a small portion to 2,5-diacetoxy-1,4-dioxane in a manner similar to that used by Summerbell and Rochen[24] to convert 2,5-dibromo-1,4-dioxane to the same derivative.

Summary

1. The reported synthesis by Lewis, Nierenstein and Rich of 2,5-diphenyl-1,4-dioxane melting at 103° is questioned.
2. Aryl dioxanes are not hydrolyzed by refluxing with aqueous alkaline solutions as previously reported.
3. The reaction of phenylmagnesium bromide with 2,5-dichlorodioxane gives rise to a pair of isomers melting at 120–121° and 173°. Evidence is presented that these are *cis*- and *trans*-2,5-diphenyl-1,4-dioxane, respectively.
4. 2,3-Diphenyl-1,4-dioxane reacts with anhydrous hydrogen bromide to yield stilbene dibromide, and with an acetic acid solution of hydrogen bromide to yield stilbene.
5. A practical synthetic method is reported for obtaining 2,5-dichloro-1,4-dioxane. A mechanism for the reaction is postulated.

EVANSTON, ILLINOIS RECEIVED AUGUST 15, 1949

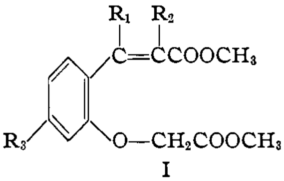
[24] Summerbell and Rochen, THIS JOURNAL, **63**, 3241 (1941).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

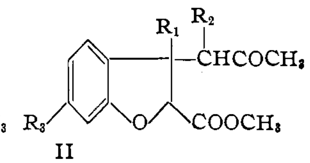
The Internal Michael Reaction. II. Formation of Arylated Coumarans, of an Indoline, a Dihydrothionaphthene and a Hydrocarbostyril[1]

BY C. F. KOELSCH AND C. R. STEPHENS, JR.

When ethyl coumarinate or a related ester (I) with an alkyl substituent on either or both the α- and β-carbons is treated with sodium alkoxide, an internal Michael reaction takes place, and a coumaran (II) is formed.[2]

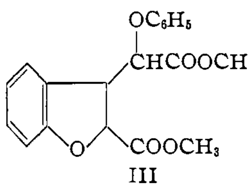


I

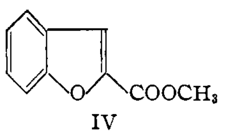


II

It has now been found that the same reaction can be effected with I when R_1 or R_2 is a phenyl. The first case (I, $R_1 = C_6H_5$, $R_2 = H$, $R_3 = CH_3$) is noteworthy because no example of the Michael reaction has been discovered previously in which the acceptor bears two aryl groups on its β-carbon. The second case ($R_1 = H$, $R_2 = C_6H_5$, $R_3 = H$) is of interest because the product of the reaction, III, tends to undergo a retrograde Michael reaction, in which it yields methyl phenylacetate and methyl coumarilate (IV).

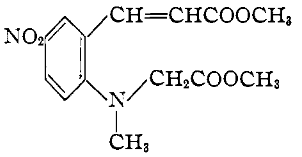


III

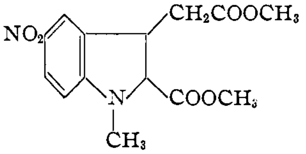


IV

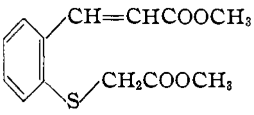
It has also been found that the internal Michael reaction can be brought about in methyl 2-methylamine-5-nitrocinnamate-N-acetate (V) and in methyl *o*-mercaptocinnamate-S-acetate (VII). From these compounds, the indoline VI and the dihydrothionaphthene VIII are formed.



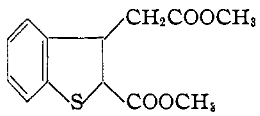
V



VI

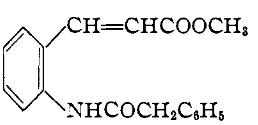


VII

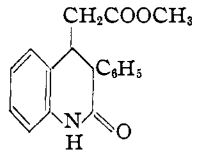


VIII

An internal Michael reaction takes place when methyl *o*-phenylacetylaminocinnamate (IX) is treated with sodium methoxide, and the hydrocarbostyril X is formed.



