Anal. Calcd for $C_{16}H_{10}O \cdot C_6H_3N_3O_7$: C, 59.06; H, 2.93; N, 9.39. Found: C, 59.13; H, 2.93; N, 9.39.

This material on admixture with the authentic picrate (mp 124°) prepared by Professor J. N. Chatterjea[4] gave no depression of melting point.[5]

8,9,10,11-Tetrahydronaphth[2,1-*b*]oxonine-8,13-dione (XI).—Twenty grams of VI was dissolved in 180 ml of glacial acetic acid and the mixture was stirred and cooled in ice. To this was added dropwise a solution of 28 g of chromium trioxide in 25 ml of water at such a rate that the temperature did not rise above 15° (1.5 hr). After the addition was completed the dark mixture was stirred for a further 3 hr at room temperature and then the crystalline deposit formed was removed by filtration. Two recrystallizations from ethanol afforded 4.6 g of XI, mp 138–139°, as colorless large square crystals: λ_{max} 218, 301, 236 (sh) mμ (ε 47,100, 4700); infrared spectrum (in KBr), 1751 (C=O, aryl lactone), 1678 cm^{-1} (C=O, aryl ketone); nmr spectrum, δ 2.09 (m) (9,10-di-CH_2, 2.68 (m) 8-CH_2 and 11-CH_2), 7.91 (d) (5-H), (J = 9 cps), 7.32 (d) (6-H) (J = 9 cps).

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.35; H, 5.55.

2-Hydroxynaphthoylvaleric Acid (XII).[10]—One gram of XI was suspended in 8 ml of 40% sodium hydroxide solution. After heating the reaction mixture for a few minutes on a steam bath a brown solution was obtained. Acidification with concentrated hydrochloric acid afforded 1 g of a brown precipitate, mp 79–81°. Recrystallization from cyclohexane gave 0.5 g of colorless crystals: mp 83–84.5°; λ_{max} 225 mμ (ε 55,056); infrared spectrum (in KBr), 1714 (CO_2H), 1625 cm^{-1} (C=O); nmr spectrum, δ 1.76 (m) 3,4-di-CH_2), 2.39 (t) (2-CH_2) (J = 6.5 cps), 3.14 (t) (5-CH_2) (J = 6.5 cps), 7.08 (d) [3-H (ar)] (J = 9 cps).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.61; H, 5.72.

Acknowledgment.—The authors gratefully acknowledge the help of Dr. E. L. Buhle and Dr. S. J. Childress in the interpretation of the spectra. Thanks are due Mr. L. E. McCardle for his skilled technical assistance.

(10) We wish to thank Dr. A. Santilli who performed this experiment.

The Syntheses, Spectra, and Thermal Isomerizations of *cis*- and *trans*-1-(*para*-Substituted phenyl)-1-cyclopropylprop-1-enes

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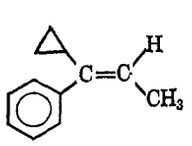
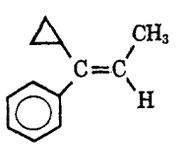
The pmr spectra of the title compounds show that in the *trans* isomers the cyclopropyl group may rotate freely, while in the *cis* isomers free rotation of the cyclopropyl group is severely restricted. In the latter systems, a configuration in which the three-membered ring lies over the π bond is highly unfavorable. Consequently, while the *trans* isomers thermally rearrange *via* a conventional vinylcyclopropane rearrangement to the corresponding cyclopentenes the *cis* isomers give a complex mixture of products which are believed to arise from diradical intermediates.

The thermally induced isomerization of vinylcyclopropanes to the corresponding cyclopentenes is considered to be a truly unimolecular reaction of the "no-mechanism" type.[1-3] Kinetic studies suggest that bond-breaking and bond-making processes are probably synchronous and thus the reaction has little, if any, radical character.[4] It is of interest to know if groups on the π bond *cis* to the cyclopropyl group can sterically inhibit the bond-forming process and thus either decrease the rate of cyclopentene formation or divert the reaction into a free-radical path where bond making and bond breaking are no longer synchronous. Such a path would presumably yield products other than substituted cyclopentenes.

To study the effect of a methyl group *cis* to a cyclopropyl group we prepared 1-phenyl-1-cyclopropylprop-1-ene by a conventional Wittig synthesis from the corresponding ketone. The two geometric isomers were obtained in approximately equal yield and were separated partially by distillation. The pure *trans* I and *cis* II isomers were then isolated by preparative vpc. To observe electronic effects, if present, the corresponding compounds in which the phenyl group was substituted in the *para* position with F, CH_3, and OCH_3 were also prepared.



I



II

Assignment of Structure by Spectroscopic Methods

Literature data on the pmr spectra of styrene and derivatives of styrene indicate that the β-olefinic proton *cis* to the aromatic ring is less shielded than the β-olefinic proton *trans* to the aromatic ring,[5-11] except in *ortho*-substituted derivatives where the plane of the aromatic ring is not nearly parallel to the plane of the double bond.[9]

In a thorough study of five isomeric pairs of *para*-substituted and unsubstituted α,β-dialkylstyrenes, Barbieux and co-workers[8] showed that other differences are present in the pmr spectra of *cis* and *trans* isomers. In the *cis* isomers, the most intense peaks formed by

(1) R. Breslow, "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 233.

