or borate buffers do not interfere with color development. At concentrations equivalent to that of the substrate, neither N,N-dimethylbenzamide nor a mercaptan (thioglycolic acid) contribute to or reduce the absorbance at 540 mμ.

**D. Ethyl Thiolbenzoate.** On completion of the hydrolysis of II (65 hr), calculation of the yield of thiol ester was made from the absorbance of reaction mixtures at 270 mμ, using molar extinction coefficients of 7700 (for methyl thiolbenzoate) and 560 (for benzamide).

**E. Spectral Analysis.** Complete ultraviolet spectra of reaction mixtures were taken on completion of the hydrolysis of each thioimidate under a variety of conditions. These spectra were compared to those of synthetic mixtures whose composition was based on the results of the above-described analyses for amine or thioester product. In general, only products expected to contribute significantly to the ultraviolet spectrum were included in the synthetic mixture. In all cases, the final spectrum of the reaction mixture agreed closely with that of the reconstituted product mixture. Some examples are (a) hydrolysis of I at pH 2.5 (HCl) and 6.2 (three different concentrations of phosphate buffer) and comparison with mixtures of ethyl thiolacetate and acetamide; (b) hydrolysis of II at pH 2.3 and 4 and comparison with mixtures of methyl thiolbenzoate and benzamide (after reaction of II at pH 9.0, the spectrum of the products was nearly identical with that of benzonitrile); (c) hydrolysis of III at pH 4.1 and comparison with a mixture of butyranilide and ethyl thiolacetate; (d) hydrolysis of IV at pH 10.0, followed by acidification to pH 3. The final spectrum was superimposable on that of N,N-dimethylbenzamide [no maximum at >220 mμ; ($\epsilon_{225}$ 8000)].

**Determination of Constants by Computer Analysis. A. Kinetic Measurements.** The best values of the constants $k_1$, $(k_3 + k_5)/k_2$, and $K_1$ for the hydrolyses of I, II, and III were obtained by a least-squares fit of the observed rate constants (corrected for hydroxide-catalyzed reactions) to eq 1 using an IBM 7094 computer. The program used (DBELL) is based on the iterative procedures discussed by Cleland.[38]

**B. Product Analysis.** Plots of the yield of amine (or thiol ester) as a function of buffer concentration (Figure 3) are rectangular hyperbolas characterized by three constants: the yield at zero buffer concentration (intercept on the *y* axis), the yield at infinite buffer concentration, and $K_{\text{app}}$ (the concentration of buffer required to achieve half of the maximum possible increase in yield). Least-squares values of these constants were obtained by two procedures. The first made use of a fit to the two-parameter hyperbola with zero intercepts, according to Bliss and James.[39] If a buffer is available which does not affect product yield, then the influence of other catalysts may be studied in the presence of the unreactive buffer. In that event, product yield in presence of the unreactive buffer may be taken as the yield at zero catalyst concentration. This situation was approached in a few experiments only (Table II, experiments 3–5) since most buffers had significant effects on the product distribution. When the *Y* intercept was not known, the best value of the yield at zero catalyst concentration was taken as that (assumed) value which gave the best fit of the data to a rectangular hyperbola.

The second procedure employed a program written for the three-parameter hyperbola (program HYPREPLT).[38] Least-squares values of the three desired constants were obtained directly and agreed closely with those determined by the first method.

The theoretical curves of Figure 4 were also calculated by use of program HYPREPLT which yielded the apparent p*K* of the sigmoid curves as well as the yields of product approached asymptotically at high and low pH.

**Acknowledgment.** We are grateful to Mrs. Madeline F. Baer for excellent assistance.

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(38) W. W. Cleland, *Nature*, **198**, 463 (1963). We are grateful to Professor Cleland, of the University of Wisconsin, for providing us with this program.

(39) C. I. Bliss and A. T. James, *Biometrics*, 22, 573 (1966). We are indebted to Dr. K. R. Hansen, of the Connecticut Agricultural Experiment Station, for the use of this program.

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# Unsaturated Neopentyl Compounds. Homoallenyl Participation in the Acetolysis of 2,2-Dimethyl-3,4-pentadienyl *p*-Bromobenzenesulfonate[1a]

**Robert S. Bly,[1b] A. R. Ballentine,[1c] and Soon U. Koock[1b]**

*Contribution from the Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208.* *Received April 12, 1967*

**Abstract:** The acetolysis of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate is about 1200 times as rapid at 75° as that of 2,2-dimethylpentyl *p*-bromobenzenesulfonate and yields a mixture containing ~12% 2-methyl-1,4,5-hexatriene, ~11% 2-methyl-2,4,5-hexatriene, and 77% 2-methyl-4,5-hexadien-2-yl acetate. Similarly, the solvolysis of the unsaturated brosylate in 95% ethanol at 75° is about 1500 times as rapid as that of the saturated brosylate and yields a mixture comprised of 5% hydrocarbons and 95% 2-methyl-4,5-hexadien-2-yl ethyl ether. A Taft–Streitwieser treatment is used to estimate that participation of the homoallenyl group enhances the acetolysis rate of the unsaturated brosylate by a factor of 8300–58,000 times at 75°. The increased participation of homoallenyl compared to homoallyl is attributed largely to the decreased stability of its ground state. The failure of solvolyzing 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate to produce cyclic products probably results from the effect of the *gem*-dimethyls which stabilize the acylic cation, dimethyl-2,3-butadienylcarbonium ion, with respect to the cyclic α-(2,2-dimethylcyclopropyl)vinyl cation.

Although the chemical literature is replete with examples of participation by isolated olefinic double bonds in both the rate- and product-determining steps of solvolytic displacement reactions,[2] there appear

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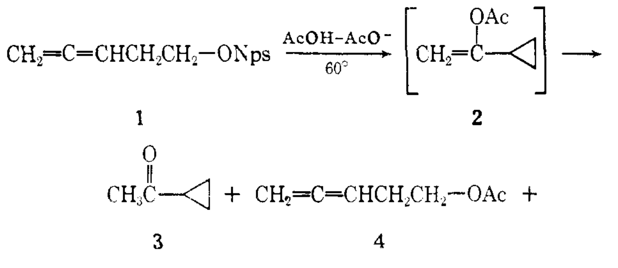
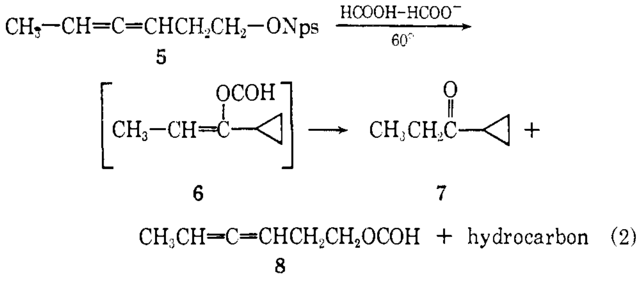
(1) (a) Portions of this work have been presented before the Southeast–Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2–4, 1965, Abstracts, p 46; at the 39th Annual Meeting of the South Carolina Academy of Science, Clinton, S. C., April 22–23, 1966 [*Bull. S. Carolina Acad. Sci.*, 28, 45 (1966)], and at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 11–16, 1966, Abstract S042; (b) to whom all correspondence should be addressed at the Department of Chemistry, the University of South Carolina; (c) Summer Research Participant at the University of South Carolina from the Department of Chemistry, The Citadel.

