TABLE III

MELTING POINTS OF α-SUBSTITUTED CINNAMALDEHYDE DERIVATIVES

Cinnamaldehyde	Semicarbazone		trans-Cinnamic acid	
	Found, °C.	Lit., °C.	Found, °C.	Lit., °C.
Methyl	209–210	207–208[a]	79–80.5[b]	81–82[c]
Ethyl	212–214	216–217[d]	103.5–105.5	104[c]
n-Propyl	179.5–181[e]	...	93–94[e]	93[f]
i-Propyl	193–195	191–192[g]		
Phenyl	199–201	194–195[h]	173–173.5	172[i]

[a] K. von Auwers, *Ber.*, **45**, 2764 (1912). [b] Mixed m.p. 79–81.5. [c] Ref. 8. [d] Y. Deux, *Compt. rend.*, **208**, 1090 (1939). [e] Neut. equiv. calcd.: 190.2; found, 191.5. [f] Ref. 9. [g] P. Shoruigin, V. Isagulyantz, E. Smolyaninova, K. Bogacheva, and S. Skoblinskaya, *J. Russ. Phys. Chem. Soc.*, **62**, 2033 (1930); *Chem. Abstr.*, **25**, 4247 (1931). [h] H. Burton, *J. Chem. Soc.*, 748 (1932). [i] Ref. 7.

in a Vigreux distillation apparatus under a vacuum chosen to give reflux at the desired initial temperature. When reaction was allowed to go to completion before distillation, completion was detected by a leveling off of temperature below the initial temperature. Products were redistilled through an 8-in. or 14-in. Vigreux column.

Analysis.—The components of the reaction product were separated and isolated by the use of a 5 ft. 1/2 in. 20% Ucon polar on firebrick gas chromatographic preparative column operated about 50° below the boiling point of the lowest boiling component in the mixture. The reaction products were then analyzed quantitatively by use of a 5 ft. 1/4 in. Ucon polar on firebrick column. The sample volume–area constants of the components for this column were determined by injecting the pure components previously separated by the preparative column. For qualitative analysis the infrared spectra of the components separated by the preparative column were used. Characteristic olefin bands in the infrared spectra[12,13] of the pure olefin products were used to identify their geometric configuration. Alkylbenzenes were identified by comparison of their spectra to cataloged infrared spectra[14] or spectra of samples prepared by a combination of Friedel-Crafts acylation and Clemmensen reduction.

Isomerization of Alkenyl Benzenes.—Isomerizations were run under nitrogen with 5 cc. alkenyl benzene samples having 0.050 g. of the catalyst mentioned above. Time errors were minimized by inserting the samples in an oil bath maintained at 180–200° and quenching the reaction mixture in an ice bath after the proper time interval. The samples were then analyzed by gas chromatography employing the 1/4 in. Ucon polar column previously mentioned.

Disproportionation of Alkenyl Benzenes.—When allylbenzene, α-methylstyrene and β-ethylstyrene were refluxed under nitrogen with 10 wt. % catalyst, amounts detectable by gas chromatography of *n*-propyl-, isopropyl-, and *n*-butylbenzene respectively were formed. A fraction, b.p. 160–161° (3 mm.) was isolated from the β-ethylstyrene disproportionation.

Anal. Calcd. for $C_{20}H_{22}$: C, 91.54; H, 8.45. Found: C, 91.90; H, 8.43.

Mol. wt. calcd. for $C_{20}H_{22}$: 262. Found by benzene boiling point elevation in a McCoy apparatus capable of an accuracy within 5 to 10%: 270.

Acknowledgment.—This work was supported by a grant from the National Science Foundation.