(2) W. von E. Doering and W. R. Roth, *Angew Chem. Intern. Ed. Engl.* **2**, 115 (1963).

(3) C. G. Overberger and A. E. Borchert, *J. Am. Chem. Soc.*, **82**, 4891 (1960).

(4) R. J. Ellis and H. M. Frey, *J. Chem. Soc.*, 4188 (1964).

(5) A. J. Berlin, L. P. Fisher, and A. D. Ketley, *Chem. Ind.* (London), 509 (1965).

(6) J. A. Pople, W. G. Schneider, and H. F. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 238–241.

(7) R. W. Fessenden and J. S. Waugh, *J. Chem. Phys.*, **31**, 996 (1959).

(8) M. Barbieux, N. Defay, J. Pecher, and R. H. Martin, *Bull. Soc. Chim. Belges*, **73**, 716 (1964).

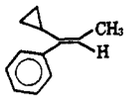
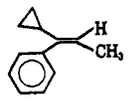
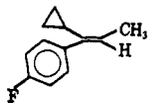
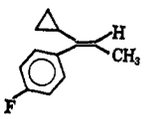
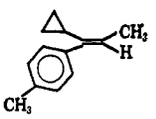
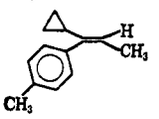
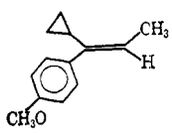
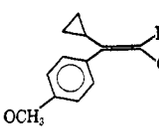
(9) H. Rottendorf, S. Sternhell, and J. R. Wilmhurst, *Australian J. Chem.*, **18**, 1759 (1965).

(10) D. T. Witiak and B. P. Chaudhari, *J. Org. Chem.*, **30**, 1467 (1965).

(11) R. W. Fessenden and J. S. Waugh, Abstracts, 132nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1957.

TABLE I

PROTON MAGNETIC RESONANCE SPECTRAL DATA OF *cis*- AND *trans*-1-(ARYL)CYCLOPROPYLPROP-1-ENE COMPOUNDS

Compd	τ values						Separation in cps between most intense peaks of A_2B_2 aromatic peaks	Cps				
	Aromatic	Olefinic	Allylic methyl	Cyclopropylmethine	Cyclopropylmethyline	Substituent $CH_3OR CH_3O$		J_3	J_4 cisoid	J_4 transoid	J_5 cisoid	J_5 transoid
	2.72	4.29	8.12	~8.4	9.1–9.9			7.0		1.5	1.1	
	~2.7	4.52	8.51	~8.4	9.4–9.7			7.0	1.0			0.8
	2.6–3.2	4.33	8.11	~8.4	9.1–9.9			6.9		1.5	1.1	
	2.8, 2.9	4.52	8.50	~8.4	9.4–9.7			7.0	1.0			0.8
	2.9	4.40	8.12	~8.4	9.1–9.9	7.70	2	7.0		1.5	1.1	
	2.85, 2.90	4.58	8.52	~8.4	9.4–9.7	7.67	~0	7.0	1.0			0.8
	2.97, 3.23	4.40	8.14	~8.4	9.1–9.8	6.27	17	7.1		1.5	1.1	
	2.85, 3.27	4.58	8.51	~8.4	9.4–9.7	6.24	7	7.0	1.0			0.8

the A_2B_2 set of aromatic protons were separated to a greater extent than in the *trans* isomers. Furthermore, these workers showed that allylic protons were shifted downfield in the *cis* isomers by 10–15 cps. Allylic four-bond coupling in *cis* isomers, $J_{4\text{-}c}$, was smaller than this coupling in *trans* isomers, $J_{4\text{-}t}$, by 0.2–1.1 cps.

Generally, the majority of measurements on cisoid ($J_{4\text{-}c}$) and transoid ($J_{4\text{-}t}$) allylic coupling indicate that the former is larger than the latter by 0.5 cps, although there are cases where the reverse is true.[9]

Homoallylic couplings in some styrene derivatives indicated that this coupling in the *trans* compounds, $J_{5\text{-}t}$, was 1.5 cps, while in the *cis* compounds, $J_{5\text{-}c}$, was 1.1 cps. Rottendorf, Sternhell, and Wilmhurst suggest that transoid homoallylic coupling would be expected to be larger than cisoid homoallylic coupling constants but that they should be closer in magnitude than allylic coupling constants in these isomers.[9] These effects have been observed.

