interaction of the sulfonio group with the benzene ring in the photo-excited state does not require a preferred steric or angular arrangement. The ultraviolet spectra of these sulfonio phenols when taken in neutral solution contain peaks corresponding to those found in alkaline solution. Since these phenols are comparatively strong acids, they evidently partially dissociate even in neutral solution.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, LOS ANGELES 24, CALIF.]

Neighboring Carbon and Hydrogen. XXXIX.[1] Complex Rearrangements of Bridged Ions. Rearrangement Leading to the Bird-cage Hydrocarbon[1]

BY LOUIS DE VRIES AND S. WINSTEIN

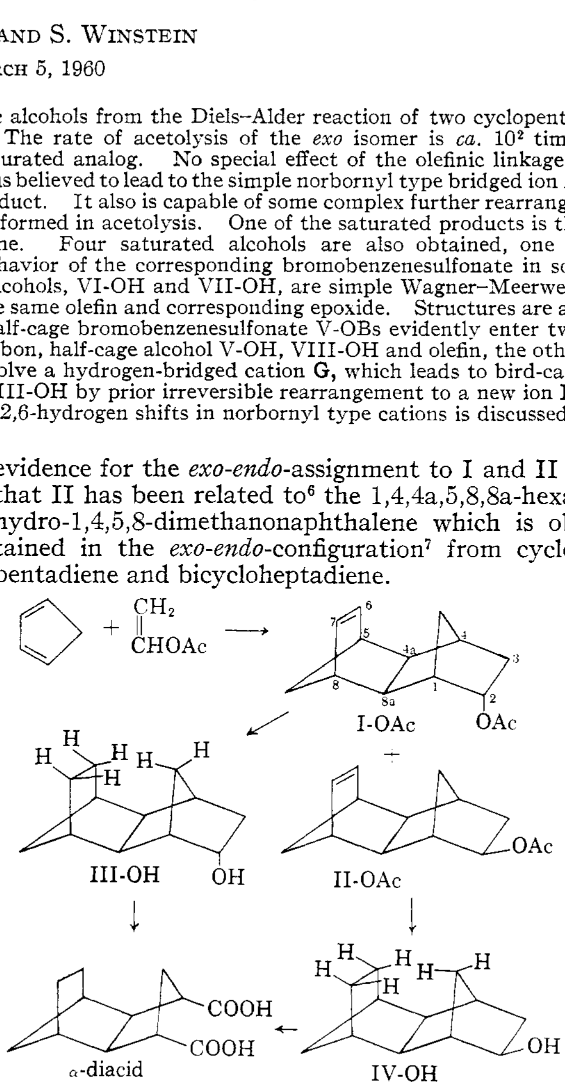
RECEIVED MARCH 5, 1960

The solvolysis of the bromobenzenesulfonates of the epimeric alcohols from the Diels–Alder reaction of two cyclopentadiene molecules with one of vinyl acetate has been studied. The rate of acetolysis of the *exo* isomer is *ca.* 10^2 times that of the *endo* and approximately the same as that of its saturated analog. No special effect of the olefinic linkage is evident in the rate-determining ionization step. Ionization is thus believed to lead to the simple norbornyl type bridged ion A. Ion A gives rise to some unrearranged unsaturated solvolysis product. It also is capable of some complex further rearrangements which lead to saturated products, *ca.* 70% of these being formed in acetolysis. One of the saturated products is the bird-cage hydrocarbon, hexacyclo$[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}]$dodecane. Four saturated alcohols are also obtained, one of them, V-OH, being unique as regards infrared spectrum and behavior of the corresponding bromobenzenesulfonate in solvolysis. This alcohol has a half-cage structure. Two of the alcohols, VI-OH and VII-OH, are simple Wagner–Meerwein isomers, and two of them, VI-OH and VIII-OH, are related to the same olefin and corresponding epoxide. Structures are assigned to alcohols VI-VIII-OH. The bridged ion **A** and the half-cage bromobenzenesulfonate V-OBs evidently enter two complex rearrangement paths, one leading to bird-cage hydrocarbon, half-cage alcohol V-OH, VIII-OH and olefin, the other leading to VI-OH, VII-OH and olefin. The first path may involve a hydrogen-bridged cation **G**, which leads to bird-cage hydrocarbon or half-cage alcohol by reaction with solvent, or VIII-OH by prior irreversible rearrangement to a new ion **H**. The analogy between the complex rearrangements of ion A and 2,6-hydrogen shifts in norbornyl type cations is discussed.

The solvolysis of the *endo* and *exo* pair of benzenesulfonates I-OBs and II-OBs was of some interest[2] because of the expected formation of a bridged cationic intermediate **A** and the possibility that it would undergo further more complex rearrangements. Therefore, solvolysis of these two materials and the corresponding saturated analogs III-OBs and IV-OBs has been examined, and some of the results of this study are presented and discussed in the present manuscript.

Results

Materials.—The mixture of *endo-* and *exo*-acetates I-OAc and II-OAc is readily available from the Diels–Alder reaction between cyclopentadiene and vinyl acetate.[3] The *exo-endo*-4a,8a-fusion of the two bicycloheptane nuclei was deduced by Soloway[4] in an excellent analysis of the stereochemistry of fused norcamphane systems. The necessary plausible assumption that the configuration of the carbon skeleton of I and II is identical with that in the bis-adduct of cyclopentadiene to ethylene has since been verified by actual conversion[5] of the vinyl acetate adduct to the ethylene analog. Other evidence for the *exo-endo*-assignment to I and II is that II has been related to[6] the 1,4,4a,5,8,8a-hexahydro-1,4,5,8-dimethanonaphthalene which is obtained in the *exo-endo*-configuration[7] from cyclopentadiene and bicycloheptadiene.



I-OAc

III-OH

II-OAc

α-diacid

IV-OH

Saponification of the bis-adduct of cyclopentadiene to vinyl acetate led to a mixture of the *endo*- and *exo*-alcohols I-OH and II-OH. These alcohols were separated by fractional crystallization of the sodium salt of the mixture of corresponding acid phthalates. Saponification of the pure acid phthalates gave rise to the pure alcohols. From these materials, the corresponding alcohols III-OH and IV-OH were obtained in nearly quantitative yield by hydrogenation.

That III-OH and IV-OH, as well as I-OH and II-OH, represent epimeric pairs of alcohols was con-

---

(1) (a) Research sponsored by the Office of Ordnance Research, U. S. Army. (b) Abstracted from Ph.D. Thesis of Louis de Vries, U.C.L.A., Jan., 1956. (c) Paper XXXIV: C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, THIS JOURNAL, **82**, 5450 (1960); paper XXXV: S. Winstein, J. Sonnenberg and L. de Vries, *ibid.*, **81**, 6523 (1959); paper XXXVI: S. Winstein, *ibid.*, **81**, 6524 (1959); paper XXXVII: P. Bruck, D. Thompson and S. Winstein, *Chemistry & Industry*, 590 (1960); paper XXXVIII: S. Winstein and C. Ordronneau, THIS JOURNAL, **82**, 2084 (1960).

(2) Much of the material reported in this manuscript was reported in outline at: (a) Symposium on "Dynamic Stereochemistry," Manchester, England, March 31, 1954; see *Chemistry & Industry*, 562 (1954); (b) XIVth International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July 21-27, 1955; S. Winstein, *Experientia Suppl. II*, 137 (1955).

(3) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

(4) S. B. Soloway, THIS JOURNAL, **74**, 1027 (1952).

(5) S. B. Soloway, Thesis, Univ. of Colorado, 1955.

(6) D. Thompson and P. Bruck, unpublished work in these laboratories.

(7) See J. K. Stille and D. A. Frey, THIS JOURNAL, **81**, 4273 (1959).

TABLE I

SUMMARY OF ACETOLYSIS RATES

ROBs[a]	Other solute	10^2 M	Temp., °C.	k, sec.$^{-}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.
I-OBs	....	..	25.00[b]	1.26×10^{-8}		
	NaOAc	3.90	25.00[b]	2.96×10^{-8}		
	....	..	50.00[b]	5.52×10^{-7}	28.3	+0.2
	NaOAc	3.90	50.00[b]	1.10×10^{-6}	27.4	−1.1
	....	..	75.00	$(1.40 \pm 0.04) \times 10^{-5}$		
	NaOAc	3.90	75.00	$(2.53 \pm .02) \times 10^{-5}$		
	....	..	100.1	$(2.33 \pm .07) \times 10^{-4}$		
	NaOAc	3.91	100.1	$(3.86 \pm .12) \times 10^{-4}$		
II-OBs	NaOAc	3.91	25.00[b]	1.45×10^{-6}		
	NaOAc	3.91	50.00[b]	4.90×10^{-5}	26.3	+3.1
	....	..	50.52	$(5.12 - 2.27) \times 10^{-5}$		
	NaOAc	3.91	50.40	$(5.16 \pm 0.07) \times 10^{-5}$		
	LiOBs	3.00	50.30	$(5.45 - 2.44) \times 10^{-5}$		
	$LiClO_4$	3.00	50.30	$(7.88 - 3.16) \times 10^{-5}$[c]		
	NaOAc	3.91	75.00	$(1.00 \pm 0.02) \times 10^{-3}$		
III-OBs	....	..	25.00[b]	3.76×10^{-8}		
	....	..	50.00[b]	1.50×10^{-6}	27.6	+0.1
	..	..	75.00	$(3.54 \pm 0.05) \times 10^{-5}$		
	....	..	99.59	$(5.24 \pm .08) \times 10^{-4}$		
	NaOAc	3.90	100.0	$(5.48 \pm .10) \times 10^{-4}$		
IV-OBs	....	..	25.00[b]	8.36×10^{-7}		
	....	..	50.00[b]	2.77×10^{-5}	26.2	+1.4
	....	..	50.40	$(2.91 \pm 0.03) \times 10^{-5}$		
	....	..	75.00	$(5.53 \pm 0.08) \times 10^{-4}$		
V-OBs	....	..	25.00	$(2.28 - 1.48) \times 10^{-4}$[d]	21.8	−0.3
	....	..	25.30	$(2.14 - 0.64) \times 10^{-4}$		
	NaOAc	3.91	25.00	$(2.27 - 0.70) \times 10^{-4}$		
	LiOBs	3.00	25.00	$(2.94 - 0.93) \times 10^{-4}$		
	$LiClO_4$	3.00	25.00	$(4.32 - 1.32) \times 10^{-4}$		
	$LiClO_4$	6.00	25.00	$(6.18 - 1.12) \times 10^{-4}$		
	....	..	35.00	$(7.25 - 3.57) \times 10^{-4}$		
VI-OBs	....	..	25.00	$(3.91 \pm 0.03) \times 10^{-5}$		
	....	..	49.92	$(8.84 \pm 0.16) \times 10^{-4}$		
	....	..	50.00[b]	8.91×10^{-4}	23.3	−0.5
VII-OBs	....	..	25.00[b]	5.70×10^{-5}	22.1	−4.0
	....	..	25.10	$(5.79 \pm 0.09) \times 10^{-5}$		
	....	..	35.02	$(1.99 \pm 0.04) \times 10^{-4}$		
VIII-OBs	....	..	25.00[b]	8.54×10^{-6}	25.8	+4.8
	....	..	25.15	$(8.70 \pm 0.08) \times 10^{-6}$		
	....	..	49.97	$(2.66 \pm 0.03) \times 10^{-4}$		

[a] *Ca.* 0.025 M. [b] Extrapolated or interpolated from the data at the other temperatures. [c] Rate constants calculated from the last three intervals: 2.40, 2.21, 2.45 × 10^{-5} sec.$^{-1}$. [d] After 10 hours at 25.10° in a similar run, k = 8.4 × 10^{-6} sec.$^{-1}$ for several reaction intervals.

firmed by oxidation of alcohols III-OH and IV-OH with potassium permanganate in pyridine to the dicarboxylic acid designated the α-diacid by Soloway.[4] That I-OH and III-OH are *endo*-alcohols, while II-OH and IV-OH are the *exo* analogs, was indicated by the much greater proportion of I-OAc over II-OAc in the 2:1 Diels–Alder adduct from cyclopentadiene and vinyl acetate. This assignment is further borne out by the relative reactivities in solvolysis of III-OBs *vs.* IV-OBs and I-OBs *vs.* II-OBs, the *exo* isomers being more reactive[8] than the *endo* by a substantial factor in both cases.