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Reactions of 2*H*,3*H*-Thieno[3,2-*b*]pyrrol-3-one. V.[1,2] The Reaction of 2,3-Disubstituted Thieno[3,2-*b*]pyrroles with Oxalyl Chloride

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The recent synthesis of 2-carbethoxy-3-hydroxythieno[3,2-*b*]pyrrole (II)[3] by carbethoxylation of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (I)[4] has made available a product which might be expected to be of value in the preparation of 6-substituted thieno[3,2-*b*]pyrrole derivatives. It was shown[3] that the dimeric enol ester II can be converted readily to the corresponding 3-tosyloxy (III) and 3-acetoxy (IV) derivatives; appropriate substitution reactions on these two products, followed by detosylation or deacetylation, decarbethoxylation, and aromatization of the sulfur-containing ring by methods employed earlier,[3,4] should therefore provide routes to 5- or 6-substituted thieno[3,2-*b*]pyrroles which are not readily accessible by direct substitution reactions.[5–8]

In studies still in progress,[8] III has been converted to the 6-formyl and 6-dimethylamino derivatives under the reaction conditions commonly employed in the preparation of analogous 3-substituted indoles. The present report concerns a study of the reactivity of III and IV towards oxalyl chloride, which in the past has found wide application in the synthesis of tryptamine analogs *via* the corresponding 3-acylindoles.[9–24]

(1) For the preceding paper, see G. W. Michel and H. R. Snyder, *J. Org. Chem.*, **27**, 2034 (1962).

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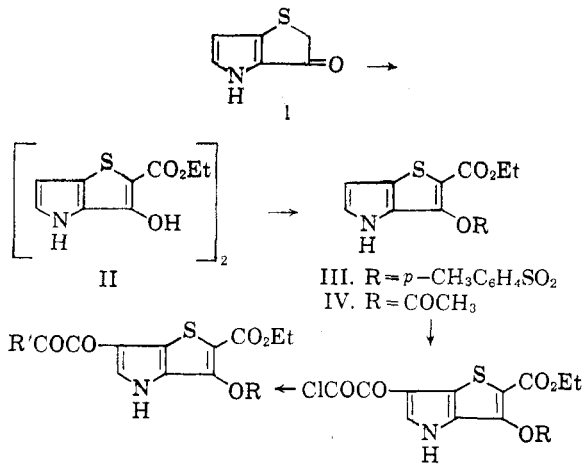

I

II

III. R = p-$CH_3C_6H_4SO_2$
IV. R = $COCH_3$

VII. R = p-$CH_3C_6H_4SO_2$, R′ = OC_2H_5
VIII. R = $COCH_3$, R′ = OC_2H_5
IX. R = H, R′ = OH
X. R = $COCH_3$, R′ = $N(CH_2C_6H_5)_2$
XI. R = H, R′ = $N(CH_2C_6H_5)_2$
XII. R = p-$CH_3C_6H_4SO_2$, R′ = OH

V. R = p-$CH_3C_6H_4SO_2$
VI. R = $COCH_3$

Treatment of IV[25] with an excess of oxalyl chloride in tetrahydrofuran solution resulted in the formation of a yellow acylation product (VI) in good yield. But whereas indole and substituted indoles are known to react with oxalyl chloride in a matter of minutes, compound IV required several hours under comparable conditions for complete reaction. When VI was heated briefly in absolute ethanol, the acid chloride was converted to the ethyl ester VIII in an over-all yield of 64%.

The structure of VIII was confirmed by the infrared spectrum, which showed four characteristic carbonyl absorptions at 1780, 1725, 1695, and 1620 cm.$^{-1}$, tentatively assigned to the *O*-acetyl group, to the two carbethoxyl functions and to the α-keto grouping, respectively, of the substituents. Evidence for substitution in the 6-position was given by the nuclear magnetic resonance (NMR) spectrum[26] of VI and VIII and their comparison with the spectrum of IV. The spectrum of IV exhibits two doublets of equal intensity centered at τ-values of 2.96 and 3.65, which are attributed,[27] respectively, to the α- and β-protons of the pyrrole ring; because of the greater electronic unshielding effect of the nitrogen atom on the α-position, the lower τ-value must be assigned to the 5-proton. In the spectrum of either VI or VIII there is only one peak in the region attributable to resonance of the 5-proton of the pyrrole ring (τ = 1.67 and 1.62, respectively) and no signal appears in the region where the 6-proton would be expected to absorb. The low τ-values of the 5-protons in both VI and VIII, as compared to IV and other 5,6-unsubstituted thieno[3,2-*b*]pyrroles,[28] can be explained by the increased unshielding effect caused by the neighboring side chain.[29] The combined spectral data are consistent only with structures VI and VIII.

