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.).

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[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

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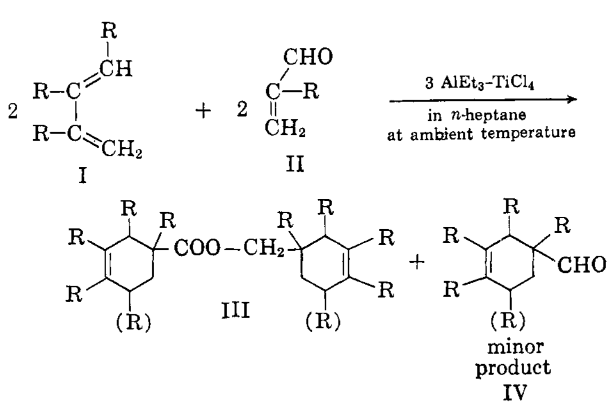
1,3-Dienes and α,β-unsaturated aldehydes have been condensed to dicarbocyclic esters in the presence of Ziegler-type catalysts. The reaction products are those that would be expected from a Diels–Alder reaction followed by a Tishchenko condensation of the intermediate adducts. Some discussion of the 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-cyclooötadiene 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$_3$

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[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).

TABLE I

REACTANTS AND PRODUCT ESTERS[a]

Diene	α,β-Unsaturated aldehyde	Product ester	Yield, %
1,3-Butadiene	Acrolein	3-Cyclohexenylmethyl 3-cyclohexenecarboxylate	19.6
Isoprene	Acrolein	4-Methyl-3-cyclohexenylmethyl 4-methyl-3-cyclohexenecarboxylate	24.5
1,3-Pentadiene	Acrolein	2-Methyl-3-cyclohexenylmethyl 2-methyl-3-cyclohexenecarboxylate[b]	12.5
2,3-Dimethyl-1,3-butadiene	Acrolein	3,4-Dimethyl-3-cyclohexenylmethyl 3,4-dimethyl-3-cyclohexenecarboxylate	21.0
1,3-Butadiene	Crotonaldehyde	None	0[c]
1,3-Butadiene	Methacrolein	1-Methyl-3-cyclohexenylmethyl 1-methyl-3-cyclohexenecarboxylate	4[d]

[a] The reactions were all carried out at room temperature with a slight exotherm observed on the slow addition of the reactants to the reaction solution. [b] No effort was made to establish the position of the methyl group in this compound. However, the literature indicates that the methyl group is in the 2-position.[9] [c] A trace of ester may have been obtained, but it was too small to characterize. [d] This is an approximate yield since the amount of ester obtained was too small to purify adequately. See Experimental for details.

TABLE II

Diene (g.)	α,β-Unsaturated aldehyde (g.)	Ester[a]			Cyclohexenecarboxaldehyde[b]		
		B.p.	n_D/°C.	G.	B.p.	n_D/°C.	G.
		(65–108°/0.6 mm.)[c]	(1.4903/20°)[c]	(2.9)[c]			
1,3-Butadiene (13.7)	Acrolein (18.3)	108–109°/0.6 mm.	1.4955/20°	4.3	55–65°/0.6 mm.	1.4701/20°	1.0
Isoprene (13.4)	Acrolein (14.4)	119–122°/0.5–0.7 mm.	1.4903/24°	6.8	48°/0.2 mm.	1.4670/23°	1.1
1,3-Pentadiene (13.6)	Acrolein (11.2)	104–112°/0.2 mm.	1.4940/22°	3.1	38–44°/0.2 mm.	1.4714/22°	0.5
2,3-Dimethyl-1,3-butadiene (16.4)	Acrolein (11.2)	130–144°/0.4 mm.	1.4967/21°	5.8	50–68°/0.2 mm.	1.4781/22°	1.7
1,3-Butadiene (12.8)	Methacrolein (14.0)	102°/0.4 mm.	1.4764/22°[d]	1.1	...	...	Small
1,3-Butadiene (12.0)	Crotonaldehyde (14.0)	Trace of uncharacterized products					

