The eluate (0.35 g) from 500 ml of ethyl acetate, a brown viscous gum, was warmed in petroleum ether from which 15 mg of a white powder and 90 mg of a hard crystalline substance separated. Recrystallization of the larger fraction from petroleum ether–ether gave white needles of 2-(N-methylacetamido)-*trans*-decalin-2β-ol (XVII): mp 109.5–110°; ν_{max}^{KBr} 3497, 3289 and 3125 (OH and NH) and 1639 cm^{-1} (amide C=O); nmr (CDCl$_3$), δ 2.26 (–CH$_2$CO–, two protons, S), 2.8 (CH$_3$, three protons, D, J = 5 cps) and 4.34 (OH, one proton, disappeared upon addition of D$_2$O); nmr (DMSO-d_6), δ 2.16 (–CH$_2$CO–, two protons, S), 2.59 (CH$_3$, three protons, D, J = 5 cps), 4.65 (OH, one proton, S), and 7.76 (NH, one proton, broad); M$^+$ in the mass spectrum at m/e 225, intense peaks at M − 18, M − 17, M − 70, M − 71, M − 89, M − 153, M − 166, and M − 195.

Anal. Calcd for C$_{13}$H$_{23}$NO$_2$: C, 69.25; H, 10.31; N, 6.21. Found: C, 69.56; H, 10.32; N, 6.27.

The smaller fraction accompanying the above compound was shown to be the dimer (XVa) by mixture melting point and ir spectra.

Elution with 400 ml of 50% ethyl acetate in benzene gave 0.47 g of a viscous liquid, considered to be the hydroxy ester (XVIa): ν_{max}^{film} 3448 (OH) and 1724 cm^{-1} (ester C=O). This material decomposed on attempted distillation under high vacuum.

Similar electrolysis of 3 g of the hydroxy acid (IIc) in 10 ml of N-methylformamide containing 1.1 ml of triethylamine for 32 hr at 10° gave, after chromatography, a 75% yield of a mixture of homodecalones XIII and XIV. The 2,4-dinitrophenylhydrazone, after recrystallization, melted at 110–132°.

Electrolysis of (2α-Hydroxy-*trans*-2-decalyl)acetic Acid (IIIc). —A total of 15 g of the hydroxy acid was electrolyzed in five 3-g lots, each in DMF containing triethylamine, and under conditions similar to those for the epimeric acid (IIc). The neutral fraction which was obtained was chromatographed on 250 g of neutral alumina. Elution with 1 l. of 1:1 benzene–ether gave 5.8 g of a mixture of the homodecalones XIII and XIV. The 2,4-dinitrophenylhydrazone melted, after recrystallization from 95% ethanol, at 113–128°. Its mass spectrum exhibited M$^+$ at m/e 346.

Anal. Calcd for C$_{17}$H$_{22}$N$_4$O$_4$: C, 58.95; H, 6.36; N, 16.19. Found: C, 59.21; H, 6.33; N, 16.07.

Elution with ether gave 1.8 g of an hydroxy ester fraction XVIb which could not be purified: ν_{max}^{film} 3448 (OH) and 1724 cm^{-1} (ester C=O).

Elution with 10% methanol in ethyl acetate gave 3.2 g of a viscous liquid. This was dissolved in warm petroleum ether and allowed to stand overnight to afford two crystalline forms (140 and 90 mg). Both showed similar ir spectra and were considered to be polymorphic forms of the dimer. Recrystallization of the larger fraction from absolute methanol gave transparent peaks of 1,2-bis(2α-hydroxy-2-*trans*-decalyl)ethane (XVb): mp 215–216.5°; ν_{max}^{KBr} 3448 cm^{-1} (OH); M$^+$ in the mass spectrum at m/e 334. The smaller fraction on recrystallization from absolute methanol gave feathery needles of the dimer (XVb): mp 152.5–153.5°; ν_{max}^{KBr} 3333 cm^{-1} (OH); M$^+$ in the mass spectrum at m/e 334.

