*Anal.* Calcd. for $C_{16}H_{23}O_4Cl$: C, 61.04; H, 7.36. Found: C, 61.03; H, 7.36.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WIS.

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# Rates of Hydrolysis of *cis*- and *trans*-3- and 4-Substituted Ethyl Cinnamates

JORDAN J. BLOOMFIELD[1] AND RICHARD FUCHS

*Received December 27, 1960*

In an earlier investigation of the transmission of electronic effects by the cyclopropane ring[2] several *m*- and *p*-substituted *trans*-ethyl 2-phenylcyclopropanecarboxylates were prepared, and their rates of alkaline hydrolysis were measured. Several *cis* esters were subsequently obtained, and their hydrolysis rates were measured.

The *cis* esters hydrolyze about one-tenth as rapidly as the *trans* esters, as would be expected on steric grounds. However, the Hammett *rho* value for these esters is 1.014,[3] whereas, for the *trans* esters *rho* is 0.812.[2,3] This unexpected result, which may be the result of a field effect between the phenyl group and the carbethoxy group in the *cis* esters, prompted an investigation of whether similar behavior would occur in the cinnamate series. Several *cis*- and *trans*-ethyl cinnamates have now been prepared, and the rates of alkaline hydrolysis have been measured. In this series *cis* esters hydrolyze slightly slower than the *trans* esters and *rho* is also smaller. Thus, for the *trans* cinnamates *rho* is 1.314[4] and for the *cis* cinnamates, 1.122. The rates of reaction of the esters are summarized in Table I.

TABLE I

RATES OF ALKALINE HYDROLYSIS OF *cis*- AND *trans*-ETHYL CINNAMATES IN 87.8% ETHANOL AT 30°

| Substituent | *cis*-Series, $k \times 10^{3a}$ | *trans*-Series, $k \times 10^{3a,b}$ |
|---|---|---|
| 4-$OCH_3$ | 0.55 | 0.79 (0.74) |
| 3,4-$CH_2O_2$ | 0.78 | 1.09 (1.02) |
| Unsubstituted | 1.07 | 1.90 (1.77) |
| 4-Cl | 2.10 | 3.98 (3.58) |
| 3-Cl | 2.69 | 6.03 (5.69) |
| 3,4-$Cl_2$ | 4.53 | 8.97 — |
| 3-$NO_2$ | — | 14.97 (13.30) |
| 4-$NO_2$ | — | 19.08 (17.25) |

[a] Liter mole$^{-1}$ sec.$^{-1}$ Each value is the average of two or more determinations. [b] Values in parentheses are those of Kindler, ref. 4.

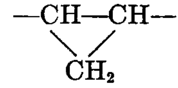
From the various data available (Table II) there appears to be an increasing influence of *m*- and *p*-substituents on the reactivity of the carbethoxy group in the order —$CH_2CH_2$—,  $\overset{\text{—CH—CH—}}{\diagdown\ \diagup \atop CH_2}$, —CH=CH—, —C≡C—, as measured by the *rho* value for ester hydrolysis. Data for the ionization constants fall in a considerably different order, only a portion of which can be attributed to solvent and temperature differences in the various studies.[5]

TABLE II

COMPARISON OF *RHO* VALUES

| Series | Ester Hydrolysis (30°) | $K_i$ (25°) |
|---|---|---|
| β-Phenylpropionic | 0.489[a] | 0.212 |
| *trans*-2-Phenylcyclopropane | 0.812[b] | 0.182[c] |
| *cis*-2-Phenylcyclopropane | 1.014[b] | — |
| *cis*-Cinnamic | 1.122 ± 0.040 (0.9998)[b] | 0.643[d] |
| *trans*-Cinnamic | 1.314 ± 0.023 (0.9991)[b] | 0.466[a] |
| Phenylpropiolic | 1.91[e] | 0.41,[f] 0.81,[g] 0.69[h] |

[a] Ref. 4. [b] This work, ref. 2, 3. Figures in parentheses are correlation coefficients. [c] E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958). [d] Calculated from data of W. A. Roth and R. Stoermer, *Ber.*, **46**, 260 (1913). [e] At 20° J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77**, 5554 (1955). [f] Ref. e; measured in 50% ethanol rather than in pure water as were the others. [g] M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77**, 5552 (1955); measured in 35% dioxane. [h] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958); measured in 50% ethanol at 24°.

Recent information[6] suggests that the Hammett *rho* value of the original equation may not be an accurate measure of the transmitting ability of various groups, because of variability in the value of *sigma* for substituents capable of resonance interaction with the reaction site. A definite separation of the possible influencing factors is not possible at this time.

