and 50% ethanol. Bicyclo[3.3.0]octane was isolated from this mixture by using preparative v.p.c. through a 6-ft. silicone oil D.C. 200 (dimethylsiloxane polymer) column at 126°. The sample showed infrared bands at 3.5, 6.9, 7.4, 7.5, 7.6, 8.1, 10.0, and 11.0 μ and the spectrum was identical with the literature spectrum of bicyclo[3.3.0]octane.[5]

The n.m.r. spectrum (Figure 4) was identical with the literature spectrum of bicyclo[3.3.0]octane.[6]

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.49, H, 11.12.

Acknowledgment.—The authors thank Mr. L. Fisher and Mr. D. Clancy for technical assistance.

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The Rearrangement of 1-*para*-Substituted Phenyl-1-cyclopropylethylenes

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There has been no systematic study reported of the effect of substituents on the rates of vinylcyclopropane rearrangements. We describe here results of part of such a study on the rates of rearrangement of a series of 1-*para*-substituted phenyl-1-cyclopropylethylenes.

Pyrolyses were initially conducted using a glass wool packed flow system at 400°. The reactions proceeded cleanly giving in each case 90% or more of the corresponding 1-*para*-substituted phenylcyclopentene.

Since the reaction rates of all except the fluoro derivative were immeasurably high at 400°, kinetic runs were made, in the gas phase, in evacuated sealed tubes at 350°. The identity of the products to those obtained at 400° was shown by v.p.c.

Figure 1 shows first-order plots for each compound. All except the fluoro derivative fall onto one line and all, consequently, have the same rate of rearrangement ($1.03 \pm 0.07 \times 10^{-4}$ sec.$^{-1}$). The *p*-fluoro derivative rearranges at approximately half this rate ($5.03 \pm 0.33 \times 10^{-5}$ sec.$^{-1}$). These values are very close to the rate constant at 350° extrapolated from Frey's and Marshall's data[1] for 1-methyl-1-cyclopropylethylene (1.15×10^{-5} sec.$^{-1}$). The vinylcyclopropane rearrangement appears, therefore, to be relatively insensitive to polar effects, at least as transmitted through the 1-carbon. This insensitivity can be explained by a mechanism in which the rate-determining step is the opening of the cyclopropyl ring either to the diradical or to the "expanded ring" **4** postulated by Schlag and Rabinovitch.[2] The lower rate of the fluorophenyl derivative may be due to the smaller conjugation of this substituent in the second step with the forming double bond of the cyclopentene. This could decrease the rate of closure of the five-membered ring below that of fission or expansion of the cyclopropyl ring. The second step would thus become rate-determining. Systems containing more strongly electron-withdrawing substituents are being studied to check this hypothesis.

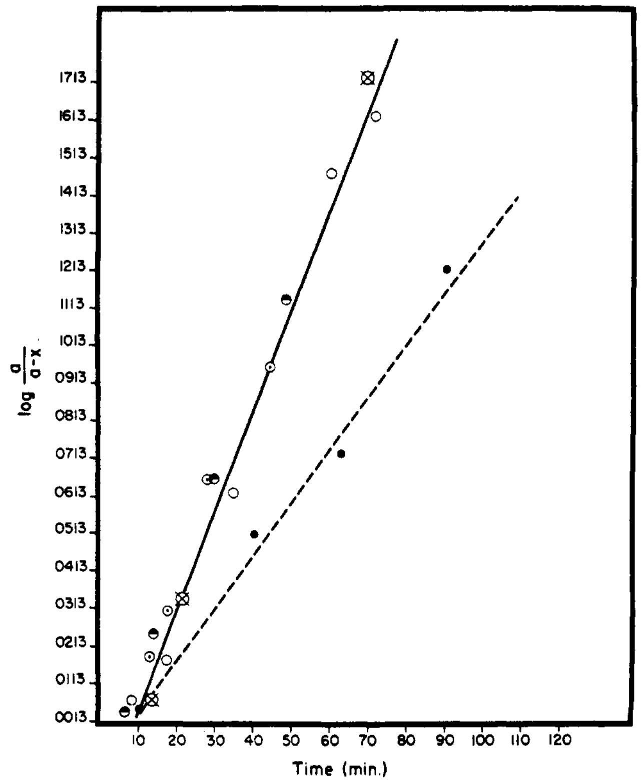
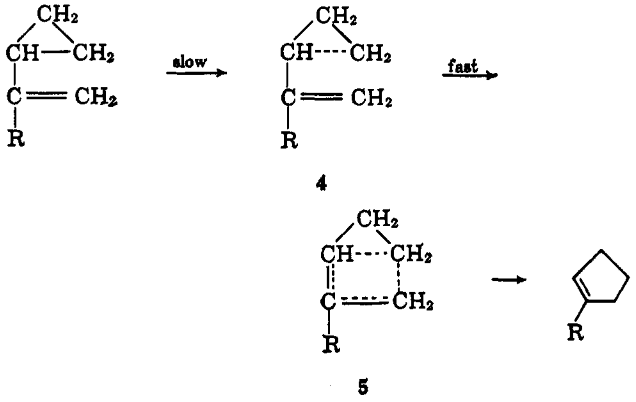


