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.

---

[24] W. H. Yanko, H. S. Mosher and F. C. Whitmore, *J. Am. Chem. Soc.*, **67**, 664 (1945).

[25] E. R. Coburn, *Org. Syntheses*, **27**, 65 (1947).

[26] K. Ziegler, *et al.*, *Ann.*, **81**, 80 (1942).

[27] J. D. Roberts, L. Urbanek and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 3049 (1949).

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

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

BY RICHARD BAIRD[2] AND S. WINSTEIN

RECEIVED OCTOBER 27, 1961

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

---

[1] Paper XL: S. Winstein and M. Battiste, *J. Am. Chem. Soc.*, **82**, 5244 (1960); paper XLI: S. Winstein and R. L. Hansen, *Tetrahedron Letters*, **No. 25**, 1 (1960); paper XLII: S. Winstein and R. L. Hansen, *J. Am. Chem. Soc.*, **82**, 8206 (1960); paper XLIII: D. Kivelson, S. Winstein, P. Bruck and R. L. Hansen, *ibid.*, **83**, 2938 (1961); paper XLIV: S. Winstein and P. Carter, *ibid.*, **83**, 4485 (1961); paper XLV: J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, in press.

[2] National Science Foundation Predoctoral Fellow, 1953–1955, 1956–1957. Present address: Dept. of Chem., Yale University, New Haven, Conn.

[3] (a) S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956); (b) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957).

[4] For similar symbolism in the case of neighboring functional groups, see F. L. Scott, R. E. Glick and S. Winstein, *Experientia*, **13**, 183 (1957).

[5] S. Winstein and R. Baird, *J. Am. Chem. Soc.*, **79**, 756 (1957).

[6] (a) L. F. Fieser and V. Desreux, *ibid.*, **60**, 2255 (1938); (b) L. F. Fieser and E. B. Hershberg, *ibid.*, **58**, 2314 (1936).

[7] E. L. Martin, *ibid.*, **58**, 1440 (1936).

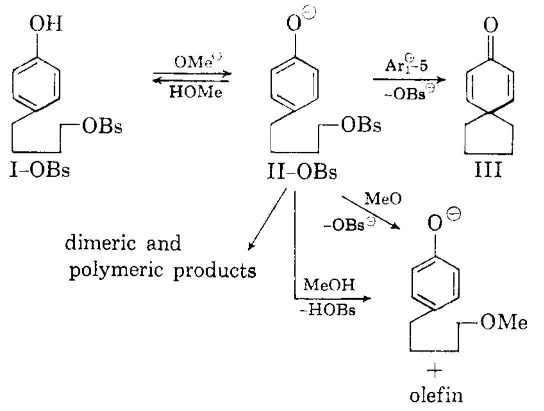
TABLE I

SUMMARY OF SOLVOLYSIS RATE CONSTANTS FOR *p*-SUBSTITUTED 4-PHENYL-1-BUTYL *p*-BROMOBENZENESULFONATES

p-Substituent	Solvent	Temp., °C.	[ROBs], 10^2 *M*	Added base	Concn., 10^2 *M*	10^5k, sec.$^{-1}$
HO	HCOOH	75.0	2.99	LiOCHO	3.35	$7.2^{a,b}$
HO	HCOOH	75.0	3.01	LiOCHO	6.96	$7.4^{a,c}$
H	MeOH	50.0	3.03	......	..	1.019 ± 0.004
CH_3O	MeOH	50.0	2.90	......	..	$1.076 \pm .005$
HO	MeOH	50.0	3.11	......	..	$1.104 \pm .006$
HO	MeOH	50.0	3.16	$NaOCH_3$	3.16	$8.3^{a,d}$
HO	MeOH	50.0	1.58	$NaOCH_3$	3.16	$8.9^{a,e}$
HO	MeOH	50.0	3.58	$NaOCH_3$	7.16	$15.4^{a,f}$
HO	MeOH	50.0	3.00	$NaOCH_3$	18.47	$30.8^{a,g}$
HO	*t*-BuOH	50.0	2.04	KOBu-*t*	2.38	49.2 ± 0.8
HO	*t*-BuOH	50.0	0.504	KOBu-*t*	0.992	49.5 ± 1.9
HO	*t*-BuOH	50.0	0.447	KOBu-*t*	0.498	49.9 ± 1.4
HO	*t*-BuOH	25.0	2.05	KOBu-*t*	2.38	4.16 ± 0.03

