4,4,14α-Trimethylallopregnan-3β-ol-20-one acetate (LXXIV) (C. S. Barnes),[52] R.D. (Fig. 10) in methanol (*c* 0.103): $[\alpha]_{700}$ +40°, $[\alpha]_{589}$ +90°, $[\alpha]_{307.5}$ +2129°, $[\alpha]_{270}$ −3479°, $[\alpha]_{265}$ −2620°.

Methyl-$\Delta^{7,9(11),24(28)}$-3β-hydroxy-16-ketoburicotrien-21-oate (LXXV) (T. G. Halsall),[49] R.D. (Fig. 10) in dioxane (*c* 0.052): $[\alpha]_{700}$ −10°, $[\alpha]_{589}$ −30°, $[\alpha]_{327.5}$ −1850°, $[\alpha]_{320}$ −1620° (sh), $[\alpha]_{280}$ +1750°.

Methyl-$\Delta^{7,9(11)}$-3β,16α-dihydroxyburicodien-21-oate (LXXVI) (T. G. Halsall),[49] R.D. in dioxane (*c* 0.106): $[\alpha]_{700}$ +31°, $[\alpha]_{589}$ +40°, $[\alpha]_{275}$ +266°.

Δ^{7}-Lanosten-3-one (LXXIX) (D. H. R. Barton), R.D. (Fig. 11) in methanol (*c* 0.084): $[\alpha]_{700}$ +2°, $[\alpha]_{589}$ −10°, $[\alpha]_{315}$ −366°, $[\alpha]_{275}$ +260°, $[\alpha]_{260}$ +174°; in dioxane (*c* 0.10) (F. S. Spring): $[\alpha]_{700}$ −31°, $[\alpha]_{589}$ −30°, $[\alpha]_{320}$ −468°, $[\alpha]_{280}$ +268°.

Δ^{8}-Lanosten-3-one (LXXX) (D. H. R. Barton), R.D. (Fig. 11) in methanol (*c* 0.111): $[\alpha]_{700}$ +57°, $[\alpha]_{589}$ +74°, $[\alpha]_{300}$ +610°, $[\alpha]_{277.5}$ +498°, $[\alpha]_{270}$ +542°.

Δ^{8}-3-Ketoburicen-21-oic acid (LXXXI) (J. S. E. Holker),[54] R.D. in methanol (*c* 0.10): $[\alpha]_{700}$ +29°, $[\alpha]_{589}$ +42°, $[\alpha]_{300}$ +437°, $[\alpha]_{260}$ −615°.

Elemenonic acid (LXXXII) (G. A. Kon[55] *via* T. G. Halsall), R.D. (Fig. 11) in dioxane (*c* 0.089): $[\alpha]_{700}$ −9°, $[\alpha]_{589}$ +17°, $[\alpha]_{315-312.5}$ +370°, $[\alpha]_{280}$ +37°.

Dihydrobutyrospermone (LXXXIII) (F. S. Spring),[21,56] R.D. in methanol (*c* 0.05): $[\alpha]_{700}$ −50°, $[\alpha]_{589}$ −50°, $[\alpha]_{310}$ −398°, $[\alpha]_{270}$ +312°.

Masticadienonic acid (LXXXIV) (D. H. R. Barton),[57] R.D. (Fig. 11) in methanol (*c* 0.1025): $[\alpha]_{700}$ −66°, $[\alpha]_{589}$ −75°, $[\alpha]_{317.5}$ −577°, $[\alpha]_{275}$ +22°, $[\alpha]_{270}$ −117° (infl.), $[\alpha]_{260}$ −606°.

Isomasticadienonic acid (LXXXV) (D. H. R. Barton),[58] R.D. (Fig. 11) in methanol (*c* 0.126): $[\alpha]_{700}$ 0°, $[\alpha]_{589}$ 0°, $[\alpha]_{305}$ +302°, $[\alpha]_{270}$ −310°, $[\alpha]_{260}$ −103°.