(2) For recent reviews, see (a) P. D. Bartlett, *Ann.*, **653**, 45 (1962); (b) J. A. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 192 ff; (c) B. Capon, *Quart. Rev.* (London), 18, 45 (1964); (d) M. J. S. Dewar and A. P. Marchand, *Ann. Rev. Phys. Chem.*, **16**, 321 (1965).

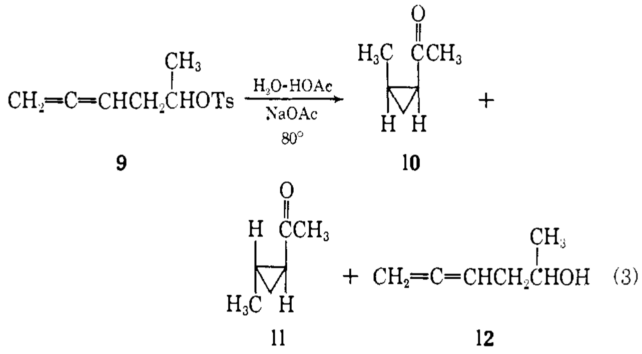
to be but two reports of allenic double bond participation. Hanack and Häffner[3] have examined the solvolyses of several primary 3,4-pentadienyl derivatives and find that the reaction mixtures usually contain a considerable amount of alkyl cyclopropyl ketone in addition to some unrearranged material and one or more hydrocarbons. For example, they report[3b] that the solvolysis for 12 days at 60° of a 0.20 *M* solution of 3,4-pentadienyl β-naphthalenesulfonate (**1**) in "absolute" acetic acid buffered with "water-free" sodium acetate yields, after an aqueous work-up, a mixture consisting of 20% methyl cyclopropyl ketone (**3**), 61% 3,4-pentadienyl acetate (**4**), and 7 and 21%, respectively, of two unidentified materials (eq 1).

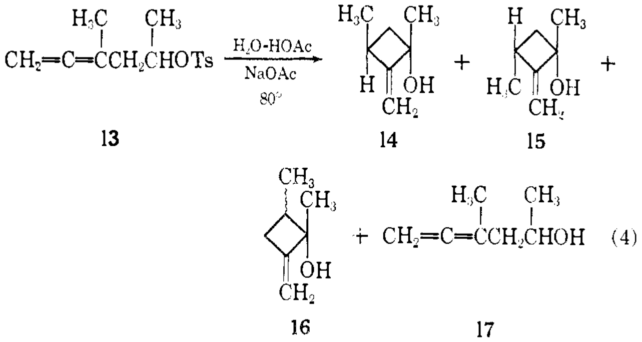


Similarly, the formolysis of 3,4-hexadienyl β-naphthalenesulfonate (**5**) is reported to produce 51% ethyl cyclopropyl ketone (**7**), 13% 3,4-hexadienyl formate (**8**), and 36% of an unsaturated hydrocarbon which was not identified (eq 2). These investigators find that



the acetolysis of **1** in unbuffered acetic acid at 60 ± 0.1° is 3.5 times as rapid as that of *n*-pentyl β-naphthalenesulfonate while **5** is 9.5 times more reactive than *n*-hexyl β-naphthalenesulfonate under similar conditions. Bertrand and Santelli[4] have investigated the hydrolysis of two homoallenic secondary tosylates in what is apparently a heterogeneous mixture of buffered, very dilute aqueous acetic acid and tosylate. They report that after 90 min at 80° 4,5-hexadien-2-yl *p*-toluenesulfonate (**9**) yields upon steam distillation a mixture comprised of ~3% hydrocarbon, 67% *cis*- and *trans*-2-methylcyclopropyl methyl ketones, **10** and **11**, respectively, and 30% 4,5-hexadien-2-ol (**12**) (eq 3). In contrast they find that under similar conditions 4-methyl-4,5-hexadien-2-yl *p*-toluenesulfonate (**13**) gives a mixture containing 17% *cis*- and 50% *trans*-1,3-dimethyl-2-methylenecyclobutanol, **14** and **15**, respectively, 17% 1,4-dimethyl-2-methylenecyclobutanol (**16**) (of unspecified stereochemistry), and 16% 4-methyl-4,5-hexadien-2-ol (**17**) (eq 4).

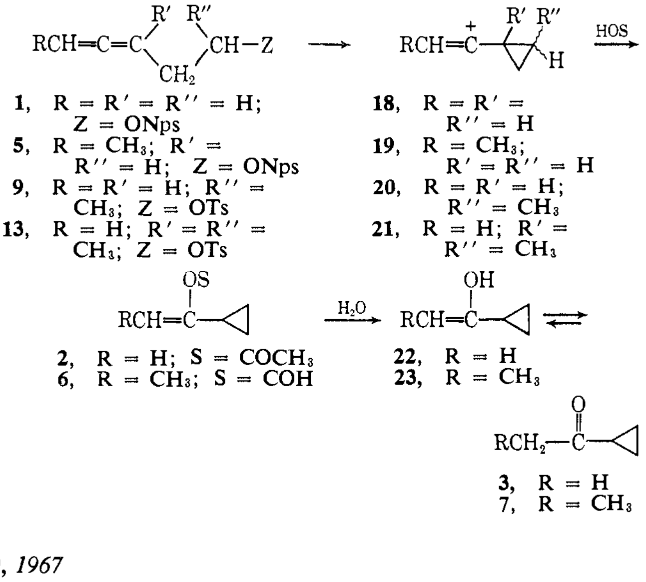




The kinetic data of Hanack and Häffner, especially when allowance is made for inductive retardation, clearly suggest homoallenic double bond participation in the rate-limiting step, but they do not provide a good quantitative estimate of the extent of such participation nor allow a meaningful comparison of the ability of a homoallyl and homoallenyl group to function in this manner. The solvolyses of these primary arenesulfonates exhibit considerable bimolecular character and hence the observed rate enhancements probably do not reflect the extent of allenic double bond participation which could occur in a truly unimolecular reaction.

The formation of nonallenic, cyclic products from the solvolysis of homoallenyl derivatives obviously involves double bond participation, but the manner in which this occurs is less apparent. Hanack and Häffner suggest the intermediacy of an enol ester such as **2** or **6** which would presumably result from the attack of solvent upon a vinyl cation (**18** or **19**) formed in the initial slow step (Scheme I), but they were able

**Scheme I**



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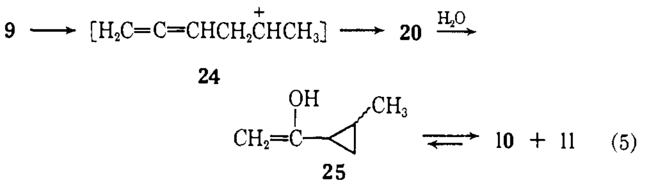
[3] (a) M. Hanack and J. Häffner, *Tetrahedron Letters*, 2191 (1964); (b) *Chem. Ber.*, **99**, 1077 (1966); (c) Professor Hanack, private communication.