[a] Extrapolated initial rate constant. [b] Integrated rate constant drifts from 6.6 at 15% to 5.2 at 91% reaction. [c] Integrated rate constant drifts from 7.3 at 12% to 5.4 at 90% reaction. [d] Instantaneous value is 4.8 at 69% reaction. [e] Instantaneous value is 7.1 at 89% reaction. [f] Instantaneous value is 8.6 at 82% reaction. [g] Instantaneous value is 28.1 at 97% reaction.

aluminum hydride provided 4-*p*-anisyl-1-butanol, and this was converted to the *p*-bromobenzenesulfonate.[3b,8]



Cleavage of the 4-*p*-anisylbutanoic acid with hydrobromic acid according to Fieser[9] provided 4-*p*-hydroxyphenylbutanoic acid. Reduction of the latter with lithium aluminum hydride under vigorous conditions provided 4-*p*-hydroxyphenyl-1-butanol (I-OH). Although 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate (I-OBs) could be obtained in fair yield directly from 4-*p*-hydroxyphenyl-1-butanol, the best route to this ester was from 4-*p*-hydroxyphenylbutanoic acid. Treatment of this material with an excess of dihydropyran and a trace of acid, followed by reduction with lithium aluminum hydride, led to 4-[*p*-(2-tetrahydropyranoxy)-phenyl]-1-butanol. This compound was converted to the *p*-bromobenzenesulfonate ester in the usual manner, and then the pyranyl group was removed by gentle acid hydrolysis.

Ar_1-5 Participation.—In searching for $Ar_1^{\ominus}$-5 participation, a combination of kinetic measurements and product examination was employed. In the kinetic exploration for $Ar_1^{\ominus}$-5 participation it was necessary to know the behavior of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate (I-OBs) in neutral solvolysis. Pertinent solvolysis rate constants for this compound and two related ones are summarized in Table I.

In formic acid solvent, the first-order solvolysis rate constant of I-OBs drifted down in a run, but this is most logically ascribed to esterification of the phenolic group which converts I-OBs to a less reactive derivative. The drift is not due to partial reaction of I-OBs by way of the phenoxide ion II-OBs or to reaction involving formate ion attack, since the initial, instantaneous first-order formolysis rate constant was insensitive to the concentration of added lithium formate. Using the initial rate constant for I-OBs, the relative formolysis rates of the *p*-hydroxy, *p*-methoxy and unsubstituted 4-phenyl-1-butyl *p*-bromobenzenesulfonates at 75° are in the sequence 2.13:1.77:1.00 (Table II). Formolysis of the 4-phenyl-1-butyl ester proceeds *ca.* 19% by the Ar_1-5-assisted route,[3b] and the *p*-methoxy derivative *ca.* 54% by this route.[3b] With the *p*-hydroxy ester I-OBs, Ar_1-5 participation is apparently slightly more important in formolysis than it is in the *p*-methoxyl case.

TABLE II

RELATIVE RATES OF SOLVOLYSIS OF *p*-SUBSTITUTED 4-PHENYL-1-BUTYL *p*-BROMOBENZENESULFONATES

p-Substituent	Relative rates HCOOH, 75°	Relative rates MeOH, 50°
H	1.00^a	1.00
CH_3O	1.77^a	1.06
HO	2.13	1.08

[a] Based on data of Heck.[3b]

In methanol in the absence of added base, the 4-*p*-hydroxyphenyl-, 4-*p*-anisyl- and 4-phenyl-1-butyl *p*-bromobenzenesulfonates solvolyze with nearly identical rate constants (Tables I and II). In the relatively nucleophilic methanol solvent, Ar_1-5-assisted ionization[3b] is essentially negligible in all three cases.