Both the acid chloride VI and the ester VIII could be hydrolyzed in the presence of base to form the α-keto acid IX in excellent yield. A solution of dibenzylamine in anhydrous ether very readily reacted with VI at room temperature, affording a practically quantitative yield of the corresponding glyoxylamide for which structure X is indicated. It was found that X can be converted to 2-carbethoxy-3-hydroxy-6-(*N*,*N*-dibenzylglyoxylamido)-thieno[3,2-*b*]pyrrole (XI) in a yield of 91% when heated with an equimolar amount of sodium hydroxide in ethanol, followed by acidification; removal of the *O*-acetyl group with the liberation of the hydroxyl group was proved by the fact that XI gave a positive ferric chloride test. Other evidence for the structure was obtained from chemical analysis and spectral data (see Experimental). Attempts to decarboxylate XI under conditions previously[3,6] applied to other 2-carbethoxy-3-hydroxythieno-[3,2-*b*]pyrrole derivatives have been unsuccessful so far. Results of further studies will be presented at a later date.

2-Carbethoxy-3-tosyloxythieno[3,2-*b*]pyrrole (III) was allowed to react with oxalyl chloride, but in order to effect substitution of III it was necessary to increase the length of reaction time (six days) as compared to that found suitable for the acylation of IV. The resulting glyoxylyl chloride V was isolated without characterization and immediately treated with an excess of 95% ethanol to give the more stable glyoxylic ester VII in 83% yield. Treatment of an ethanolic solution of VII with an equimolar amount of sodium hydroxide resulted in the hydrolysis of the α-keto ester grouping and the formation of the corresponding acid; its composition and infrared spectrum are in accordance with structure XII.

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(25) For preliminary studies, see ref. 6.
(26) The NMR spectra were recorded by Mr. Oliver W. Norton with a Varian Associates high resolution spectrometer (Model V-4300 B with superstabilizer) at a frequency of 60 Mc. per second. Spectra were obtained in 20% solutions of either chloroform or dimethyl sulfoxide (DMSO) with tetramethylsilane as an internal standard. Chemical shifts are expressed as shielding values τ in parts per million as defined by G. V. D. Tiers [*J. Phys. Chem.*, **62**, 1151 (1958)].
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(28) A list of NMR data on a number of 5,6-unsubstituted thieno-[3,2-*b*]pyrroles can be found under references 6, 8, and 27.
(29) Similarly, the 2-proton of indole-3-aldehyde shows resonance at a value which is 1.61 τ-units lower than the value of the α-proton in indole; see also ref. 8 for analogous observations.

Experimental[30]

2-Carbethoxy-3-acetoxythieno[3,2-*b*]pyrrole (IV).—The acetate IV was prepared in 96% yield from 2-carbethoxy-3-hydroxythieno[3,2-*b*]pyrrole (II) according to the procedure described by W. Carpenter and H. R. Snyder.[3] The infrared spectrum[31] (KBr pellet) of IV exhibits major absorptions at 3320 (N–H), 1748 (acetoxy C=O), 1694 (carbethoxy C=O), 1280, 1236, 1220, and 1188 cm.$^{-1}$ (C—O stretch). NMR spectrum (20% $CHCl_3$): τ = 0.76, s[32] (N—H); 2.96, d (5-proton); 3.65, d (6-proton); 5.71, q and 8.67, t (e.p.); 7.75, s (O—Ac).

