[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

Nitroalkyl Esters of Acrylic, Crotonic and Methacrylic Acids[1]

BY NELSON S. MARANS AND ROBERT P. ZELINSKI

The preparations for a number of substituted alkyl esters of acrylic, methacrylic and crotonic acids have been reported, among them those for 2-cyanoethyl acrylate,[2] 2-fluoroethyl methacrylate,[3] and various aminoalkyl acrylates and methacrylates.[4] Of the nitroalkyl acrylates and methacrylates the following are known: 2-methyl-2-nitropropyl acrylate,[5,6,7] 2-nitroamyl acrylate,[5,7] 2-nitro-1-butyl acrylate,[5,7] and 2-nitro-1-butyl α-ethyl acrylate.[8] In addition, nitro-1-alkyl esters of allyl hydrogen maleate[9] have also been recorded.

It was the purpose of this investigation to prepare and examine the polymerizability of a series of nitroalkyl esters of acrylic, methacrylic and crotonic acids. The method employed for their preparation was the acid-catalyzed alcoholysis of the methyl esters, using either *p*-toluenesulfonic acid with hydroquinone as a stabilizer or sulfuric acid with cuprous chloride (Table I). Either variation was successful in producing fair yields of the 2-nitroethyl, 2-nitropropyl, 2-nitrobutyl and 2-methyl-2-nitropropyl esters of the three unsaturated acids. However, the second appeared to furnish purer products. Under the conditions employed the reaction failed with 1-nitro-2-pentanol and 3-nitro-2-hexanol.

Polymerizability of the esters in the presence of benzoyl peroxide was also studied. All of the acrylates and methacrylates polymerized but none of the crotonates did. The acrylates formed rather soft polymers while the methacrylates yielded hard products. Copolymerization of the nitroalkyl acrylates or methacrylates with methyl acrylate was also found to be possible.

Experimental

Apparatus.—A column having about ten theoretical plates was used for all fractional distillations. It was a total condensation, partial take-off type, measured 1.1 cm. in diameter and 30 cm. in length and was packed with $^3/_{32}$ in., single turn glass helices.

Materials.—Methyl acrylate, methyl methacrylate and methyl crotonate and 2-methyl-2-nitropropanol were Eastman Kodak Co. practical grade and were used without purification. Nitroethane, nitromethane and 1-nitropropane were obtained from Commercial Solvents Corporation and redistilled before use. They were condensed with paraformaldehyde in the presence of base catalysts to form the nitroalcohols.[10] By using a 10:1 molar ratio of nitromethane to paraformaldehyde, 2-nitroethanol was prepared in 30% yield after distillation. A 2:1 molar ratio of nitroethane to paraformaldehyde gave a 45% yield of purified 2-nitro-1-propanol. This same ratio with 1-nitropropane gave a 50% yield of purified 2-nitro-1-butanol.

Preparation of Nitroalkyl Esters.—Two general methods were employed. Methods A and B illustrate the use of *p*-toluenesulfonic acid and hydroquinone; methods C and D illustrate the use of sulfuric acid and cuprous chloride.

Method A.—A mixture of 0.1 mole of nitroalcohol, 0.4 mole of methyl ester of unsaturated acid, 1–3 g. of *p*-toluenesulfonic acid, 1–3 g. of hydroquinone and 40 g. of xylene was heated under a fractionating column. The distillate, containing methanol and methyl ester, was collected and its refractive index was used to determine the amount of methanol. This was done by assuming a linear relationship in a graph of refractive index against percentage composition, and calculating from this the weight of methanol present. When the reaction either ceased or was thus shown to be 80–100% complete, the flask material was rectified at 3–10 mm. pressure.

Method B.—The procedure is approximately the same as that above, but is modified to accommodate larger runs. A mixture of 0.60–2.90 moles of nitroalcohol, 2–6 moles of methyl ester, 10–25 g. of *p*-toluenesulfonic acid, 25 g. of hydroquinone and 150–450 cc. of xylene was heated under a fractionating column until either 90–100% of the theoretical methanol had distilled or until water appeared in the column. The latter indicated nitroölefin formation. The flask material was rapidly rectified at reduced pressure and the crude product was washed twice with water. It was then dried over sodium sulfate and fractionally distilled again.

Method C.—A mixture of 1 mole of nitroalcohol, 1.5–2.0 moles of methyl ester, 10–21 g. of concentrated sulfuric acid and 10–24 g. of cuprous chloride was heated under a fractionating column until 80–100% of the theoretical amount of methanol had been distilled. The flask material was washed twice with water and rectified to yield products which were colorless, almost odorless and of constant density and refractive index.

Method D.—A mixture of 0.7 mole of nitroalcohol, 1.5–2.0 moles of methyl methacrylate, 10–20 g. of concentrated sulfuric acid, 10–25 g. of cuprous chloride and 100 g. of toluene was treated as described for Method C.

Polymerization Experiments.—One and a half gram samples of the nitroalkyl esters were heated at 100° with benzoyl peroxide in a nitrogen atmosphere. With 10 mg. of peroxide all the acrylates, except 2-methyl-2-nitropropyl acrylate, formed rather soft, viscous polymers at the end of five minutes and soft, tacky masses at the end of four hours. The 2-methyl-2-nitropropyl compound formed a fairly hard polymer. With 2 mg. of peroxide the rate of polymerization was slower and with 50 mg. of catalyst it was more rapid, but in all instances the physical characteristics at the end of four hours appeared to be similar. The methacrylates showed the same general response to peroxide concentration, but the polymers produced in four hours were much harder. On the other hand, the crotonates failed to polymerize at all.

