again with saturated brine, dried over calcium chloride, and distilled through an efficient column.

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Summary

1. The alkylation of benzene and toluene with secondary, tertiary and allyl type halides has been accomplished with boron trifluoride catalysts.

2. The presence of water, alcohol or other polar compound reactive to boron trifluoride is necessary for reaction at atmospheric pressure.

3. Lower layers which separate from these reactions have been resaturated with boron trifluoride and reused without loss of catalytic activity.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Preparation of Allyl and Methallyl Methacrylates by the Thermal Decomposition of Allyl and Methallyl α-Acetoxyisobutyrates

BY CHESSIE E. REHBERG, C. H. FISHER AND LEE T. SMITH

Considerable information concerning the thermal decomposition of α-hydroxypropionic acid and its derivatives has been collected in connection with an investigation of the pyrogenic conversion of lactic acid derivatives[1,2,3] into acrylic esters. It has been shown[4] that pyrolysis of methyl and benzyl α-acetoxypropionates (I, R = H or C_6H_5) gives high yields of methyl and benzyl acrylates, respectively. On pyrolysis ethyl and butyl α-acetoxypropionates (II, R = H or C_2H_5), which have hydrogen atoms on the beta-carbon atom of the alcohol group, yield olefins as well as acrylic esters. As a result of this undesirable side reaction (shown in equation II), the satisfactory preparation of acrylic esters by thermal decomposition of alkyl α-acetoxypropionates seems limited to derivatives, such as the methyl and benzyl esters (I), which lack hydrogen atoms on the beta-carbon atom.[5,6]

$$\begin{aligned}
&\text{(I)}\quad CH_3COOCH(CH_3)COOCH_2R \longrightarrow \\
&\quad (R = H \text{ or } C_6H_5) \\
&\qquad\qquad\qquad CH_2{=}CHCOOCH_2R + CH_3COOH \\
&\text{(II)}\quad CH_3COOCH(CH_3)COO\underset{\alpha}{CH_2}\underset{\beta}{CH_2}R \longrightarrow \\
&\quad (R = H \text{ or } C_2H_5) \\
&\qquad CH_2{=}CHR + CH_3COOCH(CH_3)COOH \longrightarrow \\
&\qquad\qquad\qquad CH_3COOH + CH_3CHO + CO
\end{aligned}$$

In a recent report[2] it was disclosed that allyl and methallyl α-acetoxypropionates, which have one hydrogen atom or none on the beta carbon atom of the alcohol group, on pyrolysis decompose into allyl and methallyl acrylates, respectively. In spite of the absence or paucity of beta hydrogen atoms, however, the desired acrylic esters were obtained only in 40% yields. The purpose of the present work was to compare the behavior of allyl and methallyl α-acetoxyisobutyrates (III) on pyrolysis with that of the corresponding α-acetoxypropionic acid derivatives and to develop satisfactory pyrogenic methods of producing allyl and methallyl methacrylates.

$$\begin{aligned}
&\text{(III)}\quad CH_3COOC(CH_3)_2COOCH_2CR{=}CH_2 \longrightarrow \\
&\quad (R = H \text{ or } CH_3) \\
&\qquad\qquad CH_3COOH + CH_2{=}C(CH_3)COOCH_2CR{=}CH_2
\end{aligned}$$

It might be predicted from previous investigations[4,7,8] that derivatives of α-hydroxyisobutyric acid, which may be regarded as a tertiary alcohol, would decompose into methacrylic esters more readily than lactic acid derivatives would decompose into acrylic esters. Comparable data reported by Burns, Jones and Ritchie[4,7] on the thermal decomposition of derivatives of lactic and α-hydroxyisobutyric acids are given in Table I. These data indicate that derivatives of α-hydroxyisobutyric acid are more suitable than lactic acid derivatives for pyrogenic conversion into unsaturated products. Milder conditions sufficed for the pyrolysis, and in most instances better yields were obtained. Burns, Jones and

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[1] Smith, Fisher, Ratchford and Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

[2] Fisher, Rehberg and Smith, THIS JOURNAL, **65**, 763 (1943).