Solvolysis Rates.—The saturated bromobenzenesulfonates III-OBs and IV-OBs displayed good first-order behavior in acetolysis, the first-order rate constants being summarized in Table I. The unsaturated *endo*-bromobenzenesulfonate I-OBs similarly displayed satisfactory first-order behavior in acetolysis. However, the inclusion of 0.04 M sodium acetate gave rise to an abnormally large salt effect,[8,9] rate being approximately doubled by this concentration of salt. It seems likely that in the absence of sodium acetate to neutralize generated bromobenzenesulfonic acid, addition of acetic acid to the double bond of the unsaturated bromobenzenesulfonate I-OBs takes place sufficiently rapidly that the observed rate constant is

---

(8) (a) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); (b) S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952); (c) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1147, 1154 (1952); (d) S. Winstein, p. 29 of Abstracts 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, N. Y., June 17–20, 1957.

(9) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2763(1956).

TABLE II

PERCENTAGE OF UNSATURATED ACETATE II-OAc RECOVERED FROM SOLVOLYSIS OF UNSATURATED BROMOBENZENESULFONATES I-OBs AND II-OBs

ROBs	Wt., g.	Solvent	Added base	Temp., °C.	Unsatd. product, II-OAc Wt., g.	Unsatd. product, II-OAc % of total recov.
endo, I-OBs	332.7 (0.1 *M*)	AcOH	0.12 *M* NaOAc	*ca.* 120	59.3	45.7
endo, I-OBs	235.7	60% Me_2CO	$CaCO_3$	65	88.4	85.2[a]
exo, II-OBs	12.8 (0.1 *M*)	AcOH	0.12 *M* NaOAc	50	1.68	30.5
exo, II-OBs	49.4	60% Me_2CO	$CaCO_3$	65	11.26	53.4[b]

[a] Solvolysis products from 60% acetone were acetylated prior to treatment with silver nitrate. [b] Alcohol II-OH obtained directly by silver nitrate treatment.

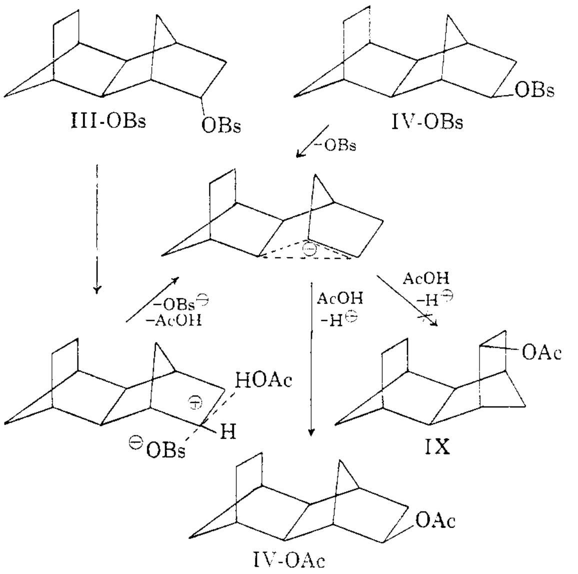
that of an acetoxy-bromobenzenesulfonate rather than of I-OBs itself. In the case of the more reactive unsaturated *exo*-bromobenzenesulfonate II-OBs, a first-order acetolysis rate constant drifts down in the absence of sodium acetate but is nicely constant in the presence of added sodium acetate. The most likely reason for the downward drift in rate constant in the absence of sodium acetate is addition of acetic acid to the double bond of the unsaturated bromobenzenesulfonate II-OBs concurrent with solvolysis, thus converting II-OBs to a less reactive acetoxy-bromobenzenesulfonate. Lithium bromobenzenesulfonate and lithium perchlorate at a concentration of 0.03 *M* gave rise to normal salt effects,[9] initial rate constants being somewhat accelerated.

Solvolysis Products.—Acetolysis of the saturated *endo*- and *exo*-bromobenzenesulfonates III-OBs and IV-OBs and subsequent saponification led to high yields of pure *exo*-alcohol IV-OH. The infrared spectrum of the distilled acetolysis product from IV-OBs before saponification matched nearly perfectly the spectrum of authentic *exo*-acetate IV-OAc.

The products from solvolysis of the unsaturated bromobenzenesulfonates I-OBs and II-OBs contained saturated as well as unsaturated materials. In the case of the product from acetolysis of 0.1 *M* *endo*-bromobenzenesulfonate in acetic acid, 0.12 *M* in sodium acetate, destruction of the unsaturated material by ozonization left a 45% yield of a saturated fraction. Saponification of this fraction led to a complex mixture composed mainly of alcohols. The unsaturated component of the acetolysis product could be isolated as a silver nitrate complex[10] by treatment of the whole solvolysis product with a large excess of saturated aqueous silver nitrate solution. This precipitated a solid complex, from which pure *exo*-acetate II-OAc was obtained in an amount corresponding to 45.7 mole per cent. of the total recovery. There were no indications of appreciable amounts of other unsaturated components which were also precipitated by the silver nitrate. Neither were there indications of appreciable quantities of unsaturated products which remained in the aqueous silver nitrate phase or the organic phase.

Solvolysis of *endo*-bromobenzenesulfonate I in 60% aqueous acetone and acetylation of the product led to a mixture from which the percentage recovery of unsaturated acetate II-OAc was now 85%, much larger than from acetolysis.

Solvolysis of the *exo*-bromobenzenesulfonate II-OBs gave rise to greater proportions of saturated products than in the case of the *endo*-analog I-OBs. From acetolysis, ozonization left a 64% yield of saturated product, while silver nitrate treatment led to a figure of 30.5 mole per cent. of total recovery for the unsaturated acetate II-OAc. From solvolysis in 60% acetone and silver nitrate treatment of the product without prior acetylation, the corresponding figure for unsaturated alcohol II-OH was 53.4%. The various percentages of unsaturated acetate or alcohol II-OAc or II-OH observed in the different solvolyses are summarized in Table II.



Separation of Saturated Products.—The products of acetolysis of the *exo*-bromobenzenesulfonate II-OBs which had been treated with silver nitrate and then permanganate to destroy residual traces of unsaturated material were reduced with lithium aluminum hydride and chromatographed over activated alumina. This gave rise to three crystalline materials and a sirup.

The first crystalline material, eluted with pentane, was a saturated hydrocarbon, $C_{12}H_{14}$, m.p. 165–167°, whose infrared spectrum is summarized in Table III. This hydrocarbon was unreactive toward bromine, potassium permanganate and ozone. In connection with an examination of its X-ray diffraction pattern, Professor J. D. McCullough[11] obtained a molecular weight of 150 ± 10 in a rough determination of its vapor density and a value of 158 ± 1 from the crystal density and the dimensions of the unit cell. Since theory for $C_{12}H_{14}$

(10) S. Winstein and H. J. Lucas, THIS JOURNAL, 60, 836 (1938).

(11) J. D. McCullough, private communication.

TABLE III

INFRARED ABSORPTION MAXIMA OF BIRD-CAGE HYDROCARBON[a,b,c] XI

μ	ν, cm.$^{-1}$	% absorb.	μ	ν, cm.$^{-1}$	% absorb.
3.42	2923	98	9.50	1052	30
3.52	2840	89	9.70	1030	22
7.67	1303	89	10.15	985	42
7.74	1291	96	10.26	975	38.5
7.83	1277	93.5	10.55	948	43.7
8.00	1250	60	10.62	942	50
8.07	1239	81	10.83	923	73
8.14	1228	72	11.20	893	31.5
8.22	1216	54	11.64	859	20
8.43	1186	64	11.92	839	37
8.94	1118	57	12.16	822	65
9.12	1096	47	12.74	785	34
			12.90	775	52

[a] Perkin-Elmer infrared spectrophotometer model 21. [b] 0.1-mm. cell; sodium chloride optics. [c] 10% solution in carbon disulfide.

is 158.3, the hydrocarbon is a simple saturated monomeric dehydration product of alcohols I-OH or II-OH.

The second crystalline material was an alcohol (V-OH), $C_{12}H_{16}O$, m.p. 130–131°, eluted with pentane–10% ether. Continuing elution gave sirupy materials, but later elution fractions contained a third crystalline material, m.p. 64–70°. Purification through the acid phthalate gave rise to another pure alcohol (VI-OH), $C_{12}H_{16}O$, m.p. 76.2–77.6°. The sirups and mother liquors yielded small amounts of alcohols V-OH and VI-OH on further chromatography, but the major portion remained uncrystallizable. Fractional crystallization of the acid phthalates obtained from the sirup did not lead to successful separation.

The same three crystalline materials mentioned above, accompanied by a sirupy fraction, were obtained from solvolysis of the *exo*-bromobenzenesulfonate II-OBs in 60% acetone and from solvolysis of the *endo*-bromobenzenesulfonate I-OBs in acetic acid and also 60% acetone. The mole percentages of materials isolated from the saturated portion of the solvolysis products are summarized in Table IV.

TABLE IV

MOLE PERCENTAGES OF COMPONENTS ISOLATED FROM SATURATED PRODUCTS OF SOLVOLYSIS OF SEVERAL BROMOBENZENESULFONATES

			Mole % products				
ROBs	Solvent	Temp., °C.	Satd. H'c. $C_{12}H_{14}$	V-OH	VI-OH	VII-OH	Syrup
II-OBs[a]	AcOH[b]	50	15	19	43		23
II-OBs[a]	60% Me_2CO[c]	65	26	27	39		8
V-OBs	AcOH[b]	50	35	29	22		14
V-OBs	60% Me_2CO[c]	65	38	41	10		11
VI-OBs	AcOH[b]	50	0[d]	0	65	22	13

[a] Based on total saturated products only. [b] 0.12 *M* sodium acetate. [c] $CaCO_3$ added. [d] No saturated hydrocarbon observed; 5% unsaturated hydrocarbon isolated.

Solvolysis of V-OBs and VI-OBs.—As summarized in Table I, the bromobenzenesulfonate of alcohol VI-OH displayed good first-order behavior in acetolysis. While the bromobenzenesulfonate of alcohol V-OH was more reactive in acetolysis, the first-order acetolysis rate constant drifted down during a run (Table I). The acetolysis rate constant at 25° was of the order of 2×10^{-4} sec.$^{-1}$ initially, but it leveled off near the end of the reaction at *ca.* 8.4×10^{-6} sec.$^{-1}$. Evidently, internal return[8,12] accompanies acetolysis of V-OBs, producing a much less reactive bromobenzenesulfonate, Z-OBs, with a rate constant of *ca.* 8.4×10^{-6} sec.$^{-1}$. The downward drift in first-order titrimetric rate constant was comparable in the presence of added sodium acetate, lithium bromobenzenesulfonate or lithium perchlorate, these salts giving rise to normal salt effects.[9,12]

Acetolysis of 0.1 *M* V-OBs in acetic acid containing 0.12 *M* sodium acetate gave only saturated products which were stable to potassium permanganate. Saponification and chromatography as in the case of the saturated products from II-OBs gave rise to the same three crystalline products, the saturated hydrocarbon, V-OH and VI-OH, as well as an accompanying sirup. As summarized in Table IV, the relative amounts of hydrocarbon and V-OH were larger and the amount of VI-OH was smaller than from II-OBs. Comparable results were obtained from solvolysis of V-OBs in 60% acetone (Table IV).