The ultraviolet absorption maxima of the *trans*-cinnamates are consistently at longer wave lengths and of higher $\epsilon_{max}$ than those of the corresponding *cis* esters (Table III), as has been found previously for the chloro- and dichlorocinnamic acids.[7] This is consistent with the notion of a superior conjugating system in the *trans* compounds.

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[1] Present address: Department of Chemistry, University of Arizona, Tucson, Ariz.

[2] R. Fuchs and J. J. Bloomfield, *J. Am. Chem. Soc.*, **81**, 3158 (1959).

[3] Complete information to be published later.

[4] *Rho* of 1.329 calculated by H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953), from data of K. Kindler, *Ann.*, **452**, 90 (1927).

[5] The ionization constants in 50% ethanol of the six series of acids in question are now being reinvestigated.

[6] H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959). R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

[7] S. Lindenfors, *Arkiv. Kemi*, **14**, 227 (1959).

TABLE IV

PHYSICAL CONSTANTS OF *cis*- AND *trans*-ETHYL CINNAMATES AND ETHYL PHENYLPROPIOLATES

| Substituent | M.P. or B.P. (Mm.) | $n_D^{30}$ | Yield, % | Calcd., % C | Calcd., % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|
| *trans*-Cinnamates | | | | | | | |
| None | 75–76 (0.02) | 1.5554 | 77 | — | — | — | — |
| 4-$OCH_3$ | 48.9–49.7 | 1.5782 | 87 | — | — | — | — |
| 4-Cl | 122–123 (0.7) | 1.5725 | 83 | — | — | — | — |
| 3,4-$Cl_2$ | 55.4–56.6[a] | 1.5831 | 79 | 53.90 | 4.11 | 54.21 | 4.11 |
| 3,4-$CH_2O_2$ | 66.6–67.3 | 1.5917 | 74 | — | — | — | — |
| 3-$NO_2$ | 74.3–74.6 | — | 64 | — | — | — | — |
| 4-$NO_2$ | 139.0–139.8 | — | [b] | — | — | — | — |
| 3-Cl | 93–94 (0.15) | 1.5640 | 92 | — | — | — | — |
| *cis*-Cinnamates | | | | | | | |
| None | 52–56 (0.01) | 1.5384 | 85 | 74.98 | 6.86 | 75.24 | 7.09 |
| 4-$OCH_3$ | 85–88 (0.03) | 1.5632 | 79 | 69.88 | 6.84 | 69.92 | 6.94 |
| 4-Cl | 75–77 (0.03) | 1.5569 | 89 | 62.71 | 5.26 | 62.82 | 4.92 |
| 3,4-$Cl_2$ | 34.4–35.1 | 1.5661 | 50 | 53.90 | 4.11 | 53.91 | 4.16 |
| 3,4-$CH_2O_2$ | 31.0–31.4 | 1.5750 | 25[c] | 65.44 | 5.49 | 65.53 | 5.33 |
| 3-Cl | 85–87 (0.05) | 1.5474 | 87 | 62.71 | 5.26 | 62.67 | 5.51 |
| Phenylpropiolates | | | | | | | |
| None | 65–66 (0.05) | 1.5476[d] | 80 | — | — | — | — |
| 4-$OCH_3$ | 100–103 (0.02) | 1.5679[e] | 77 | — | — | — | — |
| 4-Cl | 40.7–42.9[f] | — | 87 | — | — | — | — |
| 3,4-$Cl_2$ | 65.9–66.5 | — | 80 | 54.35 | 3.32 | 54.53 | 3.35 |
| 3,4-$CH_2O_2$ | 83.5–84.4 | — | 70 | 66.05 | 4.62 | 66.03 | 4.55 |
| 3-Cl | 89 (0.15) | 1.5562 | 75 | — | — | — | — |
| Phenylpropiolic Acids | | | | | | | |
| 3,4-$Cl_2$ | 182.3–183.4 dec. | — | — | 50.27 | 1.88 | 50.32 | 1.80 |
| 3,4-$CH_2O_2$ | 169–170 dec.[g] | — | — | — | — | — | — |

[a] M.p. 81°, Ng. Ph. Buu-Hoi, Ng. X. Xuong, Ng. H. Nam, F. Binon, and R. Roger, *J. Chem. Soc.*, 1358 (1953). [b] Distillation Products Ind. material recrystallized twice from ethanol. [c] After three recrystallizations. [d] $n_D^{25}$ 1.5490, ref. g, Table II. $n_D^{25}$ 1.5521, ref. e, Table II. [e] $n_D^{25}$ 1.5675, ref. g, Table II. [f] M.p. 43–44, ref. e, Table II. [g] M.p. 166°, dec., M. M. S. Baude and A. Reychler, *Bull. soc. chim. France*, [3], **17**, 616 (1897).