Kinetic Search for $Ar_1^{\ominus}$-5 Participation.—As shown in Table I, the rate of methanolysis of the 4-*p*-hydroxyphenyl-1-butyl ester I-OBs is markedly increased by addition of sodium methoxide. However, the $Ar_1^{\ominus}$-5-assisted reation of the phenoxide ion II-OBs is not the only process which is

---

(8) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956).

(9) L. F. Fieser, M. T. Leffler, *et al.*, *ibid.*, **70**, 3196 (1948).

taking place, since it would be expected to exhibit first-order kinetics. Instead, first-order rate constants depended on the added sodium methoxide concentration and also drifted down in a run. At high sodium methoxide concentrations it is evident that a higher order (presumably second-order) process is dominating, but at the lower base concentrations the initial rates are too high to be explained in this way. An additional complication occurs at low base concentrations, due to the incomplete conversion of the phenol to the phenoxide ion. Measurements of the equilibrium constant for this process, using the closely related phenol, 2-*p*-hydroxyphenylethanol,[10] indicate, however, that the phenol is initially at least 90% in the form of the phenoxide ion even at the lowest base concentrations.

While the data for basic methanol suggest that $Ar_1^{\ominus}$-5 participation is developed by addition of sodium methoxide, they also show that at no concentration of added base could the $Ar_1^{\ominus}$-5-assisted process be made dominant by a large factor over both unassisted solvolysis and reaction involving methoxide ion attack.

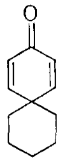
The situation in *t*-butyl alcohol as solvent is more favorable for $Ar_1^{\ominus}$-5 participation. In this solvent, good first-order kinetics, dependent only on the concentration of the phenoxide ion, are observed with 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate. The rate is independent of the base concentration, as long as sufficient *t*-butoxide is used to convert the phenol to the phenoxide ion. In basic *t*-butyl alcohol the observed first-order rate constant (Table I) is *ca.* fifty times as great as the solvolysis rate constant in neutral methanol at the same temperature. Since *t*-butyl alcohol is a poorer ionizing solvent than is methanol,[11] the unassisted as well as Ar_1-5-assisted solvolysis rates of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate in *t*-butyl alcohol would be expected to be less than those in absolute methanol. Thus it is clear that $Ar_1^{\ominus}$-5-assisted reaction of I-OBs is very dominant in basic *t*-butyl alcohol.

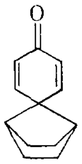
Product Isolation.—Using the kinetic data as a guide to the conditions favorable for $Ar_1^{\ominus}$-5 participation, the non-phenolic products of basic solvolysis of bromobenzenesulfonate I-OBs in both methanol and *t*-butyl alcohol were examined. From both solvents there was obtained a neutral product which led to a white crystalline solid, m.p. 34–35°, on recrystallization from pentane at low temperatures. The yield of this material was 20% from methanol and as high as 50–60% from *t*-butyl alcohol.

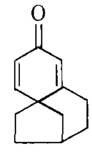
The following chemical evidence showed the above compound to be spiro-(4,5)-deca-1,4-diene-3-one[5] (III). It showed the correct carbon–hydrogen analysis for $C_{10}H_{12}O$. Also, it reacted with 2,4-dinitrophenylhydrazine and with semicarbazide to give a red 2,4-dinitrophenylhydrazone, $C_{16}H_{16}O_4N_4$, and a semicarbazone, $C_{11}H_{15}ON_3$, respectively. Quantitative hydrogenation of the compound over reduced platinum oxide required 2.04 ± 0.04 moles of hydrogen and led to a new ketone whose 2,4-dinitrophenylhydrazone showed the correct carbon–hydrogen analysis for the derivative of the tetrahydro ketone, $C_{16}H_{20}O_4N_4$. Finally, the compound underwent dienone–phenol rearrangement[12] to give an almost quantitative yield of authentic 5,6,7,8-tetrahydro-2-naphthol.

