1,4-dichloro-1-phenyl-1-butene (I) [mainly *trans*, but containing variable (2–10%) amounts of *cis*-I],[8] and ether freshly distilled from butylmagnesium bromide was treated with the activating mixture as indicated in Table I. After stirring for the times indicated at room temperature (some of the reactions were run at reflux after a time at room temperature), samples were taken and worked up as usual. The product was analyzed by g.l.p.c. on a 2-ft. column with a silicone rubber phase at 150°.

cis- **(IV) and** *trans*-**1-Phenyl-1-butene (V).**—To a Grignard reagent prepared from 88 g. of 1-bromopropane in 400 ml. of ether was added 53 g. of benzaldehyde with cooling by an ice bath. After reflux for 30 min. the mixture was treated with dilute acid and the product was isolated as usual. The product was dissolved in 200 ml. of benzene, 1 g. of toluenesulfonic acid was added, and the solution was refluxed into a phase-separating head for 1 day so that the water formed was removed. After the usual work-up[15] distillation afforded 39 g. (60%) of mixture of the isomers of 1-phenyl-1-butene, b.p. 196–198°. On analysis (g.l.p.c. using a 2-ft. silicone rubber column at 115°) the ratio of *cis* to *trans* was 12 to 88. A strong absorption at 10.4 μ indicated that the major isomer was *trans*.[16]

A solution of 20.0 g. of a 22:78 mixture of *cis–trans* isomers of 1-chloro-1-phenyl-1-butene (see below) in 135 ml. of pure dry tetrahydrofuran was added to 3.0 g. of sublimed magnesium.[5] After initiation with 0.5 ml. of 1,2-dibromoethane,[8] an exothermic reaction took place for about 1 hr. Aliquots of the reaction mixture were hydrolyzed with water and analyzed for *cis*- and *trans*-1-phenyl-1-butene (IV and V) and for *cis* and *trans*-1-chloro-1-phenyl-1-butene (VI). These analyses showed that after 1 hr. the ratio of products, as determined by g.l.p.c., was 12% IV, 36% V, 3% *cis*-VI, and 49% *trans*-VI. After 1 day the proportions were 22% IV, 72% V, and 6% *trans*-VI. Titration after 2 days showed that an 86% yield of Grignard reagent was present.

The reaction of *cis*- and *trans*-VI with magnesium in ether was much more sluggish, as after 24 hr. a solution was obtained which had only 40% of Grignard reagent. On hydrolysis this afforded a mixture which had IV and V in the ratio 17:83.

trans-**1-Chloro-1-phenyl-1-butene (VI).**—An authentic mixture of the *cis* and *trans* isomers of VI was prepared as follows. A solution of 32 g. of butyrophenone in 50 ml. of carbon tetrachloride was added to a refluxing mixture of 50 g. of phosphorus pentachloride in 100 ml. of carbon tetrachloride. After refluxing for 30 min., 110 ml. of solvent was distilled during 45 min., and the remainder was poured on ice. After the usual work-up, distillation afforded 29.5 g. (82%) of the isomers, b.p. 90–94° (5 mm.).[17] Gas phase chromatography showed this to be a mixture, 29% *cis* and 71% *trans*. In different runs slightly different ratios of *cis* and *trans* isomers were obtained. A sample of pure *trans* VI, obtained by preparative-scale gas chromatography on a 6-ft. silicone rubber column, had the following n.m.r spectrum: τ 8.93 (3H), 7.63 (2H), 3.98 (1H), and 2.76 multiplet maximum (5H). The ratios of *cis* to *trans* isomers were also determined by n.m.r. analysis.

1-Phenyl-1,3-butadiene (VII).—A sample of pure VII was prepared as described.[18] This compound proved to have a retention time exactly that of one product produced in the reaction of I with magnesium in ether and markedly different from that of 2-phenyl-1,3-butadiene.[19]

1-Phenylcyclobutene (III).—An authentic sample[18] of III was obtained. Identity with the product obtained from the reactions of I with magnesium was established by gas chromatographic analysis.