[4] M. Bertrand and M. Santelli, *Compt. Rend.*, **259**, 2251 (1964).

to isolate only its hydrolysis product, an alkyl cyclopropyl ketone (**3** or **7**). Similarly, the isolation by Bertrand and Santelli of the methyl cyclopropyl ketones **10** and **11** from the hydrolysis of **9** suggests the intervention of the vinyl cation **20** and the enol **25** as reaction intermediates (eq 5), but since the unassisted ionization

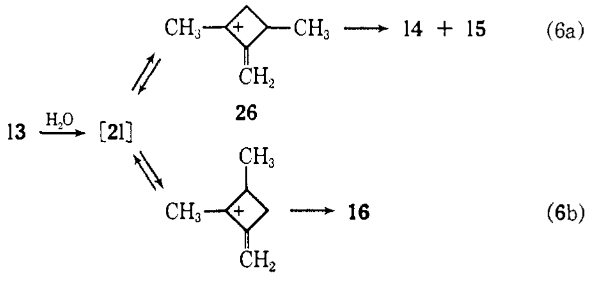


**24**

**25**

(5)

of such a secondary tosylate could produce a fairly stable cation (**24**) and because these investigators were primarily interested in the preparative aspects of the reaction and did not examine its kinetics, it is not clear that an intermediate such as **20** is actually formed in the rigid rate-limiting step. Further, the isolation of the cyclobutanols **14–16** from the hydrolysis of **13** suggests the intermediacy of the *t*-alkyl-like cyclobutyl cations **26** and **27**, but since no methyl cyclopropyl ketones were detected in this reaction it is not known whether a vinyl cation such as **21** is also involved (eq 6).



**26**

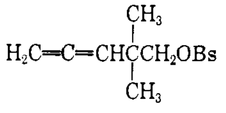
**27**

(6a)

(6b)

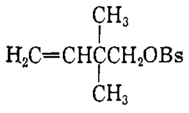
Finally, since Bertrand and Santelli evidently allowed their reaction mixtures to become acidic during work-up but do not report the stability of the products under these conditions, it is not clear that the cyclic compounds which they found result from kinetic rather than thermodynamic control.

In an effort to obtain a more realistic measure of the ability of a homoallenic double bond to participate in a solvolytic displacement reaction, we have examined the reactivity of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) in anhydrous acetic acid containing sodium acetate, in absolute ethanol buffered with pyridine, and in 50% aqueous acetone containing excess pyridine. This homoallenyl compound was chosen because of its availability,[5,6] its tendency to solvolyze in a unimolecular fashion without competing displacement, and its structural similarity to 2,2-dimethyl-3-butenyl *p*-bromobenzenesulfonate (**31**) whose acetolysis we had previously shown to occur with extensive homoallyl participation.[7]



$H_2C{=}C{=}CHC(CH_3)_2CH_2OBs$

**30**



$H_2C{=}CHC(CH_3)_2CH_2OBs$

**31**

## Results

The starting brosylate (**30**) was prepared from authentic 2,2-dimethyl-3,4-pentadienal (**28**)[5,6] in 61% over-all yield (eq 7).

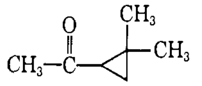
$$\underset{\mathbf{28}}{H_2C{=}C{=}CHC(CH_3)_2CHO} \xrightarrow[Et_2O]{LiAlH_4} \underset{\mathbf{29}}{H_2C{=}C{=}CHC(CH_3)_2CH_2OH} \xrightarrow[pyridine]{BsCl} \mathbf{30} \quad (7)$$

The solvolysis of a 0.04 *M* solution of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) in anhydrous acetic acid, buffered with sodium acetate and containing ~1% acetic anhydride, for 22 hr (11 half-lives) at 55° yields a mixture containing ~12%[8,9] 2-methyl-1,4,5-hexatriene (**32**), ~11%[8] 2-methyl-2,4,5-hexatriene (**33**), and 77% 2-methyl-4,5-hexadien-2-yl acetate (**34**) (eq 8). When the reaction was stopped after 0.5 half-life and the unreacted brosylate recovered, only **30** could be detected by infrared and nmr analysis. The relative amount of acetate **34** is invariant with time. Mixed gas–liquid partition chromatography (glpc) with authentic 2,2-dimethyl-3,4-pentadienyl acetate (**35**) and 2,2-dimethylcyclopropyl methyl ketone (**36**) indicated that neither was present in the reaction mixture. Since we could detect no other acetate in the product mixture and since the collected tertiary acetate appeared by nmr to consist of **34** exclusively, we believe the isomeric acetate which might be expected from methyl migration, *viz.* 3-methyl-4,5-pentadien-3-yl acetate (**37**), if present at all, must constitute less than 1% of the total product.

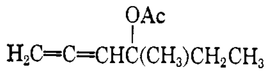
$$\mathbf{30} \xrightarrow[55^\circ]{AcOH\text{-}AcO^-} \underset{\mathbf{32}}{H_2C{=}C{=}CHCH_2C(CH_3){=}CH_2} + \underset{\mathbf{33}}{H_2C{=}C{=}CHCH{=}C(CH_3)_2} + \underset{\mathbf{34}}{H_2C{=}C{=}CHCH_2C(CH_3)_2{-}OAc} \quad (8)$$

$H_2C{=}C{=}CHC(CH_3)_2CH_2OAc$

**35**



**36**



$H_2C{=}C{=}CHC(OAc)(CH_3)CH_2CH_3$

**37**

The ethanolysis of a 0.04 *M* solution of **30** in absolute ethanol, 0.07 *M* in pyridine, at 55° for 48 hr (22 half-lives) yields a mixture[9] containing ~5% hydrocarbon(s) which were not identified and ~95% 2-methyl-4,5-hexadien-2-yl ethyl ether (**38**) (eq 9). No enol ether could be detected in the reaction by glpc.

$$\mathbf{30} \xrightarrow[pyridine]{EtOH} \underset{\mathbf{38}}{H_2C{=}C{=}CHCH_2C(CH_3)_2OC_2H_5} + \text{hydrocarbon(s)} \quad (9)$$

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[5] B. Thompson, U. S. Patent 3,236,869 and 3,236,901 (1966).

[6] We are indebted to Dr. K. C. Brannock of Tennessee Eastman Co., Kingsport, Tenn., for a generous sample of 2,2-dimethyl-3,4-pentadienal.

[7] R. S. Bly and R. T. Swindell, *J. Org. Chem.*, 30, 10 (1965).

[8] We find that 32, is partially isomerized to 33 under our glpc conditions (see Experimental Section).

[9] Uncorrected for differences in thermal conductivity, *cf.* A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, 31, 230 (1959).

Table I. Apparent First-Order Rate Constants for the Solvolysis of Neopentyl-Type Brosylates

| Run | Compd | Solvent | Temp, °C | $[ROBs]_i$ | $[NaOAc]_i$ | $10^5k$, sec$^{-1}$ |
|---|---|---|---|---|---|---|
| 1 | **30** | AcOH[a] | 40.01 | 0.0390 | 0.0487 | 1.80 |
| 2 | | | | 0.0392 | 0.0486 | 1.72 |
| 3 | | | 54.67 | 0.0392 | 0.0489 | 9.76 |
| 4 | | | 54.66 | 0.0393 | 0.0486 | 10.00 |
| 5 | | | 70.16 | 0.0398 | 0.0490 | 49.6 |
| 6 | | | | 0.0392 | 0.0495 | 50.1 |
| 7[b] | | | 54.68 | 0.0250 | 0.0340 | 9.49 |
| 8 | | EtOH[c] | 40.10 | 0.0400 | ... | 1.38 |
| 9 | | | | 0.0400 | ... | 1.33 |
| 10 | | | 54.99 | 0.0400 | ... | 8.57 |
| 11 | | | 55.00 | 0.0401 | ... | 8.62 |
| 12 | | | 68.85 | 0.0400 | ... | 42.2 |
| 13 | | | 68.88 | 0.0400 | ... | 42.4 |
| 14 | **40** | | 101.18 | 0.0400 | ... | 0.925 |
| 15 | | | | 0.0398 | ... | 0.932 |
| 16 | | | 114.70 | 0.0398 | ... | 3.43 |
| 17 | | | | 0.0400 | ... | 3.56 |

[a] Containing ~1% acetic anhydride. [b] 0.0154 *M* in sodium *p*-bromobenzenesulfonate. [c] 95 vol % ethanol, unbuffered.