2-Carbethoxy-3-acetoxythieno[3,2-*b*]pyrrolyl-6-glycoxylyl Chloride (VI).—To a solution of 0.506 g. (2 mmoles) of IV in 10 ml. of anhydrous ether and 2 ml. of anhydrous tetrahydrofuran (THF) at room temperature, 0.40 ml. (4.7 mmoles) of oxalyl chloride was added dropwise (syringe) over a period of 1 min.; the reaction mixture immediately turned yellow. After standing in a tightly stoppered flask for 1.5 hr. at 30°, the solution slowly deposited yellow needles upon scratching. The mixture was allowed to stand at room temperature for another 7 hr. and finally kept at −7° in the refrigerator overnight. The resulting yellow crystals of VI were collected, rapidly washed with anhydrous ether and dried *in vacuo* over phosphorus pentoxide and potassium hydroxide; 0.57 g. (83% yield), b.p. 178–180° dec. A sample of VI was analyzed without further purification. Infrared (KBr pellet): 3380 (N—H), 1780 (acetoxy C=O), 1765, and 1660 (CO—CO—Cl), 1695 cm.$^{-1}$ (carbethoxy C=O). NMR (20% DMSO): τ = −3.13, s (N—H); 1.67, d (5-proton); 5.74, q and 8.69, t (e.p.).[33]

Anal. Calcd. for $C_{13}H_{10}NO_6SCl$: C, 45.42; H, 2.93; N, 4.07. Found: C, 45.69; H, 3.21; N, 3.98.

2-Carbethoxy-3-acetoxy-6-ethoxyalylthieno[3,2-*b*]pyrrole (VIII).—To a solution of 0.506 g. (2 mmoles) of IV in 10 ml. of anhydrous ether and 2 ml. of anhydrous THF was slowly added at room temperature 0.40 ml. (4.7 mmoles) of oxalyl chloride as described for the preparation of VI. The reaction mixture was allowed to stand at room temperature for 2.5 hr., after which time the glyoxylyl chloride VI started to crystallize as yellow needles. After the reaction mixture had been stored at 25° for 20 hr., the bright yellow crystals were filtered, rapidly washed with a small amount of anhydrous ether and dried for 2 hr. *in vacuo* over phosphorus pentoxide and potassium hydroxide.

The acid chloride VI thus obtained was converted into the ethyl ester VIII by dissolving in 30 ml. of hot absolute ethanol and allowing the solution to cool slowly to room temperature over a period of 3 hr. After the mixture had been stored at 0–5° for 10 hr., the yellow crystals were filtered and dried *in vacuo*. The yield of VIII was 0.40 g. (57%), m.p. 201–203°. An additional amount of the ester VIII was obtained upon concentration of the ether–THF mother liquor under reduced pressure and treatment of the crude, well dried acid chloride VI with 6 ml. of hot absolute ethanol. On cooling at 0–5° for 9 hr., the solution deposited 0.05 g. of light yellow crystals, m.p. 198–201°, bringing the total yield of ester VIII to 0.45 g. (64%). An analytical sample was prepared by recrystallization from absolute ethanol to give bright yellow scales, m.p. 202–204°. Infrared (KBr pellet): 3180 (N—H), 1780 (acetoxy C=O), 1725 and 1620 (CO—$CO_2C_2H_5$), 1695 cm.$^{-1}$ (carbethoxy C=O). (20% DMSO): τ = −2.95, s (N—H); 1.62, d (5-proton); 5.57, q and 8.62, t, 5.71, q, and 8.70, t (e.p.).[33]

Anal. Calcd. for $C_{15}H_{15}NO_7S$: C, 50.98; H, 4.28; N, 3.97. Found: C, 50.80; H, 4.39; N, 4.10.