$\Delta^{7,9(11)}$-Lanostadien-3-one (LXXXVI) (D. H. R. Barton), R.D. (Fig. 12) in dioxane (*c* 0.116): $[\alpha]_{700}$ +30°, $[\alpha]_{589}$ +49°, $[\alpha]_{345-342.5}$ +203°, $[\alpha]_{330}$ +194°, $[\alpha]_{280}$ +978°, $[\alpha]_{277.5}$ +862°.

$\Delta^{7,9(11)}$-Lanostadien-3β-ol acetate (LXXXVII) (D. H. R. Barton), R.D. in dioxane (*c* 0.088): $[\alpha]_{700}$ +74°, $[\alpha]_{589}$ +100°, $[\alpha]_{250}$ +1015°.

Methyl polyporenate C (LXXXVIII) (E. R. H. Jones),[49] R.D. (Fig. 12) in methanol (*c* 0.104): $[\alpha]_{700}$ +9°, $[\alpha]_{589}$ +9°, $[\alpha]_{360}$ +38° (broad peak), $[\alpha]_{320}$ −2°, $[\alpha]_{270}$ +321°.

Δ^{7}-Ergosten-3-one (LXXXIX) (O. H. Wheeler, H. B. Henbest), R.D. (Fig. 12) in methanol (*c* 0.053): $[\alpha]_{700}$ +21°, $[\alpha]_{589}$ +51°, $[\alpha]_{307.5}$ +588°, $[\alpha]_{272.5}$ −721°, $[\alpha]_{265}$ −486°.

Δ^{8}-Cholesten-3-one (XC) (H. B. Henbest), R.D. (Fig. 12) in methanol (*c* 0.062): $[\alpha]_{700}$ +86°, $[\alpha]_{589}$ +103°, $[\alpha]_{307.5}$ +706°, $[\alpha]_{272.5}$ −540°, $[\alpha]_{260}$ −73°.

$\Delta^{8(14)}$-Ergosten-3-one (XCI) (O. H. Wheeler, H. B. Henbest), R.D. in methanol (*c* 0.086): $[\alpha]_{700}$ +15°, $[\alpha]_{589}$ +30°, $[\alpha]_{307.5}$ +635°, $[\alpha]_{270}$ −1175°, $[\alpha]_{260}$ −459°.

Δ^{14}-Ergosten-3-one (XCII) (O. H. Wheeler), R.D. in methanol (*c* 0.132): $[\alpha]_{700}$ +30°, $[\alpha]_{589}$ +58°, $[\alpha]_{305}$ +630°, $[\alpha]_{267.5}$ −743°, $[\alpha]_{255}$ −484°.

Δ^{9}-Dehydroprogesterone (XCIII) (J. Fried), R.D. in dioxane (*c* 0.184): $[\alpha]_{700}$ +100°, $[\alpha]_{589}$ +152°, $[\alpha]_{380}$ +473°, $[\alpha]_{367.5}$ +398°, $[\alpha]_{352.5}$ +463°, $[\alpha]_{350}$ +453°, $[\alpha]_{312.5}$ +3222°, $[\alpha]_{302.5}$ +1127°.

Δ^{11}-Dehydroprogesterone (XCIV) (J. Fried), R.D. in dioxane (*c* 0.060): $[\alpha]_{700}$ +100°, $[\alpha]_{589}$ +160°, $[\alpha]_{375}$ +566°, $[\alpha]_{365}$ +483°, $[\alpha]_{352.5}$ +573°, $[\alpha]_{350}$ +556°, $[\alpha]_{315}$ +2758°, $[\alpha]_{295}$ −3158°.

