change apparently is not consistent with a cyclic mechanism (see the mechanism in col. 2, p. 909) involving basic attack by oxygen on a β-hydrogen, nor with a similar bimolecular process. It is consistent with an ionic mechanism involving formation of a free carbonium ion. However, the limited extent of rearrangement discourages consideration of the latter as a unique pathway.

A more appealing explanation is that polymeric alkoxides tend to dissociate in a rate determining step, followed by a relatively rapid cyclic elimination reaction. Alkoxides with bulkier alkyl groups should form less stable polymers, with a greater degree of dissociation in the transition state. Freeing an electron pair of the oxygen atom from a bond with aluminum should greatly augment the basicity of the oxygen atom and facilitate cyclic elimination.

Alkali metal alkoxides are not able to undergo elimination unimolecularly through a five- to six-member ring. Since the oxygens are bonded covalently to one aluminum atom and are coördinated with a second in the polymeric alkoxide, aluminum alkoxides must be somewhat weaker bases then the corresponding sodium or potassium alkoxides. In accordance with this lessened basicity, the aluminum alkoxide is less likely to displace a carbanion, and reversal of the Grignard reaction does not take place, at least in the case of the *t*-butoxide, as contrasted to the formation of acetone from potassium *t*-butoxide.

The combination of these two factors, the greater ease of cyclic olefinic elimination from aluminum alkoxides and the greater basicity of alkali metal alkoxides, must lead to formation of olefin uncontaminated with aldehyde or ketone.

Transmission of Electronic Effects by the Cyclopropane Ring. Rates of Alkaline Hydrolysis of Ethyl *cis*- and *trans*-2-Phenylcyclopropanecarboxylates

RICHARD FUCHS AND JORDAN J. BLOOMFIELD[1a]

Department of Chemistry, The University of Texas, Austin 12, Texas

Received December 5, 1961

The rates of alkaline hydrolysis of a series of *m*- and *p*-substituted ethyl β-phenylpropionates and of ethyl *trans*- and *cis*-2-(substituted phenyl)cyclopropanecarboxylates in 87.8% ethanol at 30° have been measured. A comparison of Hammett ρ-values for these series, ethyl *cis* and *trans* cinnamates, and ethyl phenylpropiolates indicates that the influence of substituents on the reactivity increases in the six ester series in the order listed.

The relative abilities of the cyclopropane ring and the saturated dimethylene group (-CH_2CH_2-) to transmit electronic effects has been a continued subject of controversy. The chemical and physical evidence available in 1958 has been summarized in an article[1b] reporting the ionization constants of a series of β-phenylpropionic and *trans*-2-phenylcyclopropanecarboxylic acids. This work suggested that the three-membered ring is no better than the dimethylene group in transmitting electronic effects, in agreement with certain earlier evidence, but opposing other information. More recent information has also supported both sides of the question. The lack of hydrogen exchange and carbanion addition reactions involving diethyl 2-methylcyclopropane-1,1-dicarboxylate[2] led to the conclusion that the cyclopropane ring is poor in transmitting electronic effects to a methyl substituent β to electron withdrawing groups. In the solvolysis of *cis*- and *trans*-2-phenylcyclopropylcarbinyl β-naphthalenesulfonates and cyclopropylcarbinyl β-naphthalenesulfonate[3] rate differences were found to be fairly small, and it was concluded that little positive charge is dispersed in the transition state.

Evidence supporting the conjugative properties of the cyclopropane ring has been obtained from Raman line intensities,[4] and from the solvolysis of some cyclopropylisopropylcarbinyl *p*-nitrobenzoates,[5] wherein the three-membered ring has a strong rate-enhancing effect. Stabilization of the transition state due to the considerable π-bond character of the cyclopropane ring has been cited as the reason for the high rate of solvolysis of *p*-cyclopropyl-α,α-dimethylbenzyl chloride compared to other *p*-cycloalkyl substituted compounds.[6] Conjugation of the cyclopropane ring with the carbon–carbon double bond of α-cyclopropylstyrene apparently accounts for the 1,5 conjugate addition of maleic anhydride.[7] Recent measurements in this laboratory of the ionization constants of a series of *m*- and *p*-substituted β-phenylpropionic, *cis*- and *trans*-2-phenylcyclopropanecarboxylic acids[8] in 50% ethanol are in disagreement with Trachtenberg's earlier measurements[1b] in water; the ionization constants of the latter two acids are appreciably more affected by substituent changes than is the former, thus supporting the transmitting ability of the cyclopropane ring. A preliminary report[9] of the rates of hydrolysis of a series of ethyl *trans*-2-phenylcyclopropanecarboxylates indicated that in this case, also, the cyclopropane ring is superior to the dimethylene group. In the present paper the complete results of this investigation are reported along with similar data for the *cis* compounds and a series of ethyl β-phenylpropionates.

