Polymerizable Monomers from Castor Oil. I. Vinyl Monomers Based on Undecenoic Acid

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Abstract

Thirty-four different vinyl monomers have been synthesized, based on 10-undecenoic acid, pyrolysis product of castor oil, in 50 to 100-g lots in high purity. These include allyl ethers and esters, vinyl ethers and esters, and acrylic and methacrylic esters, all of which were characterized by their infrared spectra; purity was checked by chromatographic methods. Boiling points, refractive indices, and iodine values of the products have been reported.

Introduction

POLYMERS AND COPOLYMERS based on fatty vinyl monomers have shown considerable promise in organic surface coatings and related fields. A number of review papers (1–3) on the subject are available. Extensive work has been undertaken in this laboratory to explore the possibility of using castor oil and its derivatives for making polymerizable monomers therefrom. The present paper includes the work carried out on the preparation, purification, and characterization of vinyl monomers which are based on 10-undecenoic acid, a pyrolysis product of castor oil, and several of its derivatives. Some 50 g each of the purified samples of the monomers were sent to the United States Department of Agriculture, Western Utilization Research and Development Division, Albany, Calif., for evaluation as polymerizable monomers.

Experimental Section

Materials

10-Undecenoic acid was commercially available and was used after repeated fractional distillation. Undecanoic acid was obtained by hydrogenation of methyl undecenoate over 1% Raney nickel at 100C and 150 psig, followed by hydrolysis of the ester to the corresponding acid. 2-Bromoundecanoic acid was prepared by refluxing undecanoic acid with bromine in the presence of catalytic amounts of phosphorus trichloride (4).

11-Bromoundecanoic acid was prepared by passing dry hydrogen bromide through a well-stirred solution of undecenoic acid in dry petroleum ether, maintained at 5–10C and containing catalytic amounts of benzoyl peroxide (5). Two crystallizations of the crude acid from light petroleum gave the final product, mp 50–50.5C. This 11-bromoundecanoic acid was converted to the corresponding iodo acid by refluxing with sodium iodide in acetone (6). Two crystallizations from ligroin gave the pure acid as lustrous plates, mp 66–66.5C.

Methyl ester of 11-bromoundecanoic acid, on treatment with sodium methoxide, gave methyl 11-methoxyundecanoate (7) together with an appreciable amount of methyl undecenoate. The resultant product was carefully fractionated, hydrolyzed to free acid, and twice crystallized from light petroleum at 0C to give needles of pure 11-methoxyundecanoic acid, mp 34.5–35C. The 11-allyloxy-undecanoic acid was prepared similarly, bp 192–194C/5–6 mm Hg.

Bromination of undecenoic acid at 0–5C in pretreated light petroleum gave 10,11-dibromoundecanoic acid in about 75–80% yield (8). Two crystallizations from petroleum ether gave a waxy solid, mp 38–38.5C. Chlorination of undecenoic acid in dry carbon tetrachloride at −30 ± 5C gave 10,11-dichloroundecanoic acid in fairly good yield (9), which, when crystallized from light petroleum, furnished the pure acid, mp 32.5–33C.

Friedel-Craft's addition of methyl undecenoate to benzene, followed by hydrolysis to the corresponding acid, gave phenylundecanoic acid in about 70% yield (10). GLC studies in this laboratory (11) have shown that the product consists of three isomers, viz., 8-phenylundecanoic acid, 9-phenylundecanoic acid, and 10-phenylundecanoic acid, which are present in amounts of 44, 17, and 30% respectively.

Methyl 10(11)-hydroxyundecanoate was prepared from undecenoic acid by formylation with 98–100% formic acid in the presence of catalytic amounts of 70% perchloric acid, followed by esterification of the formoxy compound with methanol in the presence of β-naphthalenesulphonic acid (12).

Undecenol, undecanol, phenylundecanol, and 11-methoxyundecanol were obtained in good yields by the sodium reduction of methyl esters of their corresponding acids (13).

Preparative Methods

Allyl Ester. Allyl esters of the fatty acids were prepared readily by direct esterification with an acid catalyst and azeotropic removal of water with benzene (14). Alternatively, refluxing 1 mole of acid with 10 moles of allyl alcohol together with 2% *p*-toluenesulphonic acid for 6–8 hr gave excellent yields of allyl esters.