DETROIT, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Synthesis of a Series of Substituted *trans*-2-Phenylcyclopropanecarboxylic Acids

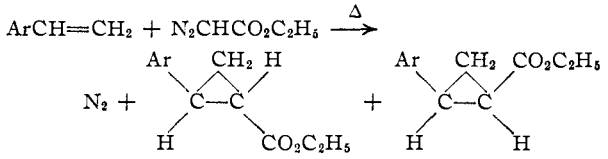
BY EDWARD N. TRACHTENBERG AND GEORGE ODIAN[1]

RECEIVED FEBRUARY 21, 1958

The syntheses, ultraviolet spectra and proofs of configuration of several *m*- and *p*-substituted *trans*-2-phenylcyclopropanecarboxylic acids are described. Further evidence is given in support of the stereochemical assignment to the isomers of 2-phenylcyclopropanecarboxylic acid melting at 106 and 93° of *cis* and *trans*, respectively.

For the purposes of the study reported in the accompanying paper,[2] it was necessary to prepare a series of *trans*-2-phenylcyclopropanecarboxylic acids substituted with *p*-nitro, *m*-nitro, *p*-chloro, *m*-chloro, *p*-acetamido, *p*-methyl and *p*-methoxy groups. In this paper are reported the syntheses, ultraviolet spectra and proofs of configuration of these compounds along with similar data for the unsubstituted acid in both the *cis* and *trans* modifications.

The method of synthesis generally employed consisted in the reaction of ethyl diazoacetate with an appropriately substituted styrene at an elevated temperature to give nitrogen and ethyl 2-arylcyclopropanecarboxylate. This led in several cases to a mixture of *cis* and *trans* isomers which was then subjected to one of the following procedures: (1) the ester mixture was saponified, the product acidified and the two isomeric acids separated by fractional crystallization; (2) the ester mixture was saponified, the product acidified, the acid mixture epimerized by refluxing with thionyl chloride in benzene and the more stable product isolated after hydrolyzing with water; (3) the ester mixture was epimerized to the more stable product by refluxing with ethanolic sodium ethoxide and the more stable isomer isolated after saponification and acidification.



In view of the fact that the various styrenes were generally made by decarboxylation of the corresponding cinnamic acids, it was held desirable to employ an alternate synthetic method involving reaction of diazomethane with a substituted cinnamic ester. However, preliminary experiments on ethyl cinnamate itself revealed that the reaction led predominantly, if not entirely, to ethyl β-methylcinnamate, isomeric with the desired product. That the diazoacetic ester reaction did not similarly yield this undesired olefinic product was tested for in all cases by use both of the permanganate test and of infrared spectroscopy.

(1) This paper is part of the work to be submitted by Mr. George Odian to the Graduate School of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4018 (1958).

The stereochemistry of 2-phenylcyclopropanecarboxylic acid has been the subject of some controversy. In 1903, Buchner isolated one of the isomers (A) melting at 106° to which he assigned the *trans* structure.[3] In support of this, he degraded the compound to the known *trans*-cyclopropane-1,2-dicarboxylic acid by a sequence of reactions involving nitration with cold fuming nitric acid, reduction of the nitro group with ferrous sulfate and ammonia and subsequent oxidation of the resultant aniline ring with alkaline permanganate. No mention is made of the exact conditions for the final oxidation, nor is it clear whether pure (A) was used for the degradation. It is significant to note that Buchner reported no isomer melting at 93° (B) despite the fact that Burger and Yost,[4] using similar experimental conditions, found this to be the major product, a conclusion which we have confirmed. Markees and Burger questioned Buchner's assignment and suggested that the *trans* structure should, instead, be assigned to the lower melting isomer (B).[5] This contention was supported by degradation of (B) to *trans*-cyclopropane-1,2-dicarboxylic acid by a reaction sequence involving nitration at room temperature with concentrated nitric acid, reduction of the nitro group with Raney nickel catalyst[6] and oxidation finally with permanganate in carbonate solution. Clearly, either Buchner or Markees and Burger had employed impure starting material or had succeeded in epimerizing the compound in the course of degradation. Independent evidence, however, strongly supports the assignment of the *trans* structure to (B). First, either acid can be converted to the lower melting compound by refluxing it with thionyl chloride in benzene solution followed by hydrolysis of the resultant acid chloride with water.[5] If one makes the entirely reasonable assumption that the *trans* structure should be thermodynamically more stable than the *cis* in this system, isomer B must be *trans*. Second, we have chemically related 2-(*p*-chlorophenyl)-cyclopropanecarboxylic acid and 2-(*m*-chlorophenyl)-cyclopropanecarboxylic acid to isomer B by unambiguous methods (see Fig. 1), and both of these substituted acids had been prepared from their corresponding esters which had previously been subjected to sodium ethoxide epimerization conditions and should, therefore, have been in the more stable, *trans* form. Third, the ultraviolet spectrum of (B) has maxima at slightly longer wave length (see Table I) than (A) in agreement with similar findings in other *cis* and *trans* isomeric cyclopropane systems.[7]