Table I lists the pmr data obtained for *cis*- and *trans*-1-(aryl)cyclopropylprop-1-enes. The assignment of stereochemistry given here fits most of the criteria for isomeric assignment given by Barbieux, *et al.* In the *cis* compounds, olefinic protons are deshielded, β-methyl groups are deshielded, and a greater chemical shift is apparent between aromatic protons than in the *trans* compounds. Both the allylic and homoallylic coupling constants do not fit the criteria given by Barbieux, *et al.*, in that the *trans* compounds show smaller coupling constants than *cis* compounds in this series. We are dealing here, however, with coupling in a system where different hybridization is present. These systems are more similar to coupling in a butadiene system, where coupling will depend on conformation owing to differing amounts of contributions of J_π and J_σ.[12,13]

Examination of Prentice Hall models which take atomic Van der Waals radii into account indicates that conformations are much different in the *cis* and *trans* isomers. Figures 1 and 2 indicate those which are most likely. These conformations aid in elucidating some unusual aspects of the pmr spectra. In the *trans* compounds the aromatic ring is pressed out of the plane of the double bond by the steric interactions of *both* the α and β groups (Figure 1). This effect has been noticed previously.[9] The cyclopropyl group in the *trans* compounds probably lies over the double bond

(12) A. A. Bothner-By and R. K. Harris, *J. Am. Chem. Soc.*, **87**, 3451 (1965).

(13) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

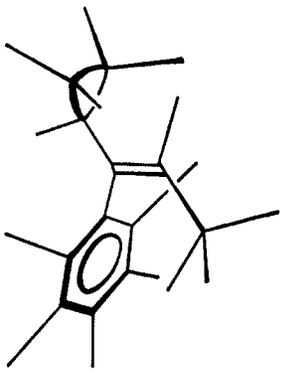


Figure 1

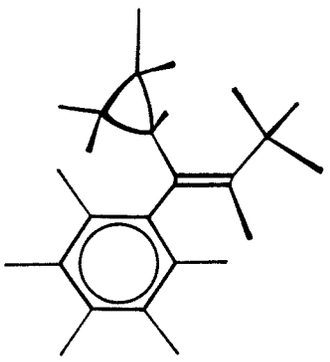


Figure 2

and may be free to rotate. Comparison of the pmr spectra reveals that the methylene cyclopropyl protons generate a much narrower group of peaks in the *trans* isomers than in the *cis* isomers. In the *cis* isomers, the angle between the aromatic ring and the plane of the double bond is small and the cyclopropyl group is forced away from the aromatic ring (Figure 2).

The unusual chemical shifts of the methyl groups in the *trans* compounds are larger than previously noted. This is because in this series of compounds the α group is cyclopropyl, about the same steric size as isopropyl, while in compounds previously examined methyl, ethyl, and *n*-propyl have been the α groups. The variation of the difference in chemical shifts between *cis* and *trans* groups and the size of the α substituent is revealed in Table II.

Long-range coupling constants support our picture of the ground-state conformations of the *cis* and *trans* compounds. Allylic coupling is known to be dependent upon conformation.[14] The angle, θ, between the C–H cyclopropyl methinyl proton bond and the plane of the double bond would be expected to be close to 0° (or 180°) in the *trans* compounds (Figure 1) and somewhere around 120° (or 60°) in the *cis* compounds (Figure 2). The long-range coupling constants would be expected to be time-averaged values in the *trans* compounds. J_{al} (J_4) is in the range of 1.3–3.1 cps for θ = 60–110° and <0.5 cps for θ <20 or >170°. Since $J_{4\text{-}c} > J_{4\text{-}t}$, these compounds agree with theoretical expectations.[15]

Homoallylic coupling, J_5, is also conformation dependent.[16] The coupling constants are determined by both the angles, θ and θ', the angle between the plane of the double bond, and the C–H methyl proton bond. If we assume that proton bonds in both isomers form the same angle θ' with the double bond then only θ is important. Since $J_{5\text{-}c}$ is larger than $J_{5\text{-}t}$, it indicates again that θ is larger in the *cis* compounds, for Karplus has shown that J_{ha} will be largest when θ and θ' are 90° and a minimum when θ and θ' are about 0°. Transoid homoallylic coupling constants have been observed to be larger than cisoid homoallylic coupling constants in similar molecules.

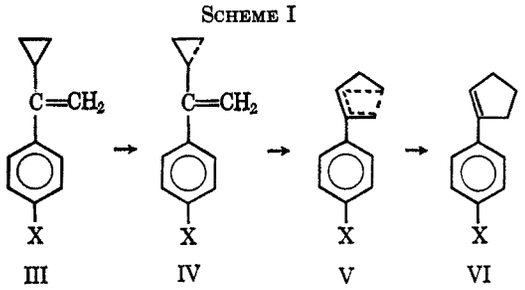
(14) E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **86**, 5563 (1964).
(15) E. W. Garbisch, Jr., *Chem. Ind.* (London), 1715 (1964).
(16) For a summary of references, see G. J. Karabatsos and F. M. Vane, *J. Am. Chem. Soc.*, **85**, 3886 (1963).

