by direct distillation of a mixture of the acid and quinoline yielded only traces of the 2-nitro-5-vinylfuran. The best procedure was adapted from the preparation of formylstyrenes by Wiley and Hobson[14] and is given below.

Five grams of 5-nitrofurylacrylic acid was dissolved in 50 ml. of hot quinoline and added dropwise to 1 g. of copper powder in a 50-ml. distilling flask, heated at 305–315° in a metal-bath. The quinoline distillate was acidified with a 50% excess of concentrated hydrochloric acid and crushed ice and steam distilled. The steam distillate was extracted with diethyl ether. The ether extracts were dried over anhydrous sodium sulfate and the residue left after removal of the ether was recrystallized from petroleum ether; yield 0.46 g. of 2-nitro-5-vinylfuran (12.5%), m. p. 48–50°. On standing overnight in a vacuum desiccator at room temperature it formed an insoluble, high melting solid. The nitrovinylfuran was relatively stable when stored in an ice-box.

Anal. Calcd. for $C_6H_5O_2N$: C, 51.80; H, 3.62; N, 10.07. Found: C, 51.98; H, 3.49; N, 10.05.

Bromination in carbon tetrachloride produced a dibromide which after two recrystallizations from petroleum ether formed colorless needles, m. p. 54–55°.

Anal. Calcd. for $C_6H_5O_3NBr_2$: N, 4.69. Found: N, 4.68.

Polymerization.—Bulk peroxide-catalyzed polymerizations were run with the nitrostyrenes. The styrenes were placed in clean glass tubes and 0.5% by weight of benzoyl peroxide added. The tubes were swept out with nitrogen, sealed and placed in an oven at 80°. The *o*-nitrostyrene exploded after four hours, apparently without polymerization. 3-Nitro-4-hydroxystyrene was a dark, viscous liquid after two weeks, while *p*-nitrostyrene formed a brittle polymer after twenty-four hours; relative viscosity 1.081 for concentration of 0.400 g. in 100 ml. of dimethyl formamide at 30°.

Persulfate–bisulfite initiated emulsion polymerizations were also attempted. *o*-Nitrostyrene and 3-nitro-4-hydroxystyrene failed to polymerize, while *p*-nitrostyrene formed a brittle polymer, relative viscosity 1.206, for a concentration of 0.400 g. in 100 ml. of dimethylformamide. A dark, brittle polymer was produced from 2-nitro-5-vinylfuran in 65% yield; relative viscosity 1.05 for 0.400 g. in 100 ml. of dimethyl formamide. The polymers could be molded to transparent, brittle films.

Boron trifluoride failed to polymerize *o*-nitrostyrene at Dry Ice–acetone temperatures in ethyl chloride or in bulk at room temperature.

Summary

3-Nitro-4-hydroxystyrene and 2-nitro-5-vinylfuran have been prepared and characterized.

p-Nitrostyrene and 2-nitro-5-vinylfuran polymerize readily to low molecular weight polymers. *o*-Nitrostyrene and 3-nitro-4-hydroxystyrene fail to polymerize or polymerize slowly with peroxide initiation.

Louisville 8, Ky. Received April 20, 1950

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[14] Wiley and Hobson, This Journal, **70**, 2429 (1948).

[Contribution from the Eastern Regional Research Laboratory[1]]

Acrylic Esters of Some Substituted Alkanols

By C. E. Rehberg, Marion B. Dixon and W. A. Faucette

In an extensive study of copolymers of alkyl acrylates used in the development of the Lactoprene type of acrylic rubber,[2,3] need arose for acrylic esters containing additional functional groups to be used in the preparation of vulcanizable copolymers of ethyl or other alkyl acrylates.

The esters reported in this paper (Table I) include chloro-, bromo-, nitro-, cyano- and aralkyl acrylates, as well as two trichloroalkyl methacylates. The methacrylates were prepared by use of methacrylic anhydride.[4] 1,3-Dichloro-2-propyl acrylate was made from acrylyl chloride.[4] All the other acrylates were prepared by the alcoholysis of methyl or ethyl acrylate.[5] Efforts to prepare 2,2,2-trichloroethyl acrylate by the alcoholysis method resulted in no reaction. This is the only instance we have found in which a primary alkanol has failed to enter into the alcoholysis reaction with methyl or ethyl acrylate.

The esters in Table I were prepared for copolymerization with ethyl acrylate; hence their homopolymerization was not studied. Several of them were polymerized by heating with benzoyl peroxide in sealed tubes, and the brittle points[6] of the polymers were determined (Table I). Chlorine or bromine seems to raise the brittle points slightly, whereas the nitro group has a much stronger effect. The effect of the phenyl group appears to be intermediate between those of the halogens and the nitro group.

The polymers having brittle points above room temperature were hard and brittle at room temperature. The others were flexible and elastic. Those containing bromo or nitro groups were amber color; the others were substantially colorless. All were clear and transparent.

Acknowledgment.—We are grateful to C. O. Willits, C. L. Ogg and their associates for analyses, and to Merck and Company for trichloroethanol.

Summary

Several bromo-, chloro-, nitro-, cyano- and aralkyl acrylates and two trichloroalkyl methacrylates were prepared.

Trichloroethanol, although a primary alcohol, did not alcoholyze ethyl acrylate.

The brittle points of alkyl polyacrylates were

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Mast, Rehberg, Dietz and Fisher, *Ind. Eng. Chem.*, **36**, 1022 (1944).

[3] Mast and Fisher, *ibid.*, **40**, 107 (1948).

[4] Rehberg, Dixon and Fisher, This Journal, **67**, 208 (1945).