Figure 1.—First-order plots for the rearrangement of *para*-substituted phenylcyclopropylethylenes; X = CH_3O (○), CH_3 (×), $(CH_3)_2CH$ (⊙), H (◒), and F (●).



Insensitivity to substituents would also fit a Cope-type mechanism proceeding directly through a transition state such as **5**. Here the group R is conjugated both with a double bond which is being formed and with one which is being destroyed and hence the effects might cancel. However, it is difficult to explain the lower rate of the fluoro derivative by this mechanism.

Experimental[3]

1-Cyclopropyl-1-phenylethylene.—Butyllithium (18 g.) in 156 ml. of dry ether was added to 87.2 g. of methyltriphenylphosphonium bromide in 600 ml. of dry ether at −3°. A 35.7-g. sample of cyclopropylphenyl ketone[4] 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, dried, and distilled; 18.7 g. of product was

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(1) H. M. Frey and D. C. Marshall, *J. Chem. Soc.*, 3981 (1962).

(2) E. W. Schlag and B. S. Rabinovitch, *J. Am. Chem. Soc.*, **82**, 5996 (1960).

(3) Carbon, hydrogen, oxygen, and fluorine analyses were by Huffman Microanalytical Laboratory, Wheatridge, Colo.

(4) All ketones were obtained from Aldrich Chemical Co.

obtained, b.p. 107° (25 mm.), b.p. 215° (763 mm.) (lit. b.p. 211–213°, $n^{25}\mathrm{D}$ 1.5312).

Infrared spectrum showed bands at 9.81 (cyclopropyl), 3.27 (aromatic C–H), and 6.31 μ (vinyl). Other bands appeared at 12.80, 12.15, 11.98, 11.25, 10.68, 9.81, 9.55, 9.26, 7.96, 7.80, 7.25, 7.03, 6.98. 6.50, and 3.20 μ.

The n.m.r. spectrum showed a multiplet (relative area 5) at τ 2.39–2.92 (phenyl H); signals at 4.88 (relative area 1), and 5.08 (relative area 1) due to olefinic protons; and complex absorptions (relative area 1) at 8.20–8.68 (cyclopropyl methyne H) and (relative area 4) at 9.13–9.55 (cyclopropyl methylene H).

Anal. Calcd. for $C_{11}H_{12}$: C, 91.66; H, 8.33. Found: C, 91.74; H, 8.46.

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

1-Cyclopropyl-1-(*p*-fluorophenyl)ethylene was obtained as a colorless liquid, yield 58%, b.p. 72° (40 mm.), and $n^{25}\mathrm{D}$ 1.5292. Infrared bands appeared at 12.12 (para-substituted phenyl), 9.80 (cyclopropyl), and 6.24 μ (C=C stretch). Other bands were at 13.01, 12.43, 11.80, 11.08, 10.76, 9.75, 9.51, 9.27, 9.08, 8.68, 8.14, 8.00, 7.23, 7.01, 6.62, 3.32, and 3.22 μ. The n.m.r. spectrum showed multiplets (relative area 4) at τ 2.42–2.65 and 2.88–3.25 (phenyl H); and signals at 4.84 (relative area 1), 8.23–8.63 (cyclopropylmethyne H), and (relative area 4) 9.03–9.50 (cyclopropyl methylene H).