Pyrolysis Results

At 360–390° *trans*-1-phenyl-1-cyclopropylprop-1-ene (I) rearranged smoothly to the corresponding cyclopentene. Side products were negligible. Good first-order rate plots were obtained and k_1 was shown to be unchanged by an eightfold change in concentration. The rate showed no inhibition by the product cyclopentene which Frey has taken to indicate the absence of a radical chain process.[17] The activation energy (52 kcal/mole) was in the expected range for a vinylcyclopropane rearrangement. Typical data show that the rates of rearrangement at 383° of *trans*-1-(*para*-substituted phenyl)-1-cyclopropylprop-1-enes are 16.23, 16.57, 16.08, and 15.96 $10^4 k_1$ (sec^{-1}), respectively, for H, F, CH_3, and OCH_3.

The rates of rearrangement were essentially independent of the substituent on the phenyl group as was found for 1-(*para*-substituted phenyl)-1-cyclopropylethylenes.[18] In the latter case, however, a lower rate was found for the fluorophenyl compound. This was interpreted by a reaction sequence (see Scheme I)

SCHEME I

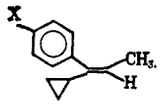
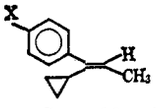


where IV contains the "expanded-ring" cyclopropane postulated by Schlag and Rabinovitch.[19] Where the π bond was activated by electron-donating groups formation of the "expanded ring" was considered to be rate determining, the step III → VI *via* the transition state V being rapid. In the case of the *p*-fluoro compound, electron withdrawal from the π bond may inhibit the bond-forming process and thus make step III → VI slower than the formation of IV and thus rate determining. This interpretation is supported by our observation that electron-withdrawing groups on the 2 carbon of 1-cyclopropylethylenes completely inhibit the vinylcyclopropane rearrangement.[20] In *trans*-1-(*p*-fluoro phenyl)-1-cyclopropylprop-1-ene, electron donation by the methyl group apparently compensates for electron withdrawal by the fluoro group and hence this compound rearranged at the same rate

(17) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962).
(18) A. D. Ketley and J. W. McClanahan, *J. Org. Chem.*, **30**, 942 (1965).
(19) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).
(20) A. D. Ketley, A. J. Berlin, and L. P. Fisher, *J. Org. Chem.*, **31**, 305 (1966).

TABLE II

THE VARIATION IN CHEMICAL SHIFT OF β-METHYL SUBSTITUENTS WITH VARIOUS α SUBSTITUENTS IN STYRENE SYSTEMS

Compd	α Substituent	β-Methyl *trans* to aromatic ring, τ	β-Methyl *cis* to aromatic ring, τ	$\Delta\tau$
cis-β-Methylstyrene	H		8.128	
				0.011[a]
trans-β-Methylstyrene	H	8.117		
β,β-Dimethylstyrene	H	8.12	8.18	0.06[a]
trans-2-Phenylbut-2-ene	CH_3		8.43	
				0.21[b]
cis-2-Phenylbut-2-ene	CH_3	8.22		
trans-2-(*p*-Methoxyphenyl)but-2-ene	CH_3		8.42	
				0.17[b]
cis-2-(*p*-Methoxyphenyl)but-2-ene	CH_3	8.25		
trans-3-(*p*-Methoxyphenyl)hex-2-ene	$CH_3CH_2CH_2$		8.47	
				0.22[b]
cis-3-(*p*-Methoxyphenyl)hex-2-ene	$CH_3CH_2CH_2$	8.25		
	Cyclopropyl		8.51	
				0.39
	Cyclopropyl	8.12		

[a] See ref 9. [b] See ref 8.

as the others in the series. Our results for these compounds are in good agreement with the results obtained by Frey for the isomerization of *trans*-1-cyclopropylbut-1-ene.[4]

cis-1-Phenyl-1-cyclopropylprop-1-ene (II) and its *para*-substituted derivatives behaved entirely differently from their geometric isomers. The rates of disappearance of the vinylcyclopropanes were again first order and there appeared to be no inhibition by product over at least 90% reaction. However, whereas in the *trans* compounds conversion to the substituted cyclopentenes was essentially quantitative, in the *cis* compounds only about 20% of the products formed at any time during the reaction were the expected substituted cyclopentenes. Most of the material (~60%) was converted to a colorless polymer.[21] Two other products were formed in 10–12% yield and 4–5% yield. These were isolated from the pyrolysis of *cis*-1-(*p*-fluorophenyl)-1-cyclopropylprop-1-ene by preparative vpc. Only the product formed in 10–12% yield could be obtained pure. It was shown by pmr and elemental analysis to be 1-(*p*-fluorophenyl)-5-ethylcyclopentene (VII). The minor product was contaminated with 1-(*p*-fluorophenyl)-5-methylcyclopentene and appeared from its pmr spectrum to be probably a mixture of methyl- and ethyl-substituted 1-(*p*-fluorophenyl)cyclopentenes which could not be separated. The corresponding products from the pyrolysis of the other *cis* isomers were not isolated. However, their retention times in the vpc suggested that they have structures analogous to those isolated from the pyrolysis of the fluoro compound.

Obviously compound VII could only be formed by a methylene insertion reaction. The only reasonable source of methylene appears to be elimination from the cyclopropyl group or from a diradical derived from it. However, since methylene is such a nonselective reagent[22] it is difficult to see why VII, one of many possible products, should be formed preferentially. An interesting possibility is that the major initial reaction is addition of methylene to the π bond of the starting material to give an excited dicyclopropane derivative which undergoes rearrangement directly to VII.

