[CONTRIBUTION FROM THE DIVISION OF DAIRY RESEARCH LABORATORIES, BUREAU OF DAIRY INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

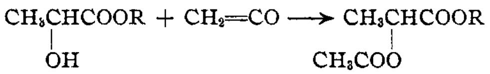
The Acetylation of Lactic Esters by Ketene

BY H. V. CLABORN AND LEE T. SMITH

The acetylation of lactic esters was accomplished first by Wislicenus[1] who acetylated ethyl lactate by means of acetyl chloride. He did not, however, report the yield obtained. More recently Burns and his co-workers[2] have used acetic anhydride for the acetylation of methyl, ethyl, butyl, and benzyl lactates. They reported yields of 81, 91, 92, and 70%, respectively. The authors have duplicated these results and in the case of methyl lactate have increased the yield to 92% of the theoretical. The improvement was due to: (1) the fact that the sulfuric acid used to catalyze the reaction was neutralized with calcium carbonate before the fractional distillation and (2) the use of a 24-inch (61-cm.) Widmer fractionating column, which proved very efficient in removing the acetic acid. This method also has been used with good results for acetylating other lactic esters.

Ketene has been used for the acetylation of alcohols,[3] primary amines,[3] amino acids,[4] ethyl mercaptan,[5] carbohydrates,[6] and phenols.[7] Hurd and Williams[5] have found that α-hydroxy acids such as benzilic and mandelic react with two moles of ketene to form acetylbenzilic acetic anhydride and acetylmandelic acetic anhydride, respectively. In order to obtain the corresponding acetoxy acids, it is necessary to decompose these anhydrides. However, the use of ketene for the acetylation of the esters of α-hydroxy acids has not been recorded.

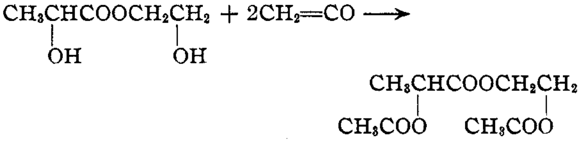
The authors have found that when a trace, one drop per mole, of sulfuric acid[8] is present to catalyze the reaction, ketene reacts very smoothly with the lactic esters, and the yield of the corresponding α-acetoxypropionate obtained is practically the theoretical.



$$CH_3\underset{\displaystyle OH}{C}HCOOR + CH_2{=}CO \longrightarrow CH_3\underset{\displaystyle CH_3COO}{C}HCOOR$$

Since the lactic esters and the acetylated esters are both liquids, no solvent is necessary. This also makes possible the use of higher temperatures and, consequently, faster rates of reaction. The ketene may be introduced directly into the ester containing the sulfuric acid catalyst. Since the ketene reacts so readily with these esters, it is necessary to use only a slight excess to complete the reaction. This method is simplified further by the fact that the ketene produced by the pyrolysis of acetone may be used without purification. The reaction product requires only an ordinary type distillation for purification and not a fractional distillation as is required to remove the acetic acid when acetic anhydride is used.

In addition to the preparation of methyl, ethyl, butyl, and benzyl α-acetoxypropionates the physical properties of which already have been recorded,[2] *n*-propyl, isopropyl, isobutyl, *n*-amyl, and isoamyl α-acetoxypropionates were prepared both with ketene and with acetic anhydride. Glycol monolactate reacts with two moles of ketene and glycol monolactate diacetate is formed.



$$CH_3\underset{\displaystyle OH}{C}HCOOCH_2\underset{\displaystyle OH}{C}H_2 + 2CH_2{=}CO \longrightarrow CH_3\underset{\displaystyle CH_3COO}{C}HCOOCH_2\underset{\displaystyle CH_3COO}{C}H_2$$

Some of the physical properties of these new compounds are recorded.

Experimental

The ketene used was prepared by the pyrolysis of acetone by the method of Hurd and Williams[5] modified by Williams.[9] The ketene was used directly as it was produced without purification. A typical example is given.

Methyl α-Acetoxypropionate.—Six moles (624 g.) of methyl lactate containing two drops of sulfuric acid was treated with ketene at the rate of 0.28 mole per hour for twenty-two hours (6.16 moles). The exothermic reaction caused the reaction flask to become quite warm after a few minutes, and it was immersed in an ice water-bath until the reaction was complete. No color change took place in the reaction flask until the end of the experiment. Then a yellow color developed which changed to a dark brown on standing overnight. This color change is an indication that the reaction is complete, for apparently it

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(1) J. Wislicenus, *Ann.*, **125**, 58 (1863).

(2) Robert Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400 (1935).

(3) N. T. M. Wilsmore, *ibid.*, **91**, 1939 (1907).

(4) Max Bergmann and F. Stern, *Ber.*, **63B**, 437 (1930).

(5) C. D. Hurd and J. W. Williams, THIS JOURNAL, **58**, 962 (1936).

(6) C. D. Hurd, S. M. Cantor and A. S. Roe, *ibid.*, **61**, 426 (1939).

(7) F. O. Rice, J. Greenberg, C. E. Waters and R. E. Volrath, *ibid.*, **56**, 1760 (1934).

(8) Since this work was completed the work by Hurd[6] has appeared in which sulfuric acid is used to catalyze the reaction of ketene with carbohydrates.

(9) Unpublished work by Dr. J. W. Williams of the University of Maryland.

TABLE I

THE PERCENTAGE YIELD, B. P., SP. GR., AND REF. INDEX OF LACTIC ESTERS

α-Acetoxypropionate esters	B. p. °C.	B. p. Mm.	B. p. 763–5 mm.	Yield, % with Ketene	Yield, % with Acetic anhydride	d^{25}_{25}	$n^{25}D$	Empirical formula	Acetyl, % Calcd.	Acetyl, % Found
Methyl	68–73	14		96.4	92					
Ethyl	73–76	11		98.0	91					
n-Butyl	94–97	8		98.0	92					
Isobutyl	90–92	9	205	94.0	87	0.9952	1.4140	$C_9H_{16}O_4$	22.86	22.86
n-Propyl	77–79	7	196	97.0	87	1.0163	1.4123	$C_8H_{14}O_4$	24.70	24.48
Isopropyl	74–78	9	183	96.5	86	0.9920	1.4069	$C_8H_{14}O_4$	24.70	24.53
n-Amyl	101–103	8	227	97.0	87	0.9822	1.4199	$C_{10}H_{18}O_4$	21.27	21.13
Isoamyl	107–110	12	222	96.0	90	0.9838	1.4190	$C_{10}H_{18}O_4$	21.27	21.14
Benzyl	145–148	7	. . .	96.0	70					
β-Acetoxyethyl*	141–145	10	265	86.0	. .	1.1489	1.4297	$C_9H_{14}O_6$	39.45	39.23

* Glycol monolactate diacetate.

is the result of polymerization of the excess ketene. If the reaction mixture is not allowed to stand for a few hours before distillation, this yellow color may later develop in the final distilled product. The reaction product distilled at 68–73° at 14 mm.; yield, 844 g. or 96.4%.

Methyl, isobutyl, *n*-propyl, isopropyl, *n*-amyl and isoamyl lactate were acetylated with acetic anhydride by the method of Burns.[2] Calcium carbonate was added to neutralize only the sulfuric acid used for catalyst, and the reaction product was fractionated in vacuum with a 24-inch (61-cm.) Widmer fractionating column.

Benzyl lactate was prepared from benzyl chloride and sodium lactate.[10]

Acknowledgment.—The authors are grateful to Dr. J. W. Williams for his helpful suggestions and kind permission to copy the ketene lamp designed by him and now in use in his laboratory at the University of Maryland.

Summary

The methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, isoamyl and benzyl lactates and glycol monolactate were acetylated with ketene in the presence of a trace of sulfuric acid as catalyst. The yields were greater than those obtained when acetic anhydride was used, being practically quantitative. Six new compounds were prepared: namely, *n*-propyl, isopropyl, isobutyl, *n*-amyl, and isoamyl α-acetoxypropionates and glycol monolactate diacetate. Some of the physical properties of these compounds are given.

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(10) M. Gomberg and C. C. Buchler, THIS JOURNAL, **42**, 2064 (1920).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF UNIVERSAL OIL PRODUCTS COMPANY]

Synthesis of *t*-Butyl- and *t*-Amylcyclopentane and of their Intermediate Products[1]

BY HERMAN PINES AND V. N. IPATIEFF

The preparation of *t*-alkylcyclopentanes has not been reported hitherto in the literature. Although the reaction of cyclopentanone with alkylmagnesium halide has been used successfully by others and also in our laboratory[2] for the preparation of several of the alkylcyclopentanes, the use of *t*-butylmagnesium halide did not yield the expected *t*-butylcyclopentanol, which would be an intermediate in the preparation of *t*-butylcyclopentane. Similarly, *t*-butylmagnesium bromide on reacting with cyclopentyl bromide gave only small yields of *t*-butylcyclopentane.

The method described in this paper for the preparation of *t*-alkylcyclopentane consists in cyclicizing alkyladipic acid to alkylcyclopentanone, a method which had been employed for the preparation of methylcyclopentanone. The starting products for the preparation of *t*-butyl- and *t*-amylcyclopentane were, respectively, *p*-*t*-butyl- and *p*-*t*-amylphenol, compounds which are now commercially available. The phenols were converted by catalytic hydrogenation to the corresponding *t*-alkylcyclohexanol; the latter on oxidation with nitric acid solution yielded β-*t*-butyl- and β-*t*-amyladipic acid. The β-*t*-alkyladipic

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(1) Presented before the Division of Organic Chemistry at the American Chemical Society Meeting, Baltimore, Md., April 3–6, 1939.

(2) Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927); Pines and Ipatieff, THIS JOURNAL, **61**, 1076 (1939).