The hydrolysis of a 0.04 *M* solution of **30** in 50 vol % aqueous acetone, 1.5 *M* in pyridine, for 24 hr at 55° yields a mixture[9] consisting of <15% of two unidentified components which we presume from their relative glpc retention times to be hydrocarbons and >85% of a single alcohol, 2-methyl-4,5-hexadien-2-ol (**39**) (eq 10). Mixed glpc with an authentic sample shows that the hydrolysis mixture contains no detectable amount (<0.1%) of 2,2-dimethylcyclopropyl methyl ketone (**36**).

$$\mathbf{30} \xrightarrow[\text{pyridine}]{H_2O\text{-}CH_3COCH_3} \underset{\mathbf{39}}{H_2C{=}C{=}CHCH_2C(CH_3)_2OH} + \text{hydrocarbons} \qquad (10)$$

The titrimetric first-order solvolytic constants for the acetolysis and ethanolysis of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) and for the ethanolysis of 2,2-dimethylpentyl *p*-bromobenzenesulfonate (**40**), determined as described in the Experimental Section, are summarized in Table I. The activation parameters for the solvolyses of **30** and **40**, computed in the usual manner as described elsewhere,[10] are recorded in Table II together with their apparent titrimetric first-order solvolysis constants corrected to 75°. Included in this table for purposes of comparison are similar data for 2,2-dimethyl-3-butenyl and 2,2-dimethylbutyl *p*-bromobenzenesulfonates **31** and **41**, respectively.[7]

Table II. Activation Parameters for the Solvolysis of Neopentyl-Type *p*-Bromobenzenesulfonates

| Compd | Solvent | $\Delta H^*$, kcal/mole | $\Delta S^*$, eu | $10^7k$, sec$^{-1}$ at 75° |
|---|---|---|---|---|
| **31**[a] | AcOH[b] | 24.6 | −7.2 | 655 |
| **41**[a] | | 29.5 | −2.4 | 6.80 |
| **41**[c] | | 28.9 | −3.9 | 6.65 |
| **30** | | 23.0 | −6.8 | 8150 |
| **40**[c] | | 29.8 | −1.3 | 7.03 |
| **30** | EtOH[d] | 24.8 | −1.7 | 8180 |
| **40** | | 27.5 | −8.5 | 5.3 |

[a] Recomputed from the data of ref 7. [b] Containing ~1% acetic anhydride and buffered with ~0.04 *M* sodium acetate. [c] Recomputed from the data in ref 11. [d] 95 vol % ethanol, unbuffered.

$CH_3CH_2CH_2C(CH_3)_2CH_2OBs$ **40**  $CH_3CH_2C(CH_3)_2CH_2OBs$ **41**

## Discussion

**The Case for π-Electron Participation.** The solvolysis of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) is accompanied by π-electron participation in the rate-limiting and product-determining step(s). As the data in Table II reflect, at 75° **30** reacts 1160 times more rapidly than 2,2-dimethylpentyl *p*-bromobenzenesulfonate (**40**) in anhydrous, buffered acetic acid ($Y = -1.633$)[12] and 1530 times more rapidly in the slightly more ionizing ($Y = -1.287$)[12] 95 vol % ethanol.[13] Since no product of bimolecular substitution is formed from **30** in either solvent (or in 50% acetone), these differences clearly reflect its enhanced unimolecular reactivity with respect to **40**. The increased driving force for ionization must derive primarily from π- rather than σ-electron participation since methyl migration, which should be able to compete favorably with the latter[14] but not the former,[7] does not occur. The only products formed are those of allenyl migration.

In considering how best to represent the course of these solvolyses, it is tempting to turn to the large body of fact and interpretation which already exists in the somewhat similar homoallyl–cyclopropylcarbinyl–cyclobutyl systems[16] and suggest that the reactions of

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(10) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, 89, 880 (1967).

(11) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *J. Org. Chem.*, 25, 2195 (1960).

(12) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, 78, 2770 (1956).

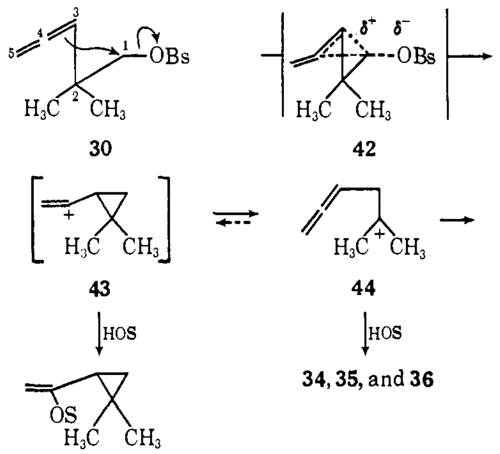
(13) The reactivity difference in acetic acid may actually be slightly larger than this since the acetolysis constant of 40 was determined in solutions that contained traces of water.[11]

(14) Methyl migration is statistically twice as favorable and the more weakly held $sp^3$–$sp^3$ σ electrons are more easily delocalized than the more tightly held $sp^2$–$sp^3$ σ electrons. Experimental confirmation of this idea may probably be inferred from the fact that the acetolysis of 2-norbornen-1-ylcarbinyl brosylate yields no vinyl-migrated products.[15]

(15) R. S. Bly and Q. E. Cooke, unpublished work (*cf.* 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug–Sept 1964, Abstract 80S.

homoallenyl neopentyl-type compounds proceed by way of one or more charge-delocalized bicyclobutonium-type cations. We do not feel, however, that such an interpretation is warranted at the present time. Roberts and co-workers have demonstrated that the substitution of a methyl or phenyl group[16b,c] appreciably alters the charge distribution in a bicyclobutonium ion and probably decreases its stability with respect to its "classical" counterparts.[16a] Substituents which grossly distort the tetrahedral-like geometry of a bicyclobutonium ion should have a similar effect.[16d] Consequently the geometry, charge distribution, and stability with respect to its charge-localized counterparts could be quite different in the case of a *gem*-dimethyl-substituted methylenebicyclobutonium ion. Further, in contrast to its homoallylic analog **31**,[7] 2,2-dimethyl-3,4-pentadieneyl *p*-bromobenzenesulfonate (**30**) yields only one nonhydrocarbon product upon solvolysis. Enantiomers excluded, there are six structurally distinguishable *gem*-dimethyl-substituted methylenebicyclobutonium cations.[16e] To suggest any specific one or more of these ions as intermediates in the solvolyses of **30** on the basis of such limited experimental evidence would be presumptuous.[17] Accordingly, until more data are available we prefer to interpret the solvolyses according to Scheme II. Although our data provide no evidence of its formation, we have included as a possible intermediate the α-(2,2-dimethylcyclopropyl)vinyl cation (**43**) on the strength of Hanack and Häffner's observations.[3]

**Scheme II**



The *gem*-dimethyl groups at C-2 would appear to affect the solvolytic behavior of **30** in three distinct ways. (1) They prevent bimolecular displacement. Not only does **30** yield no unrearranged product upon solvolysis, but its reaction rate in solvents of equivalent ionizing power[12] is not affected by changes in the nucleophilicity of the medium.[18] (2) The *gem*-dimethyl groups facilitate the hybridizational changes which occur at C-2 in the transition state (**42**) of the anchimerically assisted process (Scheme II) and thus increase the reactivity of **30** with respect to that of **1**[21]—**30** is about 350 times as reactive as **1** in anhydrous acetic acid at 60°.[3b] (3) The *gem*-dimethyl groups increase the stability of the rearranged, acyclic cation (**44**) with respect to the α-(2,2-dimethylcyclopropyl)vinyl cation (**43**) so that, in contrast to the unsubstituted homoallenyl compounds examined by Hanack and Häffner[3] and to the monosubstituted homoallenyl tosylate (**9**) studied by Bertrand and Santelli,[4] **30** yields no cyclic products upon solvolysis.