1,2-Diphenyl-1-cyclobutene (VIII).—A solution of 11.1 g. of II in 50 ml. of pure ether was added to 3.7 g. of pure magnesium.[5] The reaction was initiated by adding 0.5 ml. of 1,2-dibromoethane[8] and allowed to proceed for 19 hr. After hydrolysis and the usual work-up, there was isolated an 86% yield of 1,2-diphenyl-1-cyclobutene (VIII) as colorless crystals, m.p. 47–49°, by chromatography over Woelm neutral alumina, activity grade I. Recrystallization from Skellysolve B afforded the analytical sample, m.p. 52.0–53.5°. The n.m.r. spectrum showed a sharp singlet at τ 7.29 (4H)[20] and a multiplet centered at τ 2.68 (10H).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 93.1; H, 7.0.

The ultraviolet spectrum of VIII in alcohol had λ_{max} at 297 mμ (ϵ 19,300) and 308 mμ (ϵ 18,900).[21]

Ozonization of 96 mg. of VIII in 15 ml. of methylene chloride at −80° until the solution turned blue (15 min.) afforded 102 mg. (92%) of 1,4-diphenyl-1,4-butanedione,[22] m.p. 143.5–145.0°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found: C, 80.8, 81.0; H, 6.0, 6.1.

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[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 45.

[17] K. von Auwers [*Ber.*, **45**, 2781 (1912)] reported b.p. 102° (9 mm.).

[18] O. Brummitt and E. I. Becker, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 771.

[19] We thank James A. Smith for a sample of authentic 2-phenyl-1,3-butadiene and 1-phenylcyclobutene.

[20] K. B. Wiberg and B. J. Nist [*J. Am. Chem. Soc.*, **83**, 1226 (1961) reported a singlet at τ 7.46 for the allylic hydrogens of cyclobutene.

[21] H. H. Freedman and A. M. Frantz, Jr. [*ibid.*, **84**, 4165 (1962)], reported λ_{max} 303 mμ (ϵ 19,500) for 1,2,3,4-tetraphenylcyclobutene.

[22] R. E. Lutz and C.-K. Dien [*J. Org. Chem.*, **21**, 551 (1956)] reported m.p. 143–145°.

On the Isomers of 2-(2-Thienyl)- and 2-Phenylcyclopropanecarboxylic Acid

JAMES W. McFARLAND

Medical Research Laboratories, Chas. Pfizer & Company, Inc., Groton, Connecticut

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The geometric isomers of 2-(2-thienyl)cyclopropanecarboxylic acid have been characterized and identified. The equilibrium ratio of the *cis* and *trans* ethyl esters has been determined, along with that of the *cis* and *trans* ethyl 2-phenylcyclopropanecarboxylates. A comparison of these results with those from other cyclopropane systems is made.

For use as intermediates, the *cis*- and *trans*-2-(2-thienyl)cyclopropanecarboxylic acids have been recently prepared in these laboratories. These compounds have been reported previously, but no attempt to establish geometric relationships was ever indicated. In 1949, Burger and his co-workers[1] prepared one of the isomeric acids, m.p. 125°, and an apparently corresponding amide, m.p. 164°. Later, Burger[2] prepared the other isomeric acid, m.p. 60°. Although it was not specifically stated, the earlier reference strongly implied that the amide, m.p. 164°, was derived from the acid, m.p. 125°. The present report will demonstrate that this is not the case, and will describe the preparation, characterization, and identification of the pure acids, the amides, and the ethyl esters in both the *cis* and *trans* series.

A mixture of the isomeric ethyl 2-(2-thienyl)cyclopropanecarboxylates was prepared by the reaction of ethyl diazoacetate and 2-vinylthiophene at 125–135°.[1] Saponification of the distilled ester furnished a mixture of isomeric acids, which when recrystallized once from hexane afforded a pure isomer, m.p. 128°. However,

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[1] A. Burger, D. G. Markees, W. R. Nes, and W. L. Yost, *J. Am. Chem. Soc.*, **71**, 3307 (1949).