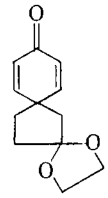
The structure of the neutral compound, m.p. 34–35°, was further verified by spectral evidence. Thus the infrared spectrum of the compound exhibited strong absorption maxima in chloroform solution at 1594, 1617, 1655 and 1707 $cm.^{-1}$, which is consistent with an α,β–α',β'-unsaturated carbonyl structure.[13] The ultraviolet absorption spectrum exhibited an absorption maximum in methanol at 242 $m\mu$ with ϵ equal to 16,000 (log ϵ 4.21). The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone, $C_{16}H_{16}O_4N_4$, possessed absorption maxima at 390, 253 and 223 $m\mu$ in methanol with log ϵ 4.53, 4.21 and 2.92, respectively. Dreiding[14a] has reported a maximum at 242.5 $m\mu$ in ethanol with log ϵ equal to 4.2 for the closely related spiro-(5,5)-undeca-1,4-diene-3-one (IV). The corresponding 2,4-dinitrophenylhydrazone possessed λ_{max} equal to 391 $m\mu$ (EtOH) (log ϵ 4.53). The infrared maxima of Dreiding's dienone are reported as 1664, 1623 and 1600 $cm.^{-1}$, in close agreement with ours. Burnell and Taylor[15] had previously reported λ_{max} equal to 235 $m\mu$ for dienone IV, but failed to specify the solvent used.

The present work shows that $Ar_1^{\ominus}$-5-assisted ionization of suitable substrates, such as the 4-*p*-hydroxyphenyl-1-butyl arenesulfonate I-OBs, can provide a useful synthetic route to spiro-dienones. Since our first report[5] of the preparation of dienone III in this way, several other dienones, such as IV,[14a] V,[14b] VI[14c] and VII[14d] have been prepared similarly.


IV


V


VI


VII

Ar_1-5 Intermediates.– There is evidence[3] that spiro-cationic intermediates such as IXa and IXb are involved in solvolyses of certain 4-*p*-anisyl-1-butyl derivatives (VIII). Some of the evidence is quite direct; for example, with VIIIb, reaction by way of the spiro-cation IXb leads to rearranged tetralin Xb. With VIIIa the evidence for the spiro-cation IXa is less direct. In interpreting the solvolysis of 4-anisyl-1-butyl *p*-bromobenzenesulfonate (VIIIa) previously,[3] the assumption was

---

(10) The equilibrium constant for this phenol will be reported in a subsequent paper.

(11) The **Y**-values for methanol and *t*-butyl alcohol are −1.090 and −3.26, respectively; A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

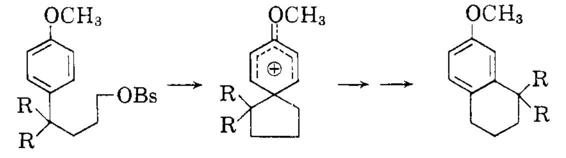
(12) A. L. Wilds and C. Djerassi, *ibid.*, **68**, 1715 (1946).

(13) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1954, p. 118.

(14) (a) A. S. Dreiding, *Helv. Chim. Acta.*, **40**, 1812 (1957); (b) R. Barner, A. S. Dreiding and H. Schmid, *Chemistry and Industry*, 1437 (1958); (c) S. Masamune, *J. Am. Chem. Soc.*, **83**, 1009 (1961); (d) S. Dorling and J. Harley-Mason, *Chemistry and Industry*, 1551 (1959).

(15) R. H. Burnell and W. I. Taylor, *J. Chem. Soc.*, 3486 (1954).

made that the spiro-cation IXa gave rise only to tetralin Xa and not to any open chain products.

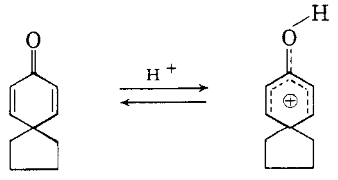


VIIIa, R = H
b, R = CH_3

IXa, R = H
b, R = CH_3

Xa, R = H
b, R = CH_3

An intermediate XI analogous to IXa can be independently obtained from the dienone III which is derived *via* $\mathrm{Ar}_1^{\ominus}$-5 participation. Thus, addition of a proton to the carbonyl oxygen atom of dienone III gives XI which is like IXa except for a hydrogen atom instead of a methyl group on oxygen. In this instance the spiran structure is pre-formed, and it is possible to determine whether tetralin is, in fact, formed from the spiro-cation and whether any ring opening occurs.



III

XI

When authentic spiro-(4,5)-deca-1,4-diene-3-one (III) was treated in buffered formic acid for one half-life of the parent bromobenzenesulfonate I-OBs, a yield in excess of 95% of authentic 5,6,7,8-tetrahydro-2-naphthol was isolated from the reaction mixture. Since the open chain products from the solvolysis of 4-*p*-anisyl-1-butyl derivatives have been shown not to cyclize under the reaction conditions,[16] the tetrahydronaphthol must have come from rearrangement of the dienone. It seems clear that spiro-cation XI leads essentially exclusively to the substituted tetralin and negligibly to open-chain products. This result serves to confirm the previous assumption[3] regarding the behavior of the related spiro-cation IXa.

Experimental

4-*p*-Anisylbutanoic acid was prepared from succinic anhydride, anisole and aluminum chloride *via* 3-*p*-anisoylpropanoic acid by the procedures of Fieser[6] and Martin.[7] The acid, b.p. 194–195.5° (9.9 mm.), m.p. 56–6.5°, was obtained in 78.5% yield from anisole.

4-*p*-Anisyl-1-butanol[3a] was prepared in 93% yield by lithium aluminum hydride reduction of the above acid; b.p. 160–160.9° (8 mm.), $n^{25}\mathrm{D}$ 1.5248, m.p. 3.0–4.0°.

4-*p*-Anisyl-1-butyl *p*-Bromobenzenesulfonate.—Preparation of this substance was carried out by the low temperature method.[8] This provided the *p*-bromobenzenesulfonate in 62% yield, m.p. 41.5–43.5° (ether–pentane), reported[3b] m.p. 43–45°.

4-*p*-Hydroxyphenylbutanoic acid was prepared from 4-*p*-anisylbutanoic acid by the method of Fieser.[9] This procedure gave rise to the desired acid in 64% yield from anisole; m.p. 106–108°, reported[9] m.p. 107–108°.

4-*p*-Hydroxyphenyl-1-butanol.—Reduction of 4-*p*-hydroxyphenylbutanoic acid with 1.5 moles of lithium aluminum hydride for 24 hours was unsuccessful, due to the formation of an insoluble salt. When a large excess of the hydride was used (4:1 molar ratio) with a longer reflux period, the acid was reduced in 92% yield. Addition of 166 g. of the acid in 1500 ml. of anhydrous ether to a slurry of 115 g. of lithium aluminum hydride in 1000 ml. of dry ether and refluxing for one week yielded 141 g. of 4-*p*-hydroxyphenyl-1-butanol, b.p. 144–146° (0.5 mm.), m.p. 55.5–58.0°. A small portion purified for analysis by sublimation melted at 56.5–57.8°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.27; H, 8.49. Found: C, 72.18; H, 8.75.

4-*p*-Hydroxyphenyl-1-butyl *p*-Bromobenzenesulfonate. From 4-*p*-Hydroxyphenyl-1-butanol.—A solution of 25 g. of 4-*p*-hydroxyphenyl-1-butanol in 300 ml. of Karl Fischer grade pyridine was cooled to −30° and to this was added 50 g. of Eastman Kodak white label *p*-bromobenzenesulfonyl chloride. After the chloride had dissolved, the solution was warmed up to 0° for 60 minutes, and the solution then poured into a large excess of ice-water. The oil was taken up in ether and the aqueous solution extracted once more with ether. The combined extracts were washed in the usual way and the bulk of the solvent was removed on the steam-bath, the remainder being taken off under reduced pressure.

When the resulting oil was dissolved in methylene chloride-hexane, it usually crystallized partially after 1–2 weeks in the ice-box.