The assignment of the *trans* configuration to the various substituted 2-phenylcyclopropanecarboxylic acids is based upon the chemical interrelationships outlined in Fig. 1, details for which are given in the Experimental.

Although the *p*-methyl derivative was not chemically related to (B), its *trans* assignment is based on the fact that its method of synthesis paralleled that for the other compounds and that only a single isomer was obtained after subjecting its corresponding ethyl ester to the sodium ethoxide epimerization conditions. The *p*-chloro and *m*-chloro compounds, whose stereochemistry is proved, also gave only a single isomer after such treatment.

TABLE I

ULTRAVIOLET SPECTRA OF THE SUBSTITUTED 2-PHENYLCYCLOPROPANECARBOXYLIC ACIDS

Substituent	Absorption maxima[a] λ, mμ	ε × 10⁻³
p-H	210–215	8.3
	222	11
	267	0.38
p-H(*cis*)	210–215	7.3
	219	7.5
	261	0.20
p-Nitro	210	8.0
	218	7.9
	287	11
m-Nitro	215	35
	267	14
p-Chloro	210	5.5
	229	15
	274	0.53
m-Chloro	212.5	14
	220	10
	273.5	0.46
p-Methyl	212.5	7.4
	225	12
	270.5	0.56
p-Methoxy	210	6.4
	233	14
	279	1.7

[a] All spectra were taken in 95% ethanol on a Cary recording spectrophotometer and unless otherwise stated are for the *trans* isomer.

Experimental[8]

Reaction of Diazomethane with Ethyl *trans*-Cinnamate.—To 500 ml. of an ether solution of 0.20–0.22 mole of diazomethane prepared from 32 g. (0.31 mole) of nitrosomethylurea and cooled to 0–5° was added over a 15-minute period with ice cooling 39 g. (0.22 mole) of ethyl cinnamate. The solution was permitted to stand in an ice-filled Dewar overnight, at the end of which time the yellow color had disappeared and a white solid had precipitated. This was filtered off, washed with ether and dried to yield 22.1 g. (50% based on diazomethane) of a solid, m.p. 99–100°. Its infrared spectrum agreed with that for a pyrazoline.

Anal. Calcd. for $C_{12}H_{14}O_2N_2$: C, 66.06; H, 6.42; N, 12.84. Found: C, 66.12; H, 6.50; N, 13.09.

Three grams of this pyrazoline was heated at 190–200° until nitrogen evolution ceased (*ca.* 5 hours). Distillation of the reaction mixture gave 2.1 g. of a clear, colorless liquid, b.p. 71–73° (0.7–0.8 mm.). This compound gave a positive permanganate test and had infrared and ultraviolet absorption spectra in agreement with its formulation as either ethyl α- or β-methylcinnamate. This ester (2.0 g.) was saponified by refluxing overnight with 0.75 g. of sodium hydroxide dissolved in a solution of 1.5 ml. of water and 6 ml. of ethanol. After concentration, excess hydrochloric acid was added to precipitate the corresponding acid. This was twice recrystallized from a dilute solution of hydrochloric acid in 20% ethanol–water to yield β-methylcinnamic acid, m.p. 98.0–98.5° (lit.[9] m.p. 98.5°).

(3) E. Buchner and J. Geronimus, *Ber.*, **36**, 3782 (1903).