Copolymerization experiments were carried out with mixtures of 1.5 g. of nitroalkyl acrylates or methacrylates

---

[1] This work was performed with the aid of U. S. Navy funds, under Subcontract number 2, Contract NOrd 9709 and Subcontract number 1, Contract NOrd 10431, both prime contracts being with the Hercules Powder Company, Allegany Ballistics Laboratory.

[2] Ratchford, Rehberg and Fisher, THIS JOURNAL, **66**, 1864 (1944).

[3] Crawford and Stanley, British Patent 580,655, September 16, 1944.

[4] *Cf.* Rehberg and Faucette, THIS JOURNAL, **71**, 3164 (1949), for an extensive bibliography.

[5] D'Alelio and Underwood, U. S. Patent 2,375,624, May 8, 1945, and U. S. Patent 2,449,804, September 21, 1948.

[6] Agre and Leckley, U. S. Patent 2,278,169, June 12, 1945.

[7] The British Thomson-Houston Co. Ltd., British Patent 547,525, September 1, 1942.

[8] Rasche and Utermohlen, U. S. Patent 2,388,844, November 13, 1945.

[9] Bruson and Butler, U. S. Patent 2,425,144, August 5, 1947.

[10] Gorski and Makarow, *Ber.*, **67**, 976 (1939).

TABLE I

Compound	Method[a]	Yield, %	B. p. °C.	B. p. Mm.	d^{25}	n^{25}_{D}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Acrylate										
2-Nitro-1-ethyl	A	47								
	B	34								
	C	53	100	5	1.204	1.4510	41.38	41.94	4.86	5.15
2-Nitro-1-propyl	A	75								
	B	45								
	C	53	92	4	1.143	1.4448	45.28	46.00	5.70	5.84
2-Nitro-1-butyl	A	89								
	B	52								
	C	52	102	6	1.112	1.4452	48.55	48.75	6.40	6.60
2-Methyl-2-nitro-1-propyl	A	61								
	B	34								
	C	58	102	8	1.112	1.4455	48.55	48.30	6.40	6.32
Crotonate										
2-Nitroethyl	A	36								
	B	10								
	C	63	111	4	1.159	1.4600	45.28	45.75	5.70	5.78
2-Nitro-1-propyl	A	58								
	B	36								
	C	51	106	4	1.109	1.4533	48.55	48.53	6.40	6.46
2-Nitro-1-butyl	A	31								
	B	43								
	C	68	111	3	1.088	1.4539	51.33	51.24	7.00	6.81
2-Methyl-2-nitro-1-propyl	A	54								
	B	54								
	C	67	115	4	1.089	1.4544	51.33	51.82	7.00	7.07
Methacrylate										
2-Nitroethyl	A	33								
	B	43								
	D	31	115	10	1.158	1.4519	45.28	45.50	5.70	5.62
2-Nitro-1-propyl	A	48								
	B	52								
	D	52	109	6	1.108	1.4470	48.55	49.16	6.40	6.60
2-Nitro-1-butyl	A	33								
	B	52								
	D	57	112	8	1.085	1.4469	51.33	51.40	7.00	6.95
2-Methyl-2-nitro-1-propyl	A	26								
	B	32								
	D	32	102	4	1.087	1.4471	51.33	51.40	7.00	6.75

[a] Constituents in Method A: xylene, 40 g.; hydroquinone, 1–3 g.; methyl ester of unsaturated acid, 0.4 mole; *p*-toluenesulfonic acid, 2–3 g., and nitroalcohol, 0.10–0.13 mole. Constituents in Method B: xylene, 30–50% by weight of mixture; hydroquinone, 25 g.; methyl ester of unsaturated acid, 2.0–6.0 moles; *p*-toluenesulfonic acid, 10.0–25.0 g.; and nitroalcohol, 0.60–2.90 moles. Constituents in Method C: cuprous chloride 10–24 g.; methyl ester of unsaturated acid, 1.5–2.0 moles; concd. sulfuric acid, 10–21 g.; and nitroalcohol, 0.62–1.24 moles. Constituents in Method D: cuprous chloride, 10–25 g.; methyl ester of unsaturated acid, 1.5–2.0 moles; 30–50% by weight of toluene; concd. sulfuric acid, 10–20 g.; and nitroalcohol, 0.34–0.71 mole.

and 1.5 g. of methyl acrylate and 10 mg. of benzoyl peroxide. The nitroalkyl acrylate-methyl acrylate copolymers were harder than the nitroalkyl acrylate homopolymers, and the nitroalkyl methacrylate-methyl acrylate copolymers were softer than the nitroalkyl methacrylate homopolymers. None of the copolymers was as hard as polymerized methyl acrylate.

Acknowledgment.—The authors wish to express their thanks to the Allegany Ballistics Laboratory, Hercules Powder Company, and particularly to Dr. Ralph Preckel of that organization. All analyses were performed by the Micro-Tech Laboratories, Skokie, Illinois.

Summary

The 2-nitroethyl, 2-nitropropyl, 2-nitrobutyl and 2-methyl-2-nitropropyl esters of acrylic, methacrylic and crotonic acids have been prepared and their physical constants have been determined.

The acrylates and methacrylates, but not the crotonates, have been found to polymerize in the presence of benzoyl peroxide and to form copolymers with methyl acrylate.

CHICAGO, ILLINOIS RECEIVED NOVEMBER 11, 1949