consumed correspond to 0.078 mole of *trans* and 0.121 mole of *cis*. The relative reactivities are *trans*, 1, and *cis*, 1.34. The yields of *t*-butyl alcohol were determined titrimetrically (nitrite ester method) and found to be 102%. The butenyl chlorides were formed in 85% yield (determined by KOH hydrolysis followed by Volhard chloride). The composition of the butenyl chloride mixture corresponding to 60–70% crotyl chloride and 40–30% 3-chlorobutene-1 was found by G.L.C. (10-foot "DEG" on Chromosorb W at 35°; 3-chlorobutene-1 2.0 min. and crotyl chloride 3.8 min.).

[CONTRIBUTION NO. 2706 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

Small-Ring Compounds. XXXVI. 3-Methylenecyclobutyl Bromide and 1-Methylcyclobut-2-enyl Bromide[1]

BY EDGAR F. KIEFER[2] AND JOHN D. ROBERTS

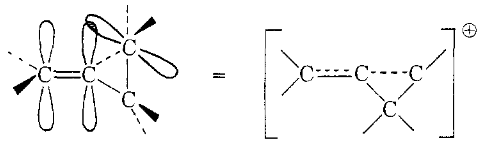
RECEIVED JUNE 10, 1961

3-Methylenecyclobutyl bromide and 1-methylcyclobut-2-enyl bromide have been synthesized from the cycloaddition products of allene with acrylonitrile and vinyl benzoate. The rate constants for solvolysis of the two bromides in aqueous ethanol have been determined and correlated with the solvolysis rates of a series of analogous bromides. 1-Methylcyclobut-2-enyl bromide appears to exhibit some rate enhancement due to cross-ring π-type interaction of the electrons formally centered on the 3-position with the electron-deficient 1-position in the transition state.

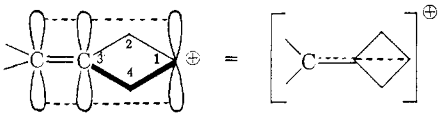
Introduction

The possibility of "homoallylic" resonance[3] in carbonium ion intermediates has received considerable attention since the suggestion by Winstein and Adams[4] that delocalization of electrons between orbitals separated by an intervening saturated carbon atom might be responsible for the unexpectedly high solvolysis reactivity of cholesteryl derivatives. Application of the simple LCAO molecular-orbital method to homoallylic systems[3,5,6] has resulted in semi-quantitative predictions and correlations of carbonium ion stabilization energies, which in certain cases have been at least qualitatively verified by experiment.

So far, virtually all cases for which homoallylic resonance is regarded as important involve carbonium ions having the proper geometry for σ-type overlap between the vacant p-orbital and one or more of the p-orbitals of a double bond, as in I. It was therefore of interest to investigate the possibility of 1,3-electron delocalization in unsaturated cations, which, if planar like cyclobutene,[7a] methylenecyclobutane,[7b] 1,3-dimethylenecyclobutane[7c] and 1-methyl-3-methylenecyclobutane,[7c] could be stabilized 1,3-π overlap (if not by the σ-bond delocalization postulated for the cations formed from the saturated cyclobutyl halides).[8] Particularly interesting in this connection are the cations II and III, for which simple MO calculations predict delocalization energies of 0.8–4.7 kcal./mole and 4.1–10.9 kcal./mole, respectively,[9] when the 1,3-resonance integrals (β_{13}) are assigned values of 0.2–0.5β which are reasonable for the distances involved.[5] While the predicted stabilizations are not large, they might be expected to lead to significant differences in the first-order solvolysis rate constants between the corresponding bromides and appropriate model compounds.