When the products of acetolysis of VI-OBs were saponified and chromatographed, no trace of the saturated hydrocarbon was obtained. Instead, a small amount of an unsaturated hydrocarbon was eluted with pentane. This material decolorized an acetone solution of potassium permanganate immediately. Elution with pentane–10% ether gave rise to a small amount of a new alcohol (VII-OH), $C_{12}H_{16}O$, m.p. 71.8–72.2° after further purification. This material was stable to permanganate. Further elution gave rise to lower melting materials of large melting range, and finally there was obtained a large amount of the original alcohol VI-OH which could be purified through the acid phthalate. There was no trace of alcohol V-OH, which is relatively easily separated from mixtures containing it.

Purification of the unsaturated hydrocarbon through the silver nitrate complex[11] and distillation gave rise to a material, $C_{12}H_{14}$, $n^{25}D$ 1.5372, whose infrared spectrum is summarized in Table V.

The bromobenzenesulfonate of alcohol VII-OH displayed good first-order behavior in acetolysis (Table I).

Relation of Unsaturated Hydrocarbon to VI-OH.—On the basis of mechanistic considerations introduced later in this paper, it seemed probable that the unsaturated hydrocarbon could be related to one or two of the saturated alcohols by way of a simple 1,2-elimination of water. In actual fact, Chugaev elimination of water from VI-OH did lead to the unsaturated hydrocarbon. A crystalline methyl xanthate was obtained from VI-OH, whose pyrolysis led to a good yield of an unsaturated hydrocarbon. After purification through the

---

(12) (a) W. G. Young, S. Winstein and H. L. Goering, THIS JOURNAL, **73**, 1958 (1951); (b) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165, 2171 (1952); (c) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956); (d) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2767 (1956); (e) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

silver nitrate complex, this material was identical in analysis, refractive index and infrared spectrum with the olefin from solvolysis of VI-OBs.

Alcohol VIII-OH.—While three saturated alcohols, V-OH, VI-OH and VII-OH, had been isolated from the various solvolyses, four such alcohols could be anticipated on mechanistic grounds. The fourth alcohol presumably corresponded to the Z-OBs recognized as a rearrangement product in the solvolysis of V-OBs, since the rate constant of this less reactive product of internal return did not correspond to V-OBs, VI-OBs or VII-OBs.

On the supposition that the fourth saturated alcohol, VIII-OH, was the second alcohol related to the unsaturated hydrocarbon along with VI-OH, an attempt was made to synthesize the new alcohol from the olefin. The latter was epoxidized with perbenzoic acid, and the epoxide was directly reduced with lithium aluminum hydride. From fractional crystallization of the acid phthalate of the alcohol mixture, there was isolated in good yield the acid phthalate of the new alcohol, $C_{12}H_{16}O$, VIII-OH, m.p. 49.5–50.5°.

TABLE V

INFRARED ABSORPTION MAXIMA OF OLEFIN[a,b,c] XII

ν, cm.$^{-1}$	Transmission, %	ν, cm.$^{-1}$	Transmission, %	ν, cm.$^{-1}$	Transmission, %	ν, cm.$^{-1}$	Transmission, %
3140	90	1152	79	1400	93	910	61
3050	30	1140	72	1332	18	895	74
2920	2	1105	60	1308	33	873	85
2860	13	1090	79	1295	23	855	79
1808	95	1052	72	1273	20	832	75
1625	85	1035	76	1258	40	798	34
1603	73	997	74	1248	51	768	51
1583	40	987	73	1235	52	730	72
1480	42	965	70	1209	55	694	6
1455	48	935	53	1172	77	680 infl.	51

[a] Perkin–Elmer infrared spectrophotometer model 21. [b] 0.03-mm. cell; sodium chloride optics. [c] Pure liquid.

In acetolysis, good first-order behavior was displayed by VIII-OBs, as summarized in Table I. The observed rate of acetolysis confirmed the supposition that the slower isomer from internal return accompanying acetolysis of V-OBs was VIII-OBs, since the first-order rate constant was equal within experimental error to the value observed in the later stages of acetolysis of V-OBs.

Solvolysis and Infrared Examination of Products.—With all four saturated alcohols available, it was possible to use infrared spectroscopy to learn more about the products of acetolysis, even in the cases where insufficient quantities of pure alcohols were available for separation and isolation of the individual alcohol products. Also, even in the other cases, more information was available from examination of the infrared spectrum of the products than from isolation, since sirupy, inseparable mixtures of alcohols constituted an appreciable fraction of the isolated product. The unsaturated *exo*-II-OBs and the saturated V-OBs, VI-OBs, VII-OBs and VIII-OBs were acetolyzed in the usual way. The product from II-OBs was freed of unsaturated materials by treatments with silver nitrate and permanganate. The products from each bromobenzenesulfonate were saponified and the hydrocarbons were separated from the alcoholic products by chromatography over alumina. The mole percentages of hydrocarbon isolated are summarized in Table VI. The alcohol products from chromatography were reconverted to acetates, and these were purified by distillation at reduced pressure. Then they were subjected to infrared examination.

TABLE VI

PRODUCT COMPOSITION FROM ACETOLYSIS[a] OF 0.1 *M* BROMOBENZENESULFONATES AT 50°

	Compn. of satd. acetates, %				Over-all product compn., %					
					Hydrocarbon		Acetates			
ROBs	V	VI	VII	VIII	Bird cage	Olefin	V	VI	VII	VIII
II-OBs[b]	27	58	6	9	15	..	23	49	5	8
V-OBs	58	18	3	21	35	0[d]	37	12	2	14
VI-OBs	0	73	27	..	0	5	0	70	26	0
VII-OBs	0	95	5	..	0	0[d]	0	95	5	0
VIII-OBs[c]	0	0	0	100	0	6	0	0	0	94

[a] 0.12 *M* NaOAc. [b] Saturated product only. [c] Acetolysis at 75°. [d] <1%.

The acetate of alcohol V-OH distinguishes itself from the other three saturated acetates by large optical densities at 1510, 1467, 1392 and 887 cm.$^{-1}$, where the optical densities of the other three acetates are low and nearly identical. Therefore, V-OAc could be detected even in very small amounts, and it was immediately obvious that formation of V-OAc was negligible in acetolysis of VI-OBs, VII-OBs and VIII-OBs.

The acetate from VIII-OBs was essentially pure VIII-OAc, the two spectra being essentially identical.

The acetates from VI-OBs and VII-OBs corresponded to mixtures of VI-OAc and VII-OAc. Regarding these mixtures as two component ones, the optical densities at a number of wave lengths led to the average compositions summarized in Table VI, and actual synthetic mixtures of VI-OAc and VII-OAc of these compositions matched the infrared spectra of the acetolysis products very closely.

In the case of the acetate mixture from V-OBs, the percentage of V-OAc was determined with considerable accuracy by treating the acetolysis mixture as a two-component mixture of V-OAc and the other acetates for those frequencies where the optical density of V-OAc is large and the values for the other three acetates are low and nearly identical. Similarly, the percentage of VI-OAc could be determined from the optical density at 742 cm.$^{-1}$, where VI-OAc exhibits a medium optical density and the other three acetates exhibit low and nearly equal optical densities. The percentage of VII-OAc could be determined analogously using the 770 cm.$^{-1}$ band. The percentage of VIII-OAc was determined with the aid of a band at 790 cm.$^{-1}$. This procedure led to the composition summarized in Table VI, and a synthetic mixture of this composition matched the infrared spectrum of the acetolysis product from V-OBs excellently.

The same procedure described above was used in the case of the acetate from II-OBs, and again a synthetic mixture with the composition indicated in Table VI matched the infrared spectrum of the saturated acetate product from II-OBs very closely.

The infrared analyses showed that VII-OAc and VIII-OAc were formed in acetolysis of II-OBs and V-OBs, even though it had not been possible to isolate the corresponding alcohols in pure form from the chromatographic experiments. The fact that it was possible to duplicate the mixtures of saturated acetates from II-OBs and V-VIII-OBs with the four acetates, V-VIII-OAc, indicates that no other saturated acetates are formed in appreciable quantities.

By combining the yields of hydrocarbon isolated chromatographically with the compositions of the acetate mixtures determined from infrared spectra, it is possible to estimate the over-all product compositions from the various acetolyses, and these are summarized also in Table VI.

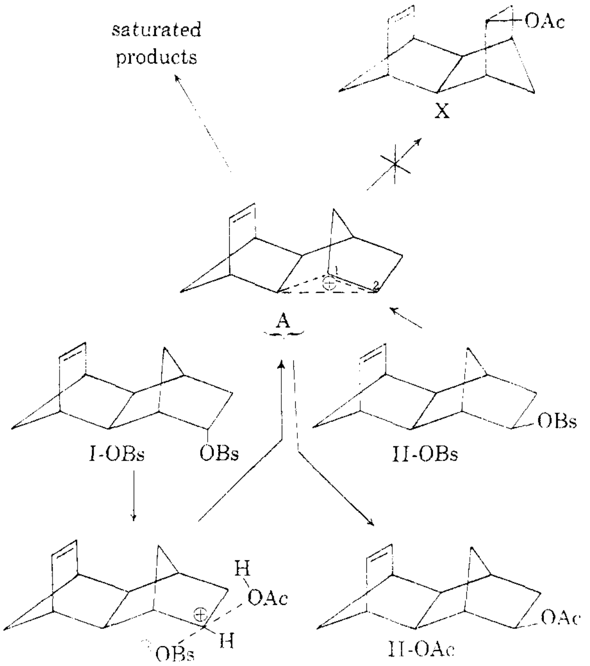
Discussion

Saturated Bromobenzenesulfonates.—The formation of saturated products during solvolysis of the unsaturated bromobenzenesulfonates, I-OBs and II-OBs, must be due to some complex rearrangements involving the olefinic linkage. However, before discussing the solvolysis of the unsaturated bromobenzenesulfonates, we should first consider the saturated analogs, III-OBs and IV-OBs, which were studied for comparison.

The behavior of the saturated bromobenzenesulfonates in acetolysis parallels to a considerable extent that of the *endo*- and *exo*-norbornyl bromobenzenesulfonates.[8] From both III-OBs and IV-OBs the product was cleanly the *exo*-IV-OAc. Also, the *exo*-bromobenzenesulfonate IV-OBs was considerably more reactive than the *endo* isomer. While the *exo:endo* reactivity ratio is sufficiently large to indicate that acetolysis of the *exo*-IV-OBs is predominantly anchimerically assisted, the ratio is only *ca.* one-tenth as large as that for the norbornyl bromobenzenesulfonates.[8] For several reasons, it is not yet possible to explain adequately this difference between III-OBs and IV-OBs and the norbornyl analogs. One of the complicating features is the unknown extent to which the solvolysis rate of IV-OBs is reduced below the ionization rate by ion pair return.[8,12] In addition, the change from the norbornyl structure to III-OBs or IV-OBs introduces subtle steric effects which we are studying and hope to report on elsewhere.

A bridged non-classical ion analogous to the norbornyl cation is apparently formed directly by ionization of the *exo*-IV-OBs and subsequent to ionization in the case of the *endo* isomer. This bridged ion gives rise to the *exo*-IV-OAc with the *exo-endo* fusion of bicycloheptane nuclei. The failure to observe any product IX with the *endo-endo* fusion parallels observations with other systems[4,13] which similarly show a preference for *exo* rather than *endo* fusion.

Unsaturated Bromobenzenesulfonates.—Turning to the solvolysis of the unsaturated I-OBs and II-OBs, there are clear indications that the complex rearrangements leading to the saturated solvolysis products occur after the rate-determining step. The first indication of this is in the rates of solvolysis. Considering first the anchimerically unaccelerated *endo*-I-OBs, we see that its rate of solvolysis is smaller by a factor of 1.4 than that of the saturated analog, III-OBs. This small rate retardation in the unsaturated I-OBs relative to its saturated analog would be expected from the rate-retarding inductive effect of the olefinic linkage.[14] In the case of the anchimerically accelerated *exo*-II-OBs, the acetolysis rate is again nearly equal to that of the saturated analog, IV-OBs. Therefore, no serious special accelerating effect of the olefinic group is indicated. The rate of II-OBs does exceed that of IV-OBs by the slight factor of 1.8, but even this cannot be ascribed to anchimeric involvement of the olefinic linkage in the first ionization step, since there are subtle steric effects on ionization rate connected with the structural change from IV-OBs to II-OBs; also, the factor by which titrimetric acetolysis rates fall below the actual ionization rates due to internal return may well be smaller for II-OBs than for IV-OBs, because the unsaturated system provides a new rearrangement path to compete with internal return. Certainly, rates provide no indication of a special anchimeric role for the olefinic linkage in the first ionization step.



