by dioxane precipitation.

Pyridine produces a precipitate with phenylmagnesium bromide which is grossly similar to the one obtained with dioxane. The precipitate can be separated by centrifuging, and the solution analyzed for basic magnesium and halogen. Typical data are plotted in Fig. 1, which shows the percentage of basic magnesium and bromide ion left in solution after the addition of a definite number of equivalents of pyridine, together with similar data for dioxane. The behavior of the two precipitants is very different in several respects. Dioxane precipitates the halomagnesium components more completely than does pyridine. Diphenylmagnesium is not precipitated by dioxane even when the latter is in large excess and high concentration. Pyridine precipitates only

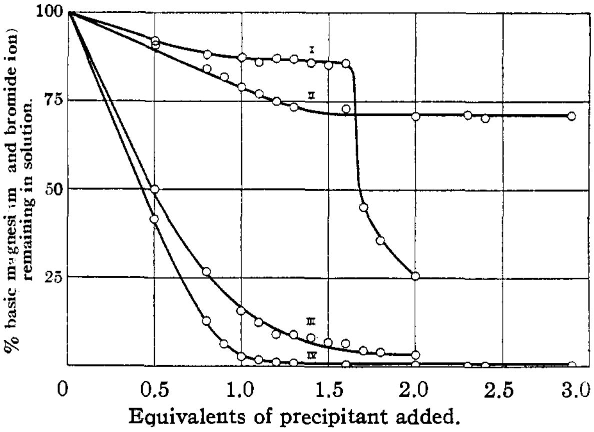

Fig. 1.—Precipitation of a phenylmagnesium bromide solution 0.2325 *N* in basic magnesium and 0.2402 *N* in bromide ion. The equivalents of precipitants are based on the normality in bromide ion. Curve I, % basic magnesium remaining in solution after precipitation with pyridine; II, % basic magnesium in solution after dioxane precipitation; III, % bromide in solution after pyridine precipitation; IV, % bromide in solution after dioxane precipitation.

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[1] Schlenk and Schlenk, *Ber.*, **62**, 920 (1929); Schlenk, *ibid.*, **64**, 734 (1931).

[2] (a) Noller and White, THIS JOURNAL, **59**, 1354 (1937); (b) Cope, *ibid.*, **57**, 2238 (1935).