The reactants were then admitted to the autoclave, the most volatile component last. Normally liquid reactants (*e.g.*, pentenes) were placed in the autoclave while still in the drybox. After all normally liquid hydrocarbons were placed in the autoclave, the vessel was sealed and removed from the drybox. Butenes were fed into the reactor as liquids under argon pressure, and propylene and ethylene, as gases under available cylinder pressure. The amounts of these volatile components charged were obtained by difference of the weights of the autoclave plus contents on a Metrogram[31] capacitance balance, to within 0.1 g.

The autoclave was then heated to the desired run temperature within 0.5 hr.; the experiment was considered to be completed when the pressure inside the autoclave had dropped to one-half of the initial maximum. The autoclave was cooled to room temperature and then depressured, while reheating slowly to 200°, into an evacuated (≤10 mm.) series of three liquid nitrogen cooled traps. The first of these traps was also the kettle of a still, being connected to the other two through a 30 × 1 cm. Vigreux column. After warming and stabilizing the cold trap condensate to room temperature, with the gas being collected in a water-displacement gas holder, the gas and liquid were sampled for analysis.

The gas samples were analyzed by gas chromatography (g.c.) on a 50 ft. × 0.25 in. column of dimethylsulfolane on firebrick, operated at 40° using 40 cc./min. of helium carrier gas and thermal conductivity detector cells. Prior calibration with authentic samples showed that this column was capable of separating and identifying individual hydrocarbons through C_6 and estimating amounts to 0.1% of the 2-ml. gas sample used. Gas samples were also routinely analyzed by mass spectrography (m.s.); m.s. and g.c. gave results in agreement to within 1–2%. Liquid samples were kept refrigerated at −20° until analyzed by g.c. on two different columns. Samples of 5-μl. volume were chromatographed on dimethylsulfolane (as above) to identify and estimate hydrocarbons through C_6; a 50 ft. × 0.25 in. column of SF-96 silicone oil[32] on firebrick operated at 125° with 50 cc./min. of helium carrier and thermal conductivity detector cells

was used to identify, by boiling point, hydrocarbons through C_{16} and estimate relative amounts to 0.1% of the 10-μl. sample charged. Within the range of overlap (*i.e.*, through C_6), agreement between the two chromatograms was within 1–2%.

Other methods used for more positive characterization of the principal products were infrared spectroscopy to determine olefin type; m.s. of compounds purified by g.c. to determine carbon skeleton by fragmentation pattern; n.m.r. to verify the 3-heptene structure (from *n*-pentene + ethylene) relative to 2-heptene. Compounds higher than C_9 remain unidentified.

Several preparative-scale experiments were made in a 1-gal. autoclave, and the products from these experiments were subjected to precision fractional distillation in a 20-plate Oldershaw column at 10:1 reflux ratio. 3-Methyl-1-pentene had b.p. 53.1°, lit.[33] b.p. 53.6°; 3-ethyl-1-pentene had b.p. 83.9–84.2°, lit.[33] b.p. 85.0°. Several of the fractions from these distillations were subjected to quantitative hydrogenation over Raney nickel to confirm olefinicity (or lack thereof, in the case of methylcyclopentane), and m.s. and g.c. of the resultant paraffins provided additional confirmation of the carbon skeleton.

In each experiment (whether 250-ml. scale or 1-gal. scale), the sum of the weights of liquid product and residue and weight of gas calculated from its volume and average molecular weight was 97–102% of the total weight of the materials charged. The total product weight was normalized to equal the charge weight before calculating product distribution.

The cooled, evacuated autoclave was opened in the drybox. The residue in nearly every case was observed to be hard, shiny, black granules which reacted briskly with isopropyl alcohol (IPA). Toluene–IPA "solutions" of the residues from a number of experiments were chromatographed to determine the boiling range of (at least part of) the organic polymer present; the failure of any component of the solution other than toluene and IPA to emerge from the g.c. column indicated that the polymer had an initial boiling point well above 300–350°. After the first several experiments, the residue was deactivated with IPA and then water, and discarded, without other than visual observation.

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(31) H. A. Hadley Associates, Inc., Burlington, Vt.
(32) Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

(33) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Co., New York, N. Y., 1943.

Reactions of 1,4-Dichloro-1-butenes with Magnesium.
A New Cyclobutene Synthesis[1]

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The reactions of *trans*-1,4-dichloro-1-phenyl-1-butene (I) and *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) with magnesium in ether afford 1-phenylcyclobutene (III) and 1,2-diphenylcyclobutene (VIII) in 5–46 and 90% yields, respectively. A study of the reaction products from I indicates that the reaction of I to form the vinyl Grignard reagent is more rapid than that to form primary Grignard reagent. Evidence that vinyl Grignard reagents do not maintain stereochemical identity is presented.