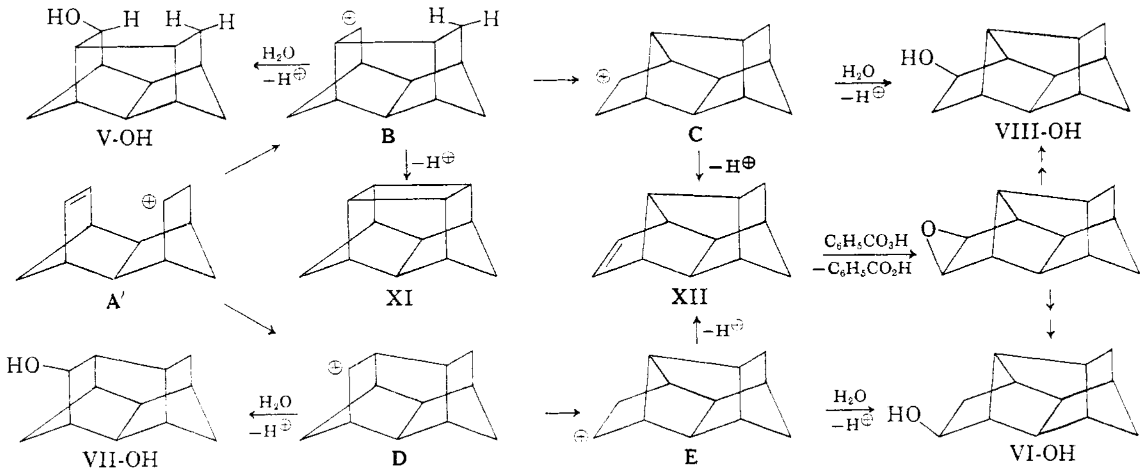
The second indication that the rearrangements leading to saturated products occurs subsequent to the first ionization step is the variation of the proportions of unsaturated and saturated products with the nature of the solvent medium. The proportion of saturated products from the anchimerically accelerated *exo*-II-OBs is considerably larger in acetic acid than in the more nucleophilic aqueous acetone solvent, and this would be understandable on the basis of a competition[2b,8] between further rearrangement of the first bridged ion **A** leading to saturated products, and nucleophilic attack on **A** leading to unsaturated product.

With the *endo*-I-OBs, the proportion of saturated products from acetolysis is also greater than from

---

(13) (a) P. D. Bartlett and A. Schneider, THIS JOURNAL, **68**, 6 (1946); (b) P. D. Bartlett, p. 1 of Abstracts, 12th National Organic Chemistry Symposium of the American Chemical Society, Denver, Colo., June 12–15, 1951.

(14) S. Winstein, H. M. Walborsky and K. Schreiber, THIS JOURNAL, **72**, 5795 (1950).



hydrolysis in aqueous acetone. In both media, the *endo*-I-OBs leads to a smaller proportion of saturated products than does the *exo* isomer II-OBs. This is presumably due to the ionization of the *endo*-I-OBs to a classical cationic intermediate, which can lead partly to unsaturated product before rearranging to the bridged ion **A** formed directly by ionization of *exo*-II-OBs. This contrast between the *endo*-I-OBs and its *exo* isomer II-OBs parallels that observed with the *endo*- and *exo*-norbornyl[8] and the *endo*- and *exo*-5-norbornenyl[2b,15] bromobenzenesulfonates.

It is interesting that no appreciable formation of the unsaturated acetate X with the *endo-endo* fusion was observed. This system, the corresponding alcohol of which has since been prepared in these laboratories by other methods,[1c,6] would arise from nucleophilic attack on C_1 of the bridged ion **A**. As already commented on, such attacks leading to *endo* instead of *exo* fusion generally fail to compete.[4,13]

Simplified Rearrangement Scheme.—For the formation of saturated products from I-OBs and II-OBs, the olefinic group must become involved in the reaction sequence, one additional ring being created in the saturated alcohols and two additional rings being formed in the saturated $C_{12}H_{14}$ hydrocarbon. One of the conceivable ways in which the olefinic linkage could become involved would involve hydrogen shifts to produce homoallylic cations which could then give rise to cyclopropane ring-containing products. However, cyclopropane rings were not detected in the saturated products. Also, hydrogen shifts appear to be relatively unimportant in solvolysis of the related saturated compounds III-OBs and IV-OBs, which were studied for comparison.

Writing classical carbonium ion structures for simplicity, we can visualize the involvement of the olefinic linkage of II-OBs with a preformed cationic center as follows. If we represent bridged ion **A** in the extreme classical form of **A′** and add the cationic center to either end of the neighboring olefinic linkage, we arrive at carbonium ions **B** or **D**. By simple Wagner–Meerwein shifts, these may be transformed to cations **C** and **E**.

With the aid of ions **B–E**, one can account for all the gross features of the observed complex rearrangements accompanying solvolysis of I-OBs and II-OBs. For example, each of the carbonium ions **B–E** may be considered related to a saturated alcohol, so four saturated alcohols (V–VIII) can be anticipated. Four are actually observed. The simplified rearrangement scheme involving ions **B–E** also allows one to accommodate various interrelationships among the various products and to go far in assigning structures to them. As for the saturated $C_{12}H_{14}$ hydrocarbon, ion **B** seems peculiarly well adapted for proton loss to yield a saturated hydrocarbon, for which the structure XI could be visualized.[2]

Bird-cage Hydrocarbon.—The saturated $C_{12}H_{14}$ hydrocarbon formed during acetolysis and hydrolysis of I-OBs, II-OBs and V-OBs was also obtained from II-OBs and V-OBs in relatively ionizing nonhydroxylic media. Thus, it was isolated in *ca.* 10% yield after II-OBs was left 48 hours at 50° in nitromethane solution. After V-OBs was left 24 hours at room temperature in the same solvent, the hydrocarbon was obtained in a yield somewhat less than from acetolysis.

The infrared spectrum of the $C_{12}H_{14}$ hydrocarbon summarized in Table III and a more extensive investigation of the infrared and Raman spectra carried out by Dr. K. Nukada[16] in the M.I.T. Spectroscopy Laboratory under the direction of Professor R. C. Lord are helpful in connection with the structure of this hydrocarbon. It fails to show an infrared absorption band in the 1000–1020 cm.$^{-1}$ region,[17] nor does it display a C–H stretching frequency[16] above 2960 cm.$^{-1}$. Therefore, it does not contain a cyclopropane ring. The spectral evidence excludes the presence of CH_3 groups,[16] but there is evidence[16] for CH_2, a band of moderate intensity at 1454 cm.$^{-1}$ in both infrared and Raman spectra suggesting the presence of a small number of CH_2 groups per molecule.[16] The analogous band in norbornadiene occurs at 1451 cm.$^{-1}$. A group of intense infrared bands at about 1300 cm.$^{-1}$ is

---

(15) H. J. Schmid, unpublished work.

(16) K. Nukada and R. C. Lord, private communication.

(17) (a) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949); (b) V. A. Slabey, *ibid.*, **76**, 3604 (1954); (c) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 27.

probably associated with tertiary C–H bending vibrations.[16] A strong band at 1310 cm.$^{-1}$ is shown by both norbornane and norbornadiene. The spectral evidence is consistent with the bird-cage hexacyclododecane structure XI, hexacyclo-[6.2.1.1^{3,6}.0^{2,7}.0^{4,10}.0^{5,9}] dodecane, suggested[2] from chemical and mechanistic considerations.

Crystals of the bird-cage hydrocarbon are highly disordered at room temperature, and this has delayed a complete analysis of the hydrocarbon structure by X-ray diffraction methods.[11] However, a thorough electron diffraction study by Schomaker and his co-workers[18] does definitely confirm the hexacyclododecane structure XI for the $C_{12}H_{14}$ hydrocarbon. The bird-cage structure is confirmed also by the proton magnetic resonance spectrum of the $C_{12}H_{14}$ hydrocarbon. The low resolution proton magnetic resonance spectrum in a 50% by weight solution in methylene chloride contains two major peaks in addition to the solvent peak. The measured ratio of peak areas is 10.0:3.84, in satisfactory agreement with the 10:4 ratio of *tertiary* to *secondary* hydrogen atoms.

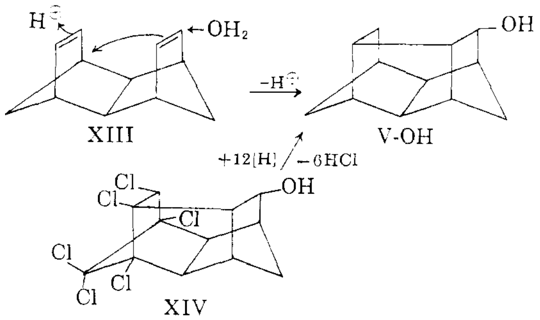
Further chemical evidence for the structure of the $C_{12}H_{14}$ hydrocarbon is its relationship to the saturated isomer of isodrin prepared by the Shell Development Co. research group.[19,20] The hexachloro-bird-cage structure for this isodrin isomer is perhaps clearest from its photochemical formation from isodrin reported by Cookson and Crundwell.[21] Dechlorination of this material with sodium in amyl alcohol by the Shell Development group[20] led to a hydrocarbon, m.p. 153–155°, which was evidently a less pure sample of the bird-cage hydrocarbon. This material was undepressed in melting point[20] and agreed in infrared spectrum[20] with our sample of the hydrocarbon, m.p. 165°, obtained from solvolysis.[22]

Half-cage Alcohol V-OH.—Of the four rearranged saturated alcohols obtained from solvolysis of the unsaturated *endo*- and *exo*-esters I-OBs and II-OBs, one of them, designated V-OH from the order in which the products were isolated, was unique, both spectroscopically and chemically. In the C–H stretching region of the infrared spectrum, V-OH shows a sharp band at 3038 cm.$^{-1}$, peculiarly high for a saturated C–H stretching frequency. No such specific absorption in the 3000–3100 cm.$^{-1}$ region is displayed by alcohols VI-OH, VII-OH and VIII-OH. However, sharp bands in this region are displayed by III-OH, IV-OH and IV-OAc. Such displaced C–H stretching frequencies are characteristic[23] of C–H groups where there exists H, H interference such as that in structures III and IV.

Of all four rearranged saturated bromobenzenesulfonates, V-OBs is the only one which leads to substantial amounts of bird-cage hydrocarbon XI in solvolysis. Also, it is the most reactive in solvolysis. Compared to the unsaturated *exo*-II-OBs it is more reactive by a factor of *ca.* 10^2, and it is faster than the *endo*-I-OBs by a factor of *ca.* 10^4.

One of the rearranged saturated structures anticipated on the basis of the simplified rearrangement scheme, the one related to ion **B**, namely, structure V, is unique. It possesses the hydrogen congestion evidenced in the infrared spectrum, which could also be expected to contribute to the anchimeric acceleration of ionization of the corresponding bromobenzenesulfonate. Also, structure V is the only one out of V-VIII which appears uniquely capable of leading to bird-cage hydrocarbon in solvolytic reactions. For these reasons, structure V-OH was assigned[2] to the rearranged saturated alcohol, m.p. 130°.