[3] Smith, Fisher, Filachione, Ratchford and Fein, "Pyrolysis of Lactic Acid Derivatives. Methyl Lactate, Acetoxypropionic Acid, Acetoxypropionyl Chloride, and Alkyl Acetoxypropionates," presented before the Division of Organic Chemistry at the 103rd meeting of the American Chemical Society, Memphis, Tenn., April 20–24, 1942.

[4] Burns, Jones and Ritchie, *J. Chem. Soc.*, 400 (1935).

[5] Bilger and Hibbert, THIS JOURNAL, **58**, 823–825 (1936).

[6] Hurd and Blunck, *ibid.*, **60**, 2419–2425 (1938).

[7] Burns, Jones and Ritchie, *J. Chem. Soc.*, 714 (1935).

[8] Ritchie, *ibid.*, 1054 (1935).

Ritchie[7] also pyrolyzed β-methoxyethyl and β-phenoxyethyl α-acetoxyisobutyrates, which have hydrogen atoms on the beta-carbon atom of the alcohol groups, and obtained the corresponding esters of methacrylic acid in moderate yields.

TABLE I

PYROLYSIS OF CORRESPONDING DERIVATIVES OF LACTIC AND α-HYDROXYISOBUTYRIC ACIDS

Ref.	Compound	Average temp., °C.	Rate, cc./min.	Unsaturated product	
				Conversion per pass, %	Yield, % of theoretical
4	Methyl acetoxypropionate	478	5.0	63.4	80
7	Methyl acetoxyisobutyrate	490	5.5	92	97
4	Acetoxypropionitrile	545	4.5	34	93.8
7	Acetoxyisobutyronitrile	430	7.0	87.2	96.3
8	Carbomethoxyethyl carbonate	425	4	27.5	51.3
8	Carbomethoxyisopropyl carbonate	450	6	84.3	84.3
8	Cyanoethyl carbonate	470	4	56.6	75.5
8	Cyanoisopropyl carbonate	440	3.5	53.8	53.8

The procedures used in the preparation of allyl and methallyl α-acetoxyisobutyrates parallel very closely those used[2] with the corresponding α-acetoxypropionates. Allyl and methallyl α-hydroxyisobutyrates were prepared by reaction of the appropriate alcohol with α-hydroxyisobutyric acid in the presence of a small quantity of p-toluenesulfonic acid. When three times the theoretical amount of alcohol was used, the initial conversion of acid to ester was about 45%. By treating the distillation residue again with alcohol, this yield was increased to 60–65%. Although strong acid catalysts frequently convert methallyl alcohol into isobutyraldehyde,[9] this difficulty was not encountered in the present work.

Allyl and methallyl α-hydroxyisobutyrates were acetylated with acetic anhydride in excellent yields.

The acetoxyisobutyrates were pyrolyzed with the equipment and general procedure described previously.[1] Satisfactory conversions were obtained at temperatures somewhat lower than those found suitable for the pyrolysis of the corresponding acetoxypropionates,[2] high conversions being obtained at 475–500°, whereas about 550° was the best temperature with the acetoxypropionates. At 475–500° conversions per pass for the acetoxyisobutyrates were 65–75%, and the yields of methacrylic esters were 70–75% of the theoretical.

Although frequent mention is made in the literature of the use of allyl and methallyl methacrylates, few data on their preparation and physical properties have been published. Bloodworth[10] reported that high yields of methallyl methacrylate were obtained by the condensation of methacrolein in the presence of an alkyl aluminate, but gave no data on the physical properties of the product. Some data were given by Barrett and Strain,[11] who prepared the methallyl and other unsaturated alcohol esters of methacrylic acid by ester interchange. From methyl methacrylate and methallyl alcohol they obtained a 60% yield of methallyl methacrylate, sodium methylate being used as catalyst. Table II gives a comparison of the physical properties with those reported in this paper.

