

reaction mixture was left at room temperature for 4 hr. On usual work-up, only 1-ethynylcyclohexanol (9) (1.5 g) was isolated.

**3-Methoxy-17-(2'- $\beta$ -methylene)estra-1,3,5(10)-triene (19) and 3-Methoxy-17-(2'- $\alpha$ -methylene)estra-1,3,5(10)-triene (20).** a. To a solution of the  $\text{LiMe}_2\text{Cu}$  reagent prepared as indicated above, 3-methoxy-17-( $\alpha$ -ethynyl)estra-1,3,5(10)-triene-17 $\beta$ -ol acetate (17) (2.0 g) was added. Chromatography gave the crystalline product **19** (0.254 g) and the starting material **17** (0.454 g). On six recrystallizations from methanol a small amount of **19** was obtained, mp 125–127°;  $[\alpha]_D^{25} +81^\circ$  ( $\text{CHCl}_3$ ); ir 1957  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ );  $\lambda_{\text{max}}^{\text{EtOH}}$  278 ( $\epsilon$  2090) and 287  $\text{m}\mu$  ( $\epsilon$  1860); nmr (100 MHz) 0.895 s (18 H), 1.640 d ( $J = 7$  Hz, 21 H), 3.770 s ( $-\text{OCH}_3$ ), 5.05–5.30 m (20 H), and 6.6–7.3 aromatic protons. *Anal.* Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}$ : C, 85.66; H, 9.15; mol wt, 308.4. Found: C, 85.61; H, 9.22; mol wt, 308 (ms).

The material that remained in the mother liquor has identical  $R_f$  value and uv spectrum to **19**, ir 1951  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ). It is a mixture of **19** and **20**, of which compound **20** could not be isolated neither by recrystallization, nor by column, or preparative thin layer chromatography (tlc). From the nmr spectrum (100 MHz) of this mixture, the chemical shifts corresponding to **20** are: 0.86 s (18 H), 1.66 d ( $J = 7$  Hz, 21 H), 3.77 s ( $\text{OCH}_3$ ), 4.78–5.14 m (20 H), and 6.6–7.3 aromatic absorption ( $\text{CDCl}_3$ ).

b. In a similar fashion 3-methoxy-17-(2'- $\beta$ -acetoxyethenylidene)estra-1,3,5(10)-triene (**23**) (1.6 g) afforded a crystalline product (0.35 g). The material is a mixture of **19** and **20**. Neither of the components could be isolated in a pure form, either by column or TLC, or by recrystallization. On repeated recrystallization from methanol mixtures ranging from mp 57–59°,  $[\alpha]_D^{25} +19^\circ$ , to mp 116–118°,  $[\alpha]_D^{25} +69^\circ$ , were obtained. The uv spectra and  $R_f$  value are identical with those of the mixtures obtained by procedure a; ir 1957  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ). The nmr spectrum (100 MHz,  $\text{CDCl}_3$ ) is identical with that of the mixture of **19** and **20**, obtained from procedure a, with the major component being **20**, the ratio of **20** to **19** in the product is approximately 2:1.

**3 $\beta$ -Acetoxy-17-(2'- $\beta$ -methylene)idene)-5 $\alpha$ -androstane (21) and 3 $\beta$ -Acetoxy-17-(2'- $\alpha$ -methylene)idene)-5 $\alpha$ -androstane (22).** a. Reaction of 3 $\beta$ ,17 $\beta$ -diacetoxy-17 $\alpha$ -ethynyl-5 $\alpha$ -androstane (**18**) (2.3 g) provided a product (1.95 g) which was chromatographed on a column (from 100 g of Florosil, in hexane). Elution with hexane-ether (95:5) gave the crystalline product (1.495 g). This material is homogenous on TLC, however it was a mixture of **21** and **22**, the pure components could not be separated by preparative TLC, column chromatography, or recrystallization. After ten recrystallizations from methanol, a material, mp 137.5–139°, was obtained—the melting point of this material could not be raised by further recrystallization;  $[\alpha]_D^{25} +19^\circ$  ( $\text{CHCl}_3$ ); ir 1961  $\text{cm}^{-1}$  ( $\text{C}=\text{C}$ ); nmr (100 MHz) (the material is a mixture of **21** and **22**) 0.740 s (19 H), 0.847 s (18 H, **22**), 0.881 s (18 H, **21**), 1.688 d ( $J = 7$  Hz, 22 H, **21**), 1.722 d ( $J = 7$  Hz, 22 H, **22**), 2.030 s ( $-\text{COCH}_3$ ), 4.60–5.05 m (3 $\alpