Chromosorb W programmed from 80 to 295°). Yield by vpc analysis was 65%.

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.60; H, 7.95. Found C, 66.31; H, 7.94.

The remainder of the ether extract was saponified with sodium hydroxide and the product recrystallized twice with water to give the isomerized product 3,5,7-decatriene-1,10-dioic acid.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.16. Found: C, 61.36; H, 6.31.

Nmr analyses showed a doublet at τ 6.48 ($>C{=}CCH_2C({=}O)$—) with a 3:2 ratio in intensity of vinyl protons to methylene protons; ultraviolet spectrum showed $\lambda_{\max}^{H_2O}$ 260, 270, and 280 mμ (Chiusoli[19] reports 258, 267, and 276 mμ in ethanol).

7-Benzamido-2,5- (3,5-) heptadienoic Acid.—A mixture of 11 g (0.1 mole) of sodium carbonate, 45 ml of water, and 150 ml of acetone was charged to the reactor. A solution of N-(4-chloro-2-butenyl) benzamide[24] (42 g, 0.2 mole) in 340 ml of acetone and 20 ml of water was fed at a rate of 0.1 mole of amide/hr. Nickel carbonyl was fed at a rate of 0.05 as an acetone solution, acetylene at 0.133, and carbon monoxide at 0.06 mole/hr. Reaction occurred at 35° and lasted 2 hr. The reaction mixture was stripped and extracted with chloroform, and a precipitate isolated from the chloroform extract after cooling was recrystallized twice from chloroform, mp 122–123°.

Anal. Calcd for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; Acid No. 228.7; Br_2 No. 128. Found: C, 67.82; H, 6.39; Acid No. 228.3; Br_2 No. 128.5.

The infrared spectrum (Nujol mull) exhibited strong bands at 3280, 2890, 1695, 1625, 1600, 1530, 1458, 1440, 977, 970, and 818 cm^{-1}. Ultraviolet absorption spectrum in methanol exhibited a strong band 210–228 mμ. Polarographic data gave $E_{1/2} = -2.4$ (butadiene, -2.5) and $E_{1/2} = -2.0$ (methyl acrylate, -2.0). Intensity ratio indicated 90% of the 3,5 and 10% of the 2,5 isomer.

Methyl 7-butoxy-2,5-heptadienoate was prepared from the reaction of 1-butoxy-4-chloro-2-butene[25] with nickel carbonyl, acetylene, carbon monoxide, methanol, and calcium carbonate. A sample of the product was isolated from an Aerograph Autoprep A700 (Apiezon L, 190°).

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.98; H, 9.50; 0, 22.61. Found: C, 67.69; H, 9.69; O, 22.50.

Infrared spectrum (neat) exhibited strong bands at 1725, 1642, 1438, 1100–1118, 968, and 818 cm^{-1}. No ultraviolet maxima appeared above 212 mμ.

Methyl 5-hydroxy-3-pentenoate was isolated from an Aerograph Autoprep A700 (5 ft × $^3/_8$ in. column 10% Carbowax 20M terminated with terepthalic acid on 70–80 mesh, acid-washed Chromosorb W, programmed 80–235°, 200 cc of helium/min) separation of a butadiene monoxide reaction product.

Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; O, 36.88. Found: C, 55.58; H, 7.78; O, 36.47.

The infrared spectrum (neat) showed strong bands at 3400, 1730, 1430, 1085, 1005, and 971 cm^{-1}. The nmr spectrum showed a doublet at τ 5.97 ($HOCH_2CH{=}$) and a doublet at 6.97 ($>CH{=}CHCH_2COOCH_3$).

Methyl 2-vinyl-3-hydroxypropionate was isolated as above.

Anal. Calcd for $C_6H_{10}O_3$: C, 55.37; H, 7.75; O, 36.88. Found: C, 55.44; H, 7.81; O, 36.89.

The infrared spectrum (neat) showed strong bands at 3400, 1730, 1650, 1440, 1040, 990, and 925 cm^{-1}.

Methyl 7-hydroxy-3,5-heptadienoate was isolated as above.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75; O, 30.73. Found: C, 61.47; H, 7.76; O, 30.50.

