***cis,cis*-2,4-*trans,trans*-6,8-(Tetratrimethylammonium bromide)-*cis*-bicyclo[3.3.0]octane.**—A sealed tube containing 3.0 g. (0.011 mole) of VI,[3] 10 ml. of methyl bromide, and 5 ml. of methyl alcohol was heated at 100–110° for 12 hr. After cooling the tube, the seal was broken and the solvent was decanted from the gummy residue. Drying the residue under reduced pressure in the presence of calcium chloride gave 4.3 g. (61%) of a tan crystalline solid which was soluble in water but insoluble in most organic solvents. This solid slowly yielded a white powder upon continuous extraction with acetonitrile. The powder decomposed above 140°.

Anal. Calcd. for $C_{20}H_{46}Br_4N_4$: C, 36.25; H, 6.95. Found: C, 36.18; H, 6.85.

Attempted Degradation of the Quaternary Bromide of VI with Phenyllithium.—To a suspension of 4.24 g. (0.00640 mole) of the quaternary bromide in 100 ml. of anhydrous ether was added an aliquot of phenyllithium solution containing 0.0256 mole of phenyllithium. The mixture was stirred for 70 hr. at room temperature and then filtered under nitrogen. The filtrate showed a small peak by vapor fractometry which could not be ascribed to ether, benzene, bromobenzene, or biphenyl. The filtrate was washed with water and dried over calcium chloride for 30 min.; the solvent was removed under reduced pressure to yield only trace amounts of an oily red residue. The infrared spectrum of this oil (neat) showed absorption maxima at 1685 and 753 cm.$^{-1}$. Not enough compound was present in any of the runs to identify this product.

Attempted Degradation of the Quaternary Bromide of VI with Potassium Amide.—To 1.64 g. (0.042 mole) of potassium metal in 100 ml. of liquid ammonia was added 5.83 g. (0.0088 mole) of the quaternary bromide. The mixture was stirred for 4 hr. at Dry Ice–acetone temperature. After removing the cooling bath, the solvent was allowed to slowly boil away over an 8-hr. period.

The residue was extracted with ether and the combined extracts were washed with 2% aqueous ammonium chloride and dried. Removal of the solvent left 0.15 g. of a red-brown oil which was dissolved in pentane and chromatographed over Woelm basic alumina using pentane as the eluent. Fractional distillation of the eluate gave 50 mg. of a yellow oil, b.p. 200° (1 mm.), which showed maxima in the infrared region which could be ascribed to carbonyl.

***cis,cis*-2,4-*trans,trans*-6,8-Tetra(acetamido)-*cis*-bicyclo[3.3.0]-octane.**—To 10.2 g. (0.10 mole) of acetic anhydride was added with stirring 3.4 g. (0.020 mole) of the tetraamine V. The precipitate was separated by filtration and recrystallized from glacial acetic acid to give a quantitative yield of pure product, m.p. above 400°. The infrared spectrum (mull) showed absorption maxima at 3330 and 3125 (N–H stretching), 1652 (C=O stretching), and 1550 cm.$^{-1}$ (C–N stretching).

Anal. Calcd. for $C_{16}H_{26}N_4O_4$: C, 56.80; H, 7.69; N, 16.57. Found: C, 56.97; H, 7.82; N, 16.38.

Attempted Degradation of *cis,cis*-2,4-*trans,trans*-6,8-Tetra-(acetamido)-*cis*-bicyclo[3.3.0]octane.—A mixture of 20 g. (0.17 mole) of thionyl chloride and 3.92 g. (0.0116 mole) of the tetraacetamide was allowed to stand at room temperature for 20 hr. and then heated at the reflux temperature for 48 hr. Removal of the solvent left a small amount of residue which was recrystallized from hexane to give trace amounts of a white crystalline solid, m.p. 119.5–120°, which was not characterized.

***cis,cis*-2,4-*trans,trans*-6,8-Tetra(benzamido)-*cis*-bicyclo[3.3.0]-octane.**—The tetraamine (V) tetrahydrochloride (0.637 g., 0.00202 mole) was dissolved in 25 ml. of water and to this solution was added 4 g. (0.10 mole) of sodium hydroxide. The solution was cooled to 10° in an ice bath and 1.4 g. (0.01 mole) of benzoyl chloride was added slowly with stirring, keeping the temperature of the solution below 20°. Stirring was continued an additional hour and the precipitate was then collected by filtration. The white solid was washed with 5% aqueous sodium hydroxide and 5% hydrochloric acid, and dried. The weight of pure product was 1.026 g. (87%), m.p. above 400°. The infrared spectrum (mull) showed absorption maxima at 3330 (N–H stretching) and 1640 cm.$^{-1}$ (C=O stretching).