**Homoallenyl and Homoallyl Participation.** A better estimate of the true driving force associated with homoallenyl π-electron participation can be made if the solvolytic rates of **30** and **40** are corrected for differences in inductive effect. Accordingly the Taft linear-free-energy relation[22] was used to compute the inductive substituent parameter, $\sigma^*$, of 2-methyl-3,4-pentadien-2-yl and 2-methyl-2-pentyl from the measured ionization constants of 2,2-dimethyl-3,4-pentadienoic and neoheptanoic acids, respectively. Using these inductive substituent parameters, an estimated reaction parameter of $\rho^* = -2$ to $-4$ for the solvolysis at 75° of a tertiary alkyl-substituted carbinyl (*i.e.*, neopentyl-type) brosylate,[19b,23] and the measured solvolytic rate constant of **40** ($k_s$), the predicted solvolytic rate constant of **30** ($k_u$) in the *absence* of π-electron participation was calculated. The actual rate enhancement provided by the homoallenyl double bond must then equal the measured $k_u/k_s$ ratio divided by the $k_u/k_s$ ratio predicted in the absence of such participation.[22,23] These calculations, together with similar estimates of homoallyl participation, are summarized in Tables III and IV. They indicate that the extent of participation is considerably greater in the homoallenic than in the homoallylic solvolysis.

The enhanced ability of a homoallyl double bond to participate by π-electron delocalization could result from an increased stability of the transition state (**42**) and/or a decreased stability of the ground state (**30**). We believe that both may occur. Mass spectral appearance potentials of cations[24] and ionization po-

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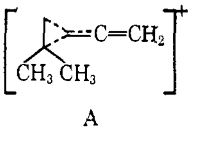
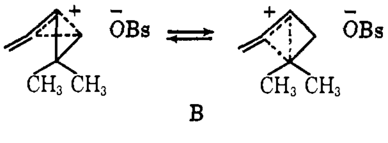
(16) (a) R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 259 ff, and references cited therein; (b) J. D. Roberts, Abstracts of the 16th National Organic Chemistry Symposium of the American Chemical Society, Seattle, Wash., June 15–17, 1959, pp 1–10; (c) K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 1331 (1965), and references cited therein; (d) M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, 19, 2, 403 (1963); (e) P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965, p 272, and papers included thereafter.

(17) An interesting example of a pitfall of prematurely complex interpretation has been provided by the two referees of this manuscript. The first suggests that the intermediate A would account for the observed products "in a more nearly straightforward fashion," the latter that B seems "intuitively more reasonable."



A



B

(18) This behavior is characteristic of compounds which solvolyze with little nucleophilic solvent participation.[19] Solvolyses which proceed with extensive nucleophilic solvent participation are much more rapid in aqueous ethanol than in aqueous acids of equivalent ionizing power but decreased nucleophilicity.[20]

(19) (a) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, 83, 618 (1961); (b) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, 88, 4475 (1966).

(20) (a) S. Winstein and H. Marshall, *ibid.*, 74, 1120 (1952); (b) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, 87, 1288 (1965).

(21) See ref 7 for a more detailed discussion of this effect.

(22) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 556 ff.

(23) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 122 ff.

(24) (a) A. Maccoll in "The Transition State," Special Publication

**Table III.** Estimation of Unassisted Acetolysis Rates at 75°

| R | p$K_a$ of RCOOH[a] | $\sigma^*$ of R | $10^7k_1$ of $RCH_2OBs$,[b] $sec^{-1}$ | Predicted $k_u/k_s$[c] |
|---|---|---|---|---|
| $H_2C{=}CHCH_2–$ | 4.35[d] | +0.22[e] | | |
| $H_2C{=}CHC(CH_3)_2–$ | | +0.02[f] | 0.31–1.5[g] | 0.22–0.047 |
| $CH_3CH_2C(CH_3)_2–$ | | −0.315[h] | 6.7[i] | |
| $H_2C{=}C{=}CHC(CH_3)_2–$ | 4.52[j] | +0.093[e] | 0.14–0.97[g] | 0.14–0.020 |
| $CH_3CH_2CH_2C(CH_3)_2–$ | 5.12[j] | −0.33[e,k] | 7.0[i] | |

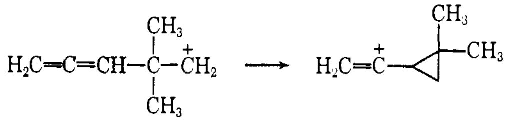
[a] In water at 25°. [b] In anhydrous acetic acid at 75°. [c] In the absence of $\pi$-electron participation. [d] J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939). [e] Computed from the p$K_a$ of RCOOH as described in ref 22, using $\rho^* = 1.4$ for the ionization of RCOOH (where R is tertiary) in water at 25°. We believe, on the basis of our fairly limited data, that this gives slightly better correlation with neo acids than the $\rho^* = 1.72$ suggested by Taft.[22] [f] Estimated as $\sigma^*(H_2C{=}CHCH_2–) + 2\sigma^*(C_2H_5–)$.[22] [g] Estimated from the Taft equation,[22] using $\rho^* = -2.0$ to $-4.0$ for the acetolysis of $RCH_2OBs$ (where R is tertiary),[19b,23] and the measured $k_1$ of saturated $RCH_2OBs$. [h] Estimated as $\sigma^*(n\text{-}C_3H_7–) + 2\sigma^*(C_2H_5–)$.[22] [i] See ref 11. [j] Measured as described in the Experimental Section. [k] Note that $\sigma^*(n\text{-}C_4H_9–) + 2\sigma^*(C_2H_5–) = -0.330$.[22]

**Table IV.** Estimation of Acetolysis Rate Enhancements at 75° Due to $\pi$-Electron Participation

| Compd | Measured $10^7k_1$,[a] $sec^{-1}$ | Obsd $k_u/k_s$ | Predicted $k_u/k_s$[b] | Estimated rate enhancement |
|---|---|---|---|---|
| $H_2C{=}CHC(CH_3)_2CH_2OBs$ | 655 | 96.0 | 0.22–0.047 | 440–2000 |
| $CH_3CH_2C(CH_3)_2CH_2OBs$ | 6.80 | | | |
| $H_2C{=}C{=}CHC(CH_3)_2CH_2OBs$ | 8150 | 1160 | 0.14–0.020 | 8300–58,000 |
| $CH_3CH_2CH_2C(CH_3)_2CH_2OBs$ | 7.03 | | | |

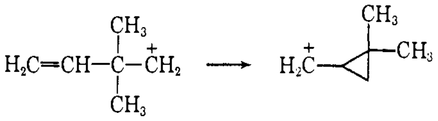
[a] *Cf.* Table II. [b] In the absence of $\pi$-electron participation, *cf.* Table III.

tentials of radicals[25] indicate the following order of increasing stability in the gas phase: $H_3\overset{+}{C} < H_2C{=}\overset{+}{C}H < CH_3\overset{+}{C}H_2$. Hence it appears that a methylene can stabilize a positive charge on carbon more effectively than can two hydrogens[26] and that an $\alpha$-cyclopropylvinyl cation such as **43** might be somewhat more stable than a cyclopropylcarbinyl, **47**.[27] Bond-energy considerations suggest that the conversion of **45** to **43**, *i.e.*



**45** **43**

is about 10 kcal/mole more exothermic than the similar rearrangement of **46** to **47**, *viz.*[28]



**46** **47**

Thus, even in the absence of any electronic stabilization by the methylene, a portion of this increased thermodynamic driving force must appear as a further rate enhancement if $\pi$-electron delocalization during the solvolysis of **30** is concerted with the loss of brosylate as our data indicate (Scheme II). Because the magnitude of the increased rate enhancement in the homoallenyl solvolysis is considerably less than the latent thermodynamic driving force, we believe that of the two effects, electronic stabilization of the transition state and thermodynamic destabilization of the ground state, the latter is probably the more important.