In the course of other work[3] quantities of *trans*-1,4-dichloro-1-phenyl-1-butene (I) and of *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) became available.[4] With the thought that interesting primary mono-Grignard reagents might be formed, ethereal solutions of I and II were allowed to react with magnesium. Treatment of the resulting solutions with water produced unexpected products. Study of these reactions revealed two facts of interest: (a) a new cyclobutene synthesis was at hand; and (b) the rate of reaction of the vinylic chloride of I (and presumably of II)

with magnesium was greater than the rate of reaction of the primary chloride.
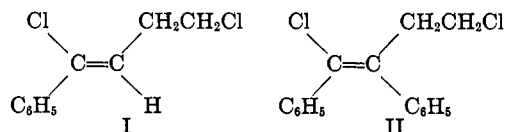
When ethereal solutions of I were allowed to react with excess sublimed magnesium[5] for periods of from 1.5 to 41 hr., reaction mixtures were obtained which on hydrolysis afforded four or five products. The results were not strictly reproducible, but examination

TABLE I

THE REACTION OF 1,4-DICHLORO-1-PHENYL-1-BUTENE (I) WITH MAGNESIUM[a]

Expt.	Concn.,[b] M	Time, hr.	III	IV (cis)	V (trans)	VI	VII	I[c]
1[d]	0.6	1.5[e]	23		33[f]	35	...	38
		4.5[e]	26		39[f]	35	...	...
2[d]	0.6	18.0	20	6	38	36	...	...
3[g]	0.6	1.5[e]	5	9	29	39	18	12
		3.0[e]	5	9	30	40	16	...
		22.0[e]	7	5	28	36	24	...
4[g]	0.6	18.0	6	6	25	35	28	...
		41.0	9	4	25	33	29	...
5[d]	0.6	17.0[e]	7	5	23	37	28	...
		40.0[e]	8	5	24	34	28	...
6[d]	0.6	3.0[e]	15	7	31	39	8	...
		21.0[e]	15	7	31	40	7	...
7[h]	0.6	15.0	24	6	27	40	3	...
8[i]	0.5	1.5	38	4	16	35	7	10
		4.0	40	5	16	35	8	...
9[j]	0.17	20.0	46		29[f]	25	...	...
10[k]	1.0	4.0	16	9	32	43	...	...

[a] All reactions were run at room temperature in ether distilled from Grignard reagent. Magnetic stirring was continuous. [b] Approximate concentration of I in ether used to react with magnesium. [c] Amount of unreacted I present in products. In most runs none found. In runs where I was present the percentage of products was calculated by subtracting the amount of recovered I first. [d] Reaction initiated with a few drops of 1,2-dibromoethane and a crystal of iodine. [e] Aliquots from same reaction mixture. [f] cis and trans isomers not separated. [g] Reaction initiated with a few drops of dibromoethane. [h] Reaction initiated with 2 ml. of dibromoethane. [i] A 1:1 molar ratio of dibromoethane and I was used. In this experiment spontaneous reflux for 25 min. occurred at the start. [j] The magnesium was allowed to react with 0.5 equiv. of dibromoethane in ether and then a 1:3 solution of I and dibromoethane in ether was added. Spontaneous refluxing occurred for 55 min. The remaining reaction was at room temperature. When part of an ethereal solution of the crude product was kept in a refrigerator for 23 days before work-up and analysis, the yield of III fell to 10% and the yield of VII rose to 36%. [k] The reaction was initiated with a few drops of dibromoethane and a little methylmagnesium iodide.
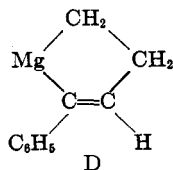
of Table I reveals that large variations in the proportions of products do not occur. The products formed were 1-phenylcyclobutene (III), cis-1-phenyl-1-butene (IV), trans-1-phenyl-1-butene (V), trans-1-chloro-1-phenyl-1-butene (VI), and 1-phenyl-1,3-butadiene (VII) (see Experimental Section for proof of structures). Scheme I can account for the observed results.

The fact that the amount of trans-1-chloro-1-phenyl-1-butene (VI) obtained does not change appreciably with time even though an excess of magnesium is available indicates that once the primary Grignard reagent A[6] has been formed no further reaction involving it occurs until hydrolysis, which yields VI. Since the amount of VI formed is in the range 25–43%, one can conclude that *the rate of formation of A is always less than that of formation of B*.