IX

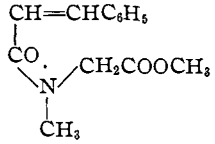


X

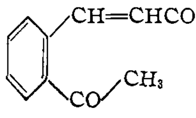
Two substances in which an internal Michael reaction appeared possible have been investigated with negative results. One of them, methyl cinnamoylsarcosinate (XI), is recovered unchanged after it has been treated with sodium methoxide. The other, methyl *o*-acetyl-allocinnamate (XII), undergoes reaction, but the product is not homogeneous, and has furnished no methyl 1-hydrindone-3-acetate or other pure substance.

[1] From the Ph.D. Thesis of Charles Robert Stephens, Jr., October, 1949.

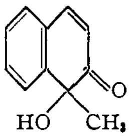
[2] Koelsch, THIS JOURNAL, **67**, 569 (1945).



XI



XII



XIII

Preparation of the substituted cinnamic esters, I (R_1 = C_6H_5, R_2 = H) and I (R_1 = H, R_2 = C_6H_5), was accomplished by treating 3- and 2-phenylcoumarin with alkali and chloroacetic acid, and by esterifying the resulting dibasic acids.

Preparation of V involved treatment of 2-chloro-5-nitrobenzaldehyde with sarcosine, to form N-(2-formyl-4-nitrophenyl)-sarcosine, conversion of this to the corresponding cinnamic acid (V, COOH instead of $COOCH_3$) by the Doebner reaction, and then esterification. Choice of V as an example for indoline synthesis was made after it had been found that neither *o*-aminocinnamic acid nor its ester could be alkylated with chloroacetic acid or ethyl chloroacetate, that *o*-iodocinnamic acid and glycine yielded carbostyril-1-acetic acid, and that *o*-chloro- or *o*-iodocinnamic acid and sarcosine furnished *o*-methylaminocinnamic acid-N-acetic acid in only small amount.

Preparation of VII was effected from diazotized *o*-aminocinnamic acid and thioglycolic acid, and in better yield from *o*-mercaptocinnamic acid and chloroacetic acid. An attempt to obtain S-(2-formyl-4-nitrophenyl)-thioglycolic acid from 2-chloro-5-nitrobenzaldehyde, thioglycolic acid, and aqueous alcoholic potassium carbonate gave only 5-nitro-2-thionaphthenecarboxylic acid[3] a result of some interest in that it indicates a strong activation of a methylene group by an attached sulfur atom.

Preparation of XII was accomplished by oxidation of 1-methyl-1,2-naphthoquinol (XIII) with periodic acid. Failure of the internal Michael reaction with XII raised some doubt as to the structure of the substance, but support for the structure given was found in oxidation with hypoiodite, which yielded known *o*-carboxycinnamic acid.

Experimental

Coumaran Syntheses. II, R_1 = C_6H_5, R_2 = H, R_3 = CH_3.—Condensation of *m*-cresol with ethyl benzoylacetate failed with 96% sulfuric acid, but when 90% sulfuric acid was used, a 25% yield of 7-methyl-4-phenylcoumarin[4] was obtained. A solution of 12 g. of this coumarin in a hot mixture of 50 ml. of alcohol and 50 ml. of 10% sodium hydroxide was treated with 15 g. of sodium chloroacetate in 20 ml. of water. The mixture was distilled for one hour, the distillate (50 ml.) being discarded. The residue was then treated with 14 g. of chloroacetic acid and 14 g. of sodium hydroxide and boiled for one hour. It was then acidified and allowed to cool. The precipitate was removed and stirred with dilute soda, giving 3 g. of unchanged coumarin and 9.5 g. (82%) of **4-methyl-β-phenylcoumarinic acid-O-acetic acid**, transparent needles from aqueous acetic acid that effluoresced when they were dried at 100°; m. p. 181–183° with gas evolution.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.2. Found: C, 69.2; H, 5.4.

The **methyl ester** (I, R_1 = C_6H_5, R_2 = H, R_3 = CH_3), obtained in 74% yield with methanol and sulfuric acid, formed colorless needles from ether–ligroin, m. p. 87–88°.

Anal. Calcd. for $C_{20}H_{20}O_5$: C, 70.6; H, 5.9. Found: C, 70.7; H, 6.1.

A mixture of 2 g. of the ester with 4 drops of a concentrated solution of sodium methoxide in methanol was warmed to 60°; the temperature of the mixture then rose spontaneously from this point to 90° during four minutes. There was obtained 1.6 g. (80%) of **methyl 3-carbomethoxymethyl-6-methyl-3-phenyl-2,3-dihydrocoumarilate** (II, R_1 = C_6H_5, R_2 = H, R_3 = CH_3), b. p. 173–175° at 1 mm.; crystallization from ether–ligroin gave prisms, m. p. 89–90°. The product depressed the m. p. of the starting material, and unlike the latter was stable to permanganate in acetone.