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA OF *cis* AND *trans* ETHYL CINNAMATES

| Substituent | *cis* Esters mμ | *cis* Esters $\epsilon_{max} \times 10^{-3}$ | *trans* Esters mμ | *trans* Esters $\epsilon_{max} \times 10^{-3}$ |
|---|---|---|---|---|
| 4-$OCH_3$ | 305 | 12.6 | 310 | 26.7 |
| 3,4-$CH_2O_2$ | 324 | 11.0 | 328 | 18.1 |
| 4-Cl | 275 | 12.9 | 284 | 24.1 |
| 3,4-$Cl_2$ | 270 | 12.5 | 278 | 25.8 |
| None | 270 | 11.7 | 277 | 24.1 |
| 3-Cl | 265 | 10.0 | | |

## EXPERIMENTAL

*trans-Cinnamates.* The cinnamic acids were prepared by the Doebner reaction.[8] The precipitated acid was washed with ethanol and the filtrates were normally discarded. When the yield of acid was less than 60% the filtrate was evaporated; the residue was dissolved in ether, and extracted with sodium bicarbonate solution, which was acidified to obtain additional product. The ether solution consisted of the ethyl ester of the acid and unchanged aldehyde.[9]

The ethyl esters were prepared by refluxing the acid, excess absolute ethanol, and a trace of *p*-toluenesulfonic acid for 24 hr. The residue from the reduced pressure evaporation of the solvent was dissolved in ether, washed with sodium bicarbonate solution and water, dried with magnesium sulfate, and either fractionally distilled, or recrystallized from petroleum ether.

*cis-Cinnamates.* Ethyl phenylpropiolates were prepared by allowing the corresponding phenylpropiolic acids,[10] excess absolute ethanol, and hydrogen chloride or concentrated sulfuric acid to stand 3 to 7 days at room temperature with occasional shaking. After the solvent was evaporated under reduced pressure the residue was dissolved in ether, washed with sodium bicarbonate solution and water, dried, and either distilled, or crystallized from petroleum ether or pentane.

The ethyl phenylpropiolates were hydrogenated over Lindlar catalyst[11] to give the *cis*-ethyl cinnamates. In a typical run 5.0 g. of the ester was mixed with 20–30 ml. of olefin-free petroleum ether, 1 g. of catalyst, and 0.5 ml. of distilled quinoline. The calculated amount of hydrogen

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(8) C. Walling and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **69**, 852 (1947).

(9) Anisaldehyde gave 56% acid, 14% ester, and 22% recovered aldehyde (total, 92%); piperonal, 47.5% acid, 20.5% ester, and 15% recovered aldehyde (total, 83%). The use of practical grade *m*-nitrobenzaldehyde gave a green reaction mixture, and lowered the yield from 87% to 67%. About 6% of the ester was isolated.

(10) Prepared by the method of T. W. Abbott, *Org. Syntheses*, **Coll. Vol. II**, 515 (1943).

(11) H. Lindlar, *Helv. chim. Acta*, **35**, 446 (1952).

was absorbed in 3-5 hr. The catalyst was removed by filtration and washed with ether. The combined filtrates were washed with cold 3*N* hydrochloric acid and with cold 10% sodium hydroxide solution, and dried. The residue after evaporation of solvent was either recrystallized from pentane or distilled.

The ultraviolet spectra were determined in 95% ethanol purified before use by distillation from potassium hydroxide. The solutions were made up to give absorbance values of 0.3–0.8 at $\lambda_{max}$. A Beckman Model DK-1 spectrophotometer was used for these measurements.

*Kinetic method.* Basic hydrolyses were carried out in 87.8% (by volume) ethanol at 30.00 ± 0.02°, in side-arm volumetric flasks, under a positive pressure of nitrogen. The initial concentration of potassium hydroxide and of ester were about 0.04*M* and 0.025*M*, respectively. Aliquots were periodically pipetted into excess sulfuric acid, and back titrated with sodium hydroxide solution using a Sargent-Malmstadt Automatic Titrator. Consistent values of the second-order rate constants were calculated, corresponding with the first 65–80% of the reaction which was followed. An infinity-time measurement was generally used, except in calculating the few slowest rate constants, for which the zero-time concentrations were accurately determined and used.

*Acknowledgment.* We wish to thank Miss Ruth Ann Cook for the ultraviolet spectra, and The University of Texas Research Institute for a Summer Grant to R.F.