The vinylic Grignard reagent B reacts further to yield 1-phenylcyclobutene (III) and to form the di-Grignard reagent C (or D[7]) which on hydrolysis affords a mixture of cis- and trans-1-phenyl-1-butene (IV and V) in the ratios shown in Table I. When an excess of ethylene dibromide was used[8] in the reaction of I with magnesium, the yield of III rose to 46% (see

Table I), but no further study of this variable was made.

The fact that pure I of trans structure affords cis and trans olefins IV and V is of interest because vinyllithium compounds have been shown not to undergo isomerization.[9] Recent studies[10] on α- and β-styryl bromides show that maintenance of stereochemistry is sensitive to solvent and other conditions during formation of the Grignard reagent. Furthermore, optically active halides in the cyclopropyl series yield optically active products on conversion into organolithium reagents[11,12] but inactive (or slightly active) products on conversion into Grignard reagents.[11,13] Accordingly, we studied briefly the behavior of cis- and trans-1-chloro-1-phenyl-1-butene (VI) on treatment with magnesium.

A 22:78% cis–trans mixture of these chloro olefins was allowed to react with magnesium in tetrahydrofuran. Hydrolysis of an aliquot after 1 hr. followed by gas chromatographic analysis showed that the recovered chloro olefin (VI, 52%), was much richer in trans-VI (6% cis, 4% trans) than at the start. This shows that cis VI reacts more rapidly with magnesium than trans VI (or that cis VI is converted to trans VI in the reaction mixture). A 48% yield of olefins IV and V was obtained and the cis–trans ratio was 1:3. Hydrolysis of the remainder of the original reaction mixture after 2 days afforded a 94% yield of IV and V in which the ratio of cis to trans was about 1 to 3.3. These results indicate that both the cis- and trans-1-phenyl-1-butenylmagnesium chlorides yield about

(6) Throughout our discussion concerning Grignard reagents it is recognized that there is doubt concerning the true structure of any Grignard reagent. Hence we use the simpler formulas.

(7) This Grignard reagent may have the structure of a cyclic magnesium derivative, D, as suggested by Dr. F. Johnson, Dow Chemical Co., Wayland, Mass. However, only that Grignard reagent which gives V could have the cyclic structure, D.

D

(8) As recommended by D. E. Pearson, D. Cowan, and J. D. Beckler, J. Org. Chem., 24, 504 (1959).

(9) F. G. Bordwell and P. S. Landis, J. Am. Chem. Soc., 79, 1593 (1957); D. Y. Curtin and J. W. Crump, ibid., 80, 1922 (1958).

(10) T. Yoshino, Y. Manabe, and Y. Kikuchi, ibid., 86, 4670 (1964).

(11) H. M. Walborsky and A. E. Young, ibid., 83, 2595 (1961).

(12) H. M. Walborsky, F. J. Impastato, and A. E. Young, ibid., 86, 3283 (1964).

(13) H. M. Walborsky and A. E. Young, ibid., 86, 3288 (1964).

SCHEME I
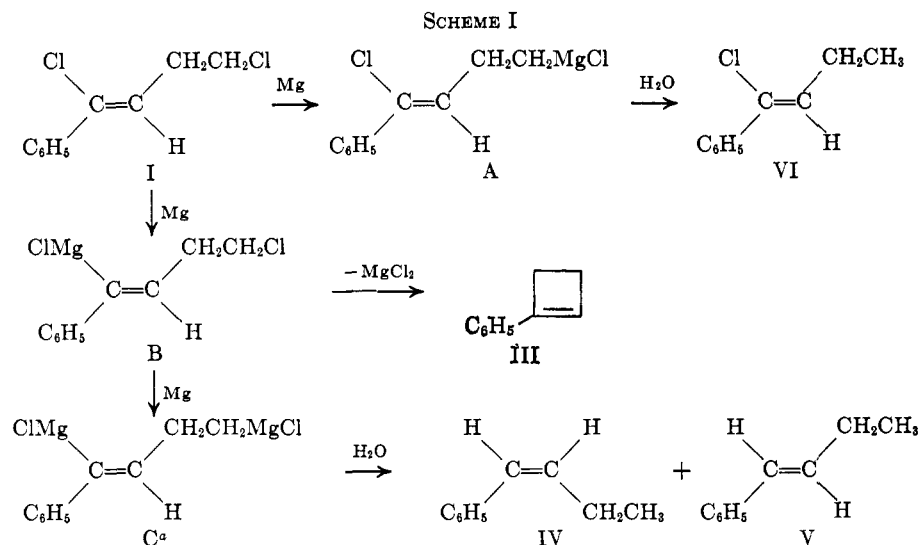
ᵃ Reference 7.