The product distribution was constant from run to run and was not dependent on concentration of starting material or on the nature of the *para* substituent.

The rates of rearrangement at 383° of *cis*-1-(*para*-substituted phenyl)-1-cyclopropylprop-1-enes were 4.61, 4.66, 4.36, and 4.89 10^4 k_1 (sec^{-1}), respectively, for H, F, CH_3, and OCH_3.

However, the first-order rate constants for the reaction of these compounds were approximately one-quarter of those obtained for their geometric isomers.

The kinetic results agree well with the interpretation of the pmr data. If the interaction of the methyl group with the cyclopropyl group in the *cis* isomers is large enough so that the conformation in Figure 2 is favored almost exclusively at room temperature, at the pyrolysis temperature a major portion of the molecular population will still have this configuration. As the cyclopropyl ring starts to break so the migration of the π cloud to form the incipient allylic radical will freeze the diradical into a conformation such that this

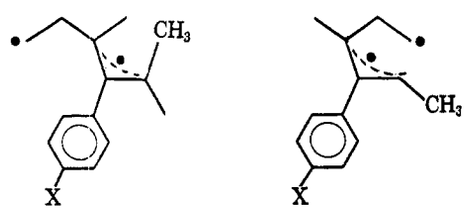
(21) Our observation that polymer is a major product in this reaction is surprising in view of the absence of high molecular weight products in the pyrolysis of 1-cyclopropyl-2-methylpropene [C. S. Elliot and H. M. Frey, *J. Chem. Soc.*, 345 (1965)]. Dr. Frey has suggested that this difference may be due to our use of clean, evacuated tubes rather than an "aged" reaction vessel. Using our experimental method we are able to obtain excellent first-order rate plots which are reproducible from run to run. We therefore feel that wall effects do not influence the rate-determining step of the reaction. However, it is not impossible that formation of polymeric material occurs after the rate-determining step and is subject to wall effects. Such an effect would not alter in any way the conclusions in this paper.

An alternative explanation for the difference between our results and those of Frey and Elliot is that phenyl-substituted dienes obtained by ring opening of 1-phenyl-1-cyclopropylpropenes would be more susceptible to polymerization than the dienes obtained in the pyrolysis of 1-cyclopropyl-2-methylpropene.

(22) W. von E. Doering, R. G. Bultery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

diradical may either reform starting material, rearrange, couple with another radical, or add to a double bond. It cannot, however, couple with itself to yield a substituted cyclopentene. Nevertheless, the reaction rate is still high and the activation energy (53 kcal/mole) is low compared with corresponding data for the thermal cleavage of cyclopropane.[23] Hence, as suggested by Benson, resonance stabilization of the transition state makes a major contribution to the lowering of the activation energy even though no energy contribution from synchronous bond formation exists.[24]

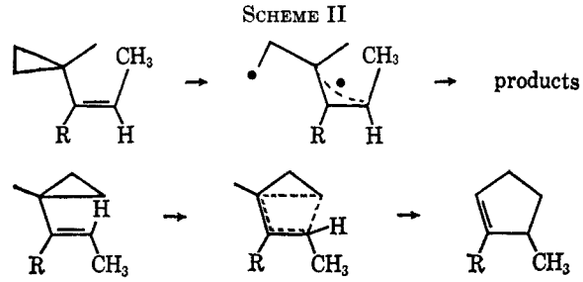
Since no products other than substituted cyclopentenes were found from the pyrolysis of the *trans* isomers, we must conclude that here bond formation is synchronous with bond cleavage. For, if this were not so, then at least part of the time the cyclopropyl ring, since it has free rotation, would break in the conformation shown in Figure 2 with the formation of products other than substituted cyclopentenes. Furthermore, the rate of formation of the radicals VIII and IX would not be expected to differ appreciably. Therefore the



VIII IX

rate of disappearance of *cis* and *trans* isomers should be the same, if both form diradical intermediates, even though the products formed would be different. The observed differences in rate can thus be best explained if the *trans* isomers undergo rearrangement with synchronous bond breaking and bond making while the *cis* isomers react *via* allylic diradicals[25] (Scheme II).

SCHEME II



Experimental Section[26]

cis- and *trans*-**1-Phenyl-1-cyclopropylprop-1-ene.**—Butyllithium (19.8 g) in 194 ml of dry ether was added to 115 g of ethyltriphenylphosphonium bromide in 600 ml of dry ether at −3°. Cyclopropyl phenyl ketone (46.0 g) in 300 ml of dry ether was added, also at −3°, and the temperature of the reaction was allowed to rise to 20°. Water (500 ml) was added and the ether layer was separated and dried over anhydrous magnesium sulfate. Ether was stripped off and the residue was fractionated through a 45 × 0.6 cm spinning-band column using a 50:1 reflux ratio. Five cuts were taken: cut 1, bp 105–110° (25 mm); cut 2, bp 110–114° (25 mm); cut 3, bp 114–116° (25 mm); cut 4, bp 117–120° (25 mm), and cut 5, bp 120–130° (25 mm). Cuts 1–4 were almost 100% isomeric mixtures of the 1-phenyl-1-cyclopropylprop-1-enes while cut 5 was predominantly unreacted ketone. The over-all yield of the two isomers was approximately 40%. Cuts 1 and 2 were rich in the *trans* isomer, cut 4 was rich in the *cis* isomer. Pure (>99%) isomers were isolated from these fractions by preparative vpc on either a 6 ft × 3/8 in. XE 60 nitrile–silicone rubber column on Chromosorb-W or a 6 ft × 3/8 in. Carbowax 20-M-TPA terminated column at 75°.