1-Cyclopropyl-1-(*p*-methoxyphenyl)ethylene was obtained as a colorless liquid, yield 46%, b.p. 116° (50 mm.), and $n^{25}\mathrm{D}$ 1.5608. Infrared bands were at 12.01 (*para*-substituted phenyl), 9.75 (cyclopropyl), and 6.25 μ (C=C stretch). Other bands appeared at 13.17, 12.96, 11.10, 10.58, 9.20, 9.08, 8.92, 8.42, 8.00, 7.71, 7.20, 7.03, 6.90, 6.85, 6.62, 6.35, 3.53, 3.40, and 3.26 μ. The n.m.r. spectrum showed multiplets (relative area 4) at τ 2.52–2.66 and 3.17–3.33 (aromatic H); signals at 4.89 (relative area 1) and 5.27 due to olefinic protons; a singlet (relative area 3) at 6.27 (methoxy H); and complex absorptions (relative area 1) at 8.34–8.67 (cyclopropylmethyne H) and (relative area 4) 9.04–9.53 (cyclopropyl methylene H).

Anal. Calcd. for $C_{12}H_{14}$: C, 90.40; H, 9.59. Found: C, 91.35; H, 9.08.

1-Phenylcyclopentene.—A 5-g. sample of 1-cyclopropyl-1-phenylethylene was passed through a 50-cm. Vicor tube packed with glass wool and heated to 400°. The crude product was distilled through a 30-plate column. 1-Phenylcyclopentene (4.6 g.) was obtained as a colorless liquid, b.p. 122° (50 mm.) and $n^{25}\mathrm{D}$ 1.5736 (lit. $n^{25}\mathrm{D}$ 1.5734), having infrared bands at 6.25 (C=C stretch), 14.20, and 13.33 μ (monosubstituted benzene). Other bands were at 11.02, 10.98, 9.60, 9.31, 7.74, 7.52, 7.42, 6.90, 6.72, 5.52, 3.98, and 3.30 μ. The n.m.r. spectrum showed a multiplet (relative intensity 5) at τ 2.5–2.8 (phenyl H); a triplet (relative intensity 1) at 3.8 (olefinic H); a complex absorption (relative intensity 9) at 7.2–7.6 (methylene H at C-3 and C-5); and a complex absorption (relative intensity 2) at 7.8–8.2 (methylene H at C-4).

Anal. Calcd. for $C_{11}H_{12}$: C, 91.66; H, 8.33. Found: C, 91.46; H, 8.27.

1-*para*-Substituted phenylcyclopentenes were prepared by similar pyrolyses of the corresponding 1-*para*-substituted phenyl-1-cyclopropylethylenes.

1-(*p*-Fluorophenyl)cyclopentene was obtained as a colorless liquid, b.p. 232° (760 mm.), $n^{25}\mathrm{D}$ 1.5578, having infrared bands at 6.24 (C=C stretch) and at 12.2 μ (*para*-substituted phenyl). Other bands appeared at 12.48, 10.43, 9.83, 9.60, 9.09, 8.17, 7.68, 7.51, 5.97, 3.52, 3.40, and 3.29 μ. The n.m.r. spectrum showed a multiplet (relative intensity 4) in the region τ 2.7–3.2 (aromatic H); a multiplet (relative intensity 1) centered at 3.95 (olefinic H); and a complex absorption (relative intensity 6) at 7.10–8.25 (methylene H).

Anal. Calcd. for $C_{11}H_{11}F$: C, 81.49; H, 6.77; F, 11.73. Found: C, 81.69; H, 6.90; F, 11.59.

1-(*p*-Methoxyphenyl)cyclopentene was obtained as colorless crystals, m.p. 81°, having infrared bands at 6.23 (C=C stretch) and 12.25 μ (*para*-substituted phenyl). Other bands were at 11.96, 10.45, 10.12, 9.67, 9.00, 8.51, 8.17, 8.03, 7.28, 4.00, 6.62, and 3.48 μ. The n.m.r. spectrum showed doublets (relative intensity 4) at τ 2.62 and 3.18 (phenyl H); a triplet at 3.95 (olefinic H); a singlet at 6.22 (methoxy H); a complex absorption at 7.30–7.65 (methylene H at C-3 and C-5); and a complex absorption at 7.75–8.20 (methylene H at C-4).