The infrared spectrum (neat) showed strong bands at 3400, 1740, 1440, 1010 (shoulders), and 990 cm^{-1}. The nmr spectrum showed a doublet at τ 5.91 ($HOCH_2CH{=}CH$—) and a doublet at 6.93 ($CH{=}CHCH_2COOCH_3$). The two doublets were of equal intensity. Polarographic data gave $E_{1/2}$ (*vs.* mercury reservoir) at -2.6 and no waves at -1.7 or -2.0 v.

1(2)-Methoxy-3-buten-1(2)-ol was isolated as above.

Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87; O, 31.33. Found: C, 58.71; H, 9.83; O, 31.87.

The infrared spectrum (neat) showed strong bands at 3400, 1070, 1040, 990, and 925 cm^{-1}. Available data did not distinguish which isomer was isolated.

Registry No.—Ia, 14565-10-7; II, 14565-19-6; methyl 7-hydroxyheptanoate, 14565-11-8; 7-hydroxyheptanoic acid amide, 14565-12-9; diethyl 2,5,8-decatriene-1,10-dioate, 14565-13-0; 7-benzamido-2,5-heptadienoic acid, 14565-14-1; methyl 7-butoxy-2,5-heptadienoate, 14565-15-2; methyl 5-hydroxy-3-pentenoate, 14565-16-3; methyl 2-vinyl-3-hydroxypropionate, 14565-17-4; methyl 7-hydroxy-3,5-heptadienoate, 14565-18-5; 7-benzamido-3,5-heptadienoic acid, 14565-33-4.

Acknowledgment.—Analytical data were obtained by various members of the Rohm and Haas analytical groups. We wish to thank Mr. R. A. Thomas, Jr. and Mr. A. Ziga for assistance in performing the experimental work.

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[24] A. Fleury, *Compt. Rend.*, **241**, 808 (1955).

[25] A. A. Petrov, *J. Gen. Chem. USSR*, **19**, 1046 (1949).

The Synthesis of α-Hydroxy Esters from α-Keto Acetals

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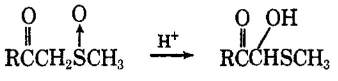
Received May 10, 1967

α-Keto acetals have been found to rearrange in the presence of water and Lewis acid catalysts, stannic chloride in particular, to give high yields of α-hydroxy esters. The mechanism of this rearrangement was shown to involve initial complexation of the keto acetal with stannic chloride followed by hydride transfer. Together with recently reported syntheses leading to α-keto acetals, this reaction comprises a convenient means of converting a carboxylic ester to an α-hydroxy ester with one more carbon in the chain. An especially attractive feature of this over-all process is that it appears to be the first of its kind which has been successfully applied to the synthesis of aliphatic hydroxy esters.

Since the discovery that β-keto sulfoxides can be conveniently prepared from carboxylic esters and methylsulfinyl carbanion,[1] considerable interest has developed in the chemistry of these compounds. Of particular bearing on the present work have been studies on the Pummerer rearrangement[2] of β-keto sulfoxides. Russell and co-workers[1b] have shown that a number of β-keto sulfoxides, primarily aromatic ones, rearrange in the presence of dilute mineral acid to give excellent yields of α-keto hemimercaptals (eq 1).



$$RC(=O)CH_2S(\rightarrow O)CH_3 \xrightarrow{H^+} RC(=O)CH(OH)SCH_3 \qquad (1)$$

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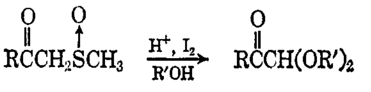
[1] (a) H.-D. Becker and G. A. Russell, *J. Org. Chem.*, **28**, 1896 (1963); (b) H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963); (c) E. J. Corey and M. Chaykovsky, *ibid.*, **86**, 1639 (1964); **87**, 1345 (1965).

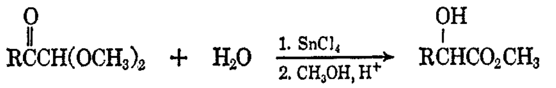
[2] R. Pummerer, *Chem. Ber.*, **42**, 2282 (1909); **43**, 1401 (1910).