The *trans* isomer had bp 113° (25 mm). Infrared spectrum showed bands at 760 (s) (monosubstituted phenyl), 1025 (s) (cyclopropyl), and 1600 cm^{-1} (m) (olefinic carbon–carbon stretch). Other bands occur at 825 (m), 875 (w), 913 (w), 955 (w), 1000 (w), 1050 (w), 1078 (w), 1176 (w), 1233 (w), 1365 (w), 1490 (s), 1485 (s), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

The pmr spectrum of this compound and the other 1-(*para*-substituted phenyl)-1-cyclopropylpropenes is discussed in detail in a previous section of this paper.

Anal. Calcd for $C_{12}H_{14}$: C, 91.13; H, 8.87. Found: C, 91.02; H, 8.79.

The *cis* isomer had bp 117° (25 mm). Infrared spectrum showed bands at 755 (s) (monosubstituted phenyl), 1030 (s) (cyclopropyl), and 1600 cm^{-1} (m) (olefinic carbon–carbon stretch). Other bands occur at 830 (m), 905 (w), 958 (w), 980 (m), 1052 (w), 1073 (w), 1308 (m), 1440 (s), 1486 (s), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{12}H_{14}$: C, 91.13; H, 8.87. Found: C, 91.45; H, 8.67.

The 1-*para*-substituted phenyl-1-cyclopropylprop-1-enes were similarly prepared by the Wittig reaction from the corresponding ketones.

trans-**1-(*p*-Fluorophenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 77° (4 mm). Infrared bands were at 825 (s) (*para*-disubstituted phenyl), 1015 (s) (cyclopropyl), 1220 (s) (C–F bond), and 1600 cm^{-1} (s) (olefinic carbon–carbon stretch). Other bands occurred at 840 (s), 875 (m), 1000 (m), 958 (w), 1052 (w), 1095 (m), 1150 (m), 1295 (w), 1340 (w), 1365 (w), 1383 (w), 1425 (w), 1447 (m), 1553 (s), 1880 (w), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{12}H_{13}F$: C, 81.89; H, 7.39; F, 10.82. Found: C, 82.10; H, 7.37; F, 10.75.

cis-**1-(*p*-Fluorophenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 83° (4 mm). Infrared bands were at 827 (s) (*para*-disubstituted phenyl), 1021 (m) (cyclopropyl), 1226 (s) (C–F bond), and 1600 cm^{-1} (s) (olefinic carbon–carbon stretch). Other bands occurred at 840 (s), 872 (w), 968 (w), 995 (m), 1049 (w), 1093 (m), 1156 (s), 1247 (w), 1310 (w), 1368 (w), 1432 (w), 1450 (m), 1508 (s), 1882 (w), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{12}H_{13}F$: C, 81.89; H, 7.39; F, 10.82. Found: C, 81.53; H, 7.35; F, 10.48.

trans-**1-(*p*-Methylphenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 93° (4 mm). Infrared bands were at 815 (s) (*para*-disubstituted phenyl), 1015 (s) (cyclopropyl), and 1600 cm^{-1} (w) (olefinic carbon–carbon stretch). Other bands occurred at 871 (m), 888 (w), 952 (w), 1000 (w), 1045 (w), 1102 (m), 1169 (w), 1180 (w), 1206 (w), 1232 (w), 1305 (w), 1342 (w), 1355 (m), 1425 (m), 1447 (s), 2820 (s), 2880 (s), 2980 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{13}H_{16}$: C, 90.69; H, 9.31. Found: C, 90.38; H, 9.08.

cis-**1-(*p*-Methylphenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 97° (4 mm). Infrared bands were at 810 (s) (*para*-disubstituted phenyl), 1020 (s) (cyclopropyl), and 1600 cm^{-1} (w) (olefinic carbon–carbon stretch). Other bands occurred at 870 (w), 905 (w), 942 (w), 967 (w), 981 (m), 1052 (m), 1105 (w), 1182 (w), 1300 (m), 1382 (m), 1424 (m), 1445 (s), 1506 (s), 2820 (s), 2980 (s), and 3050 cm^{-1} (s).

(23) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(24) K. W. Egger, D. M. Golden, and S. W. Benson, *J. Am. Chem. Soc.*, **86**, 5240 (1964).

(25) The referee has suggested that, since the aromatic ring is pushed out of the plane of the double bond in the *trans* isomers, formation of the cyclic transition state V would be a less energetic process than for the *cis* isomers since there would be less loss of resonance energy. We feel, however, that if resonance effects due to different degrees of conjugation of the phenyl group were a significant factor then we would almost certainly also observe considerable rate differences due to substituents on the phenyl group.

(26) Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Boiling points are uncorrected. Analytical vapor chromatographic analyses were carried out using a Perkin-Elmer 154D instrument with an ethylene glycol succinate polyester column (column P) at temperatures ranging from 170 to 220°. Preparative vapor chromatographic separations were carried out using a Nester-Faust Prepkro instrument with a 6 ft × 3/8 in. Wilkins 10% 20-M-TPA (Carbowax 20-M terminated with terephthalic acid) column in a temperature range of 100–135°. Helium flow rate was 300 cc/min.

Anal. Calcd for $C_{13}H_{16}$: C, 90.69; H, 9.31. Found: C, 90.47; H, 9.11.

***trans*-1-(*p*-Methoxyphenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 120° (5 mm). Infrared bands were at 820 (*para*-disubstituted phenyl), 1020 (s) (cyclopropyl), 1228 (ether linkage), and 1600 cm^{-1} (olefinic carbon–carbon stretch). Other bands occurred at 845 (s), 877 (m), 895 (w), 930 (w), 952 (w), 1040 (s), 1103 (m), 1072 (s), 1281 (s), 1328 (w), 1359 (w), 1380 (w), 1447 (m), 1455 (m), 1510 (s), 1567 (w), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.96; H, 8.52; O, 8.52. Found: C, 82.80; H, 8.47; O, 8.78.

***cis*-1-(*p*-Methoxyphenyl)-1-cyclopropylprop-1-ene** was obtained as a colorless liquid, bp 123° (5 mm). Infrared bands were at 820 (*para*-disubstituted phenyl), 1028 (cyclopropyl), 1222 (ether linkage), and 1600 cm^{-1} (olefinic carbon–carbon stretch). Other bands occurred at 830 (s), 870 (w), 903 (w), 964 (w), 979 (w), 1102 (w), 1174 (m), 1283 (m), 1358 (w), 1439 (m), 1458 (m), 1505 (s), 1570 (w), 2820 (s), 2890 (s), 2990 (s), and 3050 cm^{-1} (s).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.98; H, 8.51; O, 8.51. Found: C, 82.88; H, 8.51; O, 8.63.

1-Phenyl-5-methylcyclopentene was obtained by passing 10 g of *trans*-1-phenyl-1-cyclopropylprop-1-ene through a 0.5-m glass-wool packed column heated to 400°. The product was isolated by distillation through a 1-m spinning-band column as a colorless liquid, bp 120° (25 mm). Infrared bands were at 750 (s) (monosubstituted phenyl) and 1615 cm^{-1} (w) (olefinic carbon–carbon stretch). Other bands occurred at 690 (s), 832 (w), 905 (m), 956 (w), 1002 (w), 1018 (w), 1070 (m), 1097 (w), 1151 (w), 1176 (w), 1213 (w), 1230 (w), 1291 (w), 1326 (w), 1365 (m), 1451 (s), 1477 (w), 1560 (w), 1589 (m), 1677 (w), 1710 (w), 2880 (s), 2920 (s), and 3200 cm^{-1} (s).

The pmr spectrum showed signals centered at τ 2.8,[27a] (5),[27b] 4.05 (1),[27c] 6.6–8.8 (5),[27e] 8.95 (3).[27f]

Anal. Calcd for $C_{12}H_{14}$: C, 91.13; H, 8.87. Found: C, 90.96; H, 9.11.

1-(*p*-Methylphenyl)-5-methylcyclopentene was prepared by passing 10 g of *trans*-1-(*p*-methylphenyl)-1-cyclopropylprop-1-ene through a 0.5-m glass-wool packed column heated to 400°. The product was isolated as a colorless liquid, bp 99° (4 mm). Infrared bands were at 810 (s) (*para*-disubstituted phenyl) and 1610 cm^{-1} (w) (olefinic carbon–carbon stretch). Other bands occurred at 922 (w), 965 (w), 1004 (w), 1022 (w), 1047 (w), 1069 (w), 1110 (w), 1183 (w), 1238 (w), 1294 (w), 1305 (w), 1340 (w), 1373 (w), 1439 (m), 1510 (m), 2880 (s), 2970 (s), and 3200 cm^{-1} (s).

The pmr spectrum showed signals centered at τ 2.9 (4)[27a] 4.10 (1),[27c] 6.6–9.2 (8),[27g] and 8.95 (3).[27f]

Anal. Calcd for $C_{13}H_{16}$: C, 90.69; H, 9.31. Found: C, 90.66; H, 9.31.