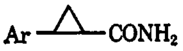
[2] A. Burger (to Smith, Kline and French Laboratories), U. S. Patent 2,638,471 (1953); *Chem. Abstr.*, **48**, 7641 (1954).

TABLE I

Ar	M.p., °C.	Recrystn. solvent	$\mathrm{p}K_\mathrm{a}$ in 50% EtOH	Neut. equiv.		Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-2-Thienyl	125–128	Hexane–acetone	6.2	168	170	57.12	57.21	4.79	4.82
trans-2-Thienyl	60–61	Hexane	5.8	168	170	57.12	57.36	4.79	4.74
cis-Phenyl	105–106	Hexane–benzene	6.4	162	162	74.05	74.14	6.22	6.22
trans-Phenyl	91–92[a]	Hexane–benzene	5.9	162	166	...	...	...	...

[a] Commercial material.

TABLE II



Ar	Prepared from acid	M.p. of amide, °C.	Recrystn. solvent	Carbon, %		Hydrogen, %		Nitrogen,	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-2-Thienyl	M.p. 128°	118–119	Benzene	57.45	57.47	5.42	5.33	8.37	8.06
trans-2-Thienyl	M.p. 61°	166–168	2-Propanol	57.45	57.34	5.42	5.37	8.37	8.06
cis-Phenyl	M.p. 106°	88–89[a]	...	74.50	...	6.88	...	8.69	...
trans-Phenyl	M.p. 92°	191–193[b]	Acetone–methanol	74.50	74.63	6.88	6.90	8.69	8.43

[a] J. Farkas, P. Kourim, and F. Šorm, *Chem. Listy*, **52**, 695 (1958). [b] D. B. Denney, J. J. Vill, and M. J. Boskin [*J. Am. Chem. Soc.*, **84**, 3944 (1962)] reported m.p. 192–193°.

preparation of the amide from this acid resulted in a product, m.p. 119°, instead of the anticipated m.p. 164°. When the crude acid from the filtrate was converted to the amide, subsequent recrystallization led to a pure substance, m.p. 168°.

The above reaction sequence was repeated. After the initially obtained acid of m.p. 128° was filtered, the crude acids in the filtrate were carefully recrystallized several times to furnish the other isomeric acid of m.p. 61°. This pure product was converted to the corresponding amide which melted at 168°, identical with the previously mentioned amide having the same melting point. Thus the relationships below were

$$\text{acid, m.p. } 128° \longrightarrow \text{amide, m.p. } 119°$$

$$\text{acid, m.p. } 61° \longrightarrow \text{amide, m.p. } 168°$$

established. Apparently, Burger, *et al.*,[1] prepared their amide, m.p. 164°, from a crude acid residue.

A clue to assigning the correct geometry to these isomeric acids was found by measuring their $\mathrm{p}K_\mathrm{a}$ values in 50% aqueous ethanol. The $\mathrm{p}K_\mathrm{a}$ of the acid of m.p. 128° was 6.2, while that of the acid of m.p. 61° was 5.8. It has been observed by others[3–5] that among isomeric pairs of 2-arylcyclopropanecarboxylic acids the *trans* isomer is invariably more acidic than its *cis* counterpart. By this criterion the acid of m.p. 61° should be designated *trans*, and the acid of m.p. 128°, *cis*. For comparison, the physical properties of these acids and the isomeric 2-phenylcyclopropanecarboxylic acids are summarized in Table I. The physical properties of the corresponding amides are summarized in Table II.

The isomeric 2-phenylcyclopropanecarboxylic acids are better known compounds, and their geometries have been established by unequivocal methods.[4,6] In subsequent efforts to confirm the aforementioned stereochemical assignments, parallel experiments with the phenyl analogs were run as controls.

In both the phenyl and 2-thienyl series, the proton magnetic resonance spectra of the isomeric acids, of their ethyl esters, and of their amides were too complex to interpret meaningfully. There were gratifying similarities between related isomers, *e.g.*, *cis*-2-(2-thienyl)- and *cis*-2-phenylcyclopropanecarboxylic acid, but, since the physical basis for these similarities was poorly understood by us, a more straightforward method of differentiation was sought.

Several approaches to the solution of this problem suggest themselves, but the one that was followed was founded on the equilibrium ratio of the isomeric ethyl 2-(2-thienyl)cyclopropanecarboxylates. It was assumed that, as with other 1,2-disubstituted cyclopropanes,[7] the *trans* isomer would predominate in an equilibrium mixture. Essential to the success of this method was an assay which could qualitatively and quantitatively differentiate the isomers in both the 2-thienyl and phenyl series. These properties were found in a gas–liquid partition chromatography (g.l.p.c.) system. A standard sample of each ester was prepared by allowing a solution of the corresponding pure acid, anhydrous hydrogen chloride, and anhydrous ethanol to stand at room temperature for several days. After acidic material was separated from the neutral ester by extraction procedures, the undistilled ester in each case was essentially 100% pure as determined by g.l.p.c. Since no isomerization could be detected under these esterifying conditions, the more laborious technique employing diazoethane was obviated. Table III summarizes the physical properties and analytical data of the four esters in question. In both the 2-thienyl and phenyl series, synthetic mixtures of the isomers were prepared to calibrate the g.l.p.c. column. The analytical method was thus shown to be accurate to ±0.5%.

Since the equilibration experiments confirm the assignments based on $\mathrm{p}K_\mathrm{a}$ data, the various isomers will be referred to by their proper prefixes in the following discussion. In approaching equilibrium from the *trans* side, pure *trans* esters were used as starting materials. However, for the approach from the *cis* side, mixtures

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

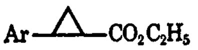
(4) H. L. de Waal and G. W. Perold, *Chem. Ber.*, **85**, 574 (1952).

(5) J. Smejkal, J. Jonas, and J. Farkas, *Collection Czech. Chem. Commun.*, **25**, 1746 (1960).

(6) Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1695 (1964).

(7) G. J. Fonken and S. Shiengthong, *J. Org. Chem.*, **28**, 3435 (1963).

Table III



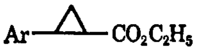
Ar	Prepared from acid	Retention time, min.[a]	% purity	n^{24}_D	d^{24}_{24}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
cis-2-Thienyl	M.p. 128°	20.7	100	1.5250	1.1445	61.19	61.41	6.17	6.31
trans-2-Thienyl	M.p. 61°	22.9	99.5	1.5259	1.1350	61.19	61.30	6.17	6.24
cis-Phenyl	M.p. 106°	17.5	100	1.5140	0.9332	75.76	75.76	7.42	7.30
trans-Phenyl	M.p. 92°	22.3	100	(M.p. 40–42°)[b]		75.76	75.88	7.42	7.43

[a] On g.l.p.c. column; conditions are described in the Experimental Section. [b] V. Grinsteins and M. Anderson [*Latvijas PSR Zinatnu Akad. Vestis, Kim. Ser.*, 106 (1963); *Chem. Abstr.*, 59, 9919c (1963)] reported m.p. 35–37°.

of isomers sufficiently enriched by the *cis* ester were employed. These latter materials were readily obtained by esterifying appropriate crude acid residues from various filtrates. The catalyst for these equilibration experiments was in each case 2 *N* sodium ethoxide in anhydrous ethanol. During equilibration, samples from each reaction mixture were analyzed periodically, affording time–course studies. The results of these studies are summarized in Table IV. In the gas chromatograms obtained from the 2-thienyl experiments, the major peak at equilibrium corresponded to that of the ester prepared from the acid of m.p. 61°, while the minor peak corresponded to that of the ester prepared from the acid of m.p. 128°. Results from the control experiment were that the major peak corresponded to that of ethyl *trans*-2-phenylcyclopropanecarboxylate and the minor peak to that of the *cis* isomer. Hence, with a high degree of certainty, it may be concluded that the acid of m.p. 128° is *cis*-2-(2-thienyl)cyclopropanecarboxylic acid, while the acid of m.p. 61° is the *trans* isomer.