Aliphatic β-keto sulfoxides, in contrast, do not react so cleanly under these conditions but give instead an equilibrium mixture of difficultly separable α-keto aldehyde derivatives. Recently, however, Moore[3] has been able successfully to rearrange aliphatic as well as aromatic β-keto sulfoxides to single products, α-keto acetals, by carrying the reaction out in the presence of iodine (eq 2).



$$\mathrm{R\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\uparrow}{S}}CH_3 \xrightarrow[\mathrm{R'OH}]{\mathrm{H^+, I_2}} R\overset{O}{\overset{\|}{C}}CH(OR')_2} \qquad (2)$$

The synthetic versatility of the aryl α-keto hemimercaptals has already been capably demonstrated by Russell and Mikol[4] who have converted these intermediates to a number of products including α-hydroxy acids. The present work, which concerns the facile rearrangement of α-keto acetals to α-hydroxy acid derivatives (eq 3),[5] suggests that α-keto acetals may have similar versatility for syntheses in the aliphatic series. This rearrangement is brought about by stannic chloride and, to a lesser extent, other Lewis acid catalysts. It is therefore notably different from the base-catalyzed process which was used to convert the α-keto hemimercaptals to α-hydroxy acids.[4]



$$\mathrm{R\overset{O}{\overset{\|}{C}}CH(OCH_3)_2 + H_2O \xrightarrow[2.\ CH_3OH,\ H^+]{1.\ SnCl_4} R\overset{OH}{\overset{|}{C}}HCO_2CH_3} \qquad (3)$$

Although examples of acid-catalyzed conversions of α-keto aldehydes to α-hydroxy acids have been reported previously,[4,6] no mention has been made of the yields obtainable from these reactions. Furthermore, it is unlikely that the conditions under which these conversions were brought about[6] would lend themselves to general or widespread usage.

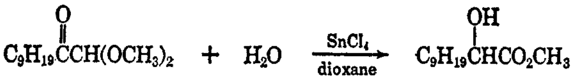
Results

Table I summarizes the results obtained from a number of rearrangements of an α-keto acetal (R = C_9H_{19}, **1**) which were run to determine optimum experimental conditions for the reaction. In general, the reaction was found to give comparable results over a fairly wide range of conditions. However, in a few instances somewhat poorer yields were obtained, and these examples serve to outline the proper experimental procedure.

Best results were obtained with equimolar amounts of the α-keto acetal and stannic chloride and a 5–10 molar excess of water. The use of less water increased tar formation, and in one case (run 1) resulted in a lower yield of product. The one run which used more than a 10 molar excess of water (run 6) also gave a reduced yield. Considerably less than an equimolar amount of catalyst could be used but this necessitated an increased reaction time (runs 9 and 10). One final requirement is that the catalyst must be added to the keto acetal prior to the addition of water. Simply reversing the order of addition of stannic chloride and water caused a more than 10% decrease in the yield of hydroxy ester (run 7). Perhaps related, is the fact that use of hydrated stannic chloride, $SnCl_4 \cdot 5H_2O$, as the catalyst–reactant gave a similarly reduced yield (run 8).

TABLE I

SYNTHESIS OF METHYL 2-HYDROXYUNDECANOATE WITH STANNIC CHLORIDE



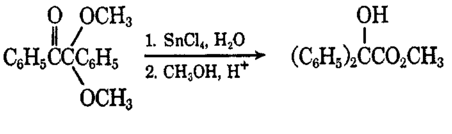
$$\mathrm{\underset{\mathbf{1}}{C_9H_{19}\overset{O}{\overset{\|}{C}}CH(OCH_3)_2} + H_2O \xrightarrow[\text{dioxane}]{SnCl_4} \underset{\mathbf{2}}{C_9H_{19}\overset{OH}{\overset{|}{C}}HCO_2CH_3}}$$