---

(1) (a) Department of Chemistry, University of Oklahoma, Norman, Okla.; (b) E. N. Trachtenberg and G. Odian, *J. Am. Chem. Soc.*, **80**, 4018 (1958).

(2) G. W. Cannon, A. A. Santilli, and P. Shenian, *ibid.*, **81**, 4265 (1959).

(3) R. D. Sneen, B. R. Smith, and I. A. Taha, Abstracts of the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960, p. 34P.

(4) R. Ya. Levina, V. N. Kostin, P. A. Genbitskii, S. M. Shostakovskii, and E. G. Treschova *J. Gen. Chem. USSR*, **30**, 2435 (1960).

(5) H. Hart and M. Sandri, *J. Am. Chem. Soc.*, **81**, 320 (1959).

(6) R. C. Hahn, T. F. Corgin, and H. Shechter, Abstracts of the 139th National Meeting of the American Chemical Soicety, St. Louis, Mo., April, 1961, p. 35-O.

(7) S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).

(8) R. Fuchs, C. A. Kaplan, J. J. Bloomfield, and L. F. Hatch, *J. Org. Chem.*, **27**, 733 (1962).

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

TABLE I

RATES OF ALKALINE HYDROLYSIS OF *m*- AND *p*-SUBSTITUTED ETHYL β-PHENYLPROPIONATES, ETHYL *cis*- AND *trans*-2-PHENYLCYCLOPROPANECARBOXYLATES IN 87.8% ETHANOL AT 30°

Phenyl substituent	Phenylpropionate series,[a] $k \times 10^3$	*cis* Series,[a] $k \times 10^3$	*trans* Series,[a] $k \times 10^3$
4'-OCH_3	5.18 (4.80)[b]		0.982
	5.17		1.03
4'-CH_3	4.95	0.0697[c]	1.07
	4.83	.0705[c]	1.06
Unsubstituted	5.78 (5.72)[b]	.0911	1.38
	5.80	.0902	1.40
4'-Cl	8.98 (8.60)[b]	.161[c]	2.37
	9.08	.163[c]	2.35
		.162[c]	
		.164[c]	
4'-Br			2.45
			2.48
3'-Cl	10.6		3.05
	10.6		3.02
3'-Br		.200	
		.202	
3',4'-Cl_2	15.3	.323	4.60
	15.3	.327	4.48
3'-NO_2		.512	5.63
		.497	5.53
4'-NO_2	18.2	.643[c]	6.37
	18.0	.665[c]	6.40

[a] Second-order rate constants (l. mole^{-1}sec.$^{-1}$) × 10^3. At time of mixing (KOH) = 0.04 *M*, (ester) = 0.025 *M*. Stated temperature regulated to ±0.02°. Solvent composition 87.8% ethanol–12.2% water by volume. The preparation and isolation of the compounds will be published elsewhere. The kinetic procedure has been described [J. J. Bloomfield and R. Fuchs, *J. Org. Chem.*, **26,** 2991 (1961)]. [b] Values in parentheses are those of K. Kindler, *Ann.*, **452,** 90 (1927). [c] Rate constants determined by permitting the small amount of *trans* ester impurity to hydrolyze completely before beginning the rate measurements.

TABLE II

COMPARISON OF REACTION CONSTANTS

Series	ρ Ester hydrolysis[a]	ρ Acid ionization[b]
β-Phenylpropionic	0.591 ± 0.032 (0.983)[c]	0.212 (0.344)[d]
trans-2-Phenylcyclopropanecarboxylic	0.812 ± 0.019 (0.996)[c]	.182 (0.473)[d]
cis-2-Phenylcyclopropanecarboxylic	1.02 ± 0.029 (0.994)[c]	(0.436)[d]
trans-Cinnamic	1.314 ± 0.023[e]	.466[f]
cis-Cinnamic	1.122 ± 0.040[e]	.643[g]
Phenylpropiolic	1.91[h]	.41,[i] 0.81,[j] 0.69[k]

[a] Alkaline hydrolysis of ethyl esters in 87.8% ethanol at 30°, unless otherwise specified. [b] Ionization constants in water at 25°, unless otherwise specified. [c] This work. Values of ρ are followed by standard deviations. The least squares treatment employed each of the rate data listed in Table I. Figures in parentheses are correlation coefficients. [d] Figures in parentheses measured in 50% ethanol at 25°; ref. 8. Other figures measured in water; ref. 1. [e] Table I, footnote *a*. [f] From compilation by H. H. Jaffé, *Chem. Rev.*, **53,** 191 (1953). [g] W. A. Roth and R. Stoermer, *Ber.*, **46,** 260 (1913). [h] At 20°; J. D. Roberts and R. A. Carboni, *J. Am. Chem. Soc.*, **77,** 5554 (1955). [i] Footnote *h*; measured in 50% ethanol. [j] M. S. Newman and S. H. Merrill, *J. Am. Chem. Soc.*, **77,** 5552 (1955); measured in 35% dioxane. [k] I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23,** 885 (1958); measured in 50% ethanol at 24°.