Anal. Calcd. for $C_{20}H_{20}O_5$: C, 70.6; H, 5.9. Found: C, 70.8; H, 6.3.

Saponification gave **3-carboxymethyl-6-methyl-3-phenyl-2,3-dihydrocoumarilic acid**, micro-needles from ethyl acetate–ligroin, m. p. 204–206°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.2. Found: C, 69.1; H, 5.4.

II, R_1 = H, R_2 = C_6H_5, R_3 = H.—Twenty grams of 3-phenylcoumarin[5] treated with sodium hydroxide and excess sodium chloroacetate yielded 2.5 g. of unchanged 3-phenylcoumarin and 22.5 g. (93%) of **α-phenylcoumarinic acid-O-acetic acid**, colorless needles from aqueous acetic acid, m. p. 197–198°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.4; H, 4.7; neut. equiv., 149. Found: C, 68.5; H, 4.8; neut. equiv., 148.

When 12 g. of the acid was boiled for five hours with 50 ml. of methanol and 6 ml. of sulfuric acid, part of it was incompletely esterified. **Methyl α-phenylcoumarinic acid-O-acetate**, separated with aqueous soda, formed long matted needles (5 g.) from methanol, m. p. 144–145°.

Anal. Calcd. for $C_{18}H_{16}O_5$: C, 69.2; H, 5.2. Found: C, 68.8; H, 5.3.

The neutral **methyl ester** (I, R_1 = H, R_2 = C_6H_5, R_3 = H) formed coarse needles (5.5 g.) from ether–ligroin, m. p. 72°.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6. Found: C, 69.9; H, 5.8.

A mixture of 2.1 g. of the neutral ester with three drops of sodium methoxide solution became red when it was warmed to 60°, and its temperature then rose spontaneously to 105°. From it were then obtained 0.9 g. of a mixture of methyl coumarilate and methyl phenylacetate, b. p. 90–140° at 2 mm., and 0.9 g. of **methyl 3-(α-carbomethoxybenzyl)-2,3-dihydrocoumarilate** (II, R_1 = H, R_2 = C_6H_5, R_3 = H), b. p. 195–197° at 2 mm. Crystallization of the latter substance from ether–ligroin gave prisms, m. p. 124–125°.

Anal. Calcd. for $C_{19}H_{18}O_5$: C, 69.9; H, 5.6. Found: C, 69.7; H, 5.6.

Saponification of II gave **3-(α-carboxybenzyl)-2,3-dihydrocoumarilic acid**, colorless plates from dilute acetic acid, m. p. 162–163°.

Anal. Calcd. for $C_{17}H_{14}O_5$: C, 68.4; H, 4.7. Found: C, 68.6; H, 5.0.

When 1 g. of II was heated at 85–120° for twenty

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[3] Fieser and Kennelly, This Journal, 57, 1611 (1935).

[4] *Cf.* Robertson, Waters and Jones, *J. Chem. Soc.*, 1688 (1932).

[5] Borsche and Streitberger, *Ber.*, 37, 3165 (1904).

minutes with a catalytic amount of sodium methoxide, it was cleaved completely to methyl coumarilate and methyl phenylacetate. This mixture, and the one formed during the preparation of II, were separated by fractional distillation. Phenylacetic acid was identified as a saponification product of one ester. **Methyl coumarilate** had b. p. 130–140° at 2 mm. and formed crystals, m. p. 54–55°; it was identified by comparison with a sample prepared from known coumarilic acid.[6]

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.2; H, 4.6. Found: C, 67.8; H, 4.9.

Indoline Synthesis.—A mixture of 25 g. of 2-chloro-5-nitrobenzaldehyde,[7] 75 ml. of alcohol, 35 g. of crude sodium sarcosinate (from saponification of ethyl sarcosinate),[8] 11.5 g. of potassium carbonate and a little copper acetate was boiled for two and one-half hours. The alcohol was then removed and replaced with water, and the product (21.3 g., 65%), m. p. 135–139°, was separated from neutral impurities by solution in soda. Crystallization from dilute acetic acid gave pure **N-(2-formyl-4-nitrophenyl)-sarcosine**, yellow prisms, m. p. 149°.