## Experimental Section[30]

**2,2-Dimethyl-3,4-pentadienol (29).** To a stirred slurry of 5.3 g (0.17 mole) of lithium aluminum hydride in 300 ml of anhydrous ether was added, at a rate sufficient to maintain reflux, 51 g (0.46 mole) of 2,2-dimethyl-3,4-pentadienal (**28**)[5,6] in 200 ml of anhydrous ether. After the addition was complete (75 min), the complex was decomposed by the sequential addition of 6 ml of water, 6 ml

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No. 16, The Chemical Society, London, 1962, p 159; (b) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press Inc., New York, N. Y., 1957, Appendix, Part I; (c) A. G. Harrison and F. P. Lossing, *J. Am. Chem. Soc.*, 82, 519 (1960).

(25) F. P. Lossing, in "Mass Spectrometry," C. A. McDowell, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, Chapter 11.

(26) There is a considerable body of evidence which indicates that a similar order of stability prevails when these ions are generated in solution under kinetically controlled conditions: for recent reviews, see (a) H. Fischer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience Publishers, Ltd., London, 1964, Chapter 13; (b) K. Griesbaum, *Angew. Chem. Intern. Ed. Engl.*, 5, 933 (1966); (c) H. G. Richey, Jr., and J. M. Richey in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967.

(27) Some support for this data may be inferred from the fact that the estimated rate enhancement due to homocroiyl participation in the acetolysis of 2,2-dimethyl-3-pentenyl *p*-bromobenzenesulfonate at 75° (unpublished work of A. R. B.) *exceeds* that due to homoallenyl participation even though a similar driving force due to ground-state destabilization is not present.

(28) This conclusion is based upon the fact that the heat of hydrogenation of allene to propane is −70 kcal/mole while that of propene to propane is ~30 kcal/mole.[29]

(29) (a) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *J. Am. Chem. Soc.*, 58, 146 (1936); (b) *ibid.*, 57, 876 (1935).

(30) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalitisches Laboratorium, Mülheim, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nmr spectra on a Varian A-60 spectrometer at ~35° using tetramethylsilane ($\delta$ = 0.00) as internal standard, and the ultraviolet spectra on a Perkin-Elmer ultraviolet–visible spectrophotometer, Model 202. The gas chromatographic analyses were carried out on an F & M Model 500 linear temperature programmed gas chromatograph. The chromatographic columns used were 0.25 in. × 20 ft or 0.25 in. × 8 ft coiled copper tubes packed with 20% Carbowax 20M on 80–100 mesh Gas-Chrom A (Applied Science Laboratories, Inc., State College, Pa.)

of 15% aqueous sodium hydroxide, and 20 ml of water.[31] The aqueous solution was extracted with four 200-ml portions of ether, and the combined ethereal solution was dried over anhydrous magnesium sulfate. After removal of the solvent by distillation at atmospheric pressure, the residue was distilled under vacuum through a 10-cm Vigreux column to yield 43 g (0.38 mole, 83%) of product; bp 73–75° (18.5 mm) (lit.[5] bp 83° (40 mm)); infrared (neat), 3360, 1046 (–$CH_2OH$), 1955 (C=C=C), 1470 (>$CH_2$), 1390, 1360 (>$C(CH_3)_2$); 840 cm$^{-1}$ ($CH_2$=C=CH–); nmr ($CCl_4$), 5.09 (1 $H_BH_BC$=C=$CH_A$–C⩽); 4.72 (2 $H_BH_BC$=C=$CH_A$–) (the resonances in the region from δ 5.15–4.60 exhibit a typical $AB_2$ pattern),[32] 3.30, singlet (2⩾$CCH_2O$–), 2.72, broad, concentration-dependent singlet (1 –OH), 1.00, singlet (6 >$C(CH_3)_2$).

*Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78; O, 14.26. Found: C, 74.85; H, 10.59; O, 14.52.

**2,2-Dimethyl-3,4-pentadienyl *p*-Bromobenzenesulfonate (30).** To an ice-cold solution of 6.6 g (0.059 mole) of 2,2-dimethyl-3,4-pentadienol (**29**) in 150 ml of anhydrous pyridine was added 16.8 g (0.0662 mole) of *p*-bromobenzenesulfonyl chloride. The mixture was cooled at −10° until pyridine hydrochloride began to precipitate (100 min) and then allowed to stand at ~0° for 19 hr. The cold solution was poured in to 400 ml of ice–water, and the resulting precipitate was separated by filtration and dried at 1 mm for 50 min. The crude material, 14.5 g (0.0438 mole, 74%), mp 35.5–36.5°, was recrystallized from *n*-hexane and dried at 1 mm for 30 min to yield 12.0 g (0.0363 mole, 62%) of white needles; mp 36.0–36.5°; infrared (KBr); 3090, 1930, 1580, 740 (>C=CH–, aromatic), 1960 (C=C=C), 1475 (>$CH_2$), 1390, 1370 (>$C(CH_3)_2$), 1370, 1190–1170 (–O–$SO_2$–), 845–810 cm$^{-1}$ ($CH_2$=C=CH–); nmr ($CCl_4$), δ 7.73, slightly perturbed singlet (4 aromatic hydrogens), 5.00 (1 $H_BH_BC$=C=$CH_A$–C⩽), 4.73 (2 $H_BH_BC$=C=$CH_A$–) (the resonances in the region from δ 5.2 to 4.5 exhibit a typical $AB_2$ pattern),[32] 3.87, slightly perturbed singlet (2 ⩾$CCH_2O$–); 1.03, slightly perturbed singlet (6 >$C(CH_3)_2$).

*Anal.* Calcd for $C_{13}H_{15}O_3BrS$: C, 47.14; H, 4.56, O, 14.49; Br, 24.13; S, 9.68. Found: C, 46.92; H, 4.61; O, 14.38; Br, 24.16; S, 9.74.

This material was used for the rate and product studies without further purification.