Anal. Calcd. for $C_{36}H_{34}N_4O_4$: C, 73.72; H, 5.80; N, 9.56. Found: C, 73.84; H, 5.89; N, 9.73.

Attempted Degradation of *cis,cis*-2,4-*trans,trans*-6,8-Tetra-(benzamido)-*cis*-bicyclo[3.3.0]octane by the von Braun Reaction.—A mixture of 5.82 g. (0.010 mole) of the tetrabenzamide and 12.5 g. (0.060 mole) of phosphorus pentachloride in 75 ml. of carbon tetrachloride was heated at the reflux temperature for 5 days. The excess phosphorus pentachloride was destroyed by the cautious addition of water. The carbon tetrachloride layer was washed with 5% aqueous sodium bicarbonate and dried. Removal of the solvent gave only trace amounts of an oily residue.

The Rearrangement of 1,1-Dicyclopropylethylene

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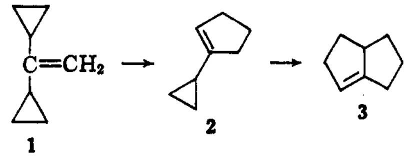
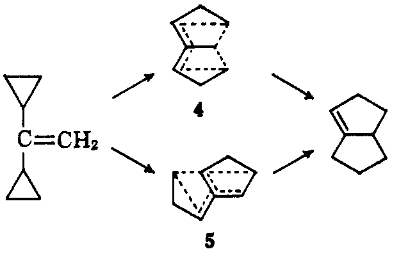
Two examples have been reported of the vinylcyclopropane rearrangement in compounds containing more than one cyclopropyl ring. Doering has studied the pyrolysis of 1-cyclopropyl-2-vinylcyclopropane[1] while Vogel and Erb have described the rearrangement of *cis*- and *trans*-1,2-dicyclopropylethylene.[2] The products in both cases were cyclopropylcyclopentenes which were stable under the conditions of the pyrolyses.

We have studied the pyrolysis of 1,1-dicyclopropylethylene (**1**) because, in this case, the rearrangement of one cyclopropyl ring leads to a product **2** containing a new vinylcyclopropane system. This in turn, would be expected to rearrange to bicyclo[3.3.0]octene-1 (**3**) in a second step. The possibility also exists in this system of the two rings opening in a concerted reaction to give **3** directly without the intermediate formation of **2**. Two transition states for the concerted reaction can be formulated, one (**4**) in which the two cyclopropyl groups simultaneously attack the 2-carbon of the vinyl group and another (**5**) in which the one cyclopropyl attacks this carbon while the other attacks the incipient cyclopentene double bond backside.





1,1-Dicyclopropylethylene was prepared from dicyclopropyl ketone by the Wittig reaction. The n.m.r. spectrum of this compound is shown in Figure 1. Pyrolysis in a glass packed tube at 400° gave, on the first pass, a material **6** showing only one major new peak in the gas chromatograph. After continuous passage through the column, **6** had grown to about 40% of the starting material. A second peak **7** began to appear at this point and grew at the expense of **6**. When the peak corresponding to the 1,1-dicyclopropylethylene

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[1] W. von Doering, *Angew. Chem., Intern. Ed. Engl.*, **2**, 115 (1963).

[2] E. Vogel and R. Erb, *ibid.*, **1**, 53 (1962).

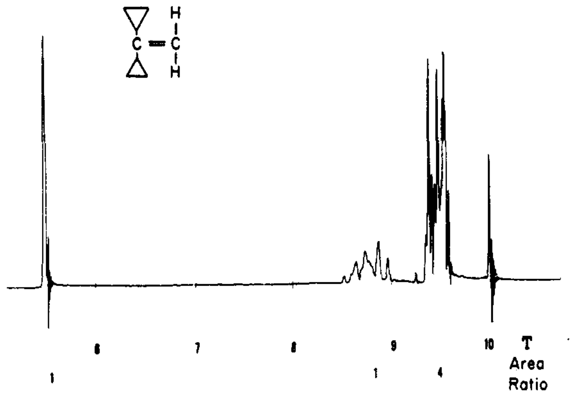

Figure 1.—N.m.r. spectrum of 1,1-dicyclopropylethylene.

