commercial production of this essential amino acid appears to involve the use of ϵ-caprolactam.

The second most practical method involves the reduction of monoethyl adipate, and conversion to 6-bromohexanoic acid.

The conversion of tetramethylene chlorobromide, tetramethylene chloride, 1-nitro-4-chlorobutane to lysine may be somewhat inferior methods but are significant in case raw material values change and the by-products formed in the reactions can be utilized.

LAFAYETTE, INDIANA RECEIVED JANUARY 17, 1949

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

Acrylic Esters of Amino Alcohols

BY C. E. REHBERG AND W. A. FAUCETTE[2]

According to the patent literature, several amino alcohols have been converted into the acrylic[3] or methacrylic[4] esters. Gilman and co-workers[5] prepared diethylaminoethyl acrylate hydrochloride, but, since their interest was in its physiological activity, they did not prepare the free ester or make any attempt to polymerize the salt.

Our principal object in preparing the aminoalkyl acrylates was to copolymerize them with alkyl acrylates and thus obtain acrylic elastomers containing basic functional groups. However, they did not readily polymerize alone, nor did they copolymerize with ethyl acrylate. Hence, their properties were not extensively studied.

It has been stated that aminoalkyl methacrylates act as polymerization inhibitors and are difficult to polymerize with benzoyl peroxide[4b] but are readily polymerized by ultraviolet light.[4b] Diethylaminoethyl methacrylate has been reported[4b,d,e] to polymerize spontaneously at 0° in the absence of light or catalysts. In general, these observations were confirmed in the present work with acrylic esters.

Experimental

Amino Alcohols.—The diethyl- and dibutylaminopropanols were obtained from Eastman Kodak Company; dimethylaminoethanol and 2-N-morpholinoethanol were kindly supplied by the Carbide and Carbon Chemicals Corporation, and we are indebted to Sharples Chemicals, Inc., for diethyl- and dibutylaminoethanol and ethyldiethanolamine. All were used after a simple distillation.

TABLE I

PREPARATION AND PROPERTIES OF AMINOALKYL ACRYLATES

Acrylate	Boiling point °C.	Mm.	Yield, %	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.	Found	Nitrogen Calcd.	Found
Dimethylaminoethyl	61	11	36	1.4375	0.9434	39.65	39.80	9.8	9.2
Diethylaminoethyl	70	5	94	1.4425	.9251	48.89	49.02	8.2	8.3
2-(1,1′-Dibutylamino)-ethyl	82	0.3	93	1.4460	.8977	67.36	67.53	6.2	6.4
3-Diethylaminopropyl	44	.1	65	1.4441	.9180	53.50	53.61	7.6	7.5
2-(1,1′-Dibutylamino)-propyl	77	.2	40	1.4440	.8880	71.98	72.20	5.8	5.4
3-(1,1′-Dibutylamino)-propyl	83	.2	85	1.4480	.8952	71.98	72.18	5.8	5.6
2-N-Morpholinoethyl	67	.2	96	1.4728	1.0711	48.33	48.49	7.6	7.6
N-Ethyl-N-(2-hydroxyethyl)-aminoethyl	77	.2	76	1.4662	1.0211	50.41	50.79	7.4	8.3

The aminoalkyl acrylates (Table I) were prepared readily, and usually in high yield, by the alcoholysis of methyl or ethyl acrylate. This method had been used previously in the preparation of alkyl,[6] alkenyl[7] and alkoxyalkyl[8] acrylates.

Monomeric Acrylates.—The esters were prepared by the alcoholysis of methyl or ethyl acrylate. Aluminum isopropoxide was used as a catalyst and phenyl-β-naphthylamine as a polymerization inhibitor. In one experiment, no inhibitor was used, and a lowered yield of monomer, together with a large distillation residue, was obtained. The procedure and equipment have been described in previous papers.[6-8]

In the one experiment in which ethyldiethanolamine was used, only one mole of methanol was produced in the reaction. The molecular refraction of the constant-boiling product agreed with the expected value for the monoacrylate. The nitrogen analysis was somewhat high for the monoacrylate, indicating that some free amine was present. However, two fractional distillations through a 3-ft. Vigreux column failed to effect any separation.

The esters were colorless liquids having mild, ammoniacal odors and appreciable water solubility.

Polymerization Experiments.—Addition of benzoyl peroxide (1%) to the monomers or to their solutions (10%) in ethyl acetate resulted in instant discoloration. Sub-

(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) Present address: Corn Products Refining Company, Argo, Illinois.

(3) Graves, U. S. Patent 2,138,031, November 29, 1938.

(4) (a) Heckert, *ibid.*, 2,168,338, August 8, 1939; (b) Graves, *ibid.*, 2,138,763, November 29, 1938; (c) Harmon, *ibid.*, 2,138,762, November 29, 1938; (d) Izard, *ibid.*, 2,129,694, September 13, 1938; (e) Barrett and Strain, *ibid.*, 2,129,662, September 13, 1938.

(5) Gilman, Heckert and McCracken, THIS JOURNAL, **50**, 437 (1928).

(6) (a) Rehberg and Fisher, THIS JOURNAL, **66**, 1203 (1944); (b) Rehberg, Faucette and Fisher, *ibid.*, 1723; (c) Rehberg, *Org. Syntheses*, **26**, 18 (1946).

(7) Rehberg and Fisher, *J. Org. Chem.*, **12**, 226 (1947).