Table IV

Equilibration Experiments[a]



Ar	Side of equil.	% *cis* — Time, min. 0	30	60	120	180	240	360
2-Thienyl	*cis*	19	12	8	6	6	..	6
2-Thienyl	*trans*	<1	3	4	5	..	6	..
Phenyl	*cis*	14	12	10	7	5	..	5
Phenyl	*trans*	0	2	3	4	..	4	..

[a] Esters in 2 *N* sodium ethoxide and anhydrous ethanol were heated under reflux. See Experimental Section for details.

Application of the conformation rule[8] to the densities of the ethyl 2-(2-thienyl)cyclopropanecarboxylates (see Table III) also leads to the correct identification of the *cis* isomer, *i.e.*, the isomer with the greater enthalpy. Ordinarily, the isomer with the greater enthalpy is also the one with the greater index of refraction, but in the present instance this is not so. However, this is in no way ambiguous since the difference between the indices of refraction is small, and the latest revision of the conformation rule[8,9] places greater reliance on the molal volume (inverse density), as the determining criterion.[10]

It should be mentioned that a change in enthalpy is not identical with a change in free energy and hence need not relate to the question of equilibrium constants. However, it is commonly accepted by stereochemists[8,9,11,12] that, as a first approximation, changes in enthalpy and free energy are nearly equal in cases such as those presently under discussion. In effect this is saying that in the equation

$$\Delta F = \Delta H - T\Delta S$$

the term $T\Delta S$ can be neglected, and further, for equilibria at room temperature or greater, ΔS is a relatively small number indeed. Hence, it may be deduced from the thermodynamic relationship

$$\mathrm{d}\Delta F = -\Delta S \mathrm{d}T$$

that ΔF will be only slightly altered with moderate temperature changes. Thus, an equilibrium constant determined at 65° may be compared directly with one determined at 80° with only negligible error. Experience in simple systems has generally confirmed these assumptions.

With this in mind the reader is invited to examine Table V for a summary of the present data in thermodynamic terms. For comparison, literature data concerning the 1,2-dimethylcyclopropane and the dimethyl 1,2-cyclopropanedicarboxylate systems have been included.

Table V

R_1	R_2	Temp., °K.	% *cis* at equil.	$K_{eq.}$	$-\Delta F°$, kcal.
CH_3	CH_3	298	14	6.4	1.1[a]
2-C_4H_3S	$CO_2C_2H_5$	353	6	16	1.9
C_6H_5	$CO_2C_2H_5$	353	4.5	21	2.2
CO_2CH_3	CO_2CH_3	338	1[b]	99	3.1[b]

[a] Estimated by Curtin, *et al.*[12] [b] See ref. 7.

The driving force for these *cis–trans* epimerizations is undoubtedly the relief of strain in the *cis* isomers. From models one would envision that the repulsive aryl–carboxylate interactions and the repulsive carboxylate–carboxylate interactions would be of the same magnitude. It is, therefore, surprising to observe a relatively large difference between the aryl ester systems and the diester system.

The fact that a methyl ester is being compared to an ethyl ester should have little bearing on this problem, since the anticipated effect is opposite to that observed. Fonken and Shiengthong[7] think that the estimated

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[8] N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

[9] N. L. Allinger and R. J. Curby, Jr., *J. Org. Chem.*, **26**, 933 (1961).

[10] It must be admitted that the conformation rule may not apply in this case since the dipole moments of the two isomers might differ significantly; the physical properties would then only fortuitously indicate the isomer of greater enthalpy.

