of 1.74 g. (6.5 mmoles) of dienestrol in nitromethane with a solution of 0.50 g. (14 mmoles) of hydrogen chloride in nitromethane and 1.50 g. (19 mmoles) of dimethyl sulfoxide as in the preceding experiment yielded 1.03 g. (45%) of III, melting at 180° with decomposition. Similarly, 0.73 g. (2.7 mmoles) of II, 0.30 g. (8 mmoles) of hydrogen chloride, and 0.47 g. (6.0 mmoles) of dimethyl sulfoxide in nitromethane gave 0.81 g. (83%) of III, melting at 182° with decomposition. Samples of III from the three sources showed identical infrared spectra and gave the same pyrolysis product.

1-Ethylidene-2-*p*-hydroxyphenyl-3-methyl-4-methylthio-5-indenol (IV).—The sulfonium salt III (1.00 g.) was heated under nitrogen at 180–185° for 5 min. The product was cooled, dissolved in benzene, and treated with activated charcoal. The solvents were evaporated, and the residue was crystallized from carbon tetrachloride, yielding 0.75 g. (90%) of yellow product, m.p. 152–153°. The analytical sample, obtained by recrystallization from carbon tetrachloride, melted at 155–156°. The apparent first pK_a, in 50% ethanol, was estimated to be approximately 10. Ultraviolet absorption maxima in methanol at 280 (ϵ 24,000) and 324 mμ (4300) were observed.

Anal. Calcd. for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.33. Found: C, 73.51; H, 5.68; S, 10.39.

The n.m.r. spectrum of IV showed the presence of eighteen hydrogen atoms with resonances, δ in p.p.m., as follows: 2.0–2.4, nine protons attributed to the three-methyl groups; 5.2, one proton exchangeable with D_2O attributed to one phenolic group; a quartet centered at 6.05, one proton attached to the olefinic carbon of the ethylidene group; 6.7–7.2 (four peaks with the most intense at 6.9), six aromatic protons; a singlet at 7.87, one proton attributed to the 5-hydroxyl group. *o*-Alkylthiophenols are known to form relatively strong hydrogen bonds.[12] A singlet at 7.95 δ was also present in the spectrum of the sulfonium salt.

The pyrolysis product (IV) (0.50 g.), 2.2 ml. of methyl sulfate in 50 ml. of benzene, and a solution of 1.00 g. of sodium hydroxide in 25 ml. of water was shaken for 5 hr. The yellow benzene solution was separated, dried, and evaporated to dryness, yielding 0.27 g. of crude methyl ether, m.p. 100–110°. This was treated with potassium permanganate in acetone at 35° until the violet color persisted. Excess permanganate was decomposed with a drop of alcohol. The mixture was filtered and the filtrate was evaporated to dryness. The residue was dissolved in water and acidified, yielding 0.09 g. of *p*-anisic acid, m.p. and m.m.p. 183–184°, with an authentic sample.

Reaction of Phenol with Dimethyl Sulfoxide in Benzene.—Hydrogen chloride was bubbled for several minutes into a solution of 5.0 g. of phenol and 3.5 g. of dimethyl sulfoxide in 50 ml. of benzene. The mixture was kept overnight at room temperature. The oily layer which had separated was washed with ether and yielded a crystalline product. This was dissolved in methanol and precipitated with ether several times to yield 1.2 g. of *p*-hydroxyphenyldimethylsulfonium chloride, m.p. 160° dec.[13,14] Heating the product several minutes above the melting point gave *p*-hydroxyphenyl methyl sulfide, m.p. 82–83°, in nearly quantitative yield in agreement with the results of Zincke and Ebel.[13]

Acknowledgment.—The authors are grateful to Dr. Charles C. Price, Chairman, Department of Chemistry, University of Pennsylvania, for constructive criticism and helpful suggestions. We are indebted to Mr. Donald P. Hollis of Varian Associates for the n.m.r. spectra.

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[12] E. A. Allan and L. W. Reeves, *J. Phys. Chem.*, **66**, 613 (1962).

[13] T. Zincke and C. Ebel, *Ber.*, **47**, 1100 (1914), report m.p. 159°.

[14] Lard and Claypole (ref. 4) report that the *ortho*-substituted derivative is the product when the reaction is carried out in excess dimethyl sulfoxide. No attempt was made to isolate the *ortho*-substituted derivative in this work.