More recently, the 130° alcohol V-OH has been obtained[1c,6] in these laboratories by routes which serve to confirm its half-cage structure. One route[1c] to the 130° alcohol involves homoconjugative hydration of the *endo-endo-diene*[20] XIII, similar to the homoconjugative additions to bicycloheptadiene.[24] Another route[6] to the 130° alcohol is dechlorination of its hexachloroderivative[20,25] XIV.



XIII V-OH XIV

Alcohols VI-VIII-OH and the Unsaturated Hydrocarbon.—Of the three remaining rearranged saturated alcohols, designated VI-OH, VII-OH and VIII-OH from their order of appearance in isolation or synthesis, two of them appear to be simple Wagner–Meerwein isomers, since a mixture of VI-OAc and VII-OAc is formed in solvolysis of either VI-OBs or VII-OBs. Two of them, namely VI-OH and VIII-OH, are related by synthesis to the same unsaturated hydrocarbon and corresponding epoxide. These relationships are exactly those which can be anticipated from the simple rearrangement scheme involving ions **B**–**E**. Structures VII-OH and VI-OH related to ions **D** and **E** would fit for the pair of Wagner–Meerwein-related alcohols of m.p. 77° and 72°, respectively, and structure VIII-OH would fit for the alcohol, m.p. 50°, which is related to the 77° alcohol by way of the same olefin and corresponding epoxide. These considerations lead to the assignment of structures VI-OH, VII-OH and VIII-OH to the alcohols designated with the

---

(18) C. Wong, A. Berndt and V. Schomaker, private communication; C. Wong and A. Berndt, Ph.D. Theses, Calif. Institute of Technology, 1957.

(19) R. E. Lidov and H. Bluestone, U. S. Patent 2,714,617 (to Shell Development Co.), Oct. 2, 1955.

(20) S. B. Soloway, *et al.*, THIS JOURNAL, **82**, 5377 (1960).

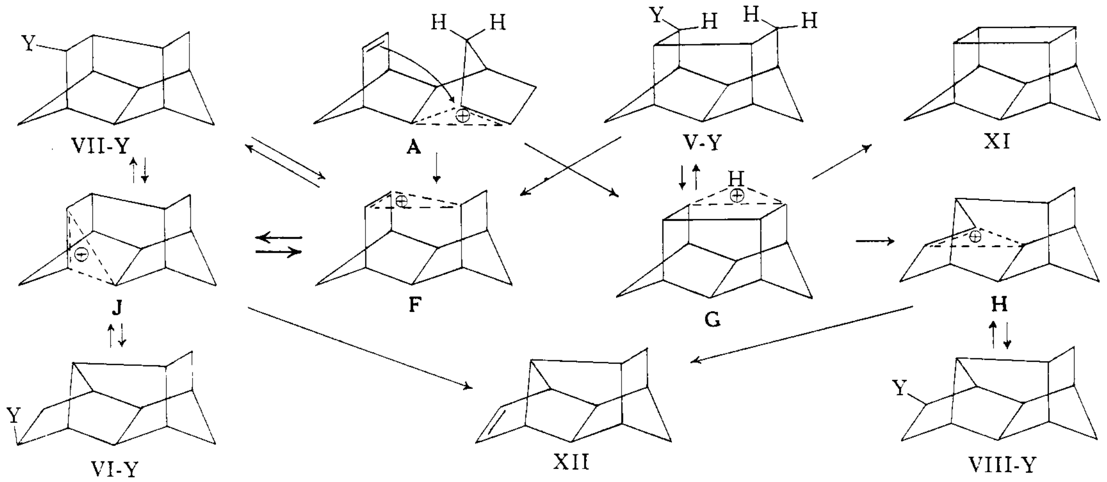
(21) R. C. Cookson and E. Crundwell, *Chemistry & Industry*, 1004 (1958); see also R. C. Cookson, E. Crundwell and J. Hudec, *ibid.*, 1003 (1958).

(22) For the heats of combustion and formation of the bird-cage hydrocarbon, see W. N. Hubbard, F. R. Frow and G. Waddington, *J. Phys. Chem.*, **62**, 821 (1958). The specially purified sample supplied for this work, m.p. 168.1–168.6°, produced an average of 99.99% of the theoretical amount of carbon dioxide in the combustion work.

(23) L. de Vries and P. R. Ryason, *J. Org. Chem.*, in press (1960).

(24) S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956).

(25) R. C. Cookson and E. Crundwell, *ibid.*, 703 (1959).



same Roman numerals from their order of appearance.

According to the simplified rearrangement scheme and the above discussion, structure XII is suggested for the unsaturated hydrocarbon which was obtained from solvolysis of VI-OBs and VIII-OBs and by Chugaev elimination from VI-OH and from which VIII-OH was synthesized. This structure for the olefin is strongly supported by its infrared spectrum summarized in Table V.

In its infrared spectrum, the $C_{12}H_{14}$ olefin displayed bands characteristic of both bicycloheptene and bicycloheptane. A strong absorption band in the C–H stretching region at 3050 cm.$^{-1}$ parallels an analogous band at 3048 cm.$^{-1}$ in the spectrum of bicycloheptene. In the double bond stretching region, three bands of increasing intensity at 1625, 1603 and 1583 cm.$^{-1}$ parallel bands at 1625, 1608 and 1568 cm.$^{-1}$ for bicycloheptene in cyclohexane solvent. In the region for the out-of-plane vibration of *cis*- olefinic hydrogen atoms, the olefin has a very strong band at 694 cm.$^{-1}$ to parallel the strong band at 706 cm.$^{-1}$ in the spectrum of bicycloheptene. A strong characteristic band in the spectrum of the olefin at 1332 cm.$^{-1}$ has its counterpart in an isolated strong band at 1337 cm.$^{-1}$ in the bicycloheptene spectrum. Another strong band at 1308 cm.$^{-1}$ is comparable to one at 1310 cm.$^{-1}$ present in the spectrum of bicycloheptane but absent from the bicycloheptene spectrum.

Rearrangement Mechanisms.—We are now in a position to inquire more intimately into the mechanisms of the rearrangements leading to the various rearranged saturated products and the rearranged olefin. In doing this we shall consider the questions of structure of the various carbonium ion intermediates and reversibility or irreversibility of the various rearrangement steps. Considering first ions **C** and **E** near the end of the two rearrangement paths leading from ion **A′**, they should be replaced by the non-classical bridged ions **H** and **J**, analogous to the norbornyl cation.[8] All three of the bromobenzenesulfonates VI-VIII-OBs are sufficiently more reactive in acetolysis than the *endo*-norbornyl analog[8] that it is clear that they are derived from *exo*-alcohols and that their ionization is anchimerically accelerated and leads to non-classical cations.

Judging by the nature of the products of solvolysis of VIII-OBs, ion **H** leads to VIII-OH and olefin XII, but not half-cage V-OH or bird-cage hydrocarbon XI, since these two substances don't arise in solvolysis of VIII-OBs. Similarly, judging by products of solvolysis of VI-OBs, ion **J** must lead only to VI-OH, VII-OH and olefin XII. Further, the rearrangement steps to ions **H** and **J** during solvolysis of II-OBs or V-OBs are not reversible back to a precursor which can lead to half-cage V-OH or bird-cage hydrocarbon XI.

Going on to pursue the mechanism of formation of bird-cage hydrocarbon and half-cage alcohol, solvolysis product compositions indicate that the bird-cage hydrocarbon XI, the half-cage alcohol V-OH and also VIII-OH occur in approximately constant ratios in solvolysis of either II-OBs or half-cage V-OBs. Thus, the ratio, VIII-OAc:V-OAc, in the solvolysis product from either II-OBs or V-OBs is (0.36 ± 0.02) from the figures in Table VI. The ratio, $C_{12}H_{14}$:V, not as accurate because the quantity of hydrocarbon is based on isolation, is approximately unity, both in acetolysis and hydrolysis of II-OBs and V-OBs (Tables IV and VI). The facts suggest common precursors for the three products whether II-OBs or V-OBs is the starting material.

The precursor of bird-cage hydrocarbon XI and half-cage alcohol V-OH cannot be written as ion **B**, this, along with **C**, being merely one of the contributing structures to the non-classical cation **H**. One of the attractive possibilities for a precursor of bird-cage hydrocarbon XI and half-cage alcohol V-OH is the hydrogen-bridged species **G**, which can be visualized to give hydrocarbon XI by proton loss and V-OH by coördination with solvent. Alternatively, **G** could lead to VIII-OH and olefin XII by prior irreversible rearrangement to **H**. If **G** is the precursor of XI, V-OH and VIII-OH, it is presumably formed by hydrogen-assisted ionization of the half-cage V-OBs or by a complex rearrangement of the first ion **A** formed by ionization of the unsaturated II-OBs.

Clearly, both half-cage V-OBs and ion **A** from II-OBs enter into another rearrangement path besides the one beginning with **G**, namely the one leading to VI-OH and VII-OH. This latter path is several times more important with ion **A** than with V-OBs, judging by the fact that the saturated solvolysis product from II-OBs contains *ca.* four times as much VI-OAc as does the product from V-OBs. This path may involve an ion such as **F** which is formed from **A** or V-OBs and which rearranges to **J**.

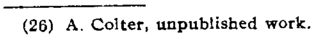
As regards the ratio of VI-OAc to VII-OAc in the solvolysis products from the various bromobenzenesulfonates (II-OBs, V-OBs, VI-OBs and VII-OBs), the data in Table VI show that this ratio is quite large (*ca.* 10–20) in the products from three of the arenesulfonates, but only *ca.* 3 in the fourth case, namely VI-OBs. The anomaly is seen the most clearly in the products from VI-OBs and VII-OBs, the former giving a 73:27 ratio and the latter a 95:5 VI:VII ratio of acetates. This difference is well outside of experimental error, VI-OBs and VII-OBs clearly giving non-identical acetate mixtures. There is another difference in the nature of the products from VI-OBs and VII-OBs in that the former leads to *ca.* 5% of olefin XII, while this material was not observed in the product from VII-OBs.

It would appear that VI-OBs and VII-OBs do not yield solvolysis products by way of completely identical intermediates. Perhaps the product anomalies mentioned above are connected with the formation of ion **F** as well as **J** by ionization of VII-OBs, while VI-OBs leads only to ion **J**. This fact taken in conjunction with ion pair considerations to be introduced in a later paper may supply an explanation of the differing products from VI-OBs and VII-OBs.

Since VII-OBs does not give rise to V-OAc or bird-cage hydrocarbon XI, certain limitations may be put on the behavior of ion **F** if it is indeed formed in ionization of VII-OBs. These limitations are that **F** does not yield V-OAc, nor does it rearrange to ion **G**.

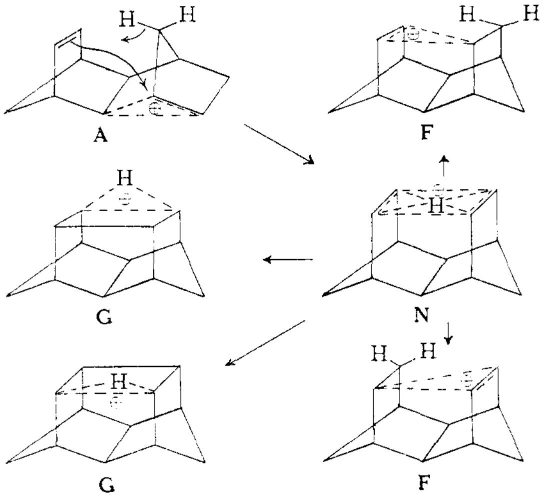
Complex Rearrangement of Bridged Ions.—Since bridged non-classical carbonium ion structures occur in many carbonium ion reactions,[2,8,12] it becomes desirable to accumulate facts and generalizations surrounding the more complex rearrangements of which these bridged structures are capable. The rearrangement of bridged ion **A** to **F** and **G** is interesting in this connection.