I



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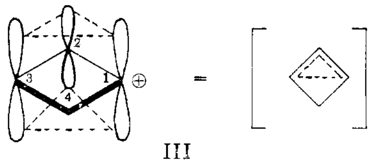

III

Results and Discussion

The synthesis of 3-methylenecyclobutyl bromide (IV) was achieved in two ways, using cycloaddition reactions[10] as shown in Fig. 1. These syntheses feature formation of a cycloadduct from vinyl benzoate and allene (vinyl acetate and allene do not undergo cycloaddition)[11] and the deamination of 3-methylenecyclobutylamine[12] to 3-methylenecyclobutanol in good yield. The uncomplicated character of this deamination is in marked contrast to the behavior of 3-methylcyclobutylamine,

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[1] Supported by the National Science Foundation and the Petroleum Research Fund of the American Chemical Society. Grateful acknowledgment is made to the Donors of the said Fund.

[2] National Science Foundation Predoctoral Fellow, 1958–1960.

[3] M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

[4] S. Winstein and R. Adams, *ibid.*, **70**, 838 (1948).

[5] W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956); see, J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1961, Chap. VII.

[6] S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959).

[7] (a) E. Goldish, K. Hedberg and V. Schomaker, *ibid.*, **78**, 2714 (1956); (b) W. Shand, Jr., V. Schomaker and J. R. Fischer, *ibid.*, **66**, 636 (1944); (c) V. Schomaker and J. P. McHugh, unpublished results.

[8] R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959), and references cited therein.

[9] S. L. Manatt, Ph.D. Thesis, California Institute of Technology, 1959.

[10] J. D. Roberts and C. M. Sharts in A. C. Cope, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. XII.

[11] Private communication from Dr. W. H. Sharkey and unpublished research in these laboratories.

[12] D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).

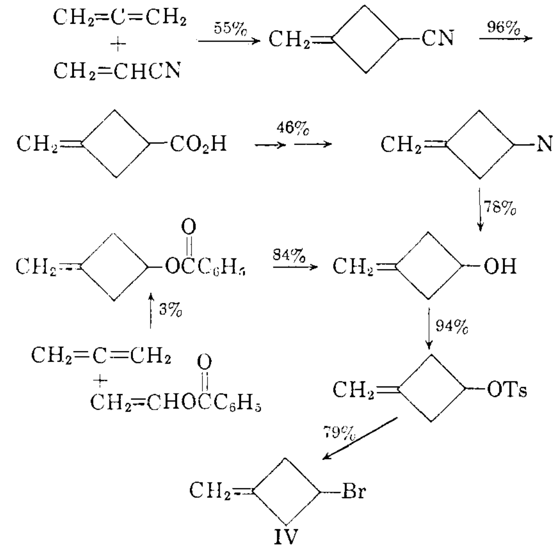


Fig. 1.

which gives principally a mixture of cyclopropylmethylcarbinol and allylmethylcarbinol.[13]

3-Methylenecyclobutylamine was prepared by Curtius degradation of 3-methylenecyclobutanecarboxylic acid as described previously.[12,14] Synthesis of 1-methylcyclobut-2-enyl bromide (V) was achieved in 66% over-all yield by dehydrobromination of IV with sodium methoxide in diethylene glycol, followed by addition of one mole of hydrogen bromide to the resulting methylenecyclobutene. The structures of IV and V were assigned on the bases of n.m.r. and infrared spectra, elemental analysis, equivalent weight as determined by solvolysis titer, chemical tests and hydrolysis and hydrogenation to a mixture of 1- and 3-methylcyclobutanols.

Attempts to convert 3-methylenecyclobutanol to 3-methylcyclobutenol by direct isomerization with acid or base, and by addition of hydrogen halide to the double bond and subsequent dehydrohalogenation, were unsuccessful. In all cases, the only new compounds detected were β-methylcrotonaldehyde and its condensation products. β-Methylcrotonaldehyde was also obtained, along with a mixture of methylcyclobutenols, from the hydrolysis of V; and it is probably formed as shown in Fig. 2.