Run	Molar ratios,[a] **1**/$SnCl_4$/H_2O	Reaction time, hr	Yield of **2**, %[b]
1	1:1:1	2	64
2	1:1:2.5	2	76
3	1:1:5	2	77
4	1:1:7	2	77
5	1:1:10	2	75
6	1:1:20	2	66
7	1:1:7[c]	2	64
8	1:1:5[d]	2	62
9	1:0.1:7	2	18
10	1:0.1:7	24	75
11	1:1:7	2	83

[a] Reaction was run on 0.005 mole of **1** in runs 1–10 and on 0.13 mole in run 11. [b] Determined by gas chromatography in runs 1–10. Determined by distillation in run 11. [c] Water was added before $SnCl_4$ in this reaction. In all others water was added after $SnCl_4$. [d] Catalyst–reactant was 0.005 mole of $SnCl_4 \cdot 5H_2O$.

The potential of the rearrangement of α-keto acetals as a preparative route to α-hydroxy acid derivatives is shown best by run 11 which was carried out on a much larger scale than the other reactions listed in Table I. This experiment gave an 83% yield of distilled hydroxy ester. Based on the results of previous work,[1c,3] aliphatic α-keto acetals can be prepared from carboxylic esters *via* a β-keto sulfoxide intermediate in up to 85% over-all yield. Thus, the entire process for converting an aliphatic ester to the α-hydroxy derivative of its next higher homolog might reasonably be expected to result in 65–70% yields. This route therefore nicely complements the one described by Russell and Mikol[4] for aromatic compounds.

The reaction was extended to α-keto ketals with the rearrangement of benzil dimethyl ketal to methyl benzilate (eq 4). In this case, however, hydrolysis of the



$$\mathrm{C_6H_5\overset{O}{\overset{\|}{C}}C(OCH_3)_2C_6H_5 \xrightarrow[2.\ CH_3OH,\ H^+]{1.\ SnCl_4,\ H_2O} (C_6H_5)_2\overset{OH}{\overset{|}{C}}CO_2CH_3} \qquad (4)$$

ketal back to benzil represents a major competing reaction and the hydroxy ester was formed in about 20% yield. Attempts to rearrange β-keto acetals to the corresponding β-hydroxy esters were unsuccessful.

Other Lewis acid catalysts can function in this reaction but none of the ones investigated performed nearly as well as stannic chloride (Table II). It should be mentioned, however, that these reactions were not studied very extensively and the poor results may have been due in part to less than optimum experimental conditions.

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[3] T. L. Moore, *J. Org. Chem.*, **32**, 2786 (1967).

[4] G. A. Russell and G. J. Mikol, *J. Am. Chem. Soc.*, **88**, 5498 (1966).

[5] After the initial stage of the reaction, the product consists of a mixture of the α-hydroxy ester and the corresponding α-hydroxy acid and lactide. For synthetic purposes this mixture was then converted to a single product, the ester, and all yields reported are based on the fully esterified product.

[6] V. Prey, H. Berbalk, and E. Steinbauer, *Monatsh. Chem.*, **91**, 1196 (1960); **93**, 237 (1962).

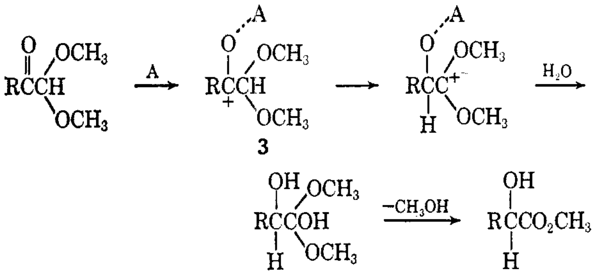
Table II
Synthesis of Methyl 2-Hydroxyundecanoate with Other Lewis Acid Catalysts

Catalyst	Molar ratio, 1/catalyst/H_2O	Yield of **2**, %[a]
$TiCl_4$	1:1:8	37
$AlCl_3$	1:1:8	33
$FeCl_3$	1:1:5	12
$BF_3\cdot(C_2H_5)_2O$	1:1:7	1–5
H_2SO_4 (conc)	*b*	1–5
H_2SO_4 (dil)	*c*	1–5

[a] Determined by gas chromatography. [b] Reactants: 0.005 mole of keto acetal and 1 ml of concentrated H_2SO_4. [c] Reactants: 0.005 mole of keto acetal and 1 ml of 20% H_2SO_4.