The complex rearrangement of ion **A** bears considerable structural and stereochemical analogy to the 2,6- hydrogen shifts[2b,8c,d] in bicycloheptane derivatives (XV). These occur by prior carbon bridging, the hydrogen shift occurring in a bridged norbornyl cation[2b,8d,26] **K**. It may be said that carbon bridging provides a mechanism for the 6,2-hydride shift.[2b,8c]



Like the 6-hydrogen atom in 6,2-hydride shift in XV, the olefinic group in II-OBs becomes involved only subsequent to formation of ion **A** with carbon bridging. The direction in which the olefinic electron cloud approaches the bridged ion structure in the rearrangement of **A** is also analogous to the 6,2-hydride shift in ion **K**.

The details which determine to what extent **F** or **G** is formed by rearrangement of **A** are not yet clear. It is possible even to conceive of a common intermediate for formation of **F** and **G** from **A**, namely an ion such as **N**. This could conceivably give rise to **F**-type or **G**-type ions by readjustments of the position of the hydrogen atom and the electronic distribution.



Many of the intimate questions of mechanism which remain in connection with the various rearrangements described in the present article can be answered by suitable stereochemical, kinetic and isotopic labeling experiments. Such work is proceeding at the present time.

Experimental Part

I- and II-Acid Phthalates.—Saponification of 427 g. of the 2:1 cyclopentadiene:vinyl acetate adduct, b.p. 85–87° (0.3 mm.) [reported[3] 140–145° (14 mm.)], gave rise to 309 g. of crude alcohol, m.p. 74.5–80°. This material was treated with 273 g. of phthalic anhydride in 168 ml. of pyridine on the steam-bath for 4 hours. The ether solution of the acid phthalate product was shaken with a dilute solution of the theoretical amount (74 g.) of sodium hydroxide. A dense white precipitate of sparingly soluble sodium salt of an acid phthalate was formed. The fine needles were filtered, recrystallized twice from hot water, and then stirred well for 4 hours with a large amount of 2 *N* hydrochloric acid. Filtration yielded 424 g. of crystalline acid phthalate, m.p. of crude dried material, 157–160°. After three recrystallizations from aqueous methanol, 382 g. of I-acid phthalate, m.p. 165–168° (Table VII), was obtained as prismatic crystals. Further recrystallization did not improve the melting point.

A second acid phthalate was obtained from the first filtrate of the precipitated sodium salt. Acidification of this filtrate yielded a yellowish crystalline precipitate, m.p. of crude dried material, 160–167°. After two recrystallizations from methanol, 51.7 g. of II-acid phthalate, m.p. 174–176° (Table VII), was obtained as small needles. Further recrystallization did not improve the melting point.

I-OH.—Saponification of a 252-g. quantity of the I-acid phthalate, m.p. 165–168°, yielded 134.5 g. of needles, m.p.

---

(26) A. Colter, unpublished work.

TABLE VII

PROPERTIES AND ANALYSES OF VARIOUS COMPOUNDS

Compound	M.p., °C. or n^{25}D	Formula	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
I-OH	107.4–108.8	$C_{12}H_{16}O$	81.77	81.69	9.15	9.30
I-$OCOC_6H_4COOH$	165–168^a	$C_{20}H_{20}O_4$	74.05	74.15	6.22	6.28
I-OBs	115.5–116.5	$C_{18}H_{19}SO_3Br$	54.68	54.50	4.84	5.13
II-OH	101–102	$C_{12}H_{16}O$	81.77	81.69	9.15	9.21
II-OAc	45–47	$C_{14}H_{20}O_2$	76.32	76.53	9.15	9.34
II-$OCOC_6H_4COOH$	174–176^a	$C_{20}H_{20}O_4$	74.05	74.10	6.22	6.47
II-OBs	102–103	$C_{18}H_{19}SO_3Br$	54.68	54.69	4.84	5.15
III-OH	99–101	$C_{12}H_{18}O$	80.85	80.73	10.18	10.20
III-OBs	111–112	$C_{18}H_{21}SO_3Br$	54.40	54.43	5.32	5.45
IV-OH	123–124	$C_{12}H_{18}O$	80.85	81.01	10.18	10.20
IV-OBs	89–90	$C_{18}H_{21}SO_3Br$	54.40	54.59	5.32	5.44
α-Diacid^b	217–219	$C_{12}H_{16}O_4$	64.30	64.06	7.19	6.99
V-OH	130–131^c	$C_{12}H_{16}O$	81.77	81.92	9.15	8.93
V-OAc	1.5247	$C_{14}H_{18}O_2$	77.02	76.90	8.33	8.53
V-$OCOC_6H_4COOH$	206–207^d	$C_{20}H_{20}O_4$	74.05	73.91	6.22	6.31
V-OBs	76.5–77.0	$C_{18}H_{19}SO_3Br$	54.68	54.75	4.84	4.98
VI-OH	76.2–77.6^e	$C_{12}H_{16}O$	81.77	81.86	9.15	9.15
VI-OAc	1.5137	$C_{14}H_{18}O_2$	77.02	76.83	8.33	8.45
VI-$OCOC_6H_4COOH$	180.5–181.0^{d,f}	$C_{20}H_{20}O_4$	74.05	74.14	6.22	6.38
VI-$OCOC_6H_4NO_2$	130–131^g	$C_{19}H_{19}O_4$	70.14	70.21	5.89	5.90
VI-OBs	97–98^h	$C_{18}H_{19}SO_3Br$	54.68	54.47	4.84	5.04
VI-$OCSSCH_3$	97–98	$C_{14}H_{18}S_2O$	63.14	63.03	6.81	7.05
VII-OH	71.5–72.6^{c,e}	$C_{12}H_{16}O$	81.77	82.01	9.15	9.33
VII-OAc	1.5144	$C_{14}H_{18}O_2$	77.02	77.12	8.33	8.29
VII-OBs	105–106	$C_{18}H_{19}SO_3Br$	54.68	54.86	4.84	4.87
VIII-OH	49.5–51.5	$C_{12}H_{16}O$	81.77	81.49	9.15	9.02
VIII-OAc	1.5138	$C_{14}H_{18}O_2$	77.02	76.80	8.33	8.47
VIII-$OCOC_6H_4COOH$	191.5–192.7^f	$C_{20}H_{20}O_7$	74.05	74.04	6.22	6.07
VIII-$OCOC_6H_4NO_2$	100.2–101.7^g	$C_{19}H_{19}O_4N$	70.14	70.47	5.89	5.86
VIII-OBs	91–92^h	$C_{18}H_{19}SO_3Br$	54.68	54.86	4.84	4.82
Bird-cage HC.XI	165–167	$C_{12}H_{14}$	91.08	91.11	8.92	8.84
Olefin XII	1.5372^i	$C_{12}H_{14}$	91.08	90.87	8.92	8.97
	1.5372^j	$C_{12}H_{14}$	91.08	91.29	8.92	9.20

$^{a,c-h}$ Pairs of compounds which show melting point depression. ^{b} From oxidation of III-OH. ^{i} From VI-OH by Chugaev elimination; b.p. 87–88° (10 mm.). ^{j} From solvolysis of VI-OBs; n^{25}D 1.5371 for olefin from solvolysis of VIII-OBs.

107.4–108.8° (Table VII). This alcohol discolored a dilute acetone solution of potassium permanganate within 1 minute.

II-OH.—Saponification of a 61.5-g. quantity of II-acid phthalate, m.p. 174–176°, yielded 31.0 g. of still slightly impure II-OH, m.p. 98.0–99.5° after one recrystallization from Skellysolve B. Further purification was obtained through recrystallization of the solid acetate.

The alcohol was dissolved in 50 ml. of pyridine, 1.5 equivalents of acetic anhydride was added, and the mixture was heated on the steam-bath for 1 hour. From this reaction mixture there was isolated 32.4 g. of solid II-OAc, m.p. 45–47° (Table VII). The acetate was treated with 3 g. of lithium aluminum hydride in ether in the usual manner. This gave rise to 25.0 g. of II-OH after one recrystallization from Skellysolve B; m.p. 101–102° (Table VII). The alcohol decolorized a dilute solution of potassium permanganate in acetone within 1 minute.

III-OH.—A 3-g. quantity of I-OH in 30 ml. of acetic acid was hydrogenated at atmospheric pressure over Adams catalyst. After one recrystallization from Skellysolve B, 2.87 g. of the saturated III-OH was obtained, m.p. 99–101° (Table VII).

A 2.40-g. quantity of potassium permanganate in 50 ml. of water was added dropwise with stirring to the refluxing solution of 1 g. of III-OH in 30 ml. of pyridine. After decoloration, the α-diacid was isolated from the reaction mixture. Recrystallization from acetone–acetonitrile gave rise to 305 mg. of the α-diacid, m.p. 217–219° (reported[4,27] 216–217°) [Table VII].

IV-OH.—From hydrogenation of a 3.00-g. quantity of II-OH there was obtained 2.79 g. of IV-OH, m.p. 123–124° (Table VII).

A 1-g. quantity of IV-OH was treated with potassium permanganate in pyridine according to the procedure described for III-OH. There was obtained the α-diacid (248 mg.), m.p. 217–219°, undepressed upon admixture of the diacid obtained from III-OH.

Acetolysis of III-OBs and IV-OBs.—A 30.5-g. quantity of III-OBs at a concentration of 0.1 *M* in acetic acid containing 0.12 *M* sodium acetate was acetolyzed for 24 hours at reflux temperature. The acetolysis products were treated with lithium aluminum hydride in the usual manner, and the alcohol product thus obtained was recrystallized from Skellysolve B. This gave rise to 11.46 g. (83.5%) of materials, m.p. 123–124°, undepressed upon admixture of IV-OH.

A 5.4-g. quantity of IV-OBs at a concentration of 0.1 *M* in acetic acid containing 0.12 *M* sodium acetate was acetolyzed for 48 hours at 50°.

The acetolysis product was distilled at 10 mm. pressure and 120° bath temperature through a small still. The infrared spectrum was found to be virtually identical with that of IV-OAc obtained from IV-OH. Small disagreements between the spectra at isolated points did not exceed 0.02 optical density unit, the average optical density of the absorption maxima being 0.7 optical density unit.

The remaining acetolysis product was treated with lithium aluminum hydride and the alcohol product thus obtained was recrystallized from Skellysolve B. This gave rise to 1.85 g. of material, m.p. 123–124°, undepressed upon admixture of IV-OH.

Acetolysis of I-OBs.—A solution of 321 g. of I-OBs in 10 l. of dry acetic acid, 0.12 *M* in sodium acetate, was refluxed for 24 hours. After being cooled, the solution was divided into several batches which were diluted with *ca.* four volumes of water and extracted three times with pen-

---

(27) K. Alder and G. Stein, *Ann.*, **496**, 204 (1932).

tane. The combined pentane extracts were washed with sodium bicarbonate solution, and the pentane was removed under aspirator vacuum to leave the crude acetolysis product.

The crude acetolysis product was shaken vigorously with 500 ml. of a saturated silver nitrate solution. The mixture thickened, and a large amount of a white solid separated. After the mixture was stirred overnight, the solid was filtered off. The filtrate contained a fair amount of an oil, the bulk of which adhered to the precipitate. This precipitate was finely ground in a mortar and then triturated thoroughly with pentane which had been precooled in a Dry Ice–acetone-bath. The pentane was filtered off, and the trituration procedure was twice repeated. The combined pentane washings were added to the first aqueous silver nitrate filtrate, and the original supernatant oil dissolved immediately into the upper layer.

The aqueous silver nitrate filtrate and the combined pentane washings of the solid silver nitrate complex were transferred to a separatory funnel, the mixture was shaken, and the pentane layer was separated. Filtration and subsequent evaporation of the pentane under aspirator vacuum left 70.3 g. of an oil. An aliquot did not form a solid complex on shaking with a saturated silver nitrate solution, but remained as a supernatant layer; however, it still decolorized a dilute solution of potassium permanganate in acetone. The combined oil was now dissolved in acetone, and powdered potassium permanganate was added in small amounts to the refluxing, rapidly stirred solution until the color persisted and no further heat was developed. The undissolved potassium permanganate and the manganese dioxide were removed by filtration, and the filtrate was decolorized by the addition of a saturated aqueous solution of sodium bisulfite. Some manganese dioxide, which did not dissolve readily, was removed by filtration. A large amount of water was now added, and the saturated acetolysis products were separated as an oil. The solution was extracted three times with pentane, in which the oil dissolved easily, and the pentane solution was washed several times with water. The pentane and remaining acetone were now removed by evaporation under aspirator vacuum. An oil (65.6 g.) was obtained which did not decolorize a solution of bromine in carbon tetrachloride.