[a] The physical constants check closely with those reported in the literature.[9] In addition, two of the esters were saponified to known acids and alcohols, and this will be described below. 3,4-Dimethyl-3-cyclohexenylmethyl 3,4-dimethyl-3-cyclohexenecarboxylate appears to be a new compound and had the following analysis: Calcd. for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21. Found: C, 77.59; H, 10.06. (Analysis performed by Huffman Microanalytical Laboratories, Wheatridge, Colo.). [b] Since the cyclohexenecarboxaldehydes were obtained in small amounts, the physical constants recorded are approximate. [c] This cut was estimated from its index of refraction to be 78% ester. [d] Ester assumed to be contaminated with aldehyde and the yield was estimated from the index of refaction.

Discussion

It is apparent that the esters described above are the products that would be obtained from a Diels–Alder reaction of a 1,3-diene with an α,β-unsaturated aldehyde followed by a Tishchenko condensation of the resulting 3-cyclohexenecarboxaldehyde. The isolation of small amounts of the corresponding 3-cyclohexenecarboxaldehyde in most cases indicated that the reaction is two-step, and the observation that no reaction took place under these conditions in the absence of catalyst shows that both steps are catalytic.[10]

It is interesting that essentially two reactions were obtained here using a 3 $AlEt_3$–$TiCl_4$ catalyst, while Robinson and Fray[7] obtained only the Diels–Alder reaction using a 2 Et_2AlCl–$TiCl_4$ catalyst. The difference in the two catalysts apparently lies in the ability of the 3 $AlEt_3$–$TiCl_4$ catalyst to form metal alkoxide bonds which catalyze the Tishchenko condensation[11] of the Diels–Alder adduct initially formed. To establish the existence of alkoxide bonds in the effective catalyst, the 3 $AlEt_3$–$TiCl_4$ catalyst was treated with acrolein in *n*-heptane and then hydrolyzed with dilute acid. A very small amount of 1-penten-3-ol was isolated, showing that, indeed, some alkoxide bonds were present in the catalyst but that their concentration is quite low. This, however, is no reason for concern since aluminum isopropoxide has been shown to be an extremely efficient Tishchenko catalyst in the system under study.[9]

This reaction appears to be subject to the same stereo requirements generally found with Ziegler catalysts. Compounds containing internal or highly substituted terminal double bonds either do not react or else react to a very limited extent.

Experimental[12]

Materials.—All chemicals used here were purchased and used without further purification—triethyl aluminum (Ethyl Corp.), titanium tetrachloride (J. T. Baker Co.), 1,3-butadiene (Matheson Co., C.P. grade), isoprene, *n*-heptane, and *n*-hentane (Phillips Petroleum Co.), 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, methacrolein, and crotonaldehyde (Matheson, Coleman and Bell Co.), acrolein (Eastman, stabilized with hyroquinone), 1-penten-3-ol (Aldrich Chemical Co.), and allyl alcohol (Merck).

General Procedure for Ester Preparation.—To a stirred solution of 3.4 g. (0.03 mole) of aluminum triethyl in about 200 cc. of pure, dry *n*-heptane was added with stirring 1.9 g. (0.01 mole) of titanium tetrachloride in a glove box as previously described.[4] The catalyst solution was brought to 600 cc. and transferred from the glove box. The α,β-unsaturated aldehyde and the diene were dissolved in 100 cc. of *n*-heptane, and this solution was added to the catalyst mixture with vigorous agitation and at ambient temperature. The addition of reactants was begun under a slow flow of prepurified nitrogen which was discontinued after a short time because of the volatility of the reactants. A mild exotherm was experienced in each case as the reactants were added, and this generally raised the reaction solution temperature to about 30°. The addition of reactants was usually carried out over a period of about 5 hr.

The reaction mixture was centrifuged to remove the insoluble catalyst,[13] the solvent stripped, and the product isolated by distillation. The details are given in Table II.

Saponification of 3-Cyclohexenylmethyl 3-Cyclohexenecarboxylate.—To 1.3 g. (0.0325 mole) of sodium hydroxide in 40 cc. of distilled water was added 4.8 g. (0.0218 mole) of 3-cyclohexenyl-

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(9) F. C. Frostick and B. Phillips, U. S. Patent 2,716,123 (August 23, 1955).

(10) Since the product yields are relatively low, it is possible that a normal, uncatalyzed Diels–Alder reaction could have taken place as the first step of the reaction followed by a catalyzed Tishchenko condensation.

(11) The literature indicates that only metal alkoxides will catalyze the Tishchenko condensation. See I. Lin and A. R. Day, *J. Am. Chem. Soc.*, **74**, 5133 (1952), for leading references.

(12) All melting and boiling points are uncorrected.

(13) A small amount of catalyst is soluble in the *n*-heptane and can be removed by dilute acid washing. However, its presence had no noticeable effect on the product work-up, and this step was generally omitted.

methyl 3-cyclohexenecarboxylate, and the mixture was refluxed with stirring for 5.5 hr. Upon cooling, the solution was dried over anhydrous potassium carbonate and distilled. 3-Cyclohexene-1-methanol distilled at 93° 19 mm., n^{25}_{D} 1.4818, and had the expected infrared spectrum. The α-naphthylurethan, m.p. 106–106.5°, and the phenylurethan, m.p. 58.0–58.5°, derivatives were prepared and found to check with those reported[14]: α-naphthylurethan, m.p. 103°, and phenylurethan, m.p. 56–57°.

The aqueous saponification solution was acidified and washed with benzene. The benzene solution was dried with anhydrous magnesium sulfate and then evaporated to dryness under vacuum. The physical constants of the crude 3-cyclohexene-1-carboxylic acid, m.p. ~19°, n^{23}_{D} 1.4791, compare closely with those in the literature,[15] m.p. 17°, n^{20}_{D} 1.4812. The p-bromophenyl ester of the acid was also prepared and found to melt at 81.5–82.0° (lit.,[16] m.p. 83–84°).

Saponification of 4-Methyl-3-cyclohexenylmethyl 4-Methyl-3-cyclohexenecarboxylate.—To 0.6 g. (0.015 mole) of sodium hydroxide in 20 cc. of distilled water was added 2.42 g. (0.01 mole) of 4-methyl-3-cyclohexenylmethyl 4-methyl-3-cyclohexenecarboxylate, and the mixture was refluxed overnight. The aqueous solution was cooled, washed with benzene, and acidified. 4-Methyl-3-cyclohexenecarboxylic acid was collected by filtration and recrystallized from water. The acid melted at 98.5–99° (lit.,[17] m.p. 99°).

Test of Diels–Alder Reaction at High Dilution and Mild Temperature.—To 13.6 g. (0.2 mole) of isoprene in 500 cc. of pure, dry n-heptane, maintained at 32°, was added 14.4 g. (.26 mole) of acrolein in 100 cc. of n-heptane over a period of about 4.75 hr. Stirring was continued for an additional 1.5 hr. and then the solution was distilled. Nothing boiling higher than n-heptane was obtained.

Reaction of Acrolein with the Catalyst.—To 7.5 g. (0.066 mole) of triethyl aluminum in about 90 cc. of dry n-heptane was added with stirring 4.2 g. (0.022 mole) of titanium tetrachloride in about 10 cc. of dry n-heptane in a glove box as described above. The catalyst was removed from the glove box, and 11.2 g. (0.2 mole) of acrolein in 20 cc. of dry n-heptane was added over a period of about 2 hr. The addition was maintained at such a rate that the temperature of the reaction solution remained between 30–35°. After standing over the week end, the catalyst suspension was centrifuged and the n-heptane removed. n-Pentane was added, the insoluble catalyst was agitated, and then centrifuged again. This procedure was repeated four or five times to remove all but a trace of n-heptane from the catalyst.[18] The catalyst was then hydrolyzed with dilute sulfuric acid (6 cc. of concentrated H_2SO_4 in 40 cc. of distilled water). A brown precipitate resulted, and additional water was added. The brown precipitate was removed by filtration and washed several times with ether and n-pentane. The brown aqueous solution was also washed several times with ether and n-pentane, and the wash solutions were combined and dried over anhydrous potassium carbonate. After drying overnight, the ether n-pentane was stripped, and 0.5 g. of a cut distilling at 80–86°, n^{20}_{D} 1.3805, and 0.8 g. of a cut distilling at 87–70°, n^{20}_{D} 1.3898, were collected. A few drops of a liquid distilling at 69–120°/0.8–1 mm., $n^{20}_{\text{D}} = 1.4681$,[19] and a very viscous orange pot residue were also obtained.