2-Carbethoxy-3-acetoxy-6-(*N*,*N*-dibenzylglyoxylamido)thieno[3,2-*b*]pyrrole (X).—To a magnetically stirred solution of 0.57 g. (2.9 mmoles) of dibenzylamine in 25 ml. of anhydrous ether was added at room temperature 0.45 g. (1.3 mmoles) of the crude acid chloride VI in small portions. Reaction took place immediately, indicated by loss of the yellow color of the suspension. Vigorous stirring was continued for 3 hr. and the resulting voluminous, colorless precipitate of X was collected, washed with ether and water, and dried in a vacuum desiccator. There was obtained 0.66 g. (96%, based on monohydrate) of X as colorless crystals, m.p. 154–156°. An analytical sample, prepared by recrystallization from ethanol–water and by drying over phosphorus pentoxide at 78° (0.025 mm.) for 16 hr., formed colorless needles, m.p. 157–158°. (It was found that a purified sample which was dried *in vacuo* at room temperature for 14 hr. had the composition of the monohydrate.) Infrared (KBr pellet): 3340–3400 (broad, N—H), 1785 (acetoxy C=O), 1713 (carbethoxy C=O), 1646 and 1630 cm.$^{-1}$ (CO—CO—N=).

Anal. Calcd. for $C_{27}H_{24}N_2O_6S$: C, 64.26; H, 4.79; N, 5.56. Found: C, 64.07; H, 4.76; N, 5.56.

2-Carbethoxy-3-hydroxy-6-(*N*,*N*-dibenzylglyoxylamido)thieno[3,2-*b*]pyrrole (XI).—To a solution of 252 mg. (0.5 mmole) of the amide X in 6 ml. of 95% ethanol was added 0.2 ml. (1 mmole) of 5 *N* sodium hydroxide with swirling. The resulting yellow solution was allowed to stand at room temperature for 5.5 hr.; after this time 5 ml. of water was added, and the mixture was neutralized with ice-cold 6 *N* hydrochloric acid, whereupon a voluminous, colorless precipitate appeared. After cooling for 1 hr. in an ice-water bath, the product was collected, washed with a small amount of water, and dried *in vacuo* overnight. The product, m.p. 171–172° weighed 0.21 g. (91%). An analytical sample of XI was prepared by dissolving the product in a minimum amount of hot 95% ethanol, gradually adding water until a slightly turbid solution was obtained, and finally cooling overnight in a refrigerator at 5°. The pure amide XI crystallized as colorless, felt-like needles, m.p. 172–173°. A solution of XI in 95% ethanol formed an intense dark blue-green color with aqueous ferric chloride solution.[34] Infrared (KBr pellet): 1645 (carbethoxy C=O), 1620–1635 cm.$^{-1}$ (broad, CO—CO—N=); (10% $CHCl_3$): 3170 (N—H), 1655 (sh, carbethoxy C=O), 1625–1640 cm.$^{-1}$ (broad, CO—CO—N=).

Anal. Calcd. for $C_{25}H_{22}N_2O_5S$: C, 64.92; H, 4.80; N, 6.05. Found: C, 64.89; H, 4.90; N, 6.08.

2-Carbethoxy-3-tosyloxy-6-ethoxylthieno[3,2-*b*]pyrrole-(VII).—To a solution of 0.20 g. (0.55 mmole) of 2-carbethoxy-3-tosyloxythieno[3,2-*b*]-pyrrole (III)[3] in 25 ml. of anhydrous ether was added at room temperature 0.1 ml. (1.2 mmoles) of oxalyl chloride. The yellow solution was allowed to stand in a stoppered flask (exclusion of moisture) at 25° for 6 days and was then evaporated under vacuum to a yellow foam-like residue, which was dissolved in 3 ml. of 95% ethanol–water (1:1). After standing at room temperature for 1 hr., the mixture was refrigerated for 2 hr., and the resulting colorless solid was filtered and washed with cold 95% ethanol. After drying *in vacuo* overnight, the product, m.p. 152–154°, weighed 0.21 g. (83%). An analytical specimen, recrystallized from absolute ethanol, formed long colorless needles and had the same melting point. Infrared (KBr pellet): 3290 (N–H), 1752 and 1658 (CO–$CO_2C_2H_5$), 1675 (carbethoxy C=O), 1390 and 1172 (—O—SO_2—), 1260 cm.$^{-1}$ (C–O stretch).

Anal. Calcd. for $C_{20}H_{19}NO_8S$: C, 51.60; H, 4.12; N, 3.01. Found: C, 51.50; H, 4.07; N, 3.09.