Approximately equal yields of allyl and methallyl esters (70 to 75% methacrylates and 35 to 40% acrylates) were obtained in the present investigation and that reported in an earlier paper.[2] Hence the allyl and methallyl groups appear to be about equally stable to thermal treatment. Comparison of available data[1,2,4,7] on the pyrogenic behavior of various acetoxypropionates and acetoxyisobutyrates indicates that allyl and methallyl groups are more stable than butyl and β-phenoxyethyl groups but less stable than methyl, ethyl and benzyl groups. Thermal stability of the allyl and methallyl groups seems to be approximately equal to that of the β-methoxyethyl group.

It was reported[12] recently that allyl acetate can be prepared by pyrolyzing the diacetate of 1,2-propylene glycol and that thermal decomposition of 1,3-butylene glycol diacetate yields α-methylallyl acetate and crotyl acetate. This may be considered as additional evidence that allyl and some substituted allyl groups are relatively stable. The indicated stability of α-methylallyl acetate ($CH_3COOCH(CH_3)CH{=}CH_2$) appears questionable, since this ester has four hydrogen atoms on the two beta-carbon atoms. Moreover, the work of Hill and Isaacs[13] indicates that α-methylallyl acetate is readily converted into butadiene and acetic acid by pyrolysis.

Because of their ability to form cross-linked polymers and copolymers, allyl and methallyl methacrylate and similar bifunctional polymerants

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[9] (a) Hearne, Tamale and Converse, *Ind. Eng. Chem.*, **33**, 805 (1941); (b) Groll and Hearne, U. S. Patent 2,046,556, July 7, 1936; (c) Groll and Tamale, *ibid.*, 2,010,076, Aug. 6, 1935.

[10] Bloodworth, U. S. Patent 2,250,520, July 29, 1941.

[11] Barrett and Strain, U. S. Patent 2,129,665, Sept. 13, 1938.

[12] Chitwood, U. S. Patent 2,251,983, Aug. 12, 1941.

[13] Hill and Isaacs, U. S. Patent 2,224,912, Dec. 17, 1940.

TABLE II

PHYSICAL PROPERTIES OF ALLYL AND METHALLYL ESTERS

Ester	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	Molecular refraction Calcd.	Molecular refraction Found	Saponification eq. Calcd.	Saponification eq. Found
Allyl hydroxyisobutyrate	73	20	1.4308	1.0010	37.24	37.27	144.2	144.5
Methallyl hydroxyisobutyrate	78	16	1.4334	0.9760	41.86	42.16	158.2	169.3
Allyl acetoxyisobutyrate	96	19	1.4280	1.0322	46.60	46.41	93.1	93.1
Methallyl acetoxyisobutyrate	106	19	1.4321	1.0126	51.22	51.29	100.1	102.4
Allyl methacrylate	67	50	1.4358	0.9335	35.25	35.32	...	...
Methallyl methacrylate	63	17	1.4400	.9231	39.86	40.02	...	...
Methallyl methacrylate[a]	57–9	15	....	.9214	...	...	400[b]	398[b]

[a] Data reported by Barrett and Strain (ref. 11). [b] Saponification number.

are of considerable interest and importance.[14] When used in even very low percentages, monomers with two active double bonds are capable of drastically modifying the properties of the copolymers produced principally from monomers having only one active double bond, such as methyl acrylate, vinyl acetate, and styrene.[15] In general, the effect is to harden and toughen the product and render it insoluble and infusible. Several of the experiments reported here showed that allyl and methallyl methacrylate profoundly affect the properties of methyl acrylate copolymers. Some change in hardness and solubility of the copolymer was detectable when only 0.1% of allyl or methallyl methacrylate was present.

The authors are grateful to the Analytical and Physical Chemistry Division for analytical data and to other members of the Carbohydrate Division for assistance in securing experimental data.

Experimental

Allyl α-Hydroxyisobutyrate.—One mole (104 g.) of α-hydroxyisobutyric acid, three moles (174 g.) of allyl alcohol, and 100 cc. of benzene were refluxed in a flask fitted with a fractionating column supporting a water trap and reflux condenser at its top. When water ceased distilling, the mixture was fractionated under vacuum. The crude ester, collected at 83–90° (40 mm.), amounted to 67.5 g., or 46.7% of the theoretical amount.