It seems noteworthy that apparently the sole product of addition of hydrogen bromide to methylenecyclobutene is 1-methylcyclobut-2-enyl bromide (V) even though four allylic and two non-allylic bromides are possible by simple addition. Bromide V was not converted to a mixture of allylic isomers even upon treatment with anhydrous zinc bromide at 100°. Since these conditions seem drastic enough to cause allylic isomerization,[12] it appears that the equilibrium must heavily favor the tertiary isomer V over the secondary isomer, 3-methylcyclobut-2-enyl bromide; this situation is the reverse of that normally observed for allylic halides.[15]

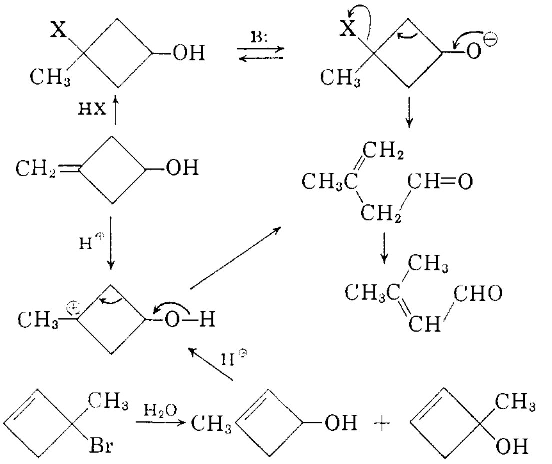
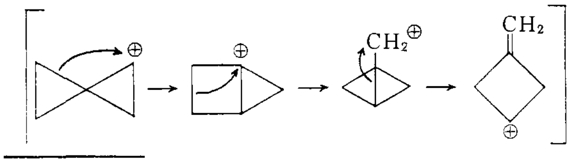


Fig. 2.

Kinetic data for the solvolyses of IV and V, together with data for some related bromides, are summarized in Tables I and II. All of the compounds studied gave good first-order rate constants except IV, which contained a small amount of a more reactive impurity so that a 35% decrease in k_1 was observed during the first 10–12% of solvolysis. Since the over-all first-order rate constant was of primary interest in this work, no effort was made to determine the nature of the impurity.

As indicated in Table I, compound IV solvolyzes more slowly than its aliphatic homoallylic analog, allylmethylcarbinyl bromide, by a factor of 160 at 99.0°. Even after corrections for ring strain and conformational effects have been made, it seems unlikely that the 3-methylenecyclobutyl carbonium ion (II) is significantly stabilized by 1,3-(homoallylic)-interactions. It is, of course, possible that a rate acceleration resulting from cross-ring interaction could be obscured by much larger rate decelerations due to inductive and hyperconjugative effects, or by incursion of a high degree of bimolecular displacement by solvent for the aliphatic model. The available data, however, do not permit an accurate evaluation of these possibilities; in any case, there is no reason to suspect that they are of considerable importance. A somewhat different conclusion has been reached by Applequist and Fanta[16] as the result of formulating the spiropentyl cation to rearrange to II by way of the 2-methylenecyclobutyl cation, which would of course mean that II is even more stable than an allylic cation. We regard this path for the rearrangement as not necessarily more likely than the following route (shown as formally involving classical cations), which avoids the necessity of ascribing greater stability to II than an allylic cation.



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[13] M. S. Silver, M. C. Caserio and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961).

[14] F. F. Caserio, Jr., S. H. Parker, R. Piccolini and J. D. Roberts, *ibid.*, **80**, 5507 (1958); F. F. Caserio, Jr., and J. D. Roberts, *ibid.*, **80**, 5837 (1958).

[15] R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

[16] D. E. Applequist and G. F. Fanta, *J. Am. Chem. Soc.*, **82**, 6393 (1960).

Each step and intermediate in this sequence of rearrangements is of a type that can be envisioned along lines analogous to those discussed previously.[8,13]

The lack of considerable reactivity of IV provides further confirmation for the notion that effective 1,3-interaction arises from arrangements of orbitals that will have σ- rather than π-overlap.[3,8,12,14]