(30) Melting points are uncorrected. Microanalyses were performed by Mr. J. Nemeth and his associates, University of Illinois.

(31) The infrared spectra were obtained from a Perkin-Elmer Model 21B spectrophotometer by Mr. D. Johnson and Miss D. Wood.

(32) The abbreviations used in describing NMR data are: s, singlet; d, doublet; t, triplet; q, quartet; (e.p.), ethyl group protons.

(33) The expected band for —CO—CH_3 is not detectable because of the resonances of the solvent (DMSO) in this region.

(34) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 4th ed., 1956, p. 112.

2-Carbethoxy-3-tosyloxythieno[3,2-*b*]pyrrolyl-6-glyoxylic Acid (XII).—To a suspension of 0.139 g. (0.3 mmole) of the glyoxylic ester VII in 5 ml. of 95% ethanol was added at room temperature 0.12 ml. (0.6 mmole) of 5 *N* sodium hydroxide solution, whereupon a clear, yellow solution was formed. After standing at 25° for 1.5 hr., a slightly yellow, amorphous precipitate began to separate; the reaction mixture was allowed to stand at room temperature 4 hr., after which time 3 ml. of water was added. The resulting clear, orange solution was then neutralized with ice-cold 6 *N* hydrochloric acid and concentrated under reduced pressure to about 2 ml. The crude acid XII, precipitated as an oily product, solidified upon cooling and scratching to form light tan crystals. The product was filtered, washed with water, and dried *in vacuo* over phosphorus pentoxide, affording 0.10 g. (75%) of the crude acid XII. Purification of XII was achieved by dissolving the crude product in 2.5 ml. of hot 95% ethanol and adding 8 ml. of water until the solution remained faintly turbid. Upon slow cooling over a period of 11 hr., the pure acid XII crystallized in slightly tan, cotton-like crystals, m.p. 215–217 dec.; the material contained 0.5 mole of water of crystallization, which was not removed by drying overnight at 78° (0.025 mm.). Infrared (KBr pellet) 3190 (N–H), 1720 and 1645, sh (CO–CO_2H), 1663 (carbethoxy C=O), 1390 and 1174 (—O—SO_2—), 1268 cm.$^{-1}$ (C—O stretch).

Anal. Calcd. for $C_{18}H_{15}NO_8S_2 \cdot 1/2H_2O$: C, 48.42; H, 3.61; N, 3.14. Found: C, 48.58; H, 3.56; N, 3.14.

2-Carbethoxy-3-hydroxythieno[3,2-*b*]pyrrolyl-6-glyoxylic Acid (IX). (A) **From 2-Carbethoxy-3-acetoxy-6-ethoxyalylthieno[3,2-*b*]pyrrole (VIII).**—To a suspension of 0.27 g. (0.76 mmole) of the ester VIII in 10 ml. of 95% ethanol and 2 ml. of water was added at room temperature 0.612 ml. (3.06 mmoles) of 5 *N* sodium hydroxide, and the resulting orange-colored solution was heated on a steam bath under reflux for 10 min. The solution was allowed to stand at room temperature for 13 hr., after which time the precipitated orange solid (Na salt) was dissolved by addition of 11 ml. of water to the mixture. After neutralization of the excess base with ice-cold 6 *N* hydrochloric acid the clear solution was poured into 10 ml. of ice water and the colorless, microcrystalline precipitate was collected, washed with water, and dried *in vacuo*. The yield of crude IX was 0.22 g. (96%). An analytical sample, obtained by very slow cooling of a solution of IX in a minimum amount of ethanol–water (1:3), formed fluffy, colorless needles, which turned bright yellow upon drying *in vacuo*, m.p. (on a preheated hot stage) 244–246° dec., darkening at 239°. Two additional recrystallizations from ethanol–water did not affect the melting point or infrared spectrum. The product was obtained as a monohydrate after drying for 16 hr. over phosphorus pentoxide *in vacuo* (0.05 mm.) at room temperature. A solution of IX in 95% ethanol gave a positive ferric chloride test[34] (intense dark green color). Infrared (KBr pellet): 3380 (broad, O—H), 3260 (N—H), 1715 and 1624 (CO—CO_2H), 1658 (carbethoxy C=O), 1265 and 1237 cm.$^{-1}$ (C—O stretch).