[11] W. Hückel and D. Rücker, *Ann.*, **666**, 30 (1963).

[12] D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer, *J. Am. Chem. Soc.*, **83**, 4838 (1961).

$-\Delta F$ for 1,2-dimethylcyclopropane is probably too small. Their skepticism is undoubtedly justified since Curtin, *et al.*,[12] extrapolated this value from gas phase data measured at 380° and higher.[13] Nevertheless, in light of the intermediate $-\Delta F$ values found for the 2-arylcyclopropanecarboxylates in the present study, and from considering the size of the methyl group, one must conclude that the value estimated by Curtin could well be correct. Without additional experimentation it is unlikely that a convincing explanation of these differences could be made; however there is no immediate plan to pursue this work further.

Experimental Section

Boiling points are uncorrected; melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) and are corrected. Analyses were made by the Physical Measurements Laboratory of Chas. Pfizer & Co.

2-Vinylthiophene was prepared according to a literature procedure.[14]

Mixed Isomers of Ethyl 2-(2-Thienyl)cyclopropanecarboxylate.—The procedure of Burger and Yost[15] was adapted to 2-vinylthiophene. The yields of distilled product were 40–65% for various runs, b.p. 92–98° (0.5–0.8 mm.) [lit.[1] b.p. 107° (3 mm.)]. Gas chromatography showed the ratio *cis–trans* to be 39:61, and revealed that essentially no other products were present.

Mixed Isomers of Ethyl 2-Phenylcyclopropanecarboxylate.—The procedure of Burger and Yost[15] was followed. The yields of distilled product were 62–78% for various runs, b.p. 104° (0.8 mm.) [lit.[15] b.p. 103–105° (0.5–0.7 mm.)]. Gas chromatography showed the ratio *cis–trans* to be 38:62, and indicated that essentially no other products were present.

***cis*-2-(2-Thienyl)cyclopropanecarboxylic Acid.**—A solution of 65.4 g. (0.333 mole) of ethyl 2-(2-thienyl)cyclopropanecarboxylate, 20 g. (0.5 mole) of sodium hydroxide, and 400 ml. of ethanol was heated under reflux for 20 hr. After the mixture had cooled to room temperature, the solvent was evaporated under reduced pressure to afford a solid residue. This was taken up in water, and was washed twice with 100-ml. portions of ether. The aqueous phase was treated with concentrated hydrochloric acid until pH 2 was attained; organic material was then extracted with three 100-ml. portions of ether. The combined extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to furnish a reddish oil, yield 53.6 g. (96%). The oil was taken up in hot hexane and upon cooling colorless crystals of *cis*-2-(2-thienyl)cyclopropanecarboxylic acid formed, yield 14.1 g. (25%), m.p. 125–128°. This material was recrystallized from acetone–hexane for analysis, yield 10.5 g., m.p. 124–126° (see Table I for analytical results).

***trans*-2-(2-Thienyl)cyclopropanecarboxylic Acid.**—The filtrates from various crystallizations and recrystallizations of the *cis* isomer were combined and evaporated to a thick oil, yield 51.0 g. (0.304 mole). This material was taken up in 500 ml. of anhydrous ethanol and was then treated with 10 ml. of acetyl chloride. After standing at room temperature for 3 days, the solution was evaporated under reduced pressure to furnish a colorless oil which was distilled to give ethyl 2-(2-thienyl)cyclopropanecarboxylate, yield 54.4 g. (91%), b.p. 110° (0.3 mm.). Gas chromatography showed the *cis–trans* isomer ratio to be 19:81.

This ester (49.0 g., 0.25 mole) was dissolved in 450 ml. of 2 *N* sodium ethoxide in anhydrous ethanol; the solution was heated under reflux for 6 hr. and then allowed to stand at room temperature overnight. The solvent was evaporated under reduced pressure to afford the mixture of esters, the *cis–trans* ratio now being 6:94.