The silver nitrate solution which had been separated from the pentane solution containing the saturated products was now extracted seven times with 200-ml. quantities of pentane. The pentane washings were combined, and the solvent was removed through a Vigreux column at steam-bath temperature. An oily residue (1.73 g.) remained, which crystallized in the refrigerator when seeded with crystals of II-OAc. After two recrystallizations from pentane, 1.19 g. of II-OAc was obtained, m.p. 44–46°, undepressed by admixture of authentic II-OAc.

The solid silver nitrate complex was warmed with concd. ammonia solution on the steam-bath. All the solid disappeared and an oily layer formed. After being cooled, the mixture was extracted with pentane which dissolved the oil. The pentane extract was concentrated under aspirator vacuum, and the residual oil was crystallized from 400 ml. of pentane. This gave rise to 54.6 g. of a crystalline solid, m.p. 45–47°, undepressed by admixture of II-OAc.

In another experiment on the acetolysis of I-OBs, a 4.00-g. quantity of the total acetolysis product was ozonized as described for the product from II-OBs described below. A 1.80-g. quantity (45% yield) of material was recovered from the ozone treatment.

Hydrolysis of I-OBs.—A 235.7-g. quantity of I-OBs was dissolved in 4800 ml. of acetone and 150 g. of powdered calcium carbonate was added. The mixture was maintained at reflux while 3200 ml. of water, which had been heated to 65°, was added gradually, so as to prevent precipitation of the dissolved *p*-bromobenzenesulfonate in difficultly soluble lumps. The mixture was kept at reflux for 21 days. After filtration, the acetone was removed through a 40-plate bubble-plate column. The residual solvolysis products were acetylated in the manner described for II-OH, the acetylated products weighing 107.4 g. Using the silver nitrate method described for the acetolysis products, 75.5 g. of II-OAc, m.p. 45–47°, was obtained from the solid silver nitrate complex and 23.4 g. of products remained which did not form a solid complex with silver nitrate but did decolorize a dilute solution of potassium permanganate in acetone within 2 minutes. These 23.4 g. of products were now shaken thoroughly with 200 ml. of a saturated silver nitrate solution. The silver nitrate layer was separated from the supernatant oily layer, and it was extracted three times with pentane. With the resulting silver nitrate solution the oily products were shaken again, and the whole procedure was repeated five times. Oily products (15.53 g.) remained, which decolorized only partially after 10 minutes a dilute solution of potassium permanganate in acetone.

From the combined pentane washings 8.0 g. of an acetate was obtained, which decolorized a dilute acetone solution of potassium permanganate virtually immediately. Treatment with 0.87 g. of lithium aluminum hydride in ether solution in the usual manner yielded a sirup, which was dissolved in pentane and subjected to chromatography on 300 g. of alumina. Using pentane containing 10% ether as an eluent, 3.07 g. of a material was obtained from the second 500-ml. fraction, which, upon recrystallization from Skellysolve B, melted at 108–109°, undepressed on admixture with I-OH, m.p. 107–109°. Continuing with the same eluent, 300 ml. followed, which contained only a trace of non-volatile material and then 500 ml. containing 2.65 g. of impure II-OH, m.p. 92–95° after recrystallization from pentane. A mixture with I-OH had m.p. 75–79° while a mixture with II-OH (m.p. 101–102°) had m.p. 97–99°. Further elution with the same solvent or pure ether did not yield appreciable amounts of products.

The small quantity of I-OH recovered from hydrolysis of I-OBs was ascribed to contamination of the original I-OBs with a little I-OH, but this point was not investigated further.

Acetolysis of II-OBs.—A 25.62-g. quantity of II-OBs was acetolyzed in 650 ml. of a 0.12 *M* solution of sodium acetate in dry acetic acid at 50° for 48 hours. One-half of the recovered product was separated into an unsaturated and a saturated fraction according to the procedure described for the acetolysis products from I-OBs. There was obtained 1.68 g. (30.5%) of II-OAc, m.p. 44.5–46.5°, along with 3.78 g. of material which did not complex with silver nitrate. Of this material, 3.55 g. was recovered after treatment with potassium permanganate in acetone.

A 4.08-g. quantity of the remaining acetolysis product from II-OBs was dissolved in 25 ml. of a 1:1 mixture of acetic acid and ethyl acetate. Oxygen containing approximately 3% ozone was bubbled through the solution until excess ozone was indicated. The solution was now treated with 50 ml. of an aqueous solution of hydrogen peroxide (8% by weight) and potassium hydroxide. After being kept at reflux for 6 hours, the mixture was cooled and placed in a separatory funnel. The aqueous layer was discarded, and, after addition of 50 ml. of pentane, the organic layer was washed with sodium bicarbonate solution until it was neutral. After the organic layer was dried over magnesium sulfate, the solvent was removed under aspirator vacuum on the steam-bath. The residue weighed 2.632 g. (64% yield). After this material was treated with lithium aluminum hydride, the reduction products could be partially crystallized from pentane after prolonged cooling. However, the material obtained by filtration had a large melting point range (45–66°), which did not improve markedly after several recrystallizations.

Hydrolysis of II-OBs.—A 49.4-g. quantity of II-OBs was solvolyzed in 2 l. of 60% aqueous acetone in the presence of excess powdered calcium carbonate. Reflux was maintained for 48 hours. The solvolysis product, recovered as in the case of I-OBs, was treated directly with a saturated silver nitrate solution without prior acetylation. The mixture was shaken, and the solid complex which formed was filtered off after the mixture had stood overnight.

The solid complex was ground, triturated thoroughly with ether and dried. This complex was quite soluble in hot water, from which it could be recrystallized. It was decomposed by heating with concd. ammonia solution as described in the case of I-OBs; however, ether was used instead of pentane to extract the product. The yield after one recrystallization from pentane was 9.05 g., m.p. 101–102°, undepressed by the original II-OH.

The ether washings of the complex were combined with the aqueous silver nitrate filtrate, the mixture was shaken, and the ether layer containing the materials which did not complex with silver nitrate was separated. After evaporation of the ether, 9.99 g. of sirupy product was obtained, which decolorized a dilute solution of potassium permanganate in acetone only slowly. Removal of all unsaturated material with permanganate as described for the solvolysis product from I-OBs left 8.98 g. of saturated products.

Separation of Saturated Hydrocarbon and V- and VI-Acid Phthalates.—A 14.20-g. quantity of saturated product from acetolysis of II-OBs, which had been freed from unsaturated materials by treatment with permanganate in acetone, was treated with 1.79 g. of lithium aluminum hydride in ether. After evaporation of the ether, 11.27 g. of a sirup was obtained. This was dissolved in 50 ml. of pyridine, the theoretical amount of phthalic anhydride was added and the solution was heated on the steam-bath for 4 hours. The solution was then cooled, diluted with ether and washed with 2 *N* hydrochloric acid. Crystals began to form in the ether solution, and these were collected by filtration; m.p. 177–179°. Three recrystallizations from acetonitrile raised the melting point to 180.5–181.0° (Table VII). The yield of this material amounted to 1.94 g.

The ether mother liquor was now extracted with concd. sodium bicarbonate solution. Evaporation of the solvent from the ether layer through a 20-plate column left a waxy solid. This material could be recrystallized from acetone, but the most effective purification was obtained by sublimation under aspirator vacuum at steam-bath temperature. A saturated hydrocarbon (1.66 g.) was obtained, m.p. 165–167° (Table VII).

Hydrochloric acid was added to the sodium bicarbonate extract, and the liberated acid phthalates were extracted three times with ether. After evaporation of the ether, the residual acid phthalates were recrystallized from acetonitrile. By cooling the hot solution to room temperature, crystals formed in the shape of coarse needles and rods. These crystals were collected by filtration and recrystallized once from acetonitrile; 1.57 g. of rod-shaped crystals was obtained, m.p. 206–207° (Table VII). This was an acid phthalate, different from the first. A mixture of the two compounds melted at 167–175°.

By concentration of the combined acetonitrile mother liquors and a five-stage fractional crystallization procedure there were obtained 0.73 g. of the acid phthalate, m.p. 206–207°, and 1.29 g. of the acid phthalate, m.p. 180.6–181.2°. After concentration of the combined mother liquors, there was obtained 3.23 g. of a much more soluble acid phthalate, m.p. 160–166°. Although this acid phthalate appeared well crystallized, it was a mixture. After five recrystallizations from acetonitrile, the melting point was 178–180°, and it still increased to 180–182° on the sixth recrystallization. This melting point was depressed by admixture of either of the two other acid phthalates.

A 6.51-g. quantity of the saturated product from hydrolysis of II-OBs in aqueous acetone was converted into acid phthalates, and the acid phthalates were subjected to fractional crystallization according to the procedure described above. There were obtained 0.63 g. of saturated hydrocarbon, m.p. 166.5–167.5°, 2.47 g. of acid phthalate, m.p. 206–207°; 1.70 g. of acid phthalate, m.p. 180.6–181.2°; and 1.86 g. of impure acid phthalate, m.p. 164–169°.

Saponification of the acid phthalate, m.p. 206–207°, led to V-OH, m.p. 130–131° (Table VII) after recrystallization from Skellysolve B. From the acid phthalate, m.p. 180.6–181.2°, was obtained VI-OH, m.p. 76.2–77.6° (Table VII). The *p*-nitrobenzoate of VI-OH had m.p. 130–131° (Table VII).

Chromatographic Separation of Saturated Products.—An 8.98-g. quantity of saturated product from hydrolysis of II-OBs was dissolved in 100 ml. of pentane and chromatographed on 400 g. of alumina. The material was eluted with 200–700-ml. quantities of solvents, pentane being employed for fractions A–C, pentane–10% ether for D–K and ether for L–M. Fractions A, C–E and M contained no eluted material. Fraction B contained a saturated hydrocarbon which did not decolorize a dilute solution of potassium permanganate in acetone in 15 minutes. It was similarly stable toward bromine in carbon tetrachloride, and it was recovered unchanged from a pentane solution subjected to an oxygen–4% ozone stream for 10 hours. After sublimation under aspirator vacuum, 1.85 g. of material, m.p. 165–167°, was obtained.

The residue from fraction F, after one recrystallization, gave rise to 0.73 g. of V-OH, m.p. 130–131°. From fraction G an impure sirupy product was obtained, from which 0.42 g. of V-OH, m.p. 129–131°, was obtained after two recrystallizations. From the combined mother liquors a sirup was recovered after evaporation of the solvent. Similar sirup fractions were obtained from fractions H and I. Fraction J gave rise to some impure VI-OH, m.p. 63–65°, after one recrystallization from pentane. More of this material, m.p. 67–69°, was obtained from fraction K, and the bulk of it from fraction L, m.p. 69–72° after one recrystallization from pentane.

The combined sirups obtained from chromatography fractions or from mother liquors, weighing 4.89 g., were rechromatographed to yield 0.56 g. of V-OH, m.p. 129–131°, 1.96 g. of sirup and 1.90 g. of impure VI-OH, m.p. 62–71. This procedure of rechromatographing the sirup was repeated twice more. All the impure VI-OH fractions were converted to acid phthalate which was recrystallized three times from aqueous methanol; m.p. 180.5–181.0°. Saponification yielded 3.04 g. of VI-OH, m.p. 76.2–77.6° after one recrystallization from pentane. Impure acid phthalate from the mother liquors (0.92 g.) gave a sirupy alcohol (0.49 g.) on saponification.