**2,2-Dimethyl-3,4-pentadienyl Acetate (35).** A solution of 1.12 g (0.0100 mole) of 2,2-dimethyl-3,4-pentadienol (**29**) and 1.2 g (0.012 mole) of acetic anhydride in 20 ml of anhydrous pyridine was heated under reflux for 10 hr. The reaction mixture was cooled to 5–10°, added to 50 ml of ice–water, and extracted with three 10-ml portions of *n*-pentane. The combined pentane extract was washed successively with 10 ml of 10% hydrochloric acid, 10 ml of saturated aqueous potassium carbonate, and two 20-ml portions of cold water, and dried over anhydrous sodium carbonate. The solvent was removed by distillation at atmospheric pressure through a 10-cm wire spiral packed column, and the residue was distilled to yield 1.0 g (6.5 mmoles, 65%) of acetate; bp 165–170° (760 mm); infrared ($CCl_4$); 1960 (C=C=C), 1750 (>C=O), 1480 (>$CH_2$), 1380, 1370 (>$C(CH_3)_2$), 1240 ($CH_3COO$–), 1039 (C–O–C), 846 cm$^{-1}$ ($CH_2$=C=CH–); nmr ($CCl_4$), δ 4.98 (1 $H_BH_BC$=C=$CH_AC$⩽), 4.72 (2 $H_BH_BC$=C=$CH_AC$⩽) (the resonances in the region from δ ~5.3 to 4.58 exhibit a typical $AB_2$ pattern),[32] 3.81, singlet (2 ⩾C-$CH_2O$–), 2.01, singlet (3 O–CO–$CH_3$), 1.05, singlet (6 >$C(CH_3)_2$).

*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15; O, 20.75. Found: C, 70.36; H, 9.21; O, 20.54.

**2,2-Dimethylcyclopropyl Methyl Ketone (36).** To a solution of methyl Grignard prepared in the usual manner from 2.4 g (0.10 g-atom) of magnesium turnings and 14.2 g (0.100 mole) of methyl iodide in 100 ml of anhydrous ether was added with stirring a solution of 4.0 g (0.042 mole) 2,2-dimethylcyclopropyl cyanide[33] in 10 ml of anhydrous ether. After the addition was complete (10 min), the reaction mixture was heated under reflux while small samples were periodically withdrawn and hydrolyzed and the ratio of nitrile to ketone determined by glpc. When the ratio of unreacted nitrile to ketone no longer appeared to decrease (28 hr), the entire reaction mixture was hydrolyzed by the sequential addition of 140 ml of water and cracked ice and 28 ml of 33 vol % dilute sulfuric acid. The light green ethereal layer was separated and extracted with seven 50-ml portions of ether. The combined ether extract was washed sequentially with two 50-ml portions of dilute potassium carbonate solution and with 50 ml of ice–water. The ethereal solution was dried over anhydrous sodium sulfate and concentrated to ~5 ml by distillation of the solvent through a 10-cm wire spiral packed column. The residue was distilled through a 3-in. Vigreux column to yield 1.3 g (0.12 mole, 28%) of ketone, bp 45.0–53.0° (20.0 mm) (lit.[34] bp 71–73° (78 mm)). A glpc analysis of this material on the 20-ft Carbowax column at 150° (helium flow 65 cc/min) reveals that the ketone is contaminated with about 15% of the unreacted nitrile: infrared ($CCl_4$), 3070, 3020 (>$CH_2$, cyclopropane), 2240 (–C≡N), 1720, 1690 ($CH_3CO$–), 1390, 1374 cm$^{-1}$ (>$C(CH_3)_2$).

**2,2-Dimethylpentyl *p*-bromobenzenesulfonate (40)** was prepared in the usual manner (*vide supra*) from 6.96 g (0.0600 mole) of 2,2-dimethylpentanol[5] and 16.8 g (0.0662 mole) of *p*-bromobenzenesulfonyl chloride in 150 ml of pyridine. The yield of crude brosylate, mp 32.5–33.0°, was 16.0 g (0.0478 mole, 80%). The crude material was recrystallized from *n*-hexane and dried at 0.05 mm for 30 min to yield 12.0 g (0.0358 mole, 60%) of white crystals; mp 33.0° (lit.[11] mp 31°); infrared (KBr), 3090, 1935, 1480, 740 (>C=CH–, aromatic), 1475 (>$CH_2$), 1390, 1370 (>$C(CH_3)_2$), 1370, 1180, 1170 cm$^{-1}$ (–O–$SO_2$–); nmr ($CCl_4$), δ 7.73, singlet (4 aromatic hydrogens), 3.69, singlet (2 ⩾C–$CH_2O$–); 1.30–0.68, multiplet superimposed on a singlet at 0.86 (12 $CH_3CH_2CH_2C$⩽ + >$C(CH_3)_2$). This material was used for the ethanolysis rate studies without further purification.

**Acetolysis of 2,2-Dimethyl-3,4-pentadienyl *p*-Bromobenzenesulfonate (30). Product Study.** A 0.0425 *M* solution of the brosylate in anhydrous acetic acid, 0.0492 *M* in sodium acetate and containing ~1% acetic anhydride, was maintained at 55° for 22 hr (11 half-lives). The solution was cooled to room temperature and poured into 200 ml of cold water, and the resulting solution was extracted with five 80-ml portions of *n*-pentane. The combined pentane extract was dried over anhydrous sodium sulfate and concentrated to ~3 ml by distillation of the pentane through a 10-cm wire spiral packed column at atmospheric pressure. When the concentrate was analyzed by glpc on the 8-ft Carbowax column[30] operated isothermally at 75° (helium flow, 70 cc/min), three peaks were evident. Samples of each were collected and identified as follows.

**The first component** was characterized by the following: retention time, 4.3 min; relative abundance,[9] 12%; infrared ($CCl_4$), 3080 (=$CH_2$), 1960 (C=C=C), 1655, 893 (>C=$CH_2$), 1445, 1380 (–$CH_3$), 847 cm$^{-1}$ ($CH_2$=C=CH–); ultraviolet (isooctane) mμ (ε), 208.5 (≈980), 245.5 (≈220), 255.2 (≈240), ~265 (≈180); nmr ($CCl_4$); δ 5.05–4.40, a complex 5-hydrogen multiplet due apparently to ($H_BH_BC$=C=$CH_ACH_2$– and –$(CH_3)C$=CHH), 2.66, a perturbed doublet (2 =CH–$CH_2$–C=), 1.72, a slightly perturbed singlet (3 –$CH_2CH(CH_3)$=CHH). We conclude that this compound is 2-methyl-1,4,5-hexatriene (**32**). When it is reinjected on the gas chromatograph, it is partially isomerized to the second component (*vide infra*).

**The second component** was characterized by the following: retention time, 8.5 min; relative abundance,[9] 11%; infrared ($CCl_4$), 1940 (C=C=CH–),[35] 1630 (>C=C<, conjugated), 1380, 1360 (=$C(CH_3)_2$), 870 (–CH=C<), 848 cm$^{-1}$ ($CH_2$=C=CH–);[35] ultraviolet (isooctane) mμ (ε), ~218.5, shoulder (≈16,000), 230.6 (≈18,000);[36] nmr ($CCl_4$), δ 6.0–5.3, a complex multiplet (2 =CH–HC=), 4.80, a perturbed doublet, $J \simeq 6.5$ cps (2 HHC=C=CH–), 1.8, a perturbed singlet (3 –HC=$C(CH_3)CH_3$), 1.73, a perturbed singlet (3 –HC=$C(CH_3)CH_3$). We conclude that this component is 2-methyl-2,4,5-hexatriene (**33**).

**The third component** was characterized by the following: retention time, 55.5 min; relative abundance,[9] 77%; infrared ($CCl_4$), 1960 (C=C=C), 1745 (>C=O), 1450 (=$CHCH_2$–), 1400, 1380 (>$C(CH_3)_2$?), 1245 ($CH_3CO$–O–), 844 cm$^{-1}$ ($CH_2$=C=CH–); ultraviolet (isooctane), 209.6 mμ (ε ≈460); nmr ($CCl_4$), δ 5.15–4.40, a complex 3-hydrogen multiplet (apparently characteristic of HHC=C=$CHCH_2$–), 2.44, a 1:2:1 triplet (1 =CHCHHC⩽), 2.32, a 1:2:1 triplet (1 =CHCHHC⩽), 1.89, singlet (3 –$OCH_3$), 1.40, singlet (6 –$C(CH_3)_2O$–).

*Anal.* Calcd for $C_9H_{14}O_2$: C, 70.17; H, 9.15; O, 20.75. Found: C, 69.89; H, 9.12; O, 21.00.

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[31] V. M. Mícovíc and M. L. Mihailovíc, *J. Org. Chem.*, 18, 1190 (1953).

[32] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Can. J. Chem.*, 35, 65 (1957).

[33] E. R. Nelson, M. Marienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, 79, 3467 (1957).

[34] M. Julia, S. Julia, and J. A. du Chaffaut, *Bull. Soc. Chim. France*, 1735 (1960).

[35] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, pp 14–15.

[36] E. R. H. Jones, H. H. Lee, and M. C. Whiting, *J. Chem. Soc.*, 341 (1960).

The retention time of this material on the 8-ft Carbowax column is different from that of authentic 2,2-dimethyl-3,4-pentadienyl acetate (**35**). We conclude that it is 2-methyl-4,5-hexadien-2-yl acetate (**34**).

When the acetolysis of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) at 55° is interrupted after 60 or 145 min (0.5 or 1.2 half-lives, respectively), the infrared spectrum of the unreacted brosylate, recovered by pouring the reaction mixture into cold water and separating the precipitated brosylate by filtration, is identical with that of the starting material, **30**.

**Kinetic Study.** Titrimetric first-order acetolysis rate constants for 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) were determined in the usual manner on ~0.025 *M* solutions of brosylate in anhydrous acetic acid containing a slight molar excess of sodium acetate and ~1% acetic anhydride. The first-order plots were linear to greater than 90% reaction. The first-order acetolysis constants computed from the plots are compared with those of McElrath, *et al.*,[11] for the acetolysis of 2,2-dimethylpentyl *p*-bromobenzenesulfonate (**40**) in Table II. The activation parameters, computed from a plot of log $(k/T)$ *vs.* $1/T$, are recorded in Table II.

**Ethanolysis of 2,2-Dimethyl-3,4-pentadienyl *p*-Bromobenzenesulfonate (30). Product Study.** A 0.042 *M* solution of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) in absolute ethanol containing 0.070 *M* pyridine was maintained at 55° for 48 hr (~21 half-lives). The ethanol was removed by distillation through a 10-in. Vigreux column at reduced pressure (25–30 mm) until pyridinium *p*-bromobenzenesulfonate began to precipitate. The concentrate (~3 ml) was then poured into 30 ml of cold water, and the resulting cloudy solution was extracted with five 50-ml portions of *n*-pentane. The combined pentane extract was dried over anhydrous magnesium sulfate, and the bulk of the solvent was removed by distillation at atmospheric pressure through a 10-cm wire spiral packed column. An isothermal glpc analysis on the 20-ft Carbowax column at 115° (helium flow 40 cc/min) shows two components in addition to solvent and pyridine. Only the second of these (retention time, 5.6 min; relative abundance,[9] >95%) was present in sufficient quantity to collect: infrared ($CCl_4$); 3060 ($=CH-$), 1960 ($C=C=C$), 1450 ($=CHCH_2-$), 1400, 1380 ($>C(CH_3)_2$), 1070 ($C-O-C$), 843 cm$^{-1}$ ($CH_2=C=CH-$); nmr ($CCl_4$), $\delta$ 5.25–4.45, a complex 3-hydrogen multiplet apparently characteristic of ($HHC=C=CHCH_2-$), 3.35, a 1:3:3:1 quartet (2 $-O-CH_2CH_3$), 2.21, a 1:2:1 triplet (1 $=CHCHHC<$), 2.09, a 1:2:1 triplet (1 $=CHCHHC<$), 1.15, singlet (6 $>C(CH_3)_2$), 1.11, a 1:2:1 triplet (3 $-CH_2CH_3$).

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.96; H, 11.54.

We conclude that this material is ethyl 2-methyl-4,5-hexadien-2-yl ether (**38**).

**Kinetic Study.** Titrimetric first-order ethanolysis constants were determined as described elsewhere[37] on ~0.04 *M* solutions of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonate (**30**) in 95 wt % aqueous ethanol. The *p*-bromobenzenesulfonic acid liberated during the reaction was titrated directly with standard sodium ethoxide in ethanol to a bromothymol blue end point. The first-order plots showed little deviation from linearity to 75% reaction. The rate and activation parameters are summarized in Tables I and II, respectively.

**The Hydrolysis of 2,2-Dimethyl-3,4-pentadienyl *p*-Bromobenzenesulfonate (30). Product Study.** A 0.038 *M* solution of the brosylate in 50 vol % aqueous acetone, 1.5 *M* in pyridine, was heated at 55° for 24 hr. The cooled solution was extracted with five 50-ml portions of *n*-pentane. The combined pentane extract was washed successively with 50 ml of water, 50 ml of dilute glacial acetic acid, 50 ml of saturated aqueous potassium carbonate solution, and 50 ml of water. The solution was dried over anhydrous sodium sulfate and concentrated to ~1 ml by distillation of the solvent through a 10-cm wire spiral packed column at atmospheric pressure. A glpc analysis of the residue on the 20-ft Carbowax column at 135° (helium flow, 60 cc/min) showed one major component (retention time, 9.6 min; relative abundance, >85%) and a couple of minor ones (retention times, 2.0 and 2.9 min; relative abundance, <15%) in addition to pentane, acetone, and pyridine. The major component was collected for identification; infrared ($CCl_4$), 3670, ~3375 ($-OH$), 3060 ($=CH_2$); 1960 ($C=C=C$), 1445 ($=CHCH_2-$), 1145, ($>COH$), 845 cm$^{-1}$ ($CH_2=C=CH-$); nmr ($CCl_4$), $\delta$ 5.25–4.5, a complex 3-hydrogen multiplet apparently characteristic of ($HHC=C=CHCH_2-$), 2.23, a 1:2:1 triplet (1 $=CHCHH-O-$), 2.10, a 1:2:1 triplet (1 $=CHCHH-O-$), 1.76 a broad, concentration dependent singlet (1 $-OH$), 1.20, singlet (6 $>C(CH_3)_2$).

*Anal.* Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.91; H, 10.84.

We conclude that this material is 2-methyl-4,5-hexadien-2-ol (**39**).

Coinjection of an authentic sample of 2,2-dimethylcyclopropyl methyl ketone with the above solvolysis mixture indicates that no ketone is formed during the hydrolysis of **30**.

**The Ethanolysis of 2,2-Dimethylpentyl *p*-Bromobenzenesulfonate (40). Kinetic Study.** First-order ethanolysis constants for this brosylate were determined exactly as described for the unsaturated brosylate (**30**), except that bromphenol blue was used as an indicator. The first-order plots were linear to about 70% reaction. The data are summarized in Tables I and II.

**The Ionization Constants of 2,2-Dimethyl-3,4-pentadienoic and Neoheptanoic Acids.** The ionization constants of 2,2-dimethyl-3,4-pentadienoic and neoheptanoic acids were determined by potentiometric titration according to the procedure of Albert and Serjeant.[38] Standard aqueous solutions of the carboxylic acids (~0.01 *M* in acid) were titrated with 0.1 *N* standard sodium hydroxide using a glass *vs.* a standard calomel electrode in conjunction with a Beckman Research pH Meter. The p$K_a$ values recorded in Table III represent averages of eight to twelve readings of two determinations for each acid.

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