When the oil was dissolved in 300–400 ml. of methanol, treated with charcoal at 0° for a few minutes and then filtered and diluted with ice-water until a second phase appeared, seeding with the above crystals usually induced extensive crystallization in *ca.* 24 hours at 0°. Filtration of the pasty solid obtained gave a material which when dissolved in methylene chloride and dried with magnesium sulfate crystallized readily on the addition of hexane to the point of oiling and seeding. A second recrystallization yielded long prisms, m.p. 59.5–61.5°, in 50% yield. This compound was completely soluble in 5% sodium hydroxide and was reprecipitated (as an oil) by carbon dioxide.

Anal. Calcd. for $C_{16}H_{17}O_4SBr$: C, 49.88; H, 4.45. Found: C, 49.74; H, 4.40.

From 4-*p*-Hydroxyphenylbutanoic Acid.—To a solution of 362 g. of Matheson, Coleman and Bell dihydropyran and 10 drops of concd. sulfuric acid in 350 ml. of anhydrous ether was added 155 g. of 4-*p*-hydroxyphenylbutanoic acid, and the solution was allowed to stand overnight at room temperature. This solution was then added over 1.5 hours to a slurry of 41 g. of lithium aluminum hydride in 1 liter of anhydrous ether, and the solution stirred under reflux for about 2.5 hours more. This solution was then treated with 82 ml. of water and 66 ml. of 10% sodium hydroxide according to the procedure of Leonard.[17] The resulting ether solution was concentrated to about 800 ml. and then washed several times with very dilute (*ca.* 1%) potassium hydroxide solution, and dried over a mixture of magnesium sulfate and potassium carbonate.

The oil resulting upon removal of the solvent was dissolved without further purification in 800 ml. of Karl Fischer grade pyridine, cooled to −20°, and treated with 286 g. of Eastman Kodak white label *p*-bromobenzenesulfonyl chloride by the low temperature method.[8] The product was isolated by pouring the mixture into ice-water and inducing it to crystallize. The solid was filtered with suction and washed thoroughly with water and then dried in vacuum over potassium hydroxide. Recrystallization from ether–pentane afforded the pyranyl ether of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate, m.p. 57–60°, in 77% yield.

The bulk of the above product (304 g.) was slurried in 2.5 liters of methanol and treated with a cooled mixture of 200 ml. of concentrated sulfuric acid and 400 ml. of water. This mixture was seeded with 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate and allowed to stand overnight in the ice-box. By this time most of the material had crystallized and water was added at intervals to bring out the rest, the final volume of solution being *ca.* 5 liters. The solid was washed with water and immediately dissolved in about 1500 ml. of methylene chloride. This solution was washed thoroughly with saturated sodium bicarbonate solution, dried and the product crystallized by the addition of hexane. The *p*-hydroxyphenylbutyl *p*-bromobenzenesulfonate, m.p. 59.3–61.7°, was obtained in 68% yield from 4-*p*-hydroxyphenylbutanoic acid.

---

(16) R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3108 (1957).

(17) N. J. Leonard, S. Swan, Jr., and J. Figueras, Jr., *J. Am. Chem. Soc.*, **74**, 4622 (1952).

5,6,7,8-Tetrahydro-2-naphthol was prepared from 2-naphthol by the method of Bamberger and Kitschalt.[18] The tetrahydronaphthol, m.p. 59.0–60.3°, $n^{25}\text{D}$ 1.5710 (supercooled), when mixed with 4-*p*-hydroxyphenyl-1-butanol, m.p. 56.5–57.8°, was liquid at room temperature.