Mechanism

It is well established that the base-catalyzed intramolecular Cannizzaro rearrangement of α-keto aldehydes to α-hydroxy acids proceeds by a hydride transfer mechanism.[7–9] Evidence supporting a hydride transfer mechanism for the acid-catalyzed rearrangement of α-keto aldehydes has also appeared.[6] Hence, it was thought probable that a mechanism requiring hydride transfer was operative for the acid-catalyzed rearrangement of α-keto acetals described here. The mechanism proposed is shown in eq 5.

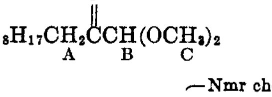


(5)

A = Lewis acid

Formation of a complex (**3**) between the metal halide (A) and the free carbonyl group of the keto acetal was verified by both nuclear magnetic resonance (nmr) and infrared spectroscopy. The pertinent nmr chemical shifts ($CDCl_3$ solution) and infrared absorptions (CCl_4 solution) of an α-keto acetal both before and immediately after the addition of 1 equiv of stannic chloride are compared in Table III. Complex formation should appear in the nmr spectrum as a downfield shift in the resonance of the methylene protons adjacent to the carbonyl group. A shift of the infrared absorption of the carbonyl group to longer wavelength should also occur. As can be seen in Table III, both of these expected changes took place upon addition of the stannic chloride.[10]

Table III
Infrared and Nmr Spectra of 1,1-Dimethoxyundecan-2-one in Absence and Presence of $SnCl_4$



$$\underset{\text{A}}{C_8H_{17}CH_2}\underset{\text{B}}{\overset{\overset{\Large O}{\|}}{C}}\underset{\text{C}}{CH}(OCH_3)_2$$

Conditions	C=O infrared absorption, μ[a]	Nmr chemical shifts, τ[b] A	B	C
$SnCl_4$ absent	5.8	7.56[c]	5.79	6.66
$SnCl_4$ present	6.0	6.94[c]	4.61	6.20

[a] CCl_4 solution. [b] $CDCl_3$ solution. [c] Triplet.

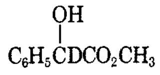
Indirect evidence consistent with this part of the mechanism comes from the fact that small amounts of a by-product (RCO_2CH_3) were found in all of the reaction mixtures. This material was not produced upon treatment of the pure α-hydroxy ester under the reaction conditions and it seems likely that it arises (as the acid) by attack of water on carbonium ion **3**.

Evidence substantiating the hydride transfer phase of the mechanism was obtained from two experiments. In the first, deuterium oxide was substituted for water in the reaction and no deuterium was found in the product (other than that arising from simple exchange with the hydroxyl proton). Since this result requires that the hydrogen atom at the α carbon of the hydroxy ester come from the keto acetal, it eliminates any type of an enolization mechanism and makes hydride transfer the most attractive alternative.

The second and most convincing proof of hydride transfer came from the reaction of a mixture of the deuterated keto acetal (**4**) and the nondeuterated keto acetal (**1**) with stannic chloride. The resulting hydroxy esters were separated by gas chromatography and it was found that the aromatic hydroxy ester (**5**) was deuterated at the α-carbon atom and that the amount of deuterium present at this position was equal to that present in the original keto acetal. The aliphatic hydroxy ester (**2**) was, correspondingly, completely free of deuterium. This result demonstrates conclusively that hydride ion is transferred from the acetal carbon to the carbonyl carbon. It also strongly suggests that the transfer is intramolecular rather than intermolecular.[11]

$$C_6H_5\overset{\overset{O}{\|}}{C}CD(OCH_3)_2$$

4



$$C_6H_5\overset{\overset{OH}{|}}{C}DCO_2CH_3$$

5

Experimental Section

General.—The β-keto sulfoxides used were gifts from Drs. D. E. O'Connor and T. L. Moore to whom the author is indebted. The catalysts used were standard reagents. Nmr spectra were obtained on a Varian HA-100 spectrometer.