(4) A. Burger and W. L. Yost, THIS JOURNAL, **70**, 2198 (1948).

(5) D. G. Markees and A. Burger, *ibid.*, **70**, 3228 (1948).

(6) We have also effected ths reduction with tin and hydrochloric acid with the same result.

(7) R. J. Mohrbacher and N. H. Cromwell, THIS JOURNAL, **79**, 401 (1957).

(8) All melting points are corrected. The elementary analyses were performed either by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Micro-tech Laboratories, Skokie, Ill.

(9) G. Schroeter, *Ber.*, **37**, 1092 (1904).

***trans*-2-Phenylcyclopropanecarboxylic acid** was obtained in 50% yield by heating a mixture of ethyl diazoacetate and styrene at 125–135° following the procedure of Burger and Yost.[4] It melted at 92–93° (lit. m.p. 93°), gave a negative permanganate test and showed the expected infrared spectrum with the characteristic cyclopropane band at about 9.8 μ.[10] It did not show the strong band at 6.2 μ which is found in *trans*-cinnamic acid and which is associated with the double bond.[11]

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.08; H, 6.12.

***cis*-2-Phenylcyclopropanecarboxylic acid** was obtained from the aqueous mother liquors from the fractional recrystallization of the *trans*-acid following the method of Burger and Yost.[4] It melted at 105.5–106.5° (lit. m.p. 106–107°), gave a negative permanganate test and had the expected infrared spectrum. It was, by far, the minor product compared to the *trans* isomer, being isolated in less than 10% yield.

Anal. Calcd. for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 74.00; H, 6.15.

***trans*-2-(*p*-Nitrophenyl)-cyclopropanecarboxylic Acid.**—Following the procedure of Markees and Burger,[5] this acid was prepared in 30% yield by the nitration of pure *trans*-2-phenylcyclopropanecarboxylic acid. After three recrystallizations from xylene, the pale yellow needles melted at 197–199° (lit. m.p. 197–199°). That the nitro group is, indeed, *para* follows from the independent synthesis of this compound from *p*-nitrostyrene by Markees and Burger.

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.18; H, 4.45; N, 6.78.

***trans*-2-(*m*-Nitrophenyl)-cyclopropanecarboxylic Acid.**—A sample of *m*-nitrocinnamic acid was prepared following the procedure of Walling.[12] Although this acid did not undergo decarboxylation at 190° as reported by Wiley,[13] the reaction could be effected smoothly at 215° to yield *m*-nitrostyrene. A solution of 21 g. (0.14 mole) of *m*-nitrostyrene in 40 ml. of xylene was heated to 120°, and to this was added over an hour period a solution of 21 g. (0.18 mole) of freshly distilled ethyl diazoacetate in 10 ml. of xylene. The resulting exothermic reaction caused the temperature to rise to 140° where it was maintained for an additional 2 hours. At this point, nitrogen evolution having ceased, the solution was concentrated and fractionated *in vacuo* to yield 80% of a yellow oil, b.p. 161° (1.0 mm.), which solidified on standing in the refrigerator. This solid, which was probably a mixture of *cis* and *trans* isomers, was hydrolyzed to the corresponding acid mixture by refluxing with a solution of acetic acid, water and sulfuric acid. The resultant acid mixture of wide melting point range was converted into the more stable *trans* compound by refluxing with thionyl chloride in benzene and then hydrolyzing the acid chloride so formed with water.[14] The *trans*-2-(*m*-nitrophenyl)-cyclopropanecarboxylic acid so produced (22% yield) melted at 155.5–156.5° after two recrystallizations from water. It gave a negative test with permanganate solution and had the expected infrared spectrum. Conclusive proof of the *trans* stereochemistry of this compound was obtained by reducing a portion of it with tin and hydrochloric acid to the corresponding amine, diazotizing the amine and removing the diazo group with hypophosphorous acid in the standard way[15] to yield *trans*-2-phenylcyclopropanecarboxylic acid identical in melting point, mixed melting point and infrared spectrum with an authentic sample.