Kinetic Measurements.—Anhydrous formic acid was prepared from J. T. Baker analyzed 98–100% formic acid. The water content, determined by density measurements, was between 0.10 and 0.14% by weight. Dioxane was purified according to Fieser.[19] Perchloric acid in dioxane was prepared by addition of the calculated amount of Merck 60% perchloric acid to purified dioxane, the solution being standardized against sodium acetate in acetic acid which in turn had been prepared by addition of a weighed amount of J. T. Baker analyzed, ACS reagent grade sodium carbonate to redistilled acetic acid. Lithium formate in anhydrous formic acid was prepared by addition of a weighed amount of anhydrous lithium formate, prepared by Arnold Fainberg, to purified formic acid, and was then standardized against the perchloric acid in dioxane. Brom cresol green was used as an indicator and the procedures used in the kinetic runs were those previously employed.[8]

Absolute methanol was prepared from J. T. Baker analyzed absolute methanol by treatment with magnesium turnings according to Lund and Bjerrum.[20] The water content, as determined by Karl Fischer titration, was 0.004% by weight. Standard solutions of sodium hydroxide and of *p*-toluenesulfonic acid in methanol were prepared by addition of the appropriate amounts of carbonate-free saturated sodium hydroxide solution and of Eastman Kodak white label *p*-toluenesulfonic acid monohydrate to absolute methanol. The sodium hydroxide solution was standardized against Mallinckrodt ACS potassium acid phthalate in a predominantly aqueous medium using phenolphthalein as the indicator, and the *p*-toluenesulfonic acid standardized against this base in the presence of excess ethanol using brom phenol blue as an indicator. When excess 4-*p*-hydroxyphenyl-1-butanol was added to the sodium hydroxide–*p*-toluenesulfonic acid titration, no detectable shift in end-point color or position was observed. Titrations in this system with phenoxides present therefore proceeded to the free phenol stage, so that phenoxide was indistinguishable from methoxide.

Sodium methoxide in absolute methanol for the kinetic measurements was made by dissolving the appropriate amounts of sodium metal, pre-washed with anhydrous methanol, in the requisite amount of the anhydrous methanol. These solutions were standardized by pipetting aliquots into an excess of standard *p*-toluenesulfonic acid in methanol and back titration of the excess acid with the standard sodium hydroxide in methanol using brom phenol blue as before. These were the same conditions as were used for the aliquots taken in the kinetic measurements, the *p*-toluenesulfonic acid solution being used as a quench for the reaction.

All of the above standard solutions were stable over a period of months and were checked at intervals.

t-Butyl alcohol was purified by distillation of Braun Co. *t*-butyl alcohol over sodium. Potassium *t*-butoxide in *t*-butyl alcohol was prepared in the same manner as was sodium methoxide in methanol. The titration techniques were identical to those used above, except that pipets had to be calibrated especially for *t*-butyl alcohol because of its high viscosity.

Kinetic runs were carried out in volumetric flasks at 25.00° or in sealed ampoules at 50.00° and 75.00°, except for the measurements in *t*-butyl alcohol at 50°. These rates were too fast to be quenched adequately at 25°, and the use of lower temperatures froze the *t*-butyl alcohol. For these measurements the rates were run in stoppered volumetric flasks at 50.0°, and aliquots quickly pipetted at room temperature in such a way that the pipet did not warm up. This procedure reduced the precision of the measurements somewhat, especially at the late points because of exposure to carbon dioxide in the air each time the flask was opened.

Product Isolation.—In 200 ml. of absolute methanol containing 0.03156 *M* sodium methoxide was dissolved an equal number of moles (2.4318 g.) of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate. This mixture was maintained at 50.0° for 40 hours. It was then cooled and diluted with an equal volume of pentane. The solution was poured into 800 ml. of an ice–water mixture, the pentane layer separated and the aqueous solution extracted 20 more times with pentane. The combined pentane extracts were washed with water, with 1% sodium hydroxide solution and with saturated salt solution, then dried over magnesium sulfate. The pentane was distilled through a 12-inch Vigreux column and the product purified by sublimation in vacuum at 100°. This sublimate was recrystallized from pentane at −70° to give white needles, m.p. 33.8–35.0°, in *ca.* 20% yield.

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 80.81; H, 8.21.

The compound possessed an absorption maximum in the ultraviolet at 242 mμ (ϵ 16,000). It gave a red 2,4-dinitrophenylhydrazone, m.p. 140.5–143.5°, $\lambda_{\max}$ (MeOH) 390, 253 and 223 mμ (log ϵ 4.53, 4.21 and 2.92, respectively).