Anal. Calcd. for $C_{10}H_{10}N_2O_5$: C, 50.4; H, 4.2. Found: C, 50.8; H, 4.3.

The **2,4-dinitrophenylhydrazone** formed an orange-red powder from alcohol–ethyl acetate, m. p. 209–210°.

Anal. Calcd. for $C_{16}H_{14}N_6O_8$: C, 45.8; H, 3.6. Found: C, 45.7; H, 3.3.

When a mixture of 3.5 g. of the aldehyde, 7 g. of malonic acid, 8 ml. of pyridine and 8 drops of piperidine was heated at 100° for two hours, there was obtained 3.6 g. (87%) of **2-methylamino-5-nitrocinnamic acid-N-acetic acid**; yellow prisms from 70% acetic acid, m. p. 211–212° dec.

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.4; H, 4.3. Found: C, 51.5; H, 4.4.

The **methyl ester** (V), obtained in 82% yield by Fischer esterification, formed yellow plates from ether; m. p. 79°.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.5; H, 5.2. Found: C, 54.5; H, 5.4.

An exothermic reaction took place when a solution of 5 g. of V in 10 ml. of benzene was treated with a few drops of sodium methoxide in methanol. The product was washed with dilute acetic acid and with soda, and then distilled, giving 3 g. of **methyl 2-carbomethoxy-1-methyl-5-nitroindoline-3-acetate, VI**, b. p. 210–220° at 1.5 mm. with some decomposition.

Anal. Calcd. for $C_{14}H_{16}N_2O_6$: C, 54.5; H, 5.2. Found: C, 55.3; H, 5.3.

Saponification in dilute methanol gave the corresponding acid; yellow needles from methanol, m. p. 175–177° dec.

Anal. Calcd. for $C_{12}H_{12}N_2O_6$: C, 51.4; H, 4.3. Found: C, 51.4; H, 4.5.

Some miscellaneous experiments on indoline synthesis involved the preparation of the following new compounds. **Carbostyril-N-acetic acid**, crystals from acetic acid, m. p. 267–268° dec., was obtained when a mixture of 2.7 g. of *o*-iodocinnamic acid,[9] 0.75 g. of glycine, 1.3 g. of potassium hydroxide, 0.7 g. of potassium carbonate and a little copper chloride was heated in 1.5 ml. of water for four hours at 120–125°.

Anal. Calcd. for $C_{11}H_9NO_3$: C, 65.0; H, 4.5. Found: C, 64.3; H, 4.7.

A similar experiment involving *o*-chlorocinnamic acid and sarcosine gave a 10.5% yield of ***o*-methylaminocinnamic acid-N-acetic acid**; yellow prisms from dilute alcohol, m. p. 143–144°.

Anal. Calcd. for $C_{12}H_{13}NO_4$: C, 61.3; H, 5.6. Found: C, 61.6; H, 5.7.

Treatment of 2-chloro-5-nitrobenzaldehyde with malonic acid in pyridine and piperidine gave a 70% yield of **2-chloro-5-nitrocinnamic acid**; amber needles from acetic acid, m. p. 220–221° dec.

Anal. Calcd. for $C_9H_6ClNO_4$: C, 47.5; H, 2.6. Found: C, 47.8; H, 2.8.

Reduction of 5 g. of 2-methylamino-5-nitrocinnamic acid-N-acetic acid by heating it for three hours with 7 g. of iron filings in 30 ml. of 5% acetic acid gave 2.5 g. of **5-amino-2-methylaminocinnamic acid-N(2)-acetic acid**, tan cubes from water containing hydrosulfite, m. p. 170° dec.

Anal. Calcd. for $C_{12}H_{14}N_2O_4$: C, 57.6; H, 5.6. Found: C, 57.7; H, 5.7.

The methyl ester of the preceding acid was obtained by Fischer esterification as an oil which was very sensitive to air. The **methyl ester dihydrochloride** formed colorless needles from methanol, m. p. 178–180° dec.

Anal. Calcd. for $C_{14}H_{18}N_2O_4 + 2HCl$: C, 47.9; H, 5.7. Found: C, 48.3; H, 6.0.