Electrolysis of α-(2-Hydroxy-2-*trans*-decalyl)propionic Acid (VIc).—A solution of 3.19 g of the hydroxy acid in 15 ml of DMF containing 0.85 ml of triethylamine was electrolyzed at a C anode and the dark brown electrolysate was worked up as above. When 3.04 g of the neutral product was diluted with petroleum ether and allowed to stand overnight, a small amount of a dark solid separated out. The residue from the mother liquors was chromatographed on 100 g of basic alumina. Elution with 1:1 benzene–ether gave 1.5 g of a mixture of *trans*-4-methylbicyclo[5.4.0]undecan-3-one (XVIII) and *trans*-3-methylbicyclo[5.4.0]undecan-4-one (XIX). Distillation in a short-path distillation tube at 120° (0.1 mm) gave a colorless liquid with a strong band in the ir at 1695 cm^{-1}. The nmr spectrum (CDCl$_3$) showed two methyl doublets (J = 7 cps) at 1.08 and 1.11 with nearly equal integrated intensities.

Anal. Calcd for C$_{12}$H$_{20}$O: 80.00; H, 11.11. Found: C, 80.16; H, 11.57.

The 2,4-dinitrophenylhydrazone was chromatographed on basic alumina and crystallized from petroleum ether, mp 72.5–76°.

Anal. Calcd for C$_{18}$H$_{24}$N$_4$O$_4$: C, 59.98; H, 6.71; N, 15.56. Found: C, 60.32; H, 6.85; N, 15.22.

Registry No.—IIa, 16666-51-6; IIb, 16666-52-7; IIc, 16666-53-8; IIIa, 16666-54-9; IIIb, 16666-55-0; IIIc, 16666-56-1; V, 16666-57-2; VIb, 16666-58-3; VIc, 16666-59-4; VIIIa, 16666-60-7; IXa, 16666-61-8; 2,4-dinitrophenylhydrazone of XIII, 16666-66-3; 2,4-dinitrophenylhydrazone of XIV, 16666-67-4; XVa, 16666-62-9; XVb, 16666-63-0; XVII, 16666-64-1; XVIII, 16666-65-2; 2,4-dinitrophenylhydrazone of XVIII, 16666-36-7; XIX, 16666-37-8; 2,4-dinitrophenylhydrazone of XIX, 16666-38-9.

The Preparation of *cis*-β-Acetylacrylic Acid[1]
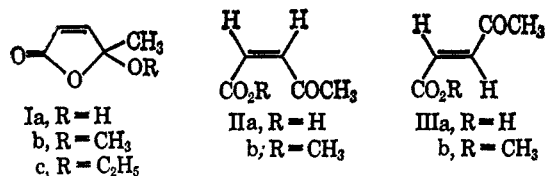
STANLEY SELTZER AND KENNETH D. STEVENS

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Kinetic studies have been carried out to determine the best conditions for the hydrolysis of the pseudo-ethyl ester of *cis*-β-acetylacrylic acid leading to the *cis* acid without the concurrent formation of the *trans* acid. *cis*-β-Acetylacrylic acid has been isolated in crystalline form. Nmr, uv, and ir spectra indicate that the *cis* acid is cyclic but that the anion exists in open form.

In connection with studies of *cis–trans*-catalyzed isomerizations[2] it became necessary to synthesize *cis*-β-acetylacrylic acid. An examination of the literature indicated that there still was some doubt in the structural assignment for the β-acetylacrylic acid isomer (mp 125–126°) that Wolff[3] had prepared more than 75 years ago by the dehydrobromination of bromolevulinic acid. Shaw[4] prepared the acid by Wolff's method but, because of its ultraviolet maximum at 220 mμ, he suggested the pseudo-acid structure, Ia, for Wolff's compound rather than IIa or IIIa. By treatment with diazomethane, Shaw isolated a methyl ester which he assigned as Ib on the basis of the similarity of its ultra-

Ia, R = H
b, R = CH$_3$
c, R = C$_2$H$_5$

IIa, R = H
b, R = CH$_3$

IIIa, R = H
b, R = CH$_3$

violet absorption to that for Ia. The ester Ib appears to be different from the ester derived from partial catalytic reduction of methyl acetylpropiolate obtained

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) K. D. Stevens, and S. Seltzer, to be published.

(3) L. Wolff, *Ann.*, **264**, 229 (1891).