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 58.01; H, 4.51; N, 7.11.

***trans*-2-(*p*-Chlorophenyl)-cyclopropanecarboxylic Acid.**—To 25 g. (0.18 mole) of *p*-chlorostyrene[12] was added 30.5 g. (0.27 mole) of freshly distilled ethyl diazoacetate. The solution was cautiously heated to 120° at which point a vigorously exothermic reaction set in necessitating cooling in an ice-bath. (The reaction could also be run in xylene solution with approximately the same yield and easier temperature control.) After the exothermic reaction had subsided, the solution was further heated at 170–180° until nitrogen evolution stopped. Fractionation of the product at reduced pressure yielded 20.5 g. (50% yield) of ethyl 2-(*p*-chlorophenyl)-cyclopropanecarboxylate as a pale yellow oil, b.p. 106–109° (0.3 mm.). This ester was saponified by refluxing overnight with 12 g. of sodium hydroxide in 80 ml. of 85% ethanol to yield after acidification, filtration and four recrystallizations from water 10% of the solid *p*-chloro acid, m.p. 115.5–116.5°. This compound had the expected infrared spectrum and did not decolorize permanganate solution. Difficulty was encountered in several subsequent attempts at the ester saponification. A low melting solid, presumably a mixture of *cis* and *trans* acids, was obtained which gave a correct elementary analysis but had infrared and ultraviolet spectra which were not as sharp as those of the pure 115.5–116.5° melting compound. Refluxing the ester with sodium ethoxide in ethanol for 90 minutes, which should have served to epimerize any *cis* to *trans* ester, overcame this

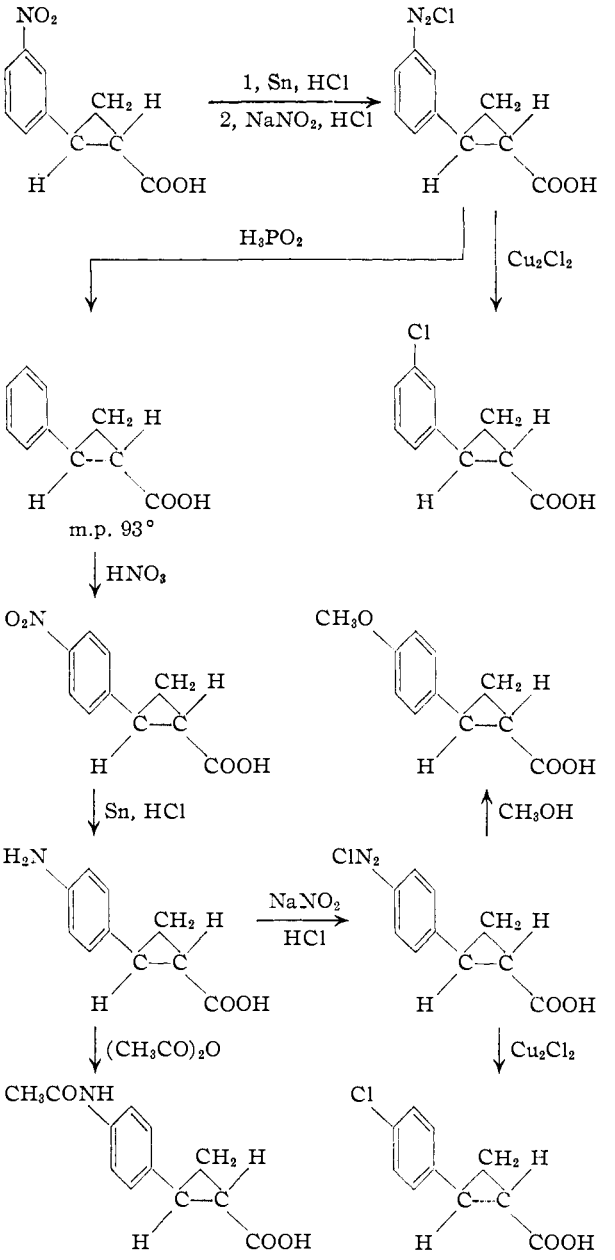


Fig. 1.—Chemical interrelationship of the *trans*-2-arylcyclopropanecarboxylic acids.