Allyl Ethers. Two methods were tried for the preparation of allyl ethers of fatty alcohols, viz., condensation of sodium alloxide with the alkyl halide, and condensation of sodium alkoxide with either allyl chloride or preferably with allyl bromide. Of the two, the second method was favored since it gives excellent yields and a better quality of allyl ether. Typically 1.1 g atom of sodium and about 750 ml of xylene were placed in a two-liter, three-necked flask, equipped with a mechanical stirrer, dropping funnel, and a reflux condenser. The xylene was heated to reflux, and the molten sodium was dispersed to fine dust by vigorous stirring.

One mole of the fatty alcohol was added dropwise to the reaction flask in about 1 hr, and the stirring and refluxing were continued for an additional hour. The temperature was lowered to 45C and maintained there, and 1.5 moles of allyl bromide or allyl chloride was added to the vigorously stirred reaction mixture in about 30 min. Stirring at this temperature was continued for another hour. The suspended sodium halide was removed by filtration through a Buchner funnel, and the filtrate, after removal of the xylene, was taken up in ether and worked up suitably to isolate the allyl ether.

Vinyl Esters. Vinyl esters of acids were generally

TABLE I

Physicochemical Characteristics of Vinyl Monomers, Based on 10-Undecenoic Acid

Monomers	BP (C/mm Hg)	Refractive index (at C)	Iodine value	
			Found	Calcd.
Allyl undecenoate	120/1–2	1.4425 (30)	225.8	226.8
Allyl undecanoate	150/4–5	1.4320 (30)	111.9	112.4
Allyl phenylundecanoate	170/1–2	1.4875 (25)	83.9	84.1
Allyl 2-bromoundecanoate	150/1–2	1.4589 (33)	81.9	83.3
Allyl-11-bromoundecanoate	165/2–3	1.4683 (24)	82.9	83.3
Allyl 11-iodoundecanoate	175/2	1.4630 (34)	....	....
Allyl 10,11-dibromoundecanoate	192/2	1.4912 (34)	65.9	66.2
Allyl 11-methoxyundecanoate	152/4	1.4430 (27)	98.6	99.2
Allyl 11-allyloxyundecanoate	162/1–2	1.4881 (28)	180.0[b]	180.2
Allyl undecenyl ether	120/1–2	1.4420 (30)	240.9[b]	241.9
Allyl undeceyl ether	150/4–5	1.4318 (30)	119.0[b]	119.8
Allyl phenylundeceyl ether	180/2–3	1.4860 (25)	....	....
Vinyl undecenoate	108–110/3	1.4418 (35)	235.4	241.9
Vinyl undecenoate	108–110/2	1.4318 (35)	120.6	119.8
Vinyl phenyl undecanoate	166–168/0.3	1.4868 (31)	90.5	88.2
Vinyl 2-bromoundecanoate	122–124/0.6	1.4552 (29)	84.6	87.3
Vinyl 11-bromoundecanoate	160/1–2	1.4541 (31)	85.4	87.3
Vinyl 11-iodoundecanoate	[a]	1.4894 (28)	....	....
Vinyl 10,11-dichloroundecanoate	144–146/0.5	1.4712 (26)	88.8	89.8
Vinyl 10,11-dibromoundecanoate	[a]	1.4872 (30)	....	....
Vinyl 11-methoxyundecanoate	108–110/0.3	1.4412 (29)	102.4	104.9
Vinyl undecenyl ether	102/1–2	1.4426 (27)	[c]	....
Vinyl undecyl ether	94–96/1.5	1.4277 (35)	[c]	....
Vinyl phenylundecyl ether	156–158/0.3	1.4865 (33)	[c]	....
Vinyl 11-methoxyundecyl ether	138–140/1–2	1.4422 (26)	[c]	....
Methyl 10(11)vinyloxy undecanoate	154–156/1	1.4382 (30)	[c]	....
Undecenyl acrylate	135/1	1.4458 (30)	225.0[b]	226.9
Undecyl acrylate	138/1	1.4375 (30)	112.6[b]	113.5
Phenyl undecyl acrylate	190/1	1.4820 (28)	....	....
10,11-Dibromoundecyl acrylate	178/0.7	1.4960 (26)	....	....
Undecenyl methacrylate	145/1	1.4475 (30)	211.4[b]	213.4
Undeceyl methacrylate	148/1	1.4390 (30)	105.5[b]	106.7
Phenyl undecyl methacrylate	200/1	1.4832 (28)	....	....
10,11-Dibromoundecyl methacrylate	195/0.8	1.4976 (26)	....	....

