[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Nitrostyrenes and 2-Nitro-5-vinylfuran[1]

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Among the variety of methods which have been used to synthesize nitrostyrenes,[3a-f] the successful decarboxylation of *m*-nitrocinnamic acid to *m*-nitrostyrene[4] has suggested the extension of this method to other nitrostyrenes. The present report concerns the preparation of nitrostyrenes and 2-nitro-5-vinylfuran by decarboxylation of the corresponding cinnamic and furylacrylic acids in quinoline with a copper catalyst. The decarboxylation of 3-nitro-4-hydroxycinnamic acid proceeded rapidly, while *o*- and *p*-nitrocinnamic acids require longer reaction times; the styrenes were isolated in yields of 40–60%. On the other hand, the yield of 2-nitro-5-vinylfuran was poor, possibly due to the sensitivity of furans to bases and the ease of polymerization of the nitrovinylfuran. A similar attempted synthesis of 3-nitro-4-methoxystyrene failed.

The polymerization and copolymerization of nitrostyrenes have been described in a number of recent papers[3d,3f,5a-e] For comparison, polymerizations were undertaken with these monomers. 3-Nitro-4-hydroxystyrene polymerized slowly in the manner of *m*-nitrostyrene[5c] while *o*-nitrostyrene failed to polymerize. Polymerization of *p*-nitrostyrene was rapid, as was the polymerization of 2-nitro-5-vinylfuran. On the basis of viscosity measurements, low molecular weight products were obtained in all cases.

The difference in polymerization rate of *p*- and *m*-nitrostyrene has been explained[6] as a result of the stabilization of the diradical formed from *p*-nitrostyrene; the nitro group probably resonates with the vinyl group, lowering the energy of activation of radical formation. 2-Nitro-5-vinylfuran, which also polymerizes rapidly is related vinylogously with *p*-nitrostyrene. On the other hand, *m*-nitrostyrene cannot have these additional resonance forms and would be expected to polymerize more slowly than the *p*-isomer as it does. The short chain length of the polymers obtained is probably due to a stabilization of the growing polymer chain by interaction with the aromatic nucleus as proposed by Price.[7]

The failure of *o*-nitro- and 2,4,6-trinitrostyrene[3f] to polymerize may be explained by steric effects. Molecular models show that the coplanar configuration necessary for the resonance of the nitro group with the vinyl group in *o*-nitrostyrenes is hindered.

Experimental

Nitrobenzaldehydes.—The *o*- and *p*-nitrobenzaldehydes were prepared by oxidation of the corresponding nitrotoluenes[8,9]; 3-nitro-4-methoxybenzaldehyde by the nitration of anisaldehyde[10]; and 3-nitro-4-hydroxybenzaldehyde by nitration of *p*-hydroxybenzaldehyde in acetic acid.[11]

Cinnamic Acids.—All nitrocinnamic acids were prepared by heating the nitrobenzaldehyde with malonic acid in the presence of pyridine on a steam plate.[12] The yields of purified acid were 80–92%. Nitration of furylacrylic acid in acetic anhydride[13] produced 5-nitrofurylacrylic acid.

Nitrostyrenes.—The nitrocinnamic acids were decarboxylated by the procedure described for *m*-nitrocinnamic acid.[3] Thirty grams of the cinnamic acid, 60 ml. of quinoline and 2 g. of copper powder were heated at the times and temperatures indicated in Table I. The *o*- and *p*-nitrostyrenes were isolated by steam distillation of the acidified reaction mixture and recrystallization from petroleum ether at 0°. Because of its low volatility, 3-nitro-4-hydroxystyrene was isolated by extraction with ether and fractionation through a small column. Decarboxylation of 3-nitro-4-methoxycinnamic acid produced a dark-brown, high-melting material.

TABLE I

Cinnamic acid	Time	Temp., °C.	Yield, %	M. p., °C.
o-Nitro	5.5 hours	160–165	40	13–14[a]
p-Nitro	5.5 hours	160–165	41	21[b]
3-Nitro-4-hydroxy	20 min.	160	60	...

[a] Reported 12°, Einhorn, *Ber.*, **16**, 2213 (1883). [b] Reported 21.4°, Strassburg, Gregg and Walling, THIS JOURNAL **69**, 2141(1947).

3-Nitro-4-hydroxystyrene thus prepared was an orange liquid, b. p. 103–108° (5 mm.); $n^{20}D$ 1.6266.

Anal. Calcd. for $C_8H_7O_3N$: C, 58.19; H, 4.27. Found: C, 58.44; H, 4.18.

3-Nitro-4-hydroxystyrene Dibromide.—Bromination of 3-nitro-4-hydroxystyrene in carbon tetrachloride yielded a dibromide. Recrystallization from petroleum ether produced yellow needles, m. p. 80–81°.

Anal. Calcd. for $C_8H_7O_3NBr_2$: C, 29.56; H, 2.17; N, 4.31. Found: C, 29.50; H, 1.93; N, 4.61.

2-Nitro-5-vinylfuran.—Decarboxylation of 5-nitrofurylacrylic acid by heating with quinoline and copper powder or

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(3) (a) Einhorn, *Ber.*, **16**, 2213 (1883). (b) Basler, *Ber.*, **16**, 3003 (1883). (c) Prausnitz, *ibid.*, **17**, 597 (1884). (d) Marvel, Overberger, Allen and Saunders, THIS JOURNAL, **68**, 736 (1946). (e) Strassburg, Gregg and Walling, *ibid.*, **69**, 2141 (1947). (f) Wiley and Behr, *ibid.*, **72**, 1822 (1950).

(4) Wiley and Smith, *ibid.*, **70**, 2295 (1948).

(5) (a) Marvel, Bailey and Inskeep, *J. Polymer Science*, **1**, 275 (1946); (b) Marvel, *et al.*, *Ind. Eng. Chem.*, **39**, 1486 (1947); (c) Wiley and Smith, *J. Polymer Science*, **3**, 444 (1948); (d) Walling, Briggs, Wolfstirn and Mayo, THIS JOURNAL, **70**, 1537 (1948); (e) Smets and Rickens, *Rec. trav. chim.*, **68**, 983 (1949).

(6) Kennedy and Morton, *J. Chem. Soc.*, 2383 (1949).

(7) Price and Durham, THIS JOURNAL, **65**, 757 (1943).

(8) Tsang, Wood and Johnson, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. 24, p. 75.

(9) Lieberman and Connor, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, p. 441.

(10) Einhorn and Grabfield, *Ann.*, **243**, 368 (1888).

(11) Paal, *Ber.*, **28**, 2413 (1895).

(12) Ittyerak and Pandya, *Proc. Indian Acad. Sci.*, **15A**, 258 (1942).

(13) Gilman and Wright, THIS JOURNAL, **52**, 2550 (1930).

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 $C_6H_5O_3N$: 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.

(14) Wiley and Hobson, THIS JOURNAL, **70**, 2429 (1948).

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.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Acrylic Esters of Some Substituted Alkanols

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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.

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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

(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).