TABLE I

SOLVOLYSIS RATES OF HOMOALLYLIC BROMIDES IN 50% AQUEOUS ETHANOL

Compound, bromide	C_0, mole/l.	Temp., °C.	$10^5 k$, sec.$^{-1}$	E^0, kcal./mole	Rel. rate at 99°
3-Methylene cyclobutyl (IV)	0.02710	86.0	0.042	27.6	
	.02562	99.0	0.16		1.0
Allylmethyl carbinyl	.01763	78.0	4.0	23.2	
	.01672	86.0	8.0		
	.02218	86.0	7.9		
	.01680	99.0	24.5		160

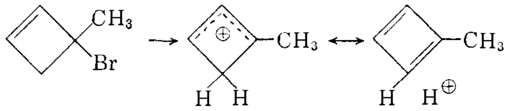
TABLE II

SOLVOLYSIS RATES OF ALLYLIC BROMIDES IN 80% ETHANOL

Compound, bromide	C_0, mole/l.	Temp., °C.	$10^5 k$, sec.$^{-1}$	E^0, kcal./mole	Rel. rate at 0°
1-Methylcyclobut-2-enyl (V)	0.00402	− 5.3 ± 0.2	0.71	21.1	1.0
	.00724	9.9 ± .2	5.65		
	.00745	10.1 ± .2	6.08		
	.00703	16.1 ± .2	14.2		
Cyclohex-2-enyl	.00555	− 0.2 ± .2	3.92	22.0	2.7
	.00645	− 0.2 ± .3	3.90		
	.00801	10.0 ± .2	17.2		
	.01094	15.0 ± .2	33.3		
α,γ-Dimethylallyl	.00709	− 9.1 ± .2	6.43	21.3	15
	.01145	− 9.0 ± .2	6.53		
	.00806	0.1 ± .2	23.4		
2-Cyclopent-2-enyl	.01140	−46.2 ± .5	4.95	18.6	3,500
	.00635	−46.1 ± .5	4.89		
	.00778	−38.8 ± .5	18.9		
	.00559	−34.8 ± .4	33.5		
α,γ,γ-Trimethylallyl	.00449	−64 ± 1	1.9	16.8	17,000
	.00638	−64 ± 1	1.7		
	.00203	−50.5 ± 1	18.1		
	.00529	−46.2 ± 0.5	43		

Of the allylic bromides studied, V has the lowest solvolytic rate constant (*cf.* Table II). Any decision regarding rate enhancement due to cross-ring electron delocalization in the resulting carbonium ion as depicted in III has to depend on the choice of suitable reference compounds. Direct comparisons with aliphatic systems may be invalid since, with the aid of available data on bending force constants[17] and conformational effects,[17,18] compound V is predicted (in the absence of cross-ring delocalization) to solvolyze more slowly than a comparable aliphatic model by a factor of 10^3 to 10^5 in 80% ethanol at 0°. Thus if proper account is taken of the net increase in strain in the formation of the carbonium ion from V, the reactivity of the compound may in fact be quite a bit larger than might be suspected otherwise.

Another complication in choosing a reference compound arises from the fact that solvolytic reactivities of allylic halides are strongly dependent on the total amount of alkyl substitution at both ends of the allylic system.[15] The allylic system of V has two alkyl substituents: the 1-methyl group and the ring methylene group, which here is counted but once because it is attached to both ends of the allylic system. If V is treated as a disubstituted allylic compound, then α,γ-dimethylallyl bromide, or perhaps α,α-dimethylallyl bromide, might be a satisfactory aliphatic allylic model. However, if some or all of the rate-enhancing ability of an alkyl group is taken to arise from hyperconjugation, then there is a possibility that hyperconjugation involving the ring methylene group will be less important than usual. The reason is that hyperconjugation would involve the resonance forms like VI, which would partake of the character of methylcyclobutadiene, and hence be unlikely to be favorable.