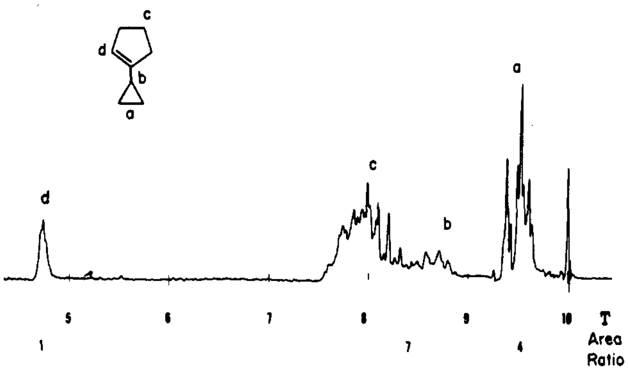

Figure 2.—N.m.r. spectrum of 1-cyclopropylcyclopentene.

had completely disappeared, the product consisted of 35% **6**, 61% **7**, and 4% minor products. Exhaustive pyrolysis resulted in conversion to 93% **7** and 7% minor products.

Compounds **6** and **7** were separated and purified by preparative v.p.c. Compound **6** was shown to be 1-cyclopropylcyclopentene by n.m.r. (Figure 2), infrared, and carbon–hydrogen analysis. Compound **7** was shown similarly (Figure 3) to be bicyclo[3.3.0]octene-1. Confirmation of the structure of **7** was obtained by conversion to bicyclo[3.3.0]octane (Figure 4).

Since, at 400°, 1,1-dicyclopropylethylene is almost half converted to 1-cyclopropylcyclopentene before any appreciable amount of bicyclo[3.3.0]octene-1 has formed, the reaction appears to be stepwise with any concerted opening of the two rings being insignificant. At 480° under otherwise identical conditions, bicyclo[3.3.0]octene-1 was observed as the only product after one pass through the tube. However, by decreasing the residence time tenfold, results similar to those at 400° were obtained. The reaction is, therefore, still stepwise at this higher temperature.

Experimental[3]

1,1-Dicyclopropylethylene.—Butyl lithium (24 g.) in 200 ml. of *n*-hexane was added to 116 g. of methyltriphenylphosphonium bromide in 600 ml. of dry ether at −3°. A 35.8-g. sample of freshly distilled dicyclopropyl ketone, b.p. 164° (763 mm.), in 300 ml. of dry ether, cooled to −3°, was then added. The complex was allowed to come to room temperature and 500 ml. of water was added. The ether layer was separated, dried over anhydrous magnesium sulfate, and distilled through a 30-plate column. 1,1-Dicyclopropylethylene (8.9 g.) was obtained: b.p. 133° (758 mm.), $n^{25}\mathrm{D}$ 1.4563. The v.p.c. of a sample showed a negligible level of impurity. The infrared spectrum had absorptions at 9.81 (cyclopropyl) and 6.13 μ (vinyl); other peaks appeared at 12.32, 11.43, 10.85, 10.52, 9.51, 9.15, 8.54, 8.25, 8.00, 7.13, 7.04, 6.87, 3.30, and 3.23 μ.

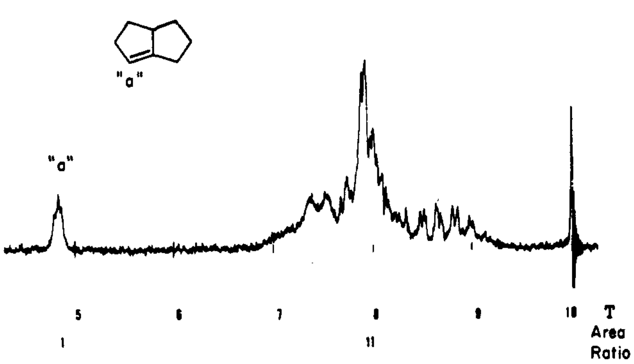

Figure 3.—N.m.r. spectrum of bicyclo[3.3.0]octene-1.

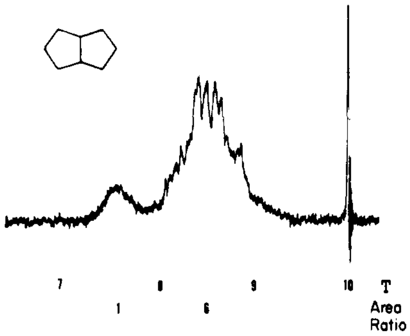

Figure 4.—N.m.r. spectrum of bicyclo[3.3.0]octane.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.44; H, 11.64.

Pyrolysis of 1,1-Dicyclopropylethylene.—A Vicor tube, 60 cm. long and 2.7 cm. in diameter, packed with glass wool, was placed vertically in a tube furnace and heated to the reaction temperature. 1,1-Dicyclopropylethylene was introduced in a stream of argon from a dropping funnel at the rate of 10 ml./hr. The vapor from the pyrolysis zone was condensed and collected in an ice-cooled flask. After each pass through the tube the composition of the material was checked on a Perkin-Elmer 154D gas chromatograph using a diisodecyl phthalate column at 105°. Part of the material containing 40% cyclopropylcyclopentene, 51% bicyclo[3.3.0]octene-1, and 7% unchanged starting material was separated, and the components were trapped using an Aerograph A350 programmed temperature gas chromatograph. A 5-ft. 80% diatomaceous earth (Chromasorb) column and a 5-ft. 20% polyethylene glycol (Carbowax 4000) column were used. The temperature was programmed from 50 to 180° at 6°/min.