[5] Rehberg and Faucette, *J. Org. Chem.*, **14**, 1094 (1949).

[6] Rehberg and Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

TABLE I

PREPARATION AND PROPERTIES OF ACRYLIC ESTERS

Acrylate	Yield, %	Boiling point, °C.	Boiling point, Mm.	n^{20}_D	d^{20}_4	Mol. refraction Calcd.	Mol. refraction Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Cl, Br or N, % Calcd.	Cl, Br or N, % Found	Brittle pt. of polymer, °C.
2-Bromoethyl	74	53	5	1.4770	1.4774	34.24	34.24	33.6	33.5	3.9	4.0	44.6	44.2	−12[a]
3-Bromopropyl	70	96	18	1.4786	1.4106	38.86	38.78	37.3	37.1	4.7	4.6	41.4	41.1	
2,3-Dibromopropyl	94	105	6	1.5220	1.7803	46.63	46.60	26.5	26.2	3.0	2.9	58.7	57.9	
1-Bromo-2-propyl	80	69	10	1.4712	1.3885	38.86	38.86					41.4	41.2	
3-Chloropropyl	95	79	14	1.4522	1.1122	35.96	36.05					23.9	23.7	−14
2,3-Dichloropropyl	94	58	0.5	1.4765	1.2603	40.83	41.00					38.7	38.5	−10
1,3-Dichloro-2-propyl		50	1	1.4725	1.2592	40.83	40.76	39.4	38.9	4.4	4.5	38.7	38.6	5
2,2,2-Trichloroethyl[b]	56	55	1	1.4718	1.3264	45.70	45.90					48.8	48.4	90
2,2,2-Trichloro-*t*-butyl[b]	83	31	1	1.4657	1.2469	54.57	54.92	39.1	38.6	4.5	4.8	43.3	42.8	75[a]
2-Cyanoethyl	81	108	12	1.4409	1.0619	30.84	31.10	57.6	57.1	5.6	6.0	11.2	11.6	
2-Methyl-2-nitro-1-propyl[c]	94	95	5	1.4470	1.1162	41.33	41.45	48.5	48.3	6.4	6.6	8.1	7.9	32
2-Nitrobutyl[c]	73	63	1	1.4480	1.1172	41.33	41.49	48.5	48.0	6.4	6.8	8.1	7.7	
2-Phenylethyl	87	104	5	1.5111	1.0369	50.59	50.93	75.0	74.8	6.9	6.9			− 2

[a] Polymer appeared to be of low molecular weight. [b] Methacrylate. [c] These compounds were reported by Marans ond Zelinski, THIS JOURNAL, **72**, 2125 (1950), after the present work had been completed. The properties reported for the monomeric esters are in substantial agreement with ours. Our 2-methyl-2-nitro-1-propyl polyacrylate was hard and brittle at room temperature, whereas Marans and Zelinski reported theirs to be softer than methyl polyacrylate (which has a brittle point of about 0°).

raised slightly by halogen substituents, moderately by the phenyl group, and considerably by the nitro group.

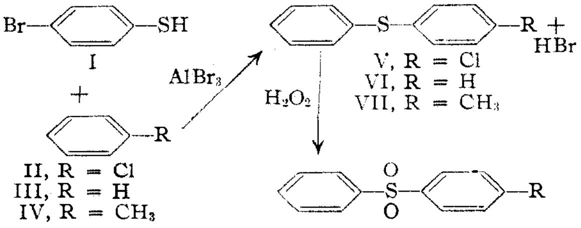
PHILADELPHIA 18, PA. RECEIVED MAY 29, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Action of Aluminum Bromide on Some Halogenated Thiophenols and Benzyl Phenyl Sulfides

BY H. F. WILSON[1] AND D. S. TARBELL

During a continuation of some investigations[2] on the cleavage of benzyl phenyl sulfides by aluminum bromide, it was noted that 4-bromothiophenol (I), in chlorobenzene solution containing a molar equivalent of aluminum bromide, showed a rapid disappearance of the thiol group, as determined by iodine titration. The product, which was formed in high yield, was found to be 4-chlorodiphenyl sulfide (V), and was characterized by oxidation to the crystalline sulfone, which was shown to be identical with an authentic sample.[3]



It was found that a similar reaction occurred in benzene and in toluene solution, leading to good yields of diphenyl sulfide (VI) and 4-methyldiphenyl sulfide (VII), respectively. 2-Bromothiophenol behaved similarly in chlorobenzene and benzene solution, but 3-bromothiophenol did not give any evidence of reaction even under conditions much more drastic than those required with 2- and 4-bromothiophenol. 4-Chlorothiophenol did not react under these conditions. The detailed data are in Table I.

The reaction of the 4-bromo compound (I) with chlorobenzene was investigated in most detail. It was found that, when the molar ratio *r* of aluminum bromide to thiophenol was one or greater, the rate of the reaction was first-order in the thiophenol, as shown in Table II; an increase in *r* from 1 to 1.5 increased the rate about fourfold, but a further increase in the ratio caused a slight decrease in rate.

Hydrogen bromide was shown to be a product of the reaction by an experiment in which the reaction mixture was swept out with dry nitrogen; the evolved gases were passed into standard base, and about 75% of the theoretical amount

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[1] du Pont Fellow, 1949–1950.

[2] Harnish and Tarbell, THIS JOURNAL, **70**, 4123 (1948).

[3] Beckurts and Otto, *Ber.*, **11**, 2066 (1878). The position of the chlorine atom is shown by other syntheses not involving the Friedel–Crafts reaction (Meyer, *Ann.*, **433**, 337, 345 (1923)).