[a] Decomposes during distillation.
[b] Iodine values were determined by using pyridine sulphate dibromide as halogenating agent (19).
[c] Percentage of vinyl ether, determined by iodometric method, ranged from 98–100.

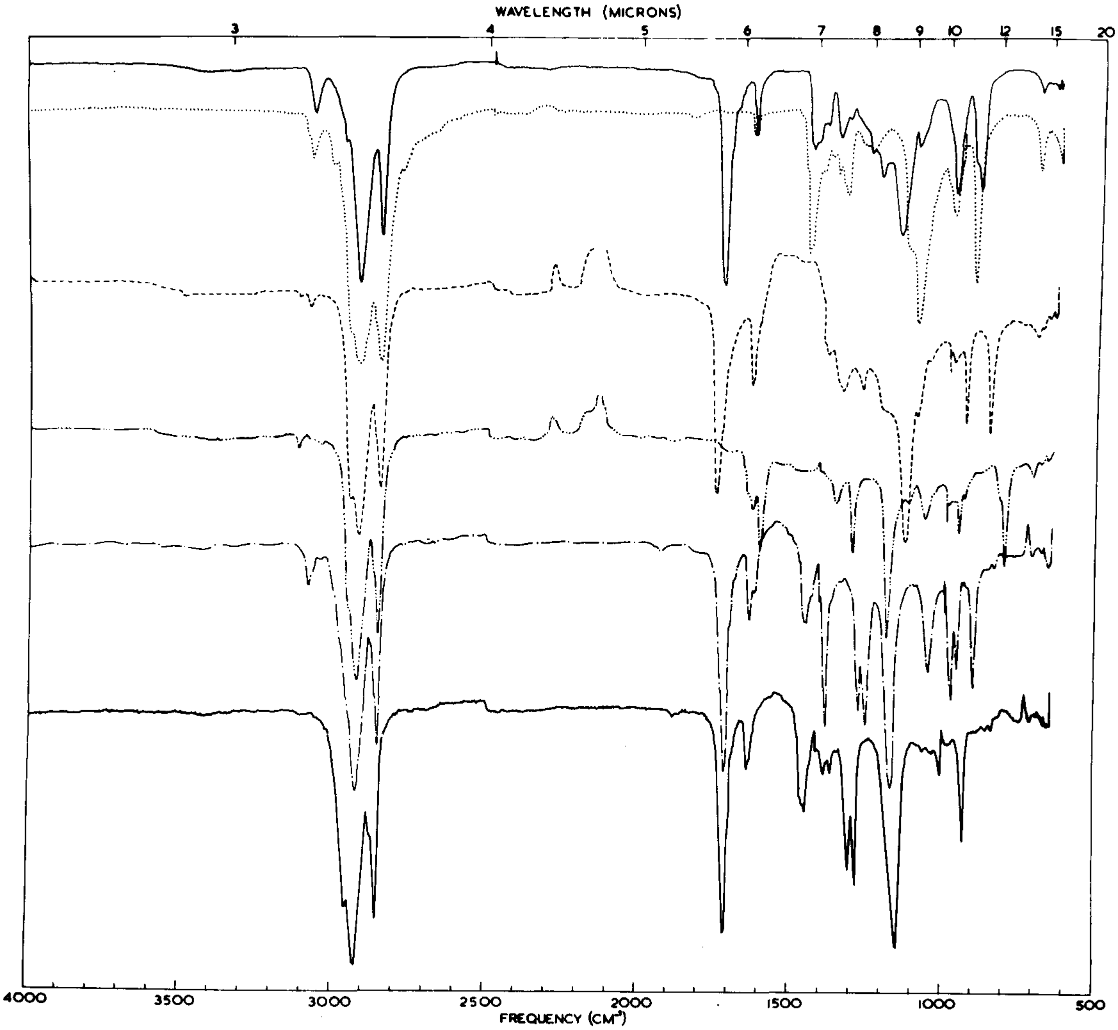

FIG. 1. Infrared spectra (from top to bottom) of allyl undecanoate, allyl undecyl ether, vinyl undecanoate, vinyl undecyl ether, undecyl acrylate, and undecyl methacrylate.