The thus equilibrated ester was dissolved in 200 ml. of ethanol containing 16 g. (0.4 mole) of sodium hydroxide. The solution was heated under reflux for 14 hr., was allowed to cool, and was then evaporated under reduced pressure to afford a solid residue. A solution of the residue in water was treated with concentrated hydrochloric acid to furnish a crystalline precipitate. The wet product was filtered, mixed with benzene, and heated under reflux in an apparatus equipped with a Dean–Stark-type moisture trap. When no more water collected in the trap, the benzene solution was allowed to cool. The addition of hexane caused crystallization of *trans*-2-(2-thienyl)cyclopropanecarboxylic acid, yield 14.5 g. (41%), m.p. 59–61°. The product was recrystallized from hexane for analysis, yield 9.8 g., m.p. 60–61° (for analytical data see Table I).

***cis*-2-Phenylcyclopropanecarboxylic Acid.**—This material was prepared according to the procedure of Burger and Yost.[15] For physical properties and analytical data see Table I.

***trans*-2-Phenylcyclopropanecarboxylic Acid.**—This material was purchased from the Aldrich Chemical Co., and was recrystallized before use. For physical properties see Table I.

Preparation of the Pure Amides.—Equimolar amounts of acid and oxalyl chloride were combined in methylene chloride, and stirred at room temperature overnight. The volatiles were evaporated under reduced pressure, and the oily residue was poured into concentrated ammonium hydroxide. The crystalline precipitate, which immediately formed, was filtered, air dried, and recrystallized. For the properties and analytical results of compounds prepared in this manner, see Table II.

Preparation of Pure Esters.—A solution of acid and 10 vol. of 1 *N* anhydrous hydrogen chloride in anhydrous ethanol was allowed to stand at room temperature for 48 hr. The solvent was evaporated under reduced pressure to furnish an oily residue. This was taken up in diethyl ether, and the resulting solution was washed twice with saturated sodium bicarbonate solution, and once with water. The ether phase was dried over anhydrous sodium sulfate, filtered, and evaporated to afford the pure ester. For physical properties and analytical results of compounds prepared by these procedures, see Table III.

Equilibration Experiments.—Anhydrous ethanol, 2 *N* in sodium ethoxide and 0.5 *M* in nonequilibrated ester, was heated under reflux for 6 hr. At the time intervals indicated in Table IV, 3-ml. samples were withdrawn from the heated solution and were rapidly mixed with 50 ml. of water. The aqueous mixtures were extracted with ether, and the extracts were dried, filtered, and evaporated to furnish the mixed isomeric esters. These mixtures were then analyzed by g.l.p.c. Table IV summarizes the results of experiments performed in this manner.

Description of Analytical Method.—For the quantitative determination of the isomeric esters described in this paper, an Aerograph Autoprep Model A-700 gas chromatography instrument was used. The column employed was 3 m. long, had a 6.35-mm. inside diameter, and was packed with (25%) tris-(tridecyl) 1,2,3-propanetricarboxylate supported on silicone-treated Chrom W (Johns–Manville), 60–80 mesh. The column operated at a temperature of 217°, and had a helium flow rate of approximately 35 cc./min.

Synthetic mixtures of the pure isomeric mixtures were used to calibrate the column, and ±0.5% accuracy was realized. For the ethyl 2-(2-thienyl)cyclopropanecarboxylate system, the ratio of isomers was best expressed by the ratio of peak heights. For the ethyl 2-phenylcyclopropanecarboxylate system, the ratio of peak areas was more accurate.

Acknowledgments.—The author wishes to thank Messrs. Richard B. James and Walter Bobinski for valuable technical assistance and to express his gratitude to Professor E. J. Corey for his helpful suggestions during the course of this work.

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[13] M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.* (London), **A257**, 122 (1960).

[14] W. S. Emerson and T. M. Patrick, Jr., "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 980.

[15] A. Burger and W. L. Yost, *J. Am. Chem. Soc.*, **70**, 2198 (1948).