1-(*p*-Fluorophenyl)-5-methylcyclopentene was prepared by pyrolysis at 400° of *trans*-1-(*p*-fluorophenyl)-1-cyclopropyl-prop-1-ene. The product was isolated by distillation as a colorless liquid, bp 85° (4 mm). Infrared bands were at 835 (s) (*para*-disubstituted phenyl), 1232 (C–F bond), and 1600 cm^{-1} (s) (olefinic carbon–carbon stretch). Other bands were at 926 (w), 955 (w), 962 (w), 1008 (w), 1070 (w), 1102 (m), 1153 (m), 1295 (w), 1338 (w), 1375 (w), 1453 (m), 1517 (s), 2880 (s), 2970 (s), and 3200 cm^{-1} (s).

(27) (a) Aromatic protons showing either A_2B_2 type spectra or complex broad peaks in the unsubstituted and fluorinated phenyl ring cases. (b) Numbers in parentheses refer to integrated area ratios. Rounded number is given when within experimental error. (c) Olefinic proton showing ill-resolved triplet characteristics. (d) Methoxy protons. (e) Nonolefinic protons on the cyclopentenyl ring. (f) Methyl doublet, $J = 7.0 \pm 0.5$ cps. (g) Protons described by 27e as well as the protons from tolyl methyl group.

The pmr spectrum showed signals centered at τ 2.95 (4),[27a] 4.10 (1),[27c] 6.6–8.8 (5)[27e] and 8.95 (3).[27f]

Anal. Calcd for $C_{12}H_{13}F$: C, 81.89; H, 7.39; F, 10.82. Found: C, 81.94; H, 7.38; F, 10.75.

1-(*p*-Methoxyphenyl)-5-methylcyclopentene was prepared by pyrolysis at 400° of *trans*-1-(*p*-methoxyphenyl)-1-cyclopropyl-prop-1-ene. The product was isolated by distillation as a colorless liquid, bp 120° (4 mm). Infrared bands were at 830 (m) (*para* disubstituted phenyl), 1253 (s) (ether linkage), and 1606 cm^{-1} (w) (olefinic carbon–carbon stretch). Other bands were at 752 (w), 811 (m), 925 (w), 967 (w), 1044 (m), 1108 (w), 1180 (m), 1293 (m), 1338 (w), 1374 (w), 1458 (m), 1513 (s), 1578 (w), 2880 (s), 2970 (s), and 3200 cm^{-1} (s).

The pmr spectrum showed signals centered at τ 2.95 (4),[27a] 4.15 (1),[27c] 6.37 (3),[27d] 6.5–9.0 (5),[27e] and 8.95 (3).[27f]

Anal. Calcd for $C_{13}H_{16}O$: C, 82.98; H, 8.51; O, 8.51. Found: C, 82.95; H, 8.49; O, 8.40.

1-(*p*-Fluorophenyl)-5-ethylcyclopentene.—*cis*-1-(*p*-Fluorophenyl)-1-cyclopropylprop-1-ene (5 ml) was passed through a 1-m glass-wooled packed column held at 425°. The product distribution was shown to be identical with that obtained in kinetic runs in sealed tubes at lower temperatures. The liquid product was removed from polymer by distillation on a vacuum line. Two peaks were found in the vpc of this material other than that due to 1-(*p*-fluorophenyl)-5-methylcyclopentene. The larger of these had a sufficiently higher retention time so that it could be trapped by preparative vpc free from the other products. The smaller peak, however, was a shoulder on the 1-(*p*-fluorophenyl)-5-methylcyclopentene peak and although it was trapped it was certainly not a pure sample. The pmr spectrum of the material from the larger peak consists of a complex signal for aromatic protons at τ 2.5–3.2 (relative area 4.3), a triplet for the olefinic proton centered at 4.1 (relative area 0.9), a complex signal for the ring and methylene protons at 7.0–8.0 (relative area 6.9), and a triplet for the methyl group centered at 8.82 (relative area 3.0).

Anal. Calcd for $C_{13}H_{15}F$: C, 82.08; H, 7.89; F, 10.03. Found: C, 82.02; H, 7.73; F, 10.21.

Rate Studies.—Degassed samples (0.1 ml) were sealed under vacuum in 10 × 2 cm glass tubes. The tubes were hung from a rack in a muffle furnace the temperature of which was controlled by a Hallikainen thermodyne relay Model 1315-A through a Hallikainen controller Model 1257-A. After equilibration for 10 min, tubes were rapidly removed at noted times and quenched in a stream of compressed air. (Tubes were cooled to room temperature in approximately 30 sec without cracking, by this method.) Five microliters from each tube were analyzed using a Perkin-Elmer 154 vapor fractometer. First-order rate constants were computed from the areas of peaks corresponding to initial and residual starting materials. The vpc showed that products obtained in kinetic runs were identical with those obtained from the larger scale preparative runs.

Pmr Spectra Determinations.—Spectra were obtained on both the Varian Associates HR-60 and A-60A instruments. Sidebanding methods were used to determine accurate chemical shifts by means of the Hewlett-Packard 200CDR audio oscillator and 522 B electronic counter. Spectra were examined in 5% v/v solutions in carbon tetrachloride and deuteriochloroform and data reported based on measurements in the carbon tetrachloride solution. Very little change is observed, however, in deuteriochloroform solution.

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