the same ratio of cis- and trans-1-phenyl-1-butene (IV and V) on hydrolysis. When a 17:83% cis–trans mixture of VI was allowed to react with excess magnesium in ether, less than 40% reacted in 19 hr. Both cis- and trans-1-phenyl-1-butene were present (in about 1:5 ratio) in the hydrolyzed product, but this experiment showed little about the stereochemical specificity of the vinylmagnesium derivative produced.

Further evidence that the precursors of IV, V, and VI were the Grignard reagents C (or D)[7] and A was obtained by carbonation of a typical reaction mixture before hydrolysis. This step decreased the amounts of IV, V, and VI formed after hydrolysis but did not appreciably affect the amount of III and VII formed. The acid mixture produced was not separated into pure components. In another experiment (expt. 4, Table I) an aliquot was titrated for Grignard reagent after 1.5 and 3.0 hr. The amount of Grignard reagent that should theoretically have been present (calculated from the amount of IV and V found multiplied by 2 plus the amount of VI formed) was quite close to that found by titration.

The formation of 1-phenyl-1,3-butadiene (VII) is difficult to explain. It cannot be formed from Grignard reagent A. There is an inverse relationship between the amounts of III and VII formed as can be seen from the results listed in Table I: the more III formed the less VII, and vice versa. In order to form VII from B, a reaction involving proton abstraction followed by chloride expulsion must occur. Grignard reagent B might undergo an intramolecular elimination of magnesium chloride with a proton transfer as shown below.
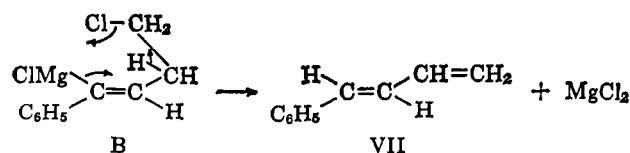
Alternately, any Grignard reagent could act as a base and abstract the allylic proton from B to initiate an elimination reaction and form a dienyl Grignard reagent, $C_6H_5C(MgCl)=CHCH=CH_2$, which would yield VII on hydrolysis.

In unpublished work[14] from this laboratory, the thermal conversion of 1-phenylcyclobutene to 2-phenyl-1,3-butadiene has been demonstrated. This shows that VII does not arise from III by a thermal reaction. In one experiment (see Table I, expt. 9) evidence that 1-phenylcyclobutene can isomerize to VII under unknown influences is presented. We have made no attempt to study further the formation of VII.

When an ethereal solution of cis-1,4-dichloro-1,2-diphenyl-1-butene (II) was allowed to react with excess sublimed magnesium[5] for 18 hr., high yields (90% by v.p.c., 86% by isolation) of 1,2-diphenylcyclobutene (VIII) were obtained, plus about 10% of 1-chloro-1,2-diphenyl-1-butene (IX). Thus, here, as in the case of the reaction of I with magnesium, if the primary Grignard reagent is formed first it undergoes no further reaction.
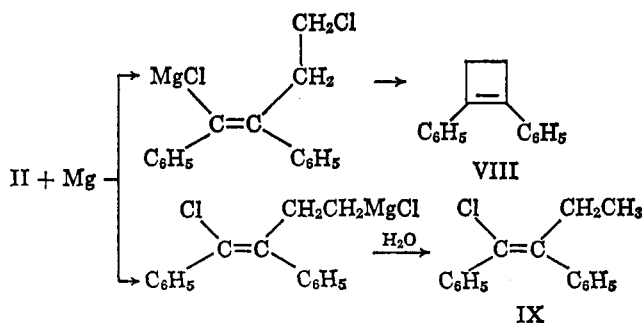
The above experiments demonstrate that the new cyclobutene synthesis described above is sensitive to the structure of the dichloride and to experimental conditions.

Experimental Section[15]

The reactions, the results of which are listed in Table I, were carried out in general as follows. A mixture consisting of an excess (three- to fivefold) of sublimed magnesium,[5] a quantity of

1,4-dichloro-1-phenyl-1-butene (I) [mainly *trans*, but containing variable (2–10%) amounts of *cis*-I],[3] 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[16] 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 λmax 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.

(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 λmax 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

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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,

(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).