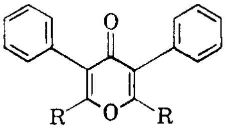
DEPARTMENT OF CHEMISTRY
THE UNIVERSITY OF TEXAS
AUSTIN 12, TEX.

## Isomeric Pyranones from Condensation of Propionic Acid with 1,3-Diphenyl-2-propanone

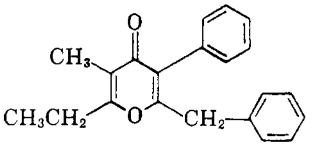
R. L. LETSINGER AND O. KOLEWE[1]

*Received December 29, 1960*

Acetic acid condenses with 1,3-diphenyl-2-propanone in polyphosphoric acid to give 2,6-dimethyl-3,5-diphenylpyran-4-one (I) in good yield.[2] A consideration of the possible pathways leading to this product indicated that an isomeric, unsymmetrical pyran-4-one might also have been produced under the reaction conditions; however, no such compound could be isolated. We now find that two pyran-4-ones are indeed formed in the reaction of propionic acid with 1,3-diphenyl-2-propanone. These products, m.p. 101.5–102° (21% yield) and m.p. 98–99° (24% yield), are assigned structures II and III, respectively, on the basis of the reaction type and analytical and spectral data. Evidence that both compounds are pyran-4-ones is provided by the infrared spectra, which show bands in the 6.0–6.4 μ region typical of pyran-4-ones. The NMR spectra strongly support formulas II and III and permit an unambiguous identification of the formulas with the reaction products.

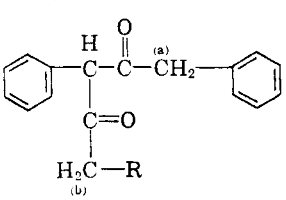


I. R = $CH_3$
II. R = $C_2H_5$



III

Formation of these pyranones may be rationalized on the basis of the pathway postulated for the analogous condensation involving acetic acid—*i.e.*, successive acylations at methylene groups α to carbonyl groups, followed by enolization and dehydration. The initial acylation would yield intermediate IV (R = $CH_3$, for propionic acid), or an equivalent acylated or phosphorylated enol derivative which would undergo a second acylation at either carbon (a) or carbon (b). Reaction at (a)



IV

would lead to II; reaction at (b), to III. The yields of II and III suggest that the two pathways are about equally probable for the propionic acid reaction. In the acetic acid condensation (R = H), the second acylation must occur preponderantly, if not exclusively, at position (a).

### EXPERIMENTAL

*Reaction of 1,3-diphenyl-2-propanone with propionic acid.* A solution containing 2.2 g. of 1,3-diphenyl-2-propanone and 25 ml. of propionic acid in 40 g. of polyphosphoric acid[3] was heated at reflux (138–145°) for 1.5 hr.; then it was cooled to room temperature, diluted with water and extracted with ether. The ether solution was washed with 10% sodium hydroxide solution, dried, and evaporated to yield a brown oil which failed to crystallize at 0°. On chromatography on alumina with petroleum ether (b.p. 60–71°)–benzene mixtures as eluent, a pale yellow band developed. Elution of this band yielded 2.0 g. of tan product, m.p. 70–93°, which was dissolved in ether and decolorized with charcoal. Recrystallization from hexane afforded 0.9 g. of product III, m.p. 90–95°. Concentration of the mother liquors gave 0.8 g. of product II, m.p. 95–100°. After several recrystallizations from pentane, III melted at 98–99°; weight, 0.8 g. (24% yield). Product II, after recrystallization from pentane, melted at 101.5–102°; weight, 0.7 g. (21%). A mixture of pure II and III melted over a range from 75–90°.

*Anal.*[4] Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.62. Found: Compound II. C, 82.67; H, 6.57. Found: Compound III. C, 82.62; H, 6.13.

*Spectral data.* Both II and III exhibited absorption in the 6.0–6.4 μ region characteristic of pyrones[2]; The infrared spectrum of II had sharp peaks at 6.06, 6.16, and 6.22 μ; that of III, peaks at 6.09 and 6.22 μ and a shoulder at 6.33 μ. Otherwise the spectra differed in numerous respects. In

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(1) National Science Foundation Undergraduate Summer Research Participant, 1960.

(2) R. L. Letsinger and J. D. Jamison, *J. Am. Chem. Soc.*, **83**, 193 (1961).

(3) The polyphosphoric acid was kindly supplied by the Victor Chemical Company.

(4) Carbon and hydrogen analyses were made by H. Beck.