(8) Rehberg and Faucette, "Acrylic Esters of Ether-Alcohols," submitted for publication in *J. Org. Chem.*

sequent heating at 90–100° had no effect. Addition of benzoyl peroxide or ammonium persulfate to aqueous emulsions of the esters had a similar result. Several attempts to copolymerize diethylaminoethyl and ethyl acrylates (weight ratio 1:10) in ethyl acetate solution and in aqueous emulsion, with benzoyl peroxide and ammonium persulfate, respectively, as catalysts, resulted in discoloration of the monomer but no appreciable polymerization. Diethyl- and dibutylaminoethyl acrylates were sealed in glass tubes and heated at 90° for one week without visible change. The tubes were than irradiated with ultraviolet light. Viscous, liquid polymers were thus formed.

No polymerization occurred when a 10% aqueous solution of the acetate of diethylaminoethyl acrylate containing 1% of benzoyl peroxide was refluxed for twenty-four hours. A 10% aqueous solution of the acrylate (salt) of diethylaminoethyl acrylate containing 0.06% (based on ester) of ammonium persulfate was placed in sunlight. After a few hours it polymerized vigorously, the entire solution being converted to a soft, pasty solid. This was soluble in water, from which it could be precipitated by sodium chloride. A sample of the polymer which had been precipitated from dilute hydrochloric acid and then from water was analyzed: N, found 2.95% (calcd. 5.75%).

A 1% aqueous solution of morpholinoethyl polyacrylate (prepared from polymer formed spontaneously while in the refrigerator) was added to a 1% aqueous solution of polyacrylic acid. A voluminous precipitate formed instantly. When dried it was hard and brittle.

Summary

The acrylic esters of eight alcohols containing tertiary amino groups were prepared by the alcoholysis of methyl or ethyl acrylate.

All attempts to polymerize the esters with benzoyl peroxide, ammonium persulfate or heat, whether in bulk, in solution or in aqueous emulsion, were failures. Ultraviolet light was effective in promoting polymerization.

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[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE]

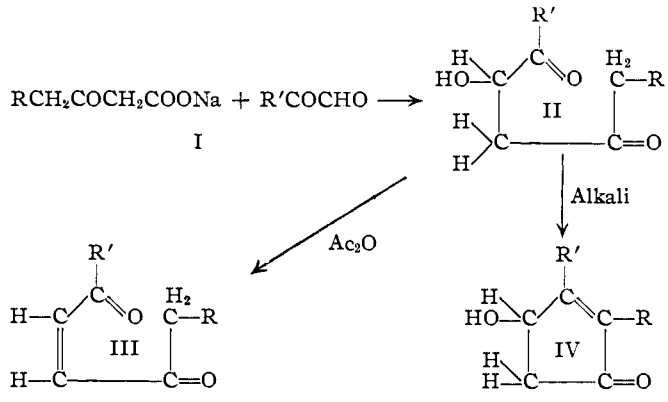
Constituents of Pyrethrum Flowers. XXIII. Cinerolone and the Synthesis of Related Cyclopentenolones[1]

BY MILTON S. SCHECHTER, NATHAN GREEN AND F. B. LAFORGE

Of the two substituted cyclopentenolones, pyrethrolone and cinerolone, the chrysanthemum acid esters of which constitute the principal insecticidal constituents of pyrethrum flowers, cinerolone, 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one, possesses the simplest structure. When it is re-esterified with *d-trans*-chrysanthemum monocarboxylic acid, the resulting cinerin I has been shown to be of about the same order of toxicity[2] as pyrethrin I, and it has the added advantage of decidedly greater stability. For these reasons cinerolone has been given first consideration from the standpoint of synthesis.

In previous articles[3,4] the synthesis of 2-*n*-butyl-4-hydroxy-3-methyl-2-cyclopenten-1-one (*dl*-dihydrocinerolone) and the corresponding 2-*n*-amyl compound (*dl*-tetrahydropyrethrolone) has been described. The method employed consisted in the introduction of bromine in the 4-position of dihydrocinerone and tetrahydropyrethrone, respectively, by the agency of N-bromosuccinimide and the replacement of the halogen by hydroxyl. This method failed[5] when the side chain was unsaturated, as it is in cinerone and pyrethrone.

It has been shown[6] that 3-methyl-2-cyclopentenones with a side chain in position 2 are readily obtained by the cyclization of 1,4-diketones con-



a, R = -*n*-C_4H_4; R′ = $-CH_3$.
b, R = $-CH_2CH{=}CHCH_3$; R′ = $-CH_3$.
c, R = $-CH_2CH{=}CH_2$; R′ = $-CH_3$.
d, R = $-CH_2C(CH_3){=}CH_2$; R′ = $-CH_3$.
e, R = $-CH_2CH_2CH{=}CH_2$; R′ = $-CH_3$.
f, R = $-CH_2CH{=}C(CH_3)_2$; R′ = $-CH_3$.
g, R = —H; R′ = $-CH_3$.
h, R = $-CH_2CH{=}CH_2$; R′ = $-C_6H_5$.

taining a $-CH_2-$ group in the 5-position. If 2-hydroxy-1,4-diketones also having a $-CH_2-$ group in the 5-position could be prepared, they might be expected to cyclize with the elimination of a molecule of water to 2,3-disubstituted-4-hydroxy-2-cyclopenten-1-ones. It will be shown that this

(1) A communication to the Editor on this subject appeared in THIS JOURNAL, 71, 1517 (1949), and an article in *Agr. Chemicals*, 4, [6], 57 (1949). This article not copyrighted.

(2) Gersdorff, *J. Econ. Entom.*, 40, 878 (1947).

(3) Soloway and LaForge, THIS JOURNAL, 69, 979 (1947).

(4) Dauben and Wenkert, *ibid.*, 69, 2074 (1947).

(5) LaForge, Green and Gersdorff, *ibid.*, 70, 3707 (1948).

(6) Hunsdiecker, *Ber.*, 75B, 455 (1942); see also Blaise, *Compt. rend.*, 158, 708 (1914).