prepared by refluxing one mole of the acid with six moles of stabilized vinyl for 3 hrs in the presence of catalytic amounts of mercuric acetate and 40% hydrofluoric acid (15). However, in some cases, vinyl ester interchange at room temperature was favored to obtain better yields.

Vinyl Ethers. Vinyl ethers of fatty alcohols were readily prepared either by direct acetylenation of the alcohol at 180C in the presence of 5% potassium hydroxide (16) or by transetherification with ethyl vinyl ether in the presence of mercuric acetate (17). In the case of methyl 10(11)-hydroxyundecanoate, which contains an alkali-sensitive group, the second method was the only choice.

Acrylic and Methacrylic Esters. Acrylic and methacrylic esters of the alcohols were prepared by Rehberg's procedure (18), involving alcoholysis of methyl acrylate or methyl methacrylate in the presence of an acidic catalyst, such as β-naphthalenesulphonic acid, and a polymerization inhibitor, such as hydroquinone, quinol, etc. Methanol formed in the reaction was continuously removed from the reaction flask by azeotropic distillation with the use of excess methyl acrylate or methyl methacrylate in the reaction.

Purification and Characterization. Each of the monomers was purified by two distillations under reduced pressure, followed by passage through a column of silica gel. The products were characterized by infrared spectroscopy, and the purity was checked by chromatographic methods. Infrared spectra of six monomers, each representative of a group, is shown in Fig. 1. Some of the physicochemical characteristics of the monomers are listed in Table I.

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REFERENCES

1. Teeter, H. M., JAOCS *40,* 143 (1963).
2. Chatterjee, P. C., and J. S. Aggarwal, Paint Manuf. *33,* 466 (1963).
3. Uzzan, A., Rev. Franc. Corps Gras. *7,* 135 (1960).
4. Birnbaun, S. M., S. C. J. Fu and J. P. Greenstein, J. Biol. Chem. *203,* 334 (1953).
5. Shirley, D. A., "Preparation of Organic Intermediates," John Wiley and Sons Inc., New York, 1951. p. 62.
6. Ashton, R., and J. C. Smith, J. Chem. Soc. 1308 (1934).
7. Brown, R. E., and R. G. Mason, Ibid. 4151 (1952).
8. Myddleton, W. W., and A. W. Barrett, J. Am. Chem. Soc. *49,* 2258 (1927).
9. Lyness, W. J., and F. W. Quackenbush, JAOCS *32,* 520 (1955).
10. Thomas, C. A., "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corporation, New York, 1941, p. 477.
11. Achaya, K. T., and P. K. Saraswathy Amma, Indian J. Chem. *5,* 109 (1967).
12. Knight, H. B., R. E. Koos and D. Swern, JAOCS *31,* 1 (1954).
13. Hansley, V. L., Ind. Eng. Chem. *39,* 55 (1947).
14. Swern, D., G. N. Billen and H. B. Knight, J. Am. Chem. Soc. *69,* 2439 (1947).
15. Chatterjee, P. C., H. Dakshinamurty and J. S. Aggarwal, Indian J. Technol. *4,* 173 (1966).
16. Teeter, H. M., E. J. Dufek, C. B. Coleman, C. A. Glass, E. H. Melvin and J. C. Cowan, JAOCS *33,* 399 (1956).
17. Teeter, H. M., L. E. Gast and J. C. Cowan, Ind. Eng. Chem. *50,* 1703 (1958).
18. Rehberg, C. E., Org. Syn. *26,* 18 (1946).
19. Stanley, E. L., "Analytical Chemistry of Polymers, Part I. High Polymer Series, Vol. 12," Interscience Publishers Inc., New York, 1959, p. 1.

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