The recovered alcohol was returned to the flask containing the residue of unconverted hydroxyisobutyric acid, 1 to 2 g. of *p*-toluenesulfonic acid was added, and the mixture was refluxed for several hours. Fractionation then gave an additional 26.5 g. of ester, thus raising the total yield to 94 g., or 64.5% of the theoretical.

Physical properties of this and other esters prepared in the present work are listed in Table II.

Methallyl α-Hydroxyisobutyrate.—Using the procedure described above for the preparation of the allyl ester, from 2 moles of hydroxyisobutyric acid and 6 moles of methallyl alcohol 220 g. (70% of the theoretical) of ester boiling at 75–80° (17 mm.) was obtained.

Allyl α-Acetoxyisobutyrate.—The hydroxy ester was acetylated by using a slight excess of acetic anhydride. To 190 g. (1.32 moles) of allyl α-hydroxyisobutyrate containing 2 cc. of phosphoric acid, 160 g. (1.58 moles) of acetic anhydride was added slowly, with stirring. During the addition of the anhydride the temperature of the mixture was maintained at 80–100° by suitable cooling. After the reagent had been added, the temperature was maintained at 100–110° for half an hour. Five grams of anhydrous sodium acetate was then added to neutralize the phosphoric acid, and the mixture was fractionated under reduced pressure. The acetoxyisobutyrate was collected at 92–96° (19 mm.). The yield was 217 g., or 88% of the theoretical.

Methallyl α-Acetoxyisobutyrate.—Using the procedure employed with the allyl ester, 161.4 g. (1.02 moles) of methallyl α-hydroxyisobutyrate was acetylated with 116 g. (1.14 moles) of acetic anhydride. In this manner 140 g. of acetoxyisobutyrate (68% of the theoretical yield) boiling at 103–106° (19 mm.) was obtained.

Pyrolysis of Allyl α-Acetoxyisobutyrate.—Using the equipment and general procedure previously described, 70 g. of material was pyrolyzed at 475° over Pyrex glass tubing at the rate of 60 drops per minute (contact time approx. 4.7 sec.). The liquid product (67.8 g.) was fractionated into two portions: (1) 58 cc. boiling at 30–50° (23 mm.) and (2) 9.5 cc. boiling at 96–98° (18 mm.). The former was a mixture of acetic acid and allyl methacrylate, whereas the latter was allyl α-acetoxyisobutyrate. Fraction (1) was washed with water and dilute sodium carbonate solution to remove acetic acid, after which it was dried and redistilled. In this manner 30.8 g. of allyl methacrylate (75% of the theoretical yield) boiling at 65–68° (50 mm.) was obtained. Only 120 cc. of uncondensed gas was formed in the pyrolysis.

Pyrolysis of Methallyl α-Acetoxyisobutyrate.—By pyrolysis of 43.4 g. of ester at 500° at the rate of 60 drops per minute (contact time approx. 12.5 sec.), 41.4 g. of liquid product was obtained. This was fractionated into two main portions: (1) 10.5 g. of acetic acid collected at 115–120° and (2) 22.2 g. (73% of the theoretical yield) of methallyl methacrylate collected at 61–64° (17 mm.). Less than a liter of gas was formed in the pyrolysis.

Polymerization Experiments.—Various proportions of allyl and methallyl methacrylate were polymerized with

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(14) H. Mark and R. Raff, "High Polymeric Reactions, Their Theory and Practice," Interscience Publishers, Inc., New York, N. Y., 1941, 476 pp.; Pollack, Muskat and Strain, U. S. Patent 2,273,891, Feb. 24, 1942.

(15) (a) Barnes, U. S. Patent 2,278,637, Apr. 7, 1942; (b) Rutovskii and Zabrodina, *Org. Chem. Ind.* (U. S. S. R.), **7**, 441 (1940) (*C. A.*, **35**, 4121 (1941)); (c) Garvey, Alexander, Kung and Henderson, *Ind. Eng. Chem.*, **33**, 1060 (1941); (d) Patnode, U. S. Patent 2,282,882, May 12, 1942.

methyl acrylate. Both mass (without solvent) and solution (20% in ethyl acetate) polymerization techniques were employed. The effects produced by the allyl and methallyl esters were similar, although that of the allyl ester was somewhat more pronounced. When the monomer mixture contained 1% or more of the allyl or methallyl ester, the polymer was noticeably harder and tougher than polymethyl acrylate and was insoluble in acetone or ethyl acetate. Some change in hardness and solubility of the polymer was detectable when only 0.1% of the allyl or methallyl methacrylate was present.