(4) E. Shaw, *J. Amer. Chem. Soc.*, **68**, 2510 (1946).

by Shen and Whiting.[5] The latter authors assigned structure IIb to their compound on the basis of the propensity for *cis* addition in catalytic reduction. By selenium dioxide dehydrogenation of methyl levulinate, Raymond[6] obtained a methyl ester identical in its properties with that prepared by Shaw and identical with the product of dehydrohalogenation of methyl bromolevulinate.[7] Structure Ib for Shaw's methyl ester was thus ruled out and, in view of Shen and Whiting's work, the ester probably has the *trans* configuration (IIIb). One might infer at this point that the starting acid (mp 125°) possesses the same configuration.

Pseudo-esters having the same basic skeleton as I have been prepared by the photosensitized 1,4 addition of oxygen to 2-methylfuran in alcoholic solution[8] and presumably could be formed by the addition, to that same molecule, of singlet oxygen, generated by the combination of sodium hypochlorite and hydrogen peroxide.[9] On acid hydrolysis of Ic, however, Schenck obtained the free acid that melted at 125° and assigned it the *trans* structure (IIIa);[10] alkaline hydrolysis of the pseudo-ethyl ester (Ic) led to polymer.[8] Milder alkaline hydrolysis of the pseudo-methyl ester (Ib), however, was claimed to lead to a mixture of the *cis* (Ia) and *trans* (IIIa) isomers although the *cis* acid was not isolated.[11] The authors report here the preparation, isolation, and properties of the *cis* acid.

Results and Discussion

β-Acetylacrylic acid was prepared by the method of Wolff;[3] the *trans* configuration is indicated by its nmr spectrum. In acetone-d_6 the spectrum consists of a singlet at τ 7.63 (methyl), an AB quartet (vinyl protons) with centers at τ 3.33 and 3.05 (J_{AB} = 16 cps), and a broad singlet (carboxyl proton) at τ 2.0 but its position varied with concentration. The areas of the three groups were in the ratio of 3:2:1. That this is the *trans* acid is shown by the large vinyl coupling constant.[12]

The ethyl pseudo-ester of β-acetylacrylic ester was prepared by Schenck's method and purified by vapor phase chromatography. In carbon tetrachloride, its nmr spectrum exhibited a triplet at τ 8.85 (methyl), a singlet at 8.38 (methyl), a quartet at 6.57 (methylene), and an AB quartet (vinyl protons) with centers at 3.80 and 2.59 (J_{AB} = 5.7 cps) with areas in the ratio of 3:3:2:1:1.

It is apparent from the previous studies[8,11] that, under normal conditions of hydrolysis of the pseudo-ester, rapid *cis*–*trans* isomerization ensues. Levisalles, however, reported that very gentle acid hydrolysis of 2,5-dimethoxy-2,5-dimethyldihydrofuran leads successfully to *cis*-3-hexene-2,5-dione which easily isomerizes to the

trans isomer under more vigorous conditions.[13] Examination of the nmr spectrum of the mixture resulting from the partial acid-catalyzed hydrolysis of the ethyl pseudo-ester of β-acetylacrylic acid, indicated the appearance of a new methyl and vinyl absorption in addition to those due to presence of pseudo-ester and *trans* acid. These new peaks were tentatively assigned to the *cis* acid and will be discussed later. In addition, shifted upfield from the methyl peak of the *trans* acid by about 0.18 ppm, was another singlet with an intensity somewhat smaller than the *trans* acid methyl peak together with a multiplet at about τ 7.05. Examination of the conditions that led to the presence of these leads us to believe that they are due to hydrated β-acetylacrylic acid (*i.e.*, α- and/or β-hydroxylevulinic acid). Support for these assignments was gained by examination of the solution after longer reaction times. By the time the ester was almost completely hydrolyzed the *cis* acid was almost completely absent; the *trans* acid and hydrate only remained.

An attempt was made to obtain approximate kinetic data in order to determine the best conditions for preparing the pure *cis* acid. A change in the concentration of the acid catalyst would not be expected to improve the ratio of *cis* to *trans* acid since both the hydrolysis and isomerization are probably first order in hydrogen ion.[14] If the activation energies for hydrolysis, hydration, and *cis*–*trans* isomerization were to be different, it might be possible to increase the fraction of the *cis* product by a suitable change in temperature. The approximate product distributions, obtained from the areas of the methyl nmr peaks due to ester, *cis*, *trans*, and hydrated acids, at two temperatures of hydrolysis, are shown in Table I. It appears that for similar large extents of hydrolysis the ratio of products is relatively insensitive to temperature.