The Hammett equation ρ-constants based on the rate constants in Table I, together with the corresponding values for the *cis* and *trans* ethyl cinnamates and ethyl phenylpropiolates are listed in Table II. ρ-Constants for the ionization of the corresponding six series of acids are also listed for comparison.

It is worth remarking that the old value of ρ for the phenylpropionates was 0.49,[10] about 17% less than the present value. The earlier value was based on only four points, one of which (4-OCH_3) falls considerably above the line. A previously reported ρ-value of 1.329[10] for the *trans* cinnamates is within experimental error of the present value of 1.31.

Insofar as these ρ-values are a measure of the relative ability of each of these groups to transmit electronic effects to the reaction site, the order of increasing effectiveness is dimethylene < *trans*-cyclopropane < *cis*-cyclopropane < *cis*-ethylene < *trans*-ethylene < acetylene. The order of the first two members of the series found here is strikingly different from the order found by Trachtenberg and Odian[1b] based on ionization of the acids. The present work indicates that the cyclopropane ring is quite good in transmitting electronic effects in the saponification of esters in 87.8% ethanol.

An apparent anomaly is that ρ for the *cis* cyclopropane esters is greater than for the *trans* compounds. It would be expected that better conjugation would be possible in the *trans* series. The greater polarizability of the *trans* system is indicated by ultraviolet measurements,[1,11] which show that the *trans* esters and acids absorb at longer wave lengths and have slightly higher extinction coefficients than the *cis* isomers. Also, the ρ-value for the ionization of *trans*-2-phenylcyclopropanecarboxylic acids is greater than that for the *cis* series (Table II), although the difference does not exceed the combined standard deviations. The rates of hydrolysis of the more hindered *cis*-ethyl 2-phenylcyclopropanecarboxylates are at least an order of magnitude slower than the rates of the *trans* isomers, but the reactivity of the *cis* series is more sensitive to substituent changes. This may result from a combination of two factors. The proximity of the aryl and carbethoxy groups may permit an electrostatic interaction through space in the *cis* esters. Although the cyclopropane ring itself may transmit electronic effects less efficiently in the *cis* configuration than in the *trans*, the electrostatic effect in the *cis* compounds more than compensates for the lesser transmission through the ring. The same effects are probably operative in the cinnamate esters, but in this case the superior transmitting ability of the *trans* ethylenic unit more than compensates for an electrostatic effect in the *cis* compounds. It may be that the phenyl and carbethoxy groups are further apart in the *cis* cinnamates than in the *cis* cyclopropane esters, for the presumably steric retardation of hydrolysis rate (compared to the *trans* isomers) amounts to a factor of less than two in the former case.

The difference in order of the ρ-values for the *cis* and *trans* cinnamic acid and cinnamate ester series as measured by ionization and hydrolysis rate experiments, respectively, may be caused by the limited availability of data. The ρ-value of 0.643 for *cis* cinnamic acids is based on data[12] for only four compounds, all having substituents with σ-values within a range of 0.35. The fit is excellent; the standard deviation in

---

(10) Table II, footnote f; based on the data of K. Kindler, *Ann.*, **452,** 90 (1927).

(11) Unpublished studies by J. J. Bloomfield and R. Fuchs.

(12) Table II, footnote *g*.

ρ is only 0.03. If data for the *trans* cinnamic acids with only the same four substituents is considered, a ρ-value of 0.66 with a standard deviation of 0.24 is obtained. This deviation points out a problem which can arise when too few points or an insufficiently wide range of σ-values are used in determining reaction constants.

Furthermore, when groups which can exhibit strong resonance interactions are present, they may alter the apparent value of ρ. It has recently been demonstrated that in certain reactions *para* σ-values are changed by direct resonance interactions with the reaction site[13] which are considerably greater than those operative in the reference reaction, the ionization of benzoic acids. Similarly, in reactions (such as the saponification of ethyl β-phenylpropionates) wherein no direct resonance interaction is possible between the substituent and reaction site, σ-values also are changed. A procedure has been recommended[13b] for making precise determinations of ρ-values for the reactions of benzene derivatives, by the use of certain *meta* substituents of nearly invariant σ-value. Although a satisfactory number of data for these substituents are not available in the present work, the ρ-values calculated from the *m*-Cl and unsubstituted compounds are 0.71 and 0.92 for the ethyl β-phenylpropionates and *trans* ethyl 2-phenylcyclopropanecarboxylates, respectively. The imperfectness of the correlation coefficient in these series results predominantly from the use of ordinary σ-values which are not completely appropriate to the systems. Regardless of the absolute magnitude of the ρ-values, the difference between them, and the greater transmitting ability of the cyclopropane ring appear to be real.