Summary

1. Satisfactory methods were developed for preparing allyl and methallyl α-hydroxyisobutyrates from hydroxyisobutyric acid and the appropriate alcohol.

2. The hydroxy esters were converted into allyl and methallyl α-acetoxyisobutyrates by treatment with acetic anhydride.

3. Under milder conditions than those required for the thermal decomposition of the corresponding acetoxypropionates, allyl and methallyl acetoxyisobutyrates were transformed satisfactorily by pyrolysis into allyl and methallyl methacrylates.

4. These results and data previously reported indicate that (1) esters of α-acetoxyisobutyric acid yield unsaturated esters more readily when pyrolyzed than do corresponding lactic acid derivatives and (2) that esters prepared from allyl and methallyl alcohols are more stable than those prepared from *n*-butyl and β-phenoxyethyl alcohols but less stable than esters prepared from methyl, benzyl and ethyl alcohols. Allyl, methallyl and β-methoxyethyl esters appear to have approximately the same thermal stability.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE B. F. GOODRICH COMPANY AND THE HYCAR CHEMICAL COMPANY]

The Geometric Isomers of Piperylene

BY DAVID CRAIG

During a current study of dienes in this Laboratory, it has been possible to effect the separation of the piperylene isomers by a variety of chemical methods and also by fractional distillation. The isomers thus secured have been found to have the properties shown in Table I. The assignment of the *trans* configuration to the lower boiling isomer, prepared but not identified by Dolliver, Kistiakowsky and Vaughan,[1] is based on the method of preparation from piperylene sulfone and on analogy to work by other investigators on the pentene-2 isomers. The assignment of *cis* configuration to the higher boiling isomer is confirmed by its behavior toward sulfur dioxide and maleic anhydride.

TABLE I

THE PROPERTIES OF THE PIPERYLENE ISOMERS

Isomer	Boiling point °C.	Boiling point Mm.	$d^{20}{}_{20}$	$n^{20}{}_{D}$	Diene content, % By hydrogenation	Diene content, % By Diels Alder reaction
cis	43.8	750	0.6916	1.4360	100	0
trans	41.7	745	.6771	1.4300	100	99+

In addition to its preparation from the sulfone *trans*-piperylene was prepared according to Lurji, *et al.*,[2] by the decomposition of the cuprous chloride addition compound. This solid derivative was secured from a C_5 fraction of a petroleum pyrolyzate by reaction with cuprous ammonium chloride. In a similar manner the corresponding solid addition compound of the *cis* isomer was secured from a higher boiling fraction. The debromination of the 1,2,3,4-tetrabromopentane racemate (m. p. 114°) supplied a mixture containing approximately equal amounts of the isomers. In agreement with Robey, Morrell and Weiss[3] *trans*-piperylene was found to react more rapidly with maleic anhydride than *cis*, thus affording a means of isolating the latter isomer. Mixtures of the isomers were also resolved by reaction with sulfur dioxide, the *cis*-isomer again reacting more slowly. These reactions are described below in considerable detail.

The presence of cyclopentene in many piperylene preparations may have escaped the attention of earlier investigators. Cyclopentene, which is also a C_5H_8 hydrocarbon, was found to form a constant boiling mixture with *cis*-piperylene.

The Chemical Properties of the Piperylene Isomers

cis-Piperylene vapor is absorbed slowly but

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(1) Dolliver, Kistiakowsky and Vaughan, THIS JOURNAL, **59**, 833, 837 (1937).

(2) Lurji, *et al.*, *Synthetic Rubber* (U. S. S. R.), **3**, No. 6, 13 (1934); *Chem. Zentr.*, **106**, II, 1977 (1935).

(3) Robey, Morrell and Weiss, THIS JOURNAL, **63**, 627 (1941).