Dihydrothionaphthene Synthesis.—When a solution of 9 g. of *o*-aminocinnamic acid in 90 ml. of 30% sulfuric acid was diazotized, filtered and then treated with 8 ml. of thioglycolic acid, a crystalline diazosulfide precipitated. This was dried and mixed with 50 ml. of ethyl acetate. The suspension was boiled for ninety minutes and then distilled to dryness under reduced pressure. A solution of the residue in dilute potassium carbonate was acidified slowly, the red-black tarry material deposited at first being discarded. There was obtained 6 g. of crude colorless product. Esterification with methanol and sulfuric acid gave 3.8 g. of a mixture, b. p. 100–180° at 5 mm., of approximately equal amounts of methyl cinnamate and **methyl *o*-mercaptocinnamate-S-acetate** (VII), b. p. 168–175° at 4 mm. The latter formed colorless crystals from ether–ligroin, m. p. 42–43°.

Anal. Calcd. for $C_{13}H_{14}O_4S$: C, 58.6; H, 5.3. Found: C, 58.4; H, 5.2.

The same compound was obtained from *o*-aminocinnamic acid (9.3 g.) through the *o,o'*-disulfide[10] (5.6 g.). Reduction of this with 2 g. of zinc dust and excess sodium hydroxide, then treatment of the sodium salt of the thiol (not isolated) with 6 g. of chloroacetic acid gave the crude acid; esterification gave the methyl ester, 4.4 g.

Saponification of the ester gave ***o*-mercaptocinnamic acid-S-acetic acid**; yellow micro crystals from acetic acid, m. p. 237–239° dec.

Anal. Calcd. for $C_{11}H_{10}O_4S$: C, 55.4; H, 4.2. Found: C, 55.2; H, 4.4.

When 2 g. of VII at 65° was treated with 4 drops of sodium methoxide in methanol, the mixture darkened and became hot (110°). There was obtained 1.5 g. of **methyl 2-carbomethoxy-2,3-dihydrothionaphthene-3-acetate** (VIII), b. p. 160–162° at 4 mm.

Anal. Calcd. for $C_{13}H_{14}O_4S$: C, 58.6; H, 5.3. Found: C, 58.9; H, 5.2.

Saponification gave mainly **2-carboxy-2,3-dihydrothionaphthene-3-acetic acid**; colorless prisms from water, m. p. 143–144°.

Anal. Calcd. for $C_{11}H_{10}O_4S$: C, 55.4; H, 4.2. Found: C, 55.4; H, 4.4.

The saponification gave also a minute amount of a water-insoluble substance, perhaps the anhydride of the acid; pink needles from aqueous acetic acid, m. p. 238–240°.

Anal. Calcd. for $C_{11}H_8O_3S$: C, 60.1; H, 3.6. Found: C, 60.5; H, 3.7.

Hydrocarbostyril Synthesis.—**Methyl *o*-Phenylacetylaminocinnamate** (IX) was obtained in 59% yield from methyl *o*-nitrocinnamate by reduction with stannous chloride and acylation of the crude amino ester with aqueous soda and phenylacetyl chloride at 0°. When pure methyl *o*-aminocinnamate was used, 2 g. of it in 20 ml. of

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[6] Fuson, Kneisley and Kaiser, "Organic Syntheses," Vol. 24, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 33.

[7] Erdmann, *Ann.*, **272**, 153 (1893).

[8] Staudt, *Z. physiol. Chem.*, **146**, 286 (1925); *C.A.*, **19**, 3254 (1925).

[9] Gabriel and Herzberg, *Ber.*, **16**, 2037 (1883).

[10] Chmelewsky and Friedländer, *ibid.*, **46**, 1903 (1913).

ether was stirred with 15 ml. of iced 10% sodium carbonate while 2 g. of phenylacetyl chloride was added slowly. In the latter experiment there was obtained 2.3 g. (67%) of product, colorless needles from toluene, m. p. 140°.

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.2; H, 5.8. Found: C, 73.1; H, 6.0.

Saponification of a portion of the ester with aqueous alcoholic sodium hydroxide gave ***o*-phenylacetylaminocinnamic acid**; colorless needles from acetic acid, m. p. 232–234°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.6; H, 5.4; neut. equiv., 281. Found: C, 72.3; H, 5.8; neut. equiv., 281.

Treatment of IX with a catalytic amount of sodium methoxide effected no change. But when a solution of 1.4 g. of the ester in 10 ml. of methanol containing 0.5 g. of sodium methoxide was boiled for two hours, cyclization was effected. There was obtained 1 g. (71%) of **methyl 3-phenylhydrocarbostyril-4-acetate (X)**; colorless rosettes from toluene–ligroin, m. p. 140–141.5°.