The products resulting from the combined procedures can be summarized as: 1.85 g. of saturated hydrocarbon, 2.12 g. of V-OH, 0.67 g. of sirup, 3.04 g. of VI-OH.

A 4.90-g. quantity of saturated product from acetolysis of II-OBs was treated with 0.60 g. of lithium aluminum hydride, 3.96 g. of a sirupy product being obtained. A separation procedure similar to that described above gave rise to 0.42 g. of saturated hydrocarbon, m.p. 165–167°, 0.59 g. of V-OH, m.p. 130–131°; 0.72 g. of sirup; and 1.32 g. of VI-OH, m.p. 76.4–77.5°.

A 7.16-g. quantity of saturated product from hydrolysis of I-OBs treated similarly gave rise to 1.50 g. of saturated hydrocarbon, m.p. 165–167°; 1.70 g. of V-OH, m.p. 129–131°; 0.60 g. of sirup; and 2.33 g. of VI-OH, m.p. 76.5–77.5°.

Acetolysis of V-OBs.—A 9.3-g. quantity of V-OBs was acetolyzed for 24 hours at 50° in 235 ml. of a 0.12 *M* solution of sodium acetate in dry acetic acid. The product (4.78 g.) was recovered by the procedure described for the acetolysis of I-OBs. This did not decolorize a dilute solution of potassium permanganate in acetone in 15 minutes. Treatment of the product with 0.51 g. of lithium aluminum hydride gave rise to 3.92 g. of a sirup. Upon dilution with pentane, V-OH began to crystallize, two recrystallizations leading to 0.61 g. of material, m.p. 129–131°. The combined mother liquors were concentrated, and the solution was chromatographed on 150 g. of alumina using the procedure described for the products of hydrolysis of II-OBs. The combined amounts of VI-OH were purified through the acid phthalate. The products resulting from the combined procedures were 1.18 g. of saturated hydrocarbon, m.p. 165–167°; 1.07 g. of V-OH, m.p. 129–131°; 0.505 g. of sirup; and 0.82 g. of VI-OH, m.p. 76.5–77.5°.

Hydrolysis of V-OBs.—A 9.24-g. quantity of V-OBs was solvolyzed for 12 hours in 700 ml. of aqueous acetone with a large excess of powdered calcium carbonate according to the method described for I-OBs. The sirupy product (3.92 g.) did not decolorize a dilute solution of potassium permanganate in acetone in 15 minutes. Dilution with pentane and two recrystallizations of the V-OH obtained gave rise to 0.96 g. of material, m.p. 129–131°. The combined mother liquors were concentrated and the solution was subjected to chromatography. The combined amounts of VI-OH were purified through the acid phthalate. The products resulting from the combined procedures were 1.23 g. of saturated hydrocarbon; 1.48 g. V-OH, m.p. 129–131°; 0.40 g. of sirup; and 0.38 g. of VI-OH, m.p. 76.5–77.5°.

Saturated Hydrocarbon from II-OBs and V-OBs in Nitromethane.—A 3.5-g. quantity of II-OBs was dissolved in 200 ml. of nitromethane which had been dried over calcium chloride and distilled, and the solution was kept at 75° for 36 hours. A small amount of a precipitate was filtered off, and the nitromethane solution was extracted four times with pentane. The combined pentane extracts were concentrated and chromatographed on alumina. From the pentane eluate a residue was recovered which led to 0.076 g. of waxy crystals, m.p. 161–163°, after one sublimation. The melting point was undepressed by admixture of the saturated hydrocarbon obtained from acetolysis of II-OBs. Also, the infrared spectra of the two materials were identical.

From a solution of 3.5 g. of V-OBs in 200 ml. of nitromethane kept 60 hours at room temperature there was similarly obtained 0.32 g. of saturated hydrocarbon, m.p. 164.2–166.5°, m.p. undepressed by admixture of the hydrocarbon obtained from solvolysis of II-OBs.

Acetolysis of VI-OBs and Isolation of VII-OH.—A 79.0-g. quantity of VI-OBs was acetolyzed at 50° for 48 hours in 2 l. of 0.12 *M* sodium acetate in acetic acid. Recovery of the product as described for I-OBs gave rise to 40.23 g. of material which decolorized a dilute acetone solution of potassium permanganate within 2 minutes. Treatment of the product with 4.5 g. of lithium aluminum hydride gave rise to 30.83 g. of sirupy material which was dissolved in 200 ml. of pentane and chromatographed on alumina. An unsaturated material which decolorized permanganate immediately was eluted by pentane. This was treated with concd. silver nitrate solution, and the solid silver nitrate complex which formed was triturated with cold pentane. The complex was decomposed with ammonia solution and the recovered olefin was distilled in a micro-still at 0.3 mm. This gave rise to 1.43 g. of material $n^{25}\text{D}$ 1.5372 (Table VII).

Elution with pentane–10% ether gave rise to a residue which could be crystallized from pentane; m.p. 61–64°. This was a saturated alcohol fraction, from which five recrystallizations from pentane gave rise to 1.88 g. of VII-OH, m.p. 71.5–72.6° (Table VII). The m.p. was depressed to 60–65° by admixture of V-OH and to 58–64° by VI-OH.

Further elution with pentane–10% ether gave rise to sirupy alcohol fractions and, finally, crystalline fractions. The latter were purified through the acid phthalate, 15.50 g. of VI-OH, m.p. 76.5–77.5°, being obtained. Sirupy fractions and material recovered from mother liquors were rechromatographed, the products obtained from the combined procedures being 1.43 g. of olefin, $n^{25}\text{D}$ 1.5372; 2.43 g. of VII-OH, m.p. 71.5–72.6°; 8.29 g. of sirup which later crystallized (m.p. 59–64°); and 15.50 g. of VI-OH, m.p. 76.5–77.5°.

Olefin XII from VI-OH.—An 11.00-g. quantity of VI-OH was dissolved in dry ether and refluxed for 48 hours with 15 g. of sodium hydride, water vapor being carefully excluded and ethyl alcohol being used to start the reaction. The mixture was now cooled, and 25 ml. of dry carbon disulfide was added slowly. This dissolved the dense white precipitate of sodium alcoholate completely and caused the ether to reflux. After some time the sodium xanthate precipitated. Reflux was continued for 6 hours, another 10 ml. of carbon disulfide was added and reflux prolonged for an additional 4 hours; 25 ml. of methyl iodide was now added, and the solution was refluxed overnight. In the morning another 10 ml. of methyl iodide was added and the reflux was continued for 4 more hours. Working up the reaction mixture and recrystallization of the product from pentane gave rise to 11.45 g. of methyl xanthate, m.p. 97–98°, in the form of large colorless needles (Table VII).

Decomposition of the 11.45-g. quantity of xanthate was carried out at 165°. The hydrocarbon product was distilled through a Claisen-head; b.p. 92.7° (13.0 mm.). It still contained sulfur compounds, as was evident from the odor, and it was purified by treatment with a concentrated silver nitrate solution. The solid olefin complex was triturated repeatedly with pentane to remove all materials that did not complex with silver nitrate. The complex was now decomposed with ammonia solution, and the recovered hydrocarbon was distilled *in vacuo*, 6.50 g. of material, b.p. 87–88° (10 mm.), $n^{25}\text{D}$ 1.5372, being obtained (Table VII). The infrared spectrum of the product was identical with that of the unsaturated hydrocarbon obtained from acetolysis of VI-OBs, except for isolated places where the disagreement did not exceed 0.02 optical density unit, the average optical density of the absorption maxima being 0.8 optical density unit.

Preparation of VIII-OH from Olefin XII.—A 9.8-g. quantity (0.0619 mole) of olefin XII from VI-OH was added slowly to 110 ml. of a 0.591 *M* chloroform solution of perbenzoic acid cooled in ice. An immediate reaction occurred, the chloroform boiling momentarily. After standing overnight in the refrigerator, the solution was washed twice with a 10% sodium hydroxide solution, then once with water and dried over sodium sulfate. The chloroform was now evaporated on the steam-bath through an efficient column under aspirator vacuum. The crude epoxide residue was reduced directly with lithium aluminum hydride.

A 100-g. quantity of purified tetrahydrofuran and 3 g. of lithium aluminum hydride were placed in a 300-ml. round-bottom flask. A solution of the epoxide in 30 ml. of tetrahydrofuran was added, and the mixture was refluxed overnight on the steam-bath. Working up the reaction mixture led to 11.79 g. of sirupy alcohol. The crude alcohol was dissolved in 100 ml. of pyridine with 9.7 g. of phthalic anhydride and heated on the steam-bath for 3 hours. The solution was cooled, diluted with ether and washed free of pyridine with 2 *N* hydrochloric acid. The acid phthalate which was obtained by evaporation of the ether was recrystallized twice from methanol and once from acetonitrile. This gave rise to 13.0 g. of an acid phthalate, m.p. 191.5–192.7°, in the form of large transparent prisms (Table VII). A 1:2 mixture of this acid phthalate with that of VI-OH showed a small melting point depression.

From saponification of the acid phthalate with 20% potassium hydroxide and one recrystallization from a small amount of pentane, 6.76 g. of VIII-OH was obtained, m.p. 49.5–51.5° (Table VII). This alcohol gave rise to a *p*-nitrobenzoate, m.p. 100.2–101.7° (Table VII), m.p. depressed by admixture of the nitrobenzoate of VI-OH.

Saturated Acetates and Acetolyses for Infrared Analysis of Products.—The acetates were prepared in 2-g. amounts from V-VIII-OH and acetic anhydride in pyridine in the usual manner, and they were once distilled at 10 mm. pressure in a micro-still. Refractive indices and analyses of the four acetates are summarized in Table VII.

Samples of II-OBs and V-VIII-OBs were acetolyzed at 0.1 *M* concentration in a dry 0.12 *M* solution of sodium acetate in acetic acid. Except for VIII-OBs, for which the temperature was 75°, the acetolyses were carried out at 50° as described earlier. In all cases the acetolysis product (for II-OBs only the portion of the acetolysis product stable to permanganate) was treated with lithium aluminum hydride and the alcohol product was freed of accompanying hydrocarbon by chromatography on alumina and elution of the latter with pentane. The alcohol product was subsequently eluted with ether. The alcohol mixture recovered after evaporation of the ether was then reconverted into the acetate in the usual manner and the acetate mixture was once distilled at 10 mm. pressure through a micro-still before it was subjected to infrared analysis.

The percentage of hydrocarbon formed during acetolysis was known for II-OBs, V-OBs and VI-OBs from the chromatographic separations of solvolysis products described earlier. With VII-OBs, chromatography of the product from 3.91 g. of VII-OBs (48 hours at 50°) gave no residue in the first 200-ml. fraction of pentane–10% ether. Since both saturated and unsaturated hydrocarbon are eluted by pure pentane, hydrocarbon formation must be negligible during acetolysis of VII-OBs. Chromatography of the product from 6.70 g. of VIII-OBs (48 hours at 75°), gave an oily residue in the pentane fraction. By distillation through a micro-still at 10 mm. pressure there was obtained 0.16 g. of a clear oil, $n^{25}\text{D}$ 1.5371, which decolorized a dilute solution of potassium permanganate in acetone within 1 minute. The infrared spectrum was identical with that of the unsaturated hydrocarbon obtained from acetolysis of VI-OBs.

Kinetics.—The anhydrous acetic acid solvent and standard sodium acetate and perchloric acid solutions were prepared as previously described.[8,9,12] Rate measurements in acetolysis of the various bromobenzenesulfonates were carried out in the usual manner.[8,9,12]

Acknowledgments.—It is a pleasure to acknowledge many helpful discussions with members[20] of the Shell Development Co. Agricultural Research Division, dating back to 1953. We are also indebted to Drs. Richard Piccolini and Daniel Kivelson in connection with the proton magnetic resonance spectrum of the bird-cage hydrocarbon, and to Professors James McCullough, Verner Schomaker and Richard Lord for other structural and spectroscopic information.