VI

Much has been written in recent years about the relative importance of inductive and hyperconjugative effects for alkyl groups,[19] but the division cannot be regarded as settled. For our purposes we shall make the conservative assumption that the 4-methylene group of V is two-thirds as effective as the γ-methyl group in α,γ-dimethylallyl bromide in stabilizing the carbonium ion, relative to hydrogen. This means that a proper (hypothetical) model for comparison with V would have log *k* for solvolysis two-thirds between the log *k* values for α,γ-dimethylallyl bromide and α-methylallyl bromide. The measured solvolysis rate of α,γ-dimethylallyl bromide (log k -2.7) and the rate calculated for α-methylallyl bromide[15] in 80% ethanol at 0° (log k -7.0) thus afford a calculated log *k* for the hypothetical model of -4.1; hence $k \sim 7 \times 10^{-5}$ sec.$^{-1}$. If this value is corrected for strain and conformational effects[17] the predicted solvolysis rate for V, in the absence of rate acceleration from 1,3-interaction, is thus somewhere in the range 7×10^{-8} to 7×10^{-10} sec.$^{-1}$ in 80% ethanol at 0°. Since the actual rate is 1.6×10^{-4} sec.$^{-1}$, it appears as though the solvolysis of V is accelerated by a factor of 10^3–10^5, which corresponds to a decrease in free energy of activation of 4.4 to 7.0 kcal./mole. If all of this additional stabilization of the solvolytic transition state (and carbonium ion)[20] is ascribed to 1,3-electron delocalization, it is interesting to note that it falls within 4.1–

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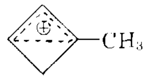
[17] *Cf.* E. F. Kiefer, Ph.D. Thesis, California Institute of Technology, 1961; the treatment, although not difficult, is rather lengthy and seems best omitted from this essentially qualitative discussion. The general approach was along the lines described by F. H. Westheimer in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956. An unpublished review kindly supplied by Professor H. J. Dauben was also used.

[18] W. G. Dauben and K. S. Pitzer, *ibid.*, p. 1; K. S. Pitzer, *Disc. Faraday Soc.*, **10**, 66 (1951); K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **75**, 2219 (1953).

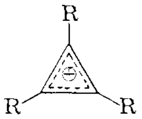
[19] For recent reviews, see E. S. Lewis, *Tetrahedron*, **5**, 143 (1958), and V. J. Shiner, *ibid.*, **5**, 243 (1958).

[20] The free energy of activation applies of course to the transition state, which, by the Hammond principle [G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 3348 (1955)], may be assumed to resemble closely the reactive carbonium ion intermediate. In any case, the stabilization energy available to the solvolysis transition state represents the minimum extra stabilization of the cationic intermediate.

10.9 kcal./mole predicted by the molecular-orbital treatment. If this argument is accepted, it seems reasonable to consider carbonium ion VII a "homocyclopropenyl" cation[12] and place it in the series of cyclopropenyl[21] (VIII), bis-homocyclopropenyl[5] (IX) and tris-homocyclopropenyl[22] (X) cations that have been formulated previously. That 1,3-π-type electronic interaction is apparently more important with VII than with II is in accord with theoretical predictions[9] and stems from the fact that the resonance energy of a triangular three-center two-electron system is greater than that of the corresponding linear system.



VII



VIII


X

Experimental

All melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin–Elmer model 21 or a Beckman model IR-7 spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were recorded with a Varian Associates high resolution n.m.r. spectrometer equipped with a Super Stabilizer. Vapor phase chromatography (v.p.c.) analyses were obtained with a Perkin–Elmer vapor fractometer, model 154-C. Elemental analyses were by Dr. Adalbert Elek, Los Angeles, Calif.

3-Methylenecyclobutyl Benzoate.—The reaction of vinyl benzoate[23] and allene was carried out several times on a preparative scale; the yields of adduct never exceeded 3%. In a typical run a 500-ml. stainless-steel Parr bomb was cooled to −40° and charged with 78 g. (0.527 mole) of vinyl benzoate, 12.6 g. (0.315 mole) of allene, 100 ml. of benzene and 0.5 g. of phenothiazine as a polymerization inhibitor. The bomb was rocked, heated to 240–260° for 4 hr. and then cooled slowly to −40°. Higher reaction temperatures caused extensive polymerization of the vinyl benzoate. Distillation of the reaction mixture through a short Vigreux column yielded allene (6 g., 48% recovery), vinyl benzoate (70 g., 90% recovery) and 3 g. of a fraction, b.p. 70–95° (1 mm.), consisting of about 75% 3-methylenecyclobutyl benzoate mixed with vinyl benzoate, benzoic acid and allene polymers. Further purification was accomplished by chromatography on alumina using pentane and 9:1 pentane–ether as eluents. All attempts to crystallize the ester failed. The structure was established by n.m.r. and infrared spectra and by reduction to 3-methylenecyclobutanol and benzyl alcohol.