Acknowledgment.—This work was supported by grants from The University of Texas Research Institute (to R. F.) and from the Research Corporation (J. J. B.).

---

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

The Condensation of 1,3-Dienes with α,β-Unsaturated Aldehydes in the Presence of a Ziegler Catalyst

E. F. Lutz

Denver Research Center of Marathon Oil Company, Littleton, Colorado

Received October 31, 1962

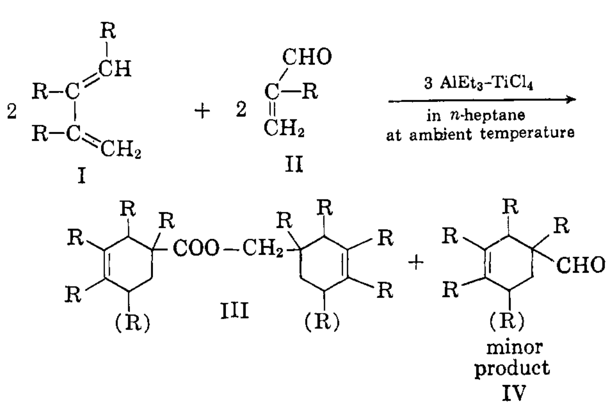
1,3-Dienes and α,β-unsaturated aldehydes have been condensed to dicarbocyclic esters in the presence of Ziegler-type catalysts. The reaction products are those that would be expected from a Diels–Alder reaction followed by a Tishchenko condensation of the intermediate adducts. Some discussion of the effective catalyst and the scope of the reaction is presented.

Introduction and Results

In recent years an increasingly large amount of research has been directed toward the study of organometallic catalysis. Of particular interest have been the Ziegler-type catalysts which have found great utility in performing stereospecific polymerizations.[1] A much less explored, but equally interesting utilization of these catalysts has been their ability to oligomerize certain monomers to dimers and trimers which are frequently inaccessible by other means. This is probably best exemplified by the work of Wilke, who has shown that 1,3-dienes can be trimerized[2] or dimerized[3] to cyclic trienes or dienes depending on the composition of the organometallic catalyst used. Thus, either 1,5,9-cyclododecatriene or 1,5-cyclooöctadiene can be readily synthesized from 1,3-butadiene.

Previous work in this laboratory[4] has shown that both monoalkyl- and dialkylacetylenes can be successfully trimerized to tri- and hexaalkylbenzenes, respectively, in the presence of Ziegler catalysts. Hoover and coworkers have reported an interesting extention of this reaction in the trimerization of vinylacetylene to, primarily, 1,2,4-trivinylbenzene in good yield.[5,6]

Recently, Robinson and Fray have reported that Lewis acids, including certain Ziegler complexes were effective catalysts in the Diels–Alder condensation of 1,3-dienes with α,β-unsaturated carbonyl compounds.[7,8] It now has been found that 1,3-dienes and α,β-unsaturated aldehydes can be condensed to dicarbocyclic esters in the presence of certain Ziegler-type catalysts. Table I lists the 1,3-dienes and dienophiles that were studied.



R = $-$H or $-CH_3$

---

[1] See W. Cooper in J. C. Robb and F. W. Peaker, "Progress in High Polymers," Vol. I, Academic Press, Inc., New York, N. Y., 1961, pp. 281–340, and C. E. H. Bawn, *Proc. Chem. Soc.*, 165 (1962), for recent reviews and leading references.

[2] G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959).

[3] G. Wilke, E. W. Müller, and M. Kröner, *Angew. Chem.*, **73**, 33 (1961).

[4] E. F. Lutz, *J. Am. Chem. Soc.*, **83**, 2551 (1961).

[5] F. W. Hoover, O. W. Webster, and C. T. Hardy, *J. Org. Chem.*, **26**, 2234 (1961).

[6] This result seems surprising since very good yields of the trimer were obtained with, apparently, little polymerization of the starting monomer or product.

[7] R. Robinson and G. I. Fray, British Patent 835,840 (1960).

[8] G. I. Fray and R. Robinson, *J. Am. Chem. Soc.*, **83**, 249 (1961).