(10) V. A. Slabey, THIS JOURNAL, **76**, 3604 (1954).

(11) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, England, 1954, p. 31.

(12) C. Walling and K. B. Wolfstirn, THIS JOURNAL, **69**, 852 (1947).

(13) R. H. Wiley and N. R. Smith, *ibid.*, **70**, 2295 (1948).

(14) The same procedure as had previously been employed in the *p*-nitro analog; see ref. 5.

(15) N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 294.

difficulty. The ester, so treated, gave on sodium hydroxide saponification and acidification 25% of the pure 115.5–116.5° product.

The *trans* configuration of this isomer was proved by independent synthesis from the known *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid. The latter was reduced with tin and hydrochloric acid and the amine so formed subjected to standard diazotization and Sandmeyer conditions.[16] Recrystallization of the dark, oily product of this reaction from water yielded *trans*-2-(*p*-chlorophenyl)-cyclopropanecarboxylic acid identical in infrared spectrum, melting point and mixed melting point with the compound prepared above from *p*-chlorostyrene.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.71; Cl, 18.03. Found: C, 61.23; H, 4.65; Cl, 18.23.

trans-2-(*m*-**Chlorophenyl**)-**cyclopropanecarboxylic Acid.**—To a solution of 27.3 g. (0.20 mole) of *m*-chlorostyrene[12] in 25 ml. of xylene heated to 140–150° was added over a period of an hour 33 g. (0.30 mole) of freshly distilled ethyl diazoacetate. Further heating at this temperature was continued until nitrogen evolution ceased at which time the solution was fractionated *in vacuo* to yield 22.0 g. (50% yield) of ethyl 2-(*m*-chlorophenyl)-cyclopropanecarboxylate as a yellow oil, b.p. 114° (0.4 mm.). To avoid the difficulties encountered in several attempts at the saponification of the *p*-chloro compound, the *m*-chloro ester was epimerized directly by treatment with sodium ethoxide in refluxing ethanol for 90 minutes. Saponification was effected by adding water to the above solution and refluxing overnight to yield, after acidification, a pale brown solid which was extracted with 50:50 ethyl acetate–cyclohexane. Concentration of the extract precipitated a lighter colored solid which could be recrystallized from water to give 15% of *trans*-2-(*m*-chlorophenyl)-cyclopropanecarboxylic acid, m.p. 108–109°. This acid had the expected infrared spectrum and did not decolorize permanganate solution.

The *trans* structure of this compound was proved by independent synthesis from the known *trans*-2-(*m*-nitrophenyl)-cyclopropanecarboxylic acid by the same sequence of reactions as was used in the *p*-chloro case (*vide supra*). Identity was established in infrared spectrum, melting point and mixed melting point.

Anal. Calcd. for $C_{10}H_9O_2Cl$: C, 61.08; H, 4.61; Cl, 18.03. Found: C, 61.21; H, 4.61; Cl, 18.16.

trans-2-*p*-**Tolylcyclopropanecarboxylic Acid.**—A solution of 11.6 g. (0.09 mole) of *p*-methylstyrene[17] and 18.0 g. (0.16 mole) of freshly distilled ethyl diazoacetate was heated cautiously to 110° and the temperature maintained for an hour. The solution was then further heated at 140–150° until nitrogen evolution ceased (*ca.* 3 hours). Vacuum distillation of the product gave 13.5 g. (80% yield) of ethyl 2-*p*-tolylcyclopropanecarboxylate as a clear, colorless oil, b.p. 71–73° (0.08–0.1 mm.). This ester was saponified by refluxing with 12 g. of sodium hydroxide in 60 ml. of 85% ethanol for 13 hours. On acidification, the desired acid precipitated. It melted at 119.5–120.5° after two recrystallizations from water (36% yield), gave a negative test with permanganate solution and had the expected infrared spectrum.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 74.97; H, 6.87. Found: C, 75.10; H, 6.65.