3-Methylenecyclobutanol. A. From 3-Methylenecyclobutylamine.—A solution of 47 g. (0.57 mole) of 3-methylenecyclobutylamine[12,14] and 120 g. of 60% perchloric acid in 800 ml. of water was cooled in ice and stirred magnetically as 90 g. (1.2 moles) of sodium nitrite in 300 ml. of water was added dropwise over 1.5 hr. The cooling bath was then removed, and stirring was continued for 4 hr. The cloudy, brown solution was then saturated with sodium chloride and extracted continuously with ether overnight. The ether extract was flash-distilled under reduced pressure and the distillate dried and redistilled through a short column packed with glass helices. The yield of 3-methylenecyclobutanol, b.p. 57–58° (20 mm.), was 37.5 g. (78%). The structure was established by n.m.r. and infrared spectra and by comparison with a sample prepared by reduction of the benzoate (see below). The n.m.r. spectrum of the product checked closely with that reported by Applequist and Fanta.[16]

Anal. Calcd. for C_5H_8O: C, 71.39; H, 9.58. Found: C, 71.26; H, 9.52.

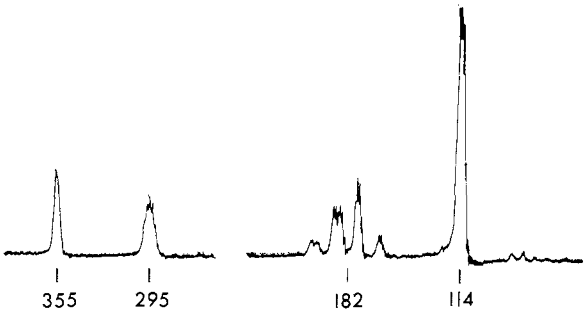


Fig. 3.—Nuclear magnetic resonance spectrum of 1-methylcyclobut-2-enyl bromide at 60 Mc. with line positions in c.p.s. taken with the zero of reference as tetramethylsilane (internal standard); increasing magnetic field from left to right. The coupling constant for the spin-spin interaction of the non-equivalent hydrogens at the 4-position is about 10 c.p.s. Small long-range couplings exist between the methyl group and the ring hydrogens; *cf.* D. R. Davis, R. P. Lutz and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961).

B. From 3-Methylenecyclobutyl Benzoate.—Because 3-methylenecyclobutanol was unstable to both strong acid and base, simple hydrolysis was not possible, and the alcohol had to be liberated by lithium aluminum hydride reduction of the ester. From 4.50 g. (0.0238 mole) of the benzoate and 1.0 g. of lithium aluminum hydride in 50 ml. of ether was obtained, after careful distillation, 1.68 g. (84%) of 3-methylenecyclobutanol identical to an authentic sample prepared from the amine. The benzyl alcohol was also collected and identified.

3-Methylenecyclobutyl Bromide (IV).—The crude *p*-toluenesulfonate ester of 3-methylenecyclobutanol was prepared in 94% yield from 17.4 g. of the alcohol, 39.2 g. of *p*-toluenesulfonyl chloride and 52 g. of 2,4,6-collidine. The tosylate (46 g., purified only by pumping under reduced pressure at room temperature) was added directly to a solution of 73 g. (4.3-fold excess) of freshly fused lithium bromide in 450 ml. of anhydrous acetone and the resulting solution heated under reflux with magnetic stirring for 2 days. The amber-colored reaction mixture, containing a small amount of precipitated lithium tosylate, was then poured into 1500 ml. of water and extracted with three 100-ml. portions of pentane. The combined pentane extracts were dried and distilled. The yield of IV was 22.7 g. (79%), b.p. 58–60° (80 mm.), $n^{25}D$ 1.4843. Although the v.p.c. (Perkin-Elmer Column A) indicated the compound to be pure, the n.m.r. spectrum showed the presence of about 10% of an impurity, which could only be removed by preparative v.p.c. using the more polar Column K. The n.m.r. and infrared spectra of the pure material were completely consistent with the assigned structure.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80; Br, 54.35. Found: C, 40.77; H, 4.85; Br, 54.40.