N.m.r. spectra were measured in carbon tetrachloride at 25° using a Varian D.P.-60 spectrometer. Tetramethylsilane was used as internal reference.

1-Cyclopropylcyclopentene had b.p. 142° (763 mm.) and $n^{25}\mathrm{D}$ 1.4768.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18. Found: C, 88.21; H, 11.07.

Bicyclo[3.3.0]octene-1 had b.p. 139° (755 mm.) and $n^{25}\mathrm{D}$ 1.4817.

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

Bicyclo[3.3.0]octane.—A 1.633-g. sample of the crude product from the exhaustive pyrolysis of dicyclopropylethylene was hydrogenated using 0.21 *N* sodium borohydride in a Brown[2] apparatus.[4] The catalyst was prepared in acetic acid which was then completely removed before carrying out the reduction in absolute ethanol. When the reduction was complete, the catalyst was filtered off and the ethanol solution was distilled through a 30-plate column. The product distilled as an azeotrope with ethanol and the first fraction consisted of approximately 50% product

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[3] Carbon and hydrogen analyses were by Huffman Microanalytical Laboratory, Denver, Colo.

[4] H. C. Brown and C. A. Barton, *J. Am. Chem. Soc.*, **84**, 2829 (1962).

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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[5] J. E. Germain and H. Blanchard, *Bull. chim. soc. France*, **54**, 473 (1960).

[6] W. B. Moniz, Ph.D. Thesis, Pennsylvania State University, 1960.

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.

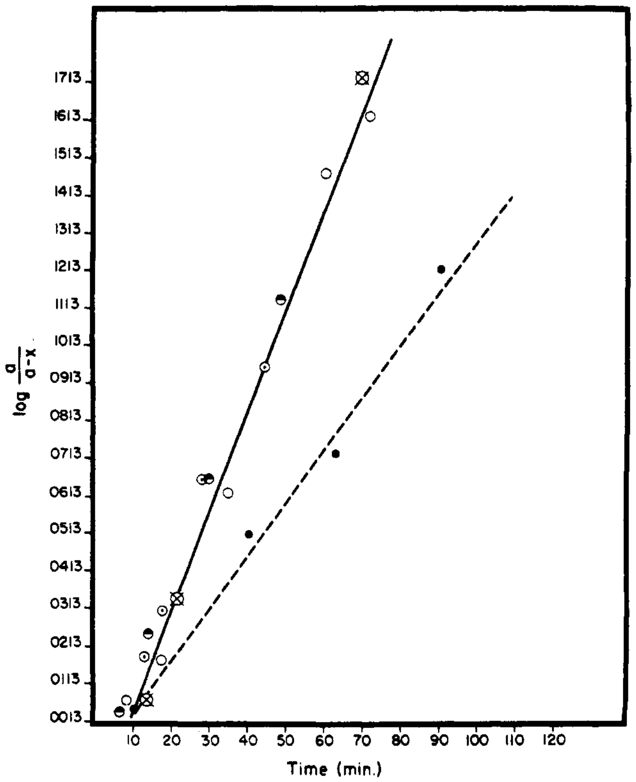
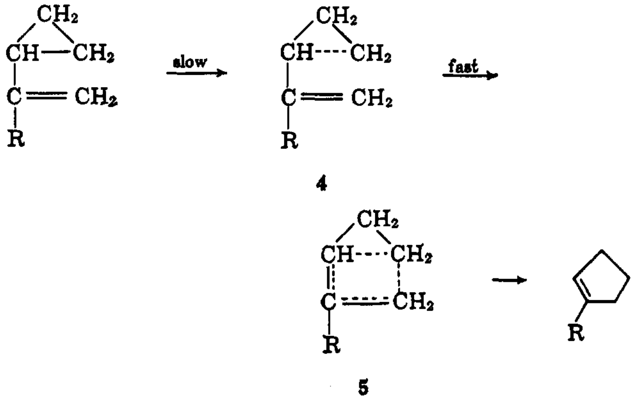


Figure 1.—First-order plots for the rearrangement of *para*-substituted phenylcyclopropylethylenes; X = CH_3O (○), CH_3 (×), $(CH_3)_2CH$ (⊙), H (◓), and F (●).



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.