Except for the variations indicated in the tables and in the text, all of the rearrangements listed in Tables I and II were carried out by the same general procedure. This procedure will be described only for the run which is considered to represent optimum conditions for the reaction (run 11, Table I). In all of the other runs, the yields of hydroxy ester were calculated from gas chromatograms obtained on a Carbowax 20 M column.

Methyl 2-Hydroxyundecanoate (Run 11, Table I).—To a solution of 30.0 g (0.13 mole) of freshly distilled 1,1-dimethoxyundecan-2-one[3] in 600 ml of dried dioxane (by distillation from molecular sieves) were added, rapidly and in succession, 34.0 g (15.2 ml, 0.13 mole) of anhydrous stannic chloride and 16.4 g (0.91 mole) of distilled water. The mixture was refluxed for 2 hr and was then poured into water and extracted with ether. After a final chloroform extraction, the combined organic extracts were dried over anhydrous magnesium sulfate and the solvents were evaporated.

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(7) H. Fredenhagen and K. F. Bonhoeffer, *Z. Physik. Chem.* (Leipzig), **A181**, 379 (1938).

(8) W. von E. Doering, T. I. Taylor, and E. F. Schoenewaldt, *J. Am. Chem. Soc.*, **70**, 455 (1948).

(9) O. K. Neville, *ibid.*, **70**, 3499 (1948).

(10) Complexation also occurs at the acetal oxygens, as indicated by the downfield shift of the $-OCH_3$ proton resonance. This, plus the fact that the usual reaction solvent, dioxane, also complexes with stannic chloride, indicates that the actual complex formed in the reaction is not so simple as depicted in eq 5.

(11) While the rates of reaction of **1** and **4** have not been determined quantitatively, our qualitative observations indicate that they are similar.

The above mixture of ester, acid, and lactide was esterified with methanol containing 1% of sulfuric acid and the crude esterification product was worked up as above. Vacuum distillation gave 23.3 g (83%) of methyl 2-hydroxyundecanoate, bp 80–82° (0.3 mm).

Anal. Calcd for $C_{12}H_{24}O_3$: C, 66.6; H, 11.2; O, 22.2. Found: C, 66.9; H, 11.4; O, 22.3.

The nmr spectrum ($CDCl_3$) is characterized by a hydroxyl doublet at τ 7.32 (1 H), a methoxyl singlet at τ 6.27 (3 H), and a methinyl multiplet at τ 5.9 (1 H). Upon deuterium exchange, the doublet disappeared and the multiplet collapsed to a triplet. The spectrum of the product obtained from this reaction was essentially identical with the spectrum of an authentic sample of methyl 2-hydroxypalmitate.

The nmr spectrum of the product obtained from the reaction in which deuterium oxide was used instead of water was unchanged from the spectrum of the normal product. The area of the multiplet at τ 5.9 remained equivalent to one proton showing that no deuterium had been incorporated at the methinyl carbon.

ω,ω-Dideuterio-ω-(methylsulfinyl)acetophenone.—A mixture of 6.0 g (0.033 mole) of ω-methylsulfinylacetophenone, 2 drops of a 25% solution of sodium deuteroxide in deuterium oxide, and 20 ml of deuterium oxide was stirred overnight at room temperature. The mixture was then extracted with chloroform and the combined extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by recrystallization from 50 ml of a 1:1 mixture of benzene–hexane gave 5.3 g of the dideuterated sulfoxide.

The nmr spectrum of the starting material (CCl_4 solution) showed resonance at τ 1.9–2.7 (aromatic), 5.78 (methylene), and 7.32 (methyl). The spectrum of the product was free of the τ 5.78 resonance.

ω-Deuterio-ω,ω-(dimethoxy)acetophenone (4)—The Pummerer rearrangement of 3.7 g (0.020 mole) of ω,ω-dideuterio-ω-(methylsulfinyl)acetophenone was carried out as described previously[3] with 2.7 g (0.011 mole) of iodine in 30 ml of methanol-d_1. Part of the product was distilled, bp 79° (1.5 mm), and another part was purified by gas chromatography. The chromatographed material was analyzed by mass spectroscopy and was found to consist of 97% of the monodeuterated and 3% of the undeuterated α-keto acetal.