Methylenecyclobutene.—In a 200-ml., three-necked, round-bottomed flask fitted with a dropping funnel, a magnetic stirrer and a short, upright condenser leading through a Dry Ice-cooled trap to a vacuum line were placed 100 ml. of diethylene glycol and 4.0 g. (0.074 mole) of sodium methoxide. The mixture was stirred and heated to 170° in a silicone-oil bath, and the pressure was reduced to about 300 mm. as 5.3 g. (0.036 mole) of 3-methylenecyclobutyl bromide (containing about 10% impurity) was added from the dropping funnel during 1.5 hr. Heating was continued for an additional 45 min. after all of the bromide had been added. The material in the Dry Ice trap was warmed to about 0° and washed twice with 10 ml. of ice-water. The crude diene was then transferred to a small pear-shaped flask and distilled into a Dry Ice-cooled receiver at 100 mm. pressure. The yield of pure methylenecyclobutene was 1.92 g. (81%). The infrared spectrum of this material was identical to that prepared in earlier work.[12]

1-Methylcyclobut-2-enyl Bromide (V).—Methylenecyclobutene (1.92 g., 0.0291 mole) and pentane (15 ml.) were cooled in Dry Ice in a tared flask, and anhydrous hydrogen bromide was passed in until 2.25 g. (0.0278 mole) had been

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[21] R. Breslow and C. Yuan, *J. Am. Chem. Soc.*, **80**, 5991 (1958), and subsequent papers.

[22] S. Winstein, J. Sonnenberg and L. DeVries, *ibid.*, **81**, 6523 (1959); S. Winstein, *ibid.*, **81**, 6524 (1959).

[23] R. L. Adelman, *J. Org. Chem.*, **14**, 1057 (1949).

absorbed. The flask was stoppered and allowed to warm slowly to 0°, and then the pentane and excess diene were distilled from an ice-bath at 100 mm. pressure. The pressure was reduced to 20 mm. and the colorless residue distilled rapidly through a short Vigreux column. The yield of V, b.p. 40° (20 mm.), was 3.31 g. (82%). The relatively high solvolytic reactivity and the presence of a methyl group and endocyclic double bond in the infrared spectrum, together with the subsequent conversion of the compound to a mixture of methylcyclobutanols, were sufficient to rule out all other structures except 3-methylcyclobut-2-enyl bromide. The latter structure was eliminated by the presence of two vinyl protons and two geminal ring protons in the n.m.r. spectrum (Fig. 3).

Hydrolysis of 1-Methylcyclobut-2-enyl Bromide.—One gram of the bromide V was hydrolyzed with 20 ml. of ice-water and the products extracted into ether and distilled rapidly below room temperature. The mixture of products (385 mg., 68% assuming C_5H_8O) consisted of 1- and 3-methylcyclobut-2-enol and β-methylcrotonaldehyde in a ratio of about 2:1:1, as determined by n.m.r. spectra. The crude mixture was hydrogenated in ether at room temperature and atmospheric pressure over 10% palladium-on-charcoal, yielding a mixture of 1-methylcyclobutanol, *cis*- and *trans*-3-methylcyclobutanol and isovaleraldehyde, all of which were identified by comparison with authentic samples.