Anal. Calcd. for $C_{16}H_{17}NO_3$: C, 73.2; H, 5.8. Found: C, 73.2; H, 6.0.

Saponification gave **3-phenylhydrocarbostyril-4-acetic acid**, colorless needles from dilute alcohol, m. p. 207–208°.

Anal. Calcd. for $C_{17}H_{15}NO_3$: C, 72.6; H, 5.4. Found: C, 72.5; H, 5.6.

Methyl Cinnamoylsarcosinate (XI).—Ten grams of sarcosinonitrile[8] was added dropwise to a stirred mixture of 50 ml. of iced 20% aqueous sodium carbonate and a solution of 17 g. of cinnamoyl chloride in ether. The resulting **cinnamoylsarcosinonitrile** (17.5 g., 87%) was removed by filtration and crystallized from toluene, giving colorless needles, m. p. 92–93°.

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 72.0; H, 6.0. Found: C, 72.3; H, 6.4.

The nitrile reacted with sodium methoxide to form sodium cyanide.

When a solution of 7 g. of the nitrile in 30 ml. of methanol was saturated with hydrogen chloride and then warmed on a steam-bath for thirty minutes, it furnished **the methyl ester, XI.** The product, isolated by evaporation, treatment with aqueous soda and ether, and distillation, was an oil, b. p. 177–180° at 3 mm., which solidified and then formed colorless plates from ether–ligroin; m. p. 59–60°, yield 5.5 g., 67%.

Anal. Calcd. for $C_{13}H_{15}NO_3$: C, 67.0; H, 6.5. Found: C, 67.3; H, 6.6.

The ester was recovered unchanged (60%) after it had been heated at 80–90° with an excess of sodium methoxide.

Saponification of the ester gave **cinnomoylsarcosine**; needles from dilute alcohol, m. p. 182–183°.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.7; H, 6.0. Found: C, 65.8; H, 6.0.

Methyl *o*-Acetyl-*allo*-cinnamate (XII).—1-Methyl-2-naphthol, obtained in 40% yield,[11] gave a 37% yield of 1-methyl-1,2-naphthoquinol[12] when it was treated with chromic acid. A solution of 5 g. of the quinol in 40 ml. of methanol was mixed with 7.6 g. of para-periodic acid in 37 ml. of water and kept in a refrigerator for forty hours. The solution was then evaporated in absence of air, and the residue was crystallized from water, giving 2.24 g. (41%) of ***o*-acetyl-*allo*-cinnamic acid**; faintly pink needles that sintered at 140°, m. p. 143–144°.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3; neut. equiv., 190. Found: C, 69.3; H, 5.6; neut. equiv., 189.

A sample of the acid was treated with iodine in potassium iodide, giving iodoform and *o*-carboxy-*allo*-cinnamic acid, m. p. 181–184°. The latter was identified by comparison with an authentic sample[12] and by conversion to phthalide–acetic acid, m. p. 150°.[13]

o-Acetyl-*allo*-cinnamic acid was esterified by treating its silver salt with excess methyl iodide. The resulting methyl ester, XII, formed colorless prisms from ligroin; m. p. 55–56°, yield 65%.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 70.8; H, 6.0.

When 0.6 g. of the ester was treated with one drop of sodium methoxide in methanol and warmed to 55°, the mixture became brown and its temperature rose to 70°. There was obtained an oil, b. p. 130–140° at 3–4 mm., which did not crystallize when it was seeded with methyl 1-hydrindone-3-acetate. Saponification gave a mixture from which a small amount of an unsaturated acid, m. p. 181–185°, was isolated.

Summary

When a cinnamic ester substituted in the *o*-position by a group $-O-CH_2COOCH_3$ is treated with sodium methoxide, cyclization takes place. This occurs even when the α,β-unsaturation bears a phenyl; similar cyclizations can be effected in cinnamic esters with the *o*-substituents $-N(CH_3)CH_2COOCH_3$, $-S-CH_2COOCH_3$ and $-NH-COOCH_2C_6H_5$. These cyclizations are internal Michael reactions. The products are, respectively, derivatives of coumaran, indoline, dihydrothionaphthene and hydrocarbostyril.

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[11] Fries and Hubner, *Ber.*, **39**, 441 (1906).

[12] Bargellini and Silvestri, *Gazz. chim. ital.*, **37**, II, 413 (1907).

[13] Böeseken and v. Konigsfeldt, *Rec. trav. chim.*, **54**, 314 (1935).