4-Bromocyclopentene by Hydride Reduction of 3,5-Dibromocyclopentene and Its Unassisted Hydrolysis

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A preparation of 4-bromocyclopentene is described by the reaction of lithium aluminum hydride with the dibromide prepared from cyclopentadiene. This homoallylic bromide undergoes solvolysis in 50% aqueous acetone about four times less rapidly than cyclopentyl bromide. Its unreactivity is discussed in the light of the acceleration by 10^{11} observed in the related but strained 7-norbornenyl sulfonates.

The anchimeric assistance to solvolysis by the double bonds in *anti*-7-norbornenyl[1] and 7-norbornadienyl[2] tosylates (by factors of 10^{11} and 10^{14}, respectively) is the greatest on record; this fact indicates that in the 7-norbornenyl cation the positive charge is effectively delocalized by the overlap of the p-orbitals at C-2, C-3, and C-7, an overlap that is between σ and π in character.

Spectral evidence indicates[3,4] that the same forces which produce a barrier to free rotation in ethane force cyclopentane to adopt a nonplanar conformation. Cyclopentene might exist preferentially, or at least permissibly, in conformation I, and its distortion might become aggravated in 4-bromocyclopentene (II). The obvious resemblance of the conformation II to the C-1-2-3-4-7 portion of 7-norbornenyl bromide led us to prepare the compound and compare its rate of hydrolysis in 50% acetone–water with that of cyclopentyl bromide.

I

II

4-Bromocyclopentene (II), b.p. 43° (35 mm.), $n^{24}\mathrm{D}$ 1.4992, is readily prepared by the S_N2' lithium aluminum hydride reduction of the 1,4-bromination product of cyclopentadiene. The bromide II prepared in this way is free of contamination by its allylic isomer because of the great ease with which the latter is further reduced by lithium aluminum hydride. The bromide II is hydrolyzed in 50% aqueous acetone to the corresponding alcohol (*p*-nitrobenzoate, m.p. 89°). The rate of this hydrolysis, carried out in sealed tubes, was followed by titration with base and compared with that of cyclopentyl bromide, with the results shown in Table I.

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[1] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

[2] S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

[3] J. G. Aston, H. L. Fink, and S. C. Schumann, *ibid.*, **65**, 341 (1943).

[4] K. S. Pitzer, *Science*, **101**, 672 (1945).

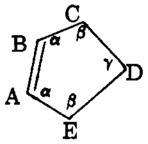
TABLE I

HYDROLYSIS OF CYCLOPENTYL BROMIDE AND OF 4-BROMOCYCLOPENTENE IN 50% ACETONE–WATER

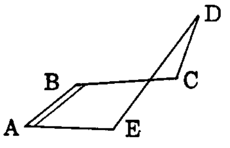
Temperature	k, sec.$^{-1}$ × 10^{-5} Cyclopentyl bromide	4-Bromocyclopentene
60.0	6.07, 5.97	1.31, 1.25
70.2	15.7, 15.7	3.23, 3.52
80.2	34.3, 38.5	8.95, 8.72
ΔH^*, kcal.	20.6	21.6
ΔS^*, cal./deg.	−11.8	−11.6

It is evident from Table I that the presence of the double bond in the homoallylic position of the five-membered ring is associated with a hydrolysis rate about 4 times slower than that of cyclopentyl bromide. It follows that the amount of purely π overlap between C-1 and C-4 must be negligible, and that the molecule of the unsaturated bromide is not bent sufficiently toward the form of 7-norbornenyl bromide to produce any significant σ overlap.

Cyclopentene has a dipole moment of 0.97 D. in hexane and 0.92 D. in carbon tetrachloride.[5] This moment, assumed to be located at the midpoint of the bisector of bonds BC and AE in III, and to be acting upon a moment of 6.5 D. in the half-ionized C–Br bond at the transition state for ionization, this bond being still directed at its original tetrahedral angle from a planar model, yields by the equation used by Winstein, Grunwald, and Ingraham[6] an estimate of 1 kcal. interaction opposing ionization. The moment here is much more effectively oriented than in *endo*-2-norbornenyl bromide, where no retardation relative to the saturated *endo* bromide is observed.[7]



III



IV

To estimate the possible effect of the double bond on the angle strain of ionization, we calculated the bond angles corresponding to minimum angle strain for planar models of cyclopentane (assumed equivalent to cyclopentyl bromide), cyclopentyl cation, cyclopentene, and Δ^3-cyclopententyl cation, locating in the last three cases the rather shallow energy minimum with respect to angle variation. We used the widely quoted[8-10] bending force constant $k = 0.8 \times 10^{-11}$ ergs/radian^2 for the C–C–C angles at saturated and unsaturated carbon alike, so that the strain energy $E = 1/2\ k\ \theta^2 = 17.5\ \theta^2$ cal./mole, where θ is the angular deflection in degrees.[11]

In all models the C–C distance was taken as 1.54 Å. for sp^3–sp^3, 1.34 Å. for sp^2–sp^2, and 1.50 Å. for sp^2–sp^3 bonds[12]; the normal angle was supposed to be 109.47° at an sp^3-hybridized carbon and 120° at an sp^2-hybridized carbon atom. Table II shows the results calculated for the hypothetical planar models and for a Δ^3-cyclopentenyl cation bent so as to afford the same degree of C-1,C-3,C-4 overlap as must be present in the 7-norbornenyl cation. This model is simply the relevant angles taken from the calculations of Sargent[13] for the benznorbornadienyl cation in its configuration of minimum strain, assuming all bridgehead angles to be equal.

Table II indicates that angle strain could be responsible for (5.3 − 3.2) − (1.5 − 0.2) = 0.8 kcal. increase in endothermicity of ionization due to the presence of the double bond in 4-bromocyclopentene, based upon planar models. This effect should be opposed by the fact that of the four molecules, cyclopentane can be the most stabilized over the planar model by puckering.[14,15,16] Torsional, or eclipsing, strain would seem to play exactly the same role in ionization of cyclopentyl and Δ^3-cyclopentenyl bromides.

The considerable strain, of the order of 17 kcal., indicated for the bent ion IV explains the lack of driving force toward ionization from the double bond in 4-bromocyclopentene. The eleven powers of ten observed in 7-norbornenyl tosylate correspond at 300° K. to a stabilization energy of only 15 kcal. available at a transition state with the degree of bending assigned to IV. This force would seem to be almost exactly counteracted by the strain required in order to establish the orbital overlap in the monocyclic compound.

Thus there is no homoallylic activation in 4-bromocyclopentene. Both the unsymmetrical type of homoallylic interaction, as in 2-norbornenyl compounds, and the symmetrical type, as in 7-norbornenyl compounds, require σ overlap of orbitals on the interacting carbon atoms. In the case of 4-bromocyclopentene the strain energy involved in reaching a suitable conformation is greater than the stabilization afforded by the orbital overlap.

Experimental

3,5-Dibromocyclopentene.[17-20]—A 175-g. sample of cyclopentadiene (2.66 moles) was dissolved in 125 ml. of petroleum ether and cooled to −30° in a 1-l. three-necked flask that was equipped with stirrer, dropping funnel, and drying tube. Bromine (427 g., 2.66 moles) was dissolved in 225 ml. of petroleum ether and added slowly during 2 hr., keeping the temperature of the reaction mixture below −30°. The mixture was poured into a 1-l. erlenmeyer flask, cooled to −80° and the solvent decanted. The residue was dissolved in ether and reduced immediately with lithium aluminum hydride.

4-Bromocyclopentene.—A solution of 44 g. of lithium aluminum hydride (1.3 moles) in 400 g. of ether was prepared in a 2-l. three-necked flask equipped with a stirrer, reflux condenser, and dropping funnel. The ether solution of 3,5-dibromocyclopentene from the previous preparation was added with cooling in an

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(5) Quoted by L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, Cambridge, Mass., 1948, from M. Puchalik, *Acta Phys. Polon.*, **4**, 145 (1945).

(6) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 825 (1948).

(7) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(8) F. H. Westheimer, "Steric Effects in Organic Chemistry," Chap. 12, M. S. Newman, Ed., John Wiley and Sons, New York, N. Y. 1956, p. 533.

(9) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

(10) C. S. Beckett, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2485 (1947).

(11) We note that the single significant figure in k has burgeoned into three in the process[8] of conversion of units (K. Mislow, remarks at the National Conference on Reaction Mechanisms, Brookhaven National Laboratory, September, 1962), and we shall round our conclusions off correspondingly.

(12) L. S. Bartell and R. A. Bonham, *J. Chem. Phys.*, **42**, 824 (1960).

(13) G. D. Sargent, thesis, Harvard University, 1963.

(14) K. S. Pitzer, *Science*, **101**, 672 (1945).

(15) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947).

(16) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

(17) E. H. Farmer and W. D. Scott, *J. Chem. Soc.*, 177 (1929).

(18) R. W. Kierstad, R. P. Linstead, B. C. L. Weedon, *ibid.*, 1803 (1953).

(19) A. T. Blomquist and W. G. Mayes, *J. Org. Chem.*, **10**, 134 (1945).

(20) E. B. Reid and J. F. Yost, *J. Am. Chem. Soc.*, **72**, 1808 (1950).

Table II

Strain at C–C–C Bond Angles in Hypothetical Five-Membered Rings

Model	∠ α, deg.	∠ β, deg.	∠ γ, deg.	Angle strain Deg.[2]	Angle strain Kcal.
Cyclopentane	108	108	108	11	0.2
Cyclopentyl cation	108.32	104.93	113.5	85	1.5
Cyclopentene (III)	112.25	104.25	107	181	3.2
Δ³-Cyclopentenyl cation, planar	112.48	101.52	112.0	304	5.3
Δ³-Cyclopentenyl cation, bent IV	109.13	97.75	98.0	997	17.5

ice bath during 2 hr. The reaction mixture was stirred at room temperature overnight and then refluxed for 36 hr. It was filtered through glass wool and the filtrate poured over ice. The ether solution was separated, dried over calcium chloride, and the ether removed by distillation at atmospheric pressure. The residue was distilled at reduced pressure and yielded 37 g. (0.25 mole, 9.5%) of 4-bromocyclopentene boiling at 43° (35 mm.), $n^{25}D$ 1.4992.[21] The infrared spectrum of 4-bromocyclopentene in carbon tetrachloride shows peaks at 3.30 (m), 3.39, 3.48, 3.53 (s), 6.29 (m), 6.93, 7.34, 7.70 (s), 8.14 (vs), 8.64, 10.32 (w), 10.77 (m), 11.04 (s), 11.40 (w), and 14.74 μ (vs).

Δ³-Cyclopentenol.—An 11-g. sample of 4-bromocyclopentene (0.075 mole) was refluxed for 12 hr. in a mixture of 75 ml. of water, 75 ml. of ethanol, and 8 g. of sodium carbonate (0.075 mole). Sodium bicarbonate precipitated and was filtered off. Most of the ethanol was removed by distillation. The residue was distilled at reduced pressure, and 2.1 g. of alcohol boiling at 83–85° (110 mm.) was obtained, $n^{25}D$ 1.4653 (lit.[22] b.p. 67–68° at 30 mm., $n^{25}D$ 1.4673).

p-Nitrobenzoate melted at 89° (from 95% ethanol).

Anal. Calcd. for $C_{12}H_{11}O_4N$: C, 61.79; H, 4.76; N, 6.01. Found: C, 61.73; H, 5.01; N, 6.12.

Measurement of Rate Constants.—The rates of solvolysis of bromocyclopentane and 4-bromocyclopentene were followed by titration of the acid produced. A solution of the bromide in 100 ml. of 50% aqueous acetone was prepared and this was evenly divided into 16 tubes which were sealed and placed in a constant temperature bath. A warm-up time of 2–3 min. was allowed and one tube was removed from the bath at this time to give an initial titer and a starting time. The tubes were cooled in Dry Ice–acetone baths for fast reactions and with running tap water for slower reactions. A 5-ml. aliquot was taken from each tube and diluted with 50 ml. of water. This mixture was then titrated with 0.01 *N* sodium hydroxide to pH 7.0 using a Beckman Autotitrator, Model K.

Product Recovery.—A 2.540-g. sample of 4-bromocyclopentene was added to 100 ml. of 50% aqueous ethanol and refluxed for 22 hr. The reflux temperature was 81°. The reaction mixture was kept neutral with1.5 *N* sodium hydroxide by keeping the brom thymol blue in the solution just green. When the hydrolysis was complete the ethanol was removed by distillation and the aqueous mixture was extracted with ether. The ethereal solution was dried over magnesium sulfate and the ether removed by distillation. The residue weighed 0.51 g., a yield of 37%. The infrared spectrum of this material was identical with that of a pure sample of 3-cyclopentenol.

When 0.592 g. of 3-cyclopentenol was dissolved in 50 ml. of 50% aqueous ethanol containing 0.6 g. of sodium bromide and refluxed for 22 hr., 0.205 g. of the alcohol was recovered using the same technique applied to the solvolysis reaction, a yield of 40.5%.

From 0.400 g. of material from the product study and 0.87 g. of *p*-nitrobenzoyl chloride, 0.495 g. of ester was obtained. From 0.400 g. of 3-cyclopentenol and 0.87 g. of *p*-nitrobenzoyl chloride, 0.50 g. of ester was obtained. Both samples melted at 89° after recrystallization from 95% ethanol and a mixture melting point showed no depression.

Acknowledgment.—This work was supported by the National Science Foundation.

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[21] In the course of work in this laboratory by Dr. Shelton Bank' this bromide has been converted into Δ³-cyclopentylacetic acid, characterized and analyzed as its *p*-bromophenacyl ester, m.p. 66–67°, and into 2-(Δ³-cyclopentenyl)ethanol, whose *p*-nitrobenzenesulfonate, prepared by Dr. George Schmid, melts at 65–66° [*cf.* R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961), m.p. 65–67°].

[22] S. Winstein, E. L. Allred, and V. Sonnenberg, *ibid.*, **81**, 5833 (1959).

Addition Reaction of Silanes to 1,5,9-Cyclododecatriene

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Monosilyl and bissilyl compounds were obtained by chloroplatinic acid-catalyzed addition of silanes, such as trichlorosilane and methyldichlorosilane, to *cis,trans,trans*-1,5,9-cyclododecatriene. These adducts were methylated, giving 1-trimethylsilyl-4,8-cyclododecadiene and bis(trimethylsilyl)cyclododecene, respectively. Catalytic hydrogenation of 1-trimethylsilyl-4,8-cyclododecadiene gave only trimethylsilylcyclododecene. The diene derivatives contained both *cis* and *trans* double bonds and the cyclododecene derivatives were mixtures of *cis* and *trans* isomers. Hydrolysis of 1-trichlorosilyl- and 1-(methyldichlorosilyl)-4,8-cyclododecadiene gave the corresponding hydroxyl derivatives.

Cyclododecatriene was prepared by trimerization of butadiene with various catalyst systems[1b] in good yields. We have found that an isomer of *cis,trans,trans*-1,5,9-cyclododecatriene also can be obtained in about 85% yield by using a catalyst of the titanium tetraalkoxide–dialkylaluminum halide system.[2] The reactions of the double bonds in the compound, *i.e.*, oxidation reactions with some organo peracids[3] and addition reactions of boranes,[4] halogen,[5] hydrogen chloride, and acetic acid,[6] have been reported by several workers. A *trans* double bond present in *cis,trans,trans*-1,5,9-cyclododecatriene is oxidized with organo per-

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[1] (a) Nishi-2-chome, Daini, Oyodoku, Osaka, Japan. (b) The catalyst systems are as follows: titanium tetrachloride–dialkylaluminum (or trialkylaluminum) chloride, chromium compounds, alkylaluminum compounds, and nickel compounds. See also G. Wilke, *Angew. Chem.*, **69**, 97 (1957); **73**, 33 (1961); **75**, 10 (1963); *J. Polymer Sci.*, **38**, 45 (1959); Studiengesellschaft Kohle m. b. H., Belgian Patents 555,180 (1957), 566,436 (1958); G. Wilke and H. Müller, German Patent 1,043,329 (1958).

[2] H. Takahasi and M. Yamaguchi, *J. Org. Chem.*, **28**, 1409 (1963).

[3] G. Wilke, *J. Polymer Sci.*, **38**, 45 (1959); L. I. Zakharkin and V. V Korneva, *Dokl. Akad. Nauk SSSR*, **132**, 1078 (1960).

[4] R. Köster, *Angew. Chem.*, **69**, 684 (1957); R. Köster and G. Griaznov, *ibid.*, **73**, 81 (1961).

[5] H. Takahasi and M. Yamaguchi, *J. Chem. Soc. Japan*, **83**, 1042 (1962).

[6] L. I. Zakharkin, V. V. Korneva, and A. V. Iogansen, *Dokl. Akad. Nauk SSSR*, **138**, 373 (1961).