Gas chromatographic (g.c.) analysis, using 150 ft. of R′ capillary column at 100°, showed that the first cut (80–86°) contained 0.8% allyl alcohol and 3.5% 1-penten-3-ol in an n-pentane-n-heptane mixture, and the second cut (87–70°) contained a trace of allyl alcohol and 4.6% 1-penten-3-ol in n-heptane. Each g.c. peak was identified by spiking the distilled fractions with authentic samples. The 1-penten-3-ol was further identified by comparison of the infrared spectrum of the second cut with that of an authentic sample and found to be superimposible between 9 and 11 μ.[20]

A small portion of the original n-heptane solution, from which the insoluble catalyst had been removed, was evaporated to dryness, leaving a slightly yellow colored powder. X-ray fluorescence spectra showed that this compound contained titanium and chlorine with no more than a trace of aluminum. The remainder of the n-heptane solution was shaken with dilute hydrochloric acid, evaporated, and dried over anhydrous potassium carbonate. The acid solution was washed with both n-heptane and ether which were then added to the previously recovered n-heptane. After concentration of the solution by fractionation through a short column, gas chromatography and infrared spectra showed that no more than a trace of penten-3-ol was formed by hydrolysis of n-heptane soluble catalyst.

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(14) E. G. E. Hawkins, D. J. G. Long, and F. W. Major, *J. Chem. Soc.*, 1465 (1955).

(15) I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. IV, Oxford University Press, New York, N. Y., 1953, p. 433.

(16) Ref. 14, p. 1466.

(17) Ref. 15, p. 449.

(18) The n-heptane was removed so that the alcohol(s) expected on catalyst hydrolysis could be more easily recovered and identified.

(19) The infrared spectrum showed a carbonyl band, and it is assumed that this is a small amount of allyl acrylate.

(20) Since the second cut was at least 95% n-heptane, only a region where 1-penten-3-ol absorbs very strongly could be used for comparison.

3-Substituted Thiophenes. XI. Abnormal Products from 3-Thenyl Grignard Reagents[1]

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A modified cyclic reactor, giving Grignard reagents from active halides in high yield, was used to prepare 3-thenylmagnesium bromide. Carbon dioxide reacts with this reagent to produce 3-thienylacetic acid (the normal product) and 3-methyl-2-thenoic acid (the abnormal product) in a ratio of 2:3, thus confirming the hypothesis that abnormal products are formed more readily when the reaction site is activated toward electrophilic substitution. 3-Thenylmagnesium bromide reacts with ethyl chlorocarbonate, acetyl chloride, and formaldehyde to give the abnormal products, as shown by comparison to authentic samples.

In an attempt to prepare 3-thienylacetic acid by carbonation of 3-thenylmagnesium bromide, Campaigne and Le Suer[3] found that the principal acidic product was 3-methyl-2-thenoic acid. This observation led to the suggestion that this substance might have been formed as the abnormal carbonation product of the 3-thenyl Grignard reagent, although such abnormal products from Grignard reagents and carbon dioxide were then unknown. It was further suggested that the high activity of the alpha position of thiophene at which carbonation had occurred, may have been responsible for the observed result. Subsequently, abnormal carbonation was found to be the rule, rather than the exception, in reactions with Grignards derived from

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(1) Taken from a thesis submitted by O. E. Yokley for the degree Doctor of Philosophy at Indiana University, June 1954. For the previous paper in the series, see E. Campaigne and R. L. Patrick, *J. Am. Chem. Soc.*, **77**, 5425 (1955).

(2) Sterling-Winthrop Fellow in Chemistry, 1952–1953.

(3) E. Campaigne and W. M. Le Seur, *J. Am. Chem. Soc.*, **70**, 1555 (1948).