trans-2-(*p*-**Acetamidophenyl**)-**cyclopropanecarboxylic Acid.**—A solution of 2.00 g. (0.0097 mole) of *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid and 4.5 g. (0.038 mole) of tin in 12 ml. of concentrated hydrochloric acid was stirred and heated on the steam-bath for an hour. The solution was made alkaline by addition of concentrated ammonium hydroxide and the precipitated tin hydroxides filtered. The filtrate was then made slightly acid with glacial acetic acid and evaporated to dryness. The solid residue was extracted with acetone and the extract evaporated to dryness to yield 1.59 g. (93% yield) of *trans*-2-(*p*-aminophenyl)-cyclopropanecarboxylic acid. This amino acid could not be purified, as also was found to be the case when the reduction had been effected catalytically, but could be acetylated directly with acetic anhydride following the procedure of Markees and Burger to give *trans*-2-(*p*-acetamidophenyl)-cyclopropanecarboxylic acid which after successive recrystallizations from a 1:9 mixture of glacial acetic acid–*n*-butyl ether and then water melted at 206–208° (lit.[5] m. p. 205–208°).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.50; H, 6.12; N, 6.49.

trans-2-*p*-**Anisylcyclopropanecarboxylic Acid.**—A solution of 10 g. (0.077 mole) of *p*-methoxystyrene[12] and 15.0 g. (0.135 mole) of freshly distilled ethyl diazoacetate was heated at 130–140° until nitrogen evolution ceased (*ca.* 3 hours. Fractionation of the reaction mixture *in vacuo* yielded 11.3 g. (77% yield) of ethyl 2-*p*-anisylcyclopropanecarboxylate as a clear, colorless oil, b.p. 150° (3 mm.), which solidified in the receiver vessel. This ester was saponified by refluxing with 12 g. of potassium hydroxide in 25 ml. of 85% ethanol for 8 hours to yield 15% of the corresponding acid, m.p. 112–113° after three recrystallizations from water. This acid gave a negative test with permanganate solution and had the expected infrared spectrum.

The *trans* stereochemistry of this compound was proved by its independent synthesis from the known *trans*-2-(*p*-nitrophenyl)-cyclopropanecarboxylic acid following the procedure of Hodgson and Foster involving a sequence of reactions in which the nitro group is reduced with tin and hydrochloric acid and the amine group so formed diazotized and replaced by methoxyl.[18] The compound formed in this way agreed with that synthesized from *p*-methoxystyrene in infrared spectrum, melting point and mixed melting point.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29. Found: C, 68.60; H, 6.15.

(16) C. S. Marvel and S. M. McElvain, "Organic Syntheses," Coll. Vol. 1, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 170.

(17) N. Sulzbacher and E. Bergmann, *J. Org. Chem.*, **13**, 303 (1948).

(18) H. H. Hodgson and C. K. Foster, *J. Chem. Soc.*, 581 (1942).

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Conjugative Transmission in Cyclopropane Systems

BY EDWARD N. TRACHTENBERG AND GEORGE ODIAN[1]

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The *pK*'s of a series of *m*- and *p*-substituted *trans*-2-phenylcyclopropanecarboxylic acids in dilute aqueous solution at 25° were determined potentiometrically and the Hammett ρ for the reaction calculated. Comparison to the ρ for the dissociation of *trans*-cinnamic acid and β-phenylpropionic acid indicates that the cyclopropane ring does not transmit conjugation.

It has long been recognized that cyclopropane is quite different in both its physical and chemical properties from its strainless higher homologs and that it bears some marked resemblance to an olefin. One of the most interesting properties is the ability of the three-membered ring to enter into conjugation. It is well known that there is delocalization of electrons in an alternating system of single and double bonds with concomitant transmission of electrical effects along the chain. In the case of

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