Other Allylic Bromides.—The open-chain allylic bromides were prepared from the corresponding alcohols and phosphorus tribromide in ether. Allylmethylcarbinol was prepared from allylmagnesium bromide and acetaldehyde by the method of Whitmore.[24] 2-Penten-4-ol was prepared from methylmagnesium iodide and crotonaldehyde by the procedure of Coburn.[25] 2-Methyl-2-penten-4-ol was prepared by reduction of mesityl oxide with lithium aluminum hydride. Cyclopentenyl bromide was prepared by addition of hydrogen bromide to cyclopentadiene in pentane at −30°. Cyclohexenyl bromide was prepared by allylic bromination of cyclohexene as described by Ziegler, *et al.*[26]

Kinetic Measurements.—The solvolytic measurements for 3-methylenecyclobutyl bromide (IV) and allylmethylcarbinyl bromide in 50% (by volume) ethanol–water were carried out as described previously,[27] except that a mixed indicator was used consisting of 0.1% brom thymol blue and 0.1% brom cresol purple in 50% ethanol, which gave a sharp end-point at *p*H 7.0–7.2. The solvolysis rates of the faster allylic bromides were measured by dissolving approximately 100-mg. samples of the bromide in 100 ml. of 80% (by volume) ethanol–water that had previously been brought to temperature in a 500-ml., three-necked, round-bottomed flask fitted with a calibrated low temperature thermometer, a ball joint sealed stirrer, an Ascarite tube and a 10-ml. buret. Temperature control in the range −64 to −30° was maintained with a cooling bath of liquid nitrogen and methanol in a large Dewar flask. At higher temperatures, the coolant was an ice–salt slurry. The reaction was followed by intermittent titration with 0.1 *N* NaOH in 80% ethanol to the brom thymol blue end-point. This method gave good results for temperatures at which the half-lives were 5–60 min. With more reactive bromides, the precision of the time readings was less; with half-lives of more than one hour, maintenance of constant temperature became difficult.

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Neighboring Carbon and Hydrogen. XLVI.[1] Spiro-(4,5)-deca-1,4-diene-3-one from Ar$_1^{\ominus}$-5 Participation

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When the aryl group is *p*-hydroxyphenyl, Ar$_1$-5 participation in the phenoxide anion of 4-aryl-1-butyl arenesulfonates, designated by the symbol Ar$_1^{\ominus}$-5, should lead to the corresponding spiro-dienones. Kinetic investigation of the behavior of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate in basic solution shows that conditions are relatively unfavorable for Ar$_1^{\ominus}$-5 participation in methanol but are quite favorable in *t*-butyl alcohol as solvent. Correspondingly, spiro-(4,5)-deca-1,4-diene-3-one is isolated in low yield from reaction in methanol and in much better yield from *t*-butyl alcohol as a reaction medium. In the dienone–phenol rearrangement of the dienone to 5,6,7,8-tetrahydro-2-naphthol, the protonated dienone intermediate is analogous to the spiro-cationic intermediate in Ar$_1$-5-assisted solvolysis of 4-*p*-anisyl-1-butyl bromobenzenesulfonate. Therefore, the quantitative conversion of dienone to the tetrahydronaphthol in formic acid furnishes further insight into the behavior of spiro-cationic intermediates from Ar$_1$-5 participation.

With suitable 4-aryl-1-butyl arenesulfonates, Ar$_1$-5-assisted ionization[3] leads to spiro-cationic intermediates which give rise to tetralins as final products. When the aryl group is *p*-hydroxyphenyl, as in 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate (I-OBs), one can conceive of a process involving participation of the phenoxide ion group of the anion II-OBs. This would lead to the spiro-dienone III. Modifying the Ar$_1$-5 symbol[3] to indicate the anionic nature of the participating group,[4] such formation of dienone III from anion II-OBs can be designated Ar$_1^{\ominus}$-5. As indicated already in a preliminary Communication,[5] it is possible to find conditions which favor conversion of II-OBs to dienone III, and the results of this study of the formation and behavior of III are presented and discussed in the present manuscript.

Syntheses.—Most of the compounds in this study were prepared from 4-*p*-anisylbutanoic acid, which was obtained by the procedures of Fieser[6] and Martin.[7] Reduction of this acid with lithium

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