Anal. Calcd. for $C_{12}H_{19}O$: C, 82.76; H, 8.05; O, 9.20. Found: C, 82.47; H, 8.14; O, 9.68.

1-(*p*-Methylphenyl)cyclopentene was obtained as colorless crystals, m.p. 53°, having infrared bands at 6.1 (C=C stretch) and 12.30 μ (*para*-substituted phenyl). Other bands were at 11.11, 10.12, 9.62, 8.92, 8.83, 8.43, 8.07, 7.63, 7.44, 7.28, 6.89, 6.57, 6.38, and 3.48 μ. The n.m.r. spectrum showed a quartet (relative intensity 4) in the region τ 2.6–3.2 (aromatic H); a multiplet (relative intensity 1) centered at 4.0 (olefinic H); a complex absorption (relative intensity 6) at 7.0–8.9 (methylene H); and a singlet (relative intensity 3) at 7.68 (methyl H).

Anal. Calcd. for $C_{12}H_{14}$: C, 90.40; H, 9.59. Found: C, 90.81; H, 8.89.

1-(*p*-Isopropylphenyl) cyclopentene was obtained as a colorless liquid, b.p. 120° (4.0 mm.), having infrared bands at 6.22 (C=C stretch) and 12.32 μ (*para*-substituted phenyl). Other bands were at 11.98, 10.40, 9.79, 9.62, 9.45, 7.68, 7.30, 7.21, 7.04, 6.86, 6.60, and 3.48 μ. The n.m.r. spectrum showed a multiplet (relative intensity 4) at τ 2.61–3.02 (phenyl H); a triplet (relative intensity 1) at 3.95 (olefinic H); complex absorptions (relative intensity 7) at 7.15–8.21 (methylene and methyne protons); and a sharp doublet (relative intensity 6) at 8.73 (methyl H).

Anal. Calcd. for $C_{14}H_{18}$: C, 90.32; H, 9.68. Found: C, 90.34; H, 9.90.

***p*-Methylphenylcyclopentane**—A 1.75-g. portion of the crude product from the pyrolysis of 1-cyclopropyl-1-(*p*-methylphenyl)-ethylene was hydrogenated with sodium borohydride in a Brown[2] apparatus.[5] The catalyst was filtered off and the ethanol solvent was removed by distillation. *p*-Methylphenylcyclopentane (88% yield) was obtained as a colorless liquid after purification by preparative v.p.c. on a silicone oil column at 162°. The n.m.r. spectrum showed a singlet (relative intensity 4) centered at τ 2.82 (aromatic H); a broad absorption (relative intensity 1) centered at 7.12 (aliphatic H on carbon adjacent to phenyl); a singlet (relative intensity 3) centered at 7.67 (methyl H); and broad absorptions at 7.6–9.1 (relative intensity 8) assignable to methylene protons.

Anal. Calcd. for $C_{11}H_{14}$: C, 90.41; H, 9.59. Found: C, 90.50; H, 9.48.

Rate Studies.—Samples (0.1 ml.) were sealed under vacuum in 10 × 2 cm. glass tubes. The tubes were placed in a muffle furnace equipped with an electronic controller which kept the temperature (350°) within ±0.5°. After equilibration for 10 min., tubes were rapidly removed at noted times and quenched in a stream of compressed air. Five microliters from each tube was analyzed using an F and M gas chromatograph with an integrating recorder. First-order rate constants were computed from the areas of the peaks corresponding to initial and residual starting materials.

Acknowledgment.—The authors are indebted to Mr. L. Fisher and Mr. D. Clancy for technical assistance.

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Disilyldihydronaphthalenes from Alkali Metal Naphthalenides and Chlorosilanes

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Although the reaction of chlorosilanes and alkali metal naphthalenides is known to give disilyldihydronaphthalenes,[1,2] the previous data do not rigorously establish the positions of the silyl groups in these struc-

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[2] J. F. Brown, Jr., U. S. Patent 2,967,160 (1961); *Chem. Abstr.* **55**, 6456*b* (1961).