Reaction of Stannic Chloride with a Mixture of ω-Deuterio-ω,ω-(dimethoxy)acetophenone and 1,1-Dimethoxyundecan-2-one.—This reaction was performed as described above using 0.45 g (0.0025 mole) of ω-deuterio-ω,ω-(dimethoxy)acetophenone, 0.58 g (0.0025 mole) of 1,1-dimethoxyundecan-2-one, 1.3 g (0.59 ml, 0.005 mole) of anhydrous stannic chloride, and 0.63 g (0.035 mole) of water in 20 ml of dry dioxane. After esterification, the aliphatic and aromatic hydroxy esters were separated by gas chromatography and each was analyzed by nmr.

The nmr spectrum of the aliphatic hydroxy ester showed a multiplet at τ 5.9 (HCO), the area of which was equivalent to one (full) proton. The level of methinyl proton in the aromatic hydroxy ester was determined by comparing the area of the HCO peak in the nmr spectrum with the area of the C^{13} satellite of the CH_3O peak. This analysis was made with the aid of a Varian C-1024 time-averaging computer and showed that less than 2% of undeuterated aromatic hydroxy ester was present.[12]

Rearrangement of Benzil Dimethyl Ketal.—Benzil dimethyl ketal[13] (2.0 g, 0.0078 mole), 6.0 g (2.6 ml, 0.023 mole) of stannic chloride, and 0.99 g (0.055 mole) of water reacted in 20 ml of dry dioxane according to the general procedure described for the rearrangement of α-keto acetals. The esterification product (1.7 g) was found by infrared spectroscopy and gas and thin layer chromatography to consist of both benzil and methyl benzilate. Quantitative thin layer chromatography, using appropriate standard mixtures, indicated that the sample contained 20–25% of methyl benzilate. This represents an 18–22% yield of the ester.

Registry No.—2, 14919-24-5; 5, 14919-25-6; 1,1-dimethoxyundecan-2-one, 13133-49-8; ω,ω-dideuterio-ω-(methylsulfinyl)acetophenone, 7714-34-3.

Acknowledgments.—The author is grateful for the encouragement and helpful discussions which were provided by Dr. W. I. Lyness and Dr. D. E. O'Connor during the course of this work. He also wishes to express his appreciation to Mr. M. C. Coleman, Jr., for excellent technical assistance.

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[12] The author wishes to thank Dr. J. J. McLeskey, III, for this analysis.

[13] R. Kuhn and H. Trischmann, *Chem. Ber.*, **94**, 2258 (1961).

Conformational Studies in the Ethyl 3-*t*-Butylcyclobutanecarboxylate System[1]

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Received February 20, 1967

The syntheses of ethyl *cis*- and *trans*-3-*t*-butylcyclobutanecarboxylates and the corresponding carboxylic acids are reported. The conformational studies made on these compounds are basic equilibration and rates of saponification of the esters and ionization constants of the acids. The results are explained on the basis of both planar and nonplanar conformers.

The cyclobutane ring has been shown to be nonplanar in a large number of cases such as cyclobutane,[2-5] octafluorocyclobutane,[6] octachlorocyclobutane,[7] *gem*-difluorocyclobutanes,[8] bromocyclobutane,[9] chlorocyclobutane,[10] methyl 3-methylcyclobutanecarboxylate,[11] 3-isopropylcyclobutyl alcohols and amines,[12] methyl 3-isopropylcyclobutanecarboxylate,[13] 2,2,4,4-tetramethylcyclobutane-1,3-dinitrile,[14] 1,3-dibromocyclobutane,[15] and *cis*-1,3-cyclobutanedicarboxylic acid.[16b] The nonplanar conformations lead to axial and equatorial positions similar to those of cyclohexane as indicated in Chart I.[17] However, whereas the

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[17] The Dreiding model of cyclobutane has been used. The bond angles are as follows: C–C–C, 88°; H–C–H, 113°; dihedral angle, 26°; bond lengths for C–C bonds in ring, 1.54 A. These values closely approximate the values obtained for bromocyclobutane, ref 9a.