Anal. Calcd. for $C_{11}H_9NO_6S \cdot H_2O$: C, 43.85; H, 3.86; N, 4.65. Found: C, 43.72; H, 3.84; N, 4.62.

(B) **From 2-Carbethoxy-3-acetoxythieno[3,2-*b*]pyrrolyl-6-glyoxylyl Chloride (VI).**—To a suspension of 0.343 g. (1 mmole) of glyoxylyl chloride VI in 20 ml. of water was added 1 ml. (5 mmoles) of 5 *N* sodium hydroxide at room temperature. The resulting clear orange solution was heated on a steam bath for 15 min., then allowed to stand at room temperature for 23 hr. and finally neutralized with ice-cold 6 *N* hydrochloric acid. The mixture was chilled for 30 min. and the pale yellow precipitate was collected, washed with a small amount of water, and dried *in vacuo;* wt. 0.28 g. (93%). Purification of the crude product by the method given under procedure A afforded yellow needles, m.p. 243–245° dec. A mixture melting point determination and the infrared spectrum (KBr) confirmed the identity of the product with the acid IX prepared according to procedure A.

The Structure of Xanthinin

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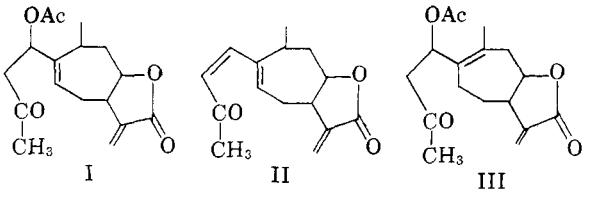
The structures of xanthinin (I) and xanthatin (II), sesquiterpene lactones derived from *Xanthium pennsylvanicum* (cocklebur), were first proposed by Deuel and Geissman in 1957.[1] In the same year, Dolejš and his collaborators[2] described their studies on these compounds and agreed that the structure for II was correct, but proposed the structure III for xanthinin. Structures III and I differ only in the position assigned to one of the double bonds. In the work of Deuel and Geissman the assignment was made on the basis of the characteristic infrared absorption associated with the —CH=$\overset{|}{C}$— grouping, while the Czech workers arrived at the alternative conclusion from the results of an oxidative degradation.



The structure of xanthinin has now been reexamined with the aid of NMR. The results are clear and unequivocal, and substantiate the structure (I) originally put forward by Deuel and Geissman. The relevant portions of the NMR spectrum are shown in Fig. 1. The presence of the secondary

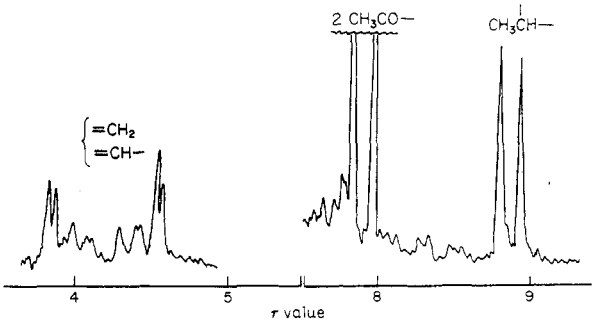


Fig. 1.—NMR spectrum of xanthinin (60 mc. $CDCl_3$), shown for τ = 4 to 5, 8 to 9 regions.

methyl group is shown by the symmetrical doublet at τ = 8.9. No methyl group singlet of the type CH_3—C=C, as would be required for structure III,

(1) P. G. Deuel and T. A. Geissman, *J. Am. Chem. Soc.*, **79**, 3778 (1957).

(2) L. Dolejš, V. Herout, and F. Šorm, *Chem. Listy*, **51**, 1521 (1957); *Coll. Czech. Chem. Commun.*, **23**, 504 (1958).