TABLE I

DISTRIBUTION OF PRODUCTS FROM ACID HYDROLYSIS OF THE ETHYL PSEUDO-ESTER OF *cis*-β-ACETYLACRYLIC ACID AT DIFFERENT TEMPERATURES[a]

Temp, °C	Reaction, time	% hydrolysis	β-Acetylacrylic acid [*cis*]/[*trans*]	[*cis* acid]/ [*trans* + hydrated acid]
49	2.5 hr	76	7.4	6.4
49	4 hr	89	3.9	3.6
49	39 hr	98	0.12	0.096
98	2 min	63	12	12
98	4 min	85	4.6	4.3
98	8 min	93	0.81	0.77
98	23 min	99	0.087	0.078

[a] The initial reaction mixture was a 1:1 (v/v) ester–0.138 *M* hydrochloric acid mixture. The two phases initially present became completely miscible before the first nmr spectrum was recorded. The quantities shown here are from integration of nmr signals.

Additional experiments revealed that the *cis/trans* ratio could be increased by increasing the initial ratio of acid solution to ester. The results of these studies are shown in Table II. The hydrolysis reaction is rapidly reversible and in the presence of a high concentration of ethanol, as in the case where equal volumes of ester and aqueous acid are mixed initially, the hy-

(5) T. Y. Shen and M. C. Whiting, *J. Chem. Soc.*, 1772 (1950).

(6) S. Raymond, *J. Amer. Chem. Soc.*, **72**, 4304 (1950).

(7) H. Pauly, R. Gilmour, and G. Will, *Ann.*, **403**, 119 (1914).

(8) G. O. Schenck, *ibid.*, **584**, 156 (1953); K. Gollnick and G. O. Schenck in "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press Inc., New York, N. Y., 1967, p 255.

(9) C. Foote and S. Wexler, *J. Amer. Chem. Soc.*, **86**, 3879 (1964).

(10) There appears to be no discussion in ref 8 for the basis of this assignment.

(11) G. Fuchs and N. Hellstrom, *Lantbrukshogskol. Ann.*, **30**, 615 (1964).

(12) J. W. Emsley, J. Feeney, and J. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press Inc., New York, N. Y., 1966, pp 710–730.

(13) J. Levisalles, *Bull. Soc. Chim. Fr.*, 997 (1957).

(14) See, *e.g.*, K. Nozaki and R. A. Ogg, Jr., *J. Amer. Chem. Soc.*, **63**, 2583 (1941); A. J. Deyrup, *ibid.*, **56**, 60 (1934); R. P. Bell and A. D. Norris, *J. Chem. Soc.*, 118 (1941).

drolysis is retarded with respect to the isomerization. By decreasing the available ethanol, the hydrolysis proceeds to a greater extent before substantial isomerization takes place. The preparative method follows from these results. After incomplete hydrolysis, the unhydrolyzed ester is extracted from the neutral aqueous solution and the *cis* acid extracted from the remaining acidified aqueous solution. The small amount of hydrated acid is apparently extracted at a much slower rate. The crystalline *cis* isomer melts almost 100° lower than the *trans* acid.

TABLE II

DISTRIBUTION OF PRODUCTS FROM ACID HYDROLYSIS OF THE
ETHYL PSEUDO-ESTER OF *cis*-β-ACETYLACRYLIC ACID[a]

Aqueous acid/ester (v/v)	Reaction time, min	% hydrolysis	β-Acetylacrylic acid [cis]/[trans]	[cis acid]/ [trans + hydrated acid]
1	30	72	30	13
1	50	89	9.2	4.0
1	125	94	1.8	0.88
5[b]	8	66	86	26
5[b]	12	86	85	28
5[b]	16	93	74	20
5[b]	20	97	49	13
10[b]	8	80	>300	>150
10[b]	12	94	55	20
10[b]	16	96	54	14

[a] All hydrolyses were carried out at 98°. Concentrations shown here are from integration of nmr signals. [b] The aqueous acid solution was 1.0×10^{-3} M hydrochloric acid; all others were 1.5×10^{-3} M.

The nmr spectrum of *cis*-β-acetylacrylic acid is decidely different from that of the *trans* acid, but in some respects similar to the spectrum of the pseudo-ester. The *cis* acid in chloroform-*d* exhibits a singlet at τ 8.30 (methyl), an AB quartet with centers at 3.88 and 2.56 (vinyl protons, $J_{AB} = 5.6$ cps), and broad singlet at 3.88 (hydroxyl). The areas are in the ratio of 3:2:1. That this is the *cis* isomer is shown by the small vinyl proton coupling constant.[12] The nmr spectrum is consistent with the *cis* acid existing in the cyclic form (Ia). Support for this structure comes from the examination of the chemical shift of the methyl peak and the vinyl proton coupling constant.

It has been shown that conversion of a carbonyl group into a *gem*-diol (*i.e.*, hydration) is accompanied by an upfield shift of the protons α to the original carbonyl group.[15] α protons of hydrated aldehydes and ketones are shifted +0.7 to +0.9 ppm relative to their unhydrated forms.[15,16] Smaller effects are observed for β protons. In the *trans* acid the methyl group appears at τ 7.63. If the acid were the open *cis* acid (IIa) the position of the methyl group would not be expected to differ substantially from that for the *trans* compound. As will be shown below, the anion, a derivative of the hypothetical open *cis* acid, exhibits a methyl peak only 0.08 ppm away from that of the methyl peak of the *trans* acid. Cyclization as in Ia, however, alters the magnetic anisotropy of the carbonyl group in a way exactly analogous to the hydration of the carbonyl group. The position of the methyl peak in the *cis* acid, τ 8.30, is in line with the expected shift.

The magnitude of coupling constants of *cis*-olefinic protons incorporated in a ring show a marked dependence on the size of the ring.[17] For five-membered cyclic olefins and unsaturated ketones, the coupling constant was found to be between 5.4 and 7.0 cps.[18] The coupling constant increases with increased ring size; for six-membered rings the constant is found to be between 9.9 and 10.5 cps. It should be recalled that the vinyl coupling constant of the ethyl pseudo-ester is 5.7 cps which fits well within the predicted range. The *cis* acid's vinyl coupling constant is essentially the same as in the pseudo-ester, and it too must have a cyclic pseudo-acid structure. It is interesting that this structure is maintained in aqueous solution as shown by the presence of the same coupling constant.

The pK_a of the pseudo-acid was found[2] to be 4.48. This is to be contrasted with a pK_a of 3.24 for the *trans* acid.[19] It was of interest to examine the nmr spectrum of the conjugate base. In aqueous bicarbonate solution an interesting change takes place. The methyl peak moves downfield 0.59 ppm toward the position where the methyl peak of the *trans* acid anion can be found. Moreover, the vinyl proton coupling constant changes to 12.2 cps. From the previous discussion both of these changes are consistent with an open structure (IV) for the conjugate base of the *cis* acid. Cycli-

IV
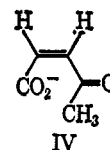
zation is reversible upon reacidification as shown by the return of the methyl peak and vinyl coupling constant to previous values for the *cis* acid.

The ultraviolet spectra of the *cis* acid and its conjugate base and the *trans* acid were recorded in aqueous solution and shown in Figure 1. As reported previously[4] an aqueous solution of the *trans* acid exhibits a maximum at 220 mμ. The *cis* acid in acidic solution (pH <2.5), however, exhibits a maximum at 195 mμ. The ultraviolet spectra of the pseudo-ester and *cis* acid are similar as they should be if both have a cyclic structure; in aqueous solution the ester has a maximum at 195 mμ. In 95% ethanol the single maximum of the pseudo-ester moves to 200 mμ. The rules that are used to preduct ultraviolet maxima for α,β-unsaturated compounds are well known.[20] Application of these rules to the ester and *cis* acid suggests that the skeletal structure (V), the γ-lactone of 4-hydroxycrotonic acid,

V

should exhibit a maximum at 202 mμ in ethanol. Only partial vertification of this predicted maximum exists; it appears to be somewhere below 210 mμ (log ε >3.8).[21] Further substitution on the γ carbon

(15) E. Lombardi and P. G. Sogo, *J. Chem. Phys.*, **32**, 635 (1960).
(16) P. Greenzaid, Z. Luz, and D. Samuel, *J. Amer. Chem. Soc.*, **89**, 749 (1967).
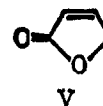(17) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, pp 53, 54.
(18) O. L. Chapman, *J. Amer. Chem. Soc.*, **85**, 2014 (1963).
(19) M. Sanesi, *Ann. Chim.* (Rome), **50**, 997 (1960).
(20) A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Ltd., London, 1955, pp 90–99.
(21) R. J. D. Smith and R. N. Jones, *Can. J. Chem.*, **37**, 2092 (1959).

in V, as to produce the ester and acid, would not expect to change appreciably the position of the maximum.

An almost neutral aqueous solution (pH >5.5) of the *cis* acid results in the appearance of a new maximum at 240 mμ and a shift of the low-wavelength peak to 198 mμ. The spectrum of the cyclic pseudo-acid reappears upon reacidification of the neutral solution. The behavior of *cis*-β-acetylacrylic acid in neutral and acidic media parallels that of β-formylacrylic acid.[22] The latter compound also develops a maximum at 240 mμ with increasing pH where the change has been suggested to involve ring opening.[23]

The infrared spectra of the cyclic ester and *cis* acid are given in the Experimental Section. They exhibit strong carbonyl absorption at 5.61 and 5.63 μ, respectively. γ-Lactones characteristically absorb at about 5.64 μ. α,β-unsaturation generally increases this to about 5.70 μ.[24] The low-wavelength carbonyl band in the *cis* acid also supports the cyclic acid structure. In summary the nmr, uv, and ir spectra are in accord with a cyclic *cis* acid but with an open carboxylate anion.

Experimental Section

All ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer. Nmr spectra were obtained on a Varian A-60 spectrometer. Infrared spectra were obtained on a Perkin-Elmer Infracord. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory.

trans-β-**Acetylacrylic acid** was prepared from bromolevulinic acid by the method of Wolff.[3] The product was recrystallized from petroleum ether (bp 30–60°)–benzene, mp 125–126°.

Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.47; H, 5.37.

Pseudo-ethyl ester of *cis*-β-**acetylacrylic acid** was prepared from 2-methylfuran by the method reported by Schneck[5] with some modification. 2-Methylfuran (42 g, 0.513 mol), eosin Y (0.635 g), vanadium pentoxide (0.135 g), and 2.35 l. of absolute ethanol were mixed and placed in a water-cooled photoreactor connected to a 3.5-l. gas buret containing oxygen. The light source was a 100-W 20-V unfrosted incandescent lamp (GE No. 100T8/1DC) which was cooled by a rapid stream of air. In addition, the solution was stirred during reaction. After about 65% of the required oxygen had been consumed, the fluorescence due to the eosin Y diminished considerably, and the rate of oxygen consumption was reduced significantly. At this point another 0.62 g of eosin Y was added, and the reaction was allowed to continue until, after 3 days, a total of 11.60 l. (STP) (0.518 mol) of oxygen had been consumed. Five-hundred-milliliter aliquots of the ethanolic solution and 500 ml of saturated aqueous ferrous sulfate were shaken and allowed to remain in contact for 30 min to destroy any remaining peroxides. The resulting mixture was further diluted with 500 ml of water, and then the whole solution was extracted with one 300-ml plus three 100-ml portions of ether. The combined ether extracts were dried over magnesium sulfate. After filtering and removal of the ether, the dark orange residue was distilled: bp 55° (0.5 mm); yield 30 g, 41%. The distillate was purified further by gas chromatography on an Aerograph A-700 instrument (Carbowax 20M column, 0.375 in. × 10 ft; injector, 205°; column, 165°; detector, 205°; collector, 170°; helium flow, 275 cc/min). The material collected was light yellow and showed no impurities by nmr; n^{25}D 1.4432 (reported 1.4360,[5] 1.4460[11]). The purified ester exhibited strong bands at 3.36, 3.40, 3.47, 5.61, 7.90, 8.45, 9.10 (doublet), 9.50 (doublet), and 10.90 μ (doublet).
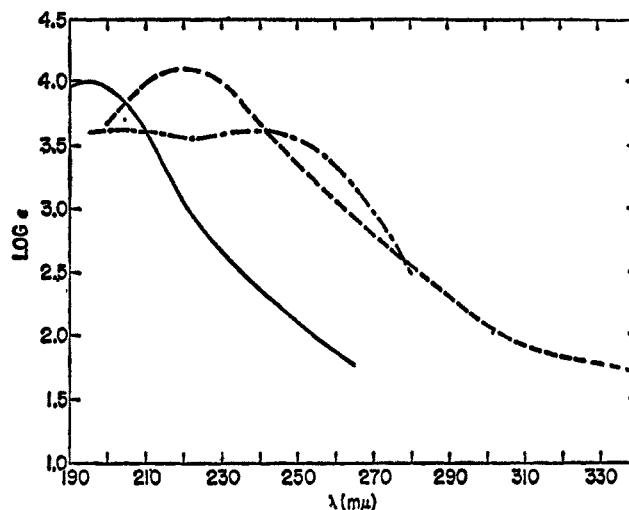
Figure 1.—The ultraviolet spectrum of *cis*-β-acetylacrylic acid (solid line), *trans*-β-acetylacrylic acid (dashed line), and the carboxylate anion of *cis*-β-acetylacrylic acid (dash–dot line).

The nmr and uv spectra are discussed in the Results and Discussion.

Pseudo-*cis*-acetylacrylic Acid.—Hydrochloric acid (50 ml, 1.0×10^{-3} M) was heated in a boiling-water bath. Pseudo-ester (3 ml) was added to the stirred acid solution. Heating and stirring was continued for 8 min after which time the flask was removed and placed in crushed ice and the sitrring continued. After the solution was cool, the pH was adjusted to 7 with sodium carbonate solution and the reaction mixture extracted with three 30-ml portions of ether. The pH was then adjusted to 2.5 with hydrochloric acid and extracted continuously for 18 hr with ether. The ether layer was dried over anhydrous sodium sulfate overnight and filtered. Evaporation of the filtered solvent left a pale yellow liquid which was dried for 3 days over phosphorus pentoxide under vacuum. The pale yellow liquid was molecularly distilled at room temperature. The acid is very hydroscopic and therefore all transfers from this point on were made in a drybox. The distillate was a clear water white liquid. Upon refrigeration in the presence of a drying agent, it crystallized to a white solid. Four successive room temperature sublimations were carried out. It was noticed that after the earlier sublimations a very small yellow liquid residue, probably polymer, remained. This was almost completely absent when the sublimations were carried out in the dark. Integration of nmr methyl signals indicated that the *cis* acid was at least 99% pure. The large melting point range, 33.8–36.4° (sealed tube under nitrogen), is thought to be due to some thermal polymerization of the neat material during heating.

Anal. Calcd for $C_5H_6O_3$: C, 52.63; H, 5.30. Found: C, 52.51, 53.03; Y, 5.30, 5.57.

The nmr and uv spectra are given in the Results and Discussion. The following strong infrared bands were observed: 2.96 (broad, associated hydroxyl), 5.63 (carbonyl), 7.90, 8.35, 9.09, 10.92 μ (doublet).

Kinetic studies were performed with small quantities of ester and acid solution contained in sealed nmr tubes. After mixing the two components, the sealed nmr tube was placed in a refluxing cyclopentane bath (49°) or boiling-water bath (98°) for a specified time. The reaction was quenched by cooling in ice, and the nmr integrals for the methyl peaks of the ester, *trans* acid, and hydrated acid were determined with the aid of a CAT-1024. After satisfactory analyses were obtained the same tube was returned to the bath for an additional reaction period and the process repeated several times until the ester was essentially completely hydrolyzed.

Registry No.—Ia, 14300-71-1; Ic, 2833-26-3; IIa, 2833-21-8; IIIa, 2833-28-5; carboxylate anion of IIa, 16504-49-7.

(22) G. O. Schenck and R. Appel, *Naturwissenschaften*, **33**, 122 (1946).

(23) N. Hellstrom, *Nature*, **187**, 146 (1960).

(24) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, p 186.