Anal. Calcd. for $C_{16}H_{16}O_4N_4$: C, 58.53; H, 4.91. Found: C, 58.63; H, 5.08.

In 995 ml. of 0.0253 *N* potassium *t*-butoxide in anhydrous *t*-butyl alcohol was dissolved 7.71 g. of 4-*p*-hydroxyphenyl-1-butyl *p*-bromobenzenesulfonate, and the solution was held for 5 hours at 50.0°. The solution was then diluted with 1 liter of pentane and poured into *ca.* 3 liters of a mixture of ice and water. The pentane was separated and the solution extracted 4 more times with pentane and then twice with 50% pentane–ether. The combined extracts were washed 3 times with water and then dried with magnesium sulfate. The bulk of the solvent was distilled through a Vigreux column until the boiling point rose to about that of *t*-butyl alcohol. The residue was dissolved in ether and washed 3 times more with water, re-dried and the solvent removed on the steam-bath, the last traces being taken off under reduced pressure. The product, b.p. 83.5–85.0° (1.3 mm.), obtained in 50% yield (a high boiling residue remaining in the pot), crystallized on standing; m.p. 35–36.2°. Recrystallized from pentane, the product, m.p. 35.5–36.5°, was identical in all respects with that obtained from methanol. In addition to the red 2,4-dinitrophenylhydrazone, it formed a semicarbazone, m.p. 224–225.5° dec.

Anal. Calcd. for $C_{11}H_{15}ON_3$: C, 64.36; H, 7.37. Found: C, 64.56; H, 7.19.

Dienone–Phenol Rearrangement of spiro-(4,5)-Deca-1,4-diene-3-one in Formic Acid.—In 113 ml. of anhydrous formic acid containing 0.03349 *M* lithium formate was dissolved 0.4981 g. of the dienone isolated from *t*-butyl alcohol, and the solution was then heated at 75° for 2.8 hours in a flask protected from moisture. The solution was then cooled and the formic acid was distilled at reduced pressure keeping the pot temperature at or below 40°.

When all of the acid had been removed, the residue was dissolved in dry ether and filtered through glass wool to remove most of the salts. The flask and salts were washed with dry ether and the combined ether solutions were treated with 1.1 g. of lithium aluminum hydride and allowed to stand overnight. The excess hydride was discharged with ethyl acetate, followed by water and then 40% hydrochloric acid, and the product isolated by extraction with ether. Distillation at reduced pressure provided an oil which yielded a *ca.* 100% yield of 5,6,7,8-tetrahydro-2-naphthol, m.p. 56–60° (without recrystallization), when seeded with a minute seed of the naphthol. The melting point of a mixture of the product with authentic 5,6,7,8-tetrahydro-2-naphthol was undepressed (58–60.5°). Recrystallization of 0.46 g. of the product from hexane gave 0.40 g. of material with m.p. 60.5–61.0°.

Quantitative Hydrogenation of Spiro-(4,5)-deca-1,4-diene-3-one.—When 0.1008 g. of spiro-(4,5)-deca-1,4-diene-3-one, dissolved in 18 ml. of absolute *t*-butyl alcohol, was hydrogenated in the presence of reduced platinum oxide, 2.04 ± 0.04 moles of hydrogen was rapidly absorbed. The catalyst was removed by filtration and the solvent distilled through an 18-inch Podbielniak column. The residue was converted to a 2,4-dinitrophenylhydrazone, orange in color, m.p. 161.9–162.8°, 0.11 g. being obtained. In the ultraviolet the 2,4-dinitrophenylhydrazone possessed $\lambda_{\max}$ (MeOH) 363 and 229 mμ, with ϵ 22,500 and 17,000, respectively.

Anal. Calcd. for $C_{16}H_{20}O_4N_4$: C, 57.82; H, 6.07. Found: C, 57.93; H, 6.11.

---

[18] E. Bamberger and M. Kitschalt, *Ber.*, **23**, 885 (1890).

[19] L. F. Fieser, "Experiments in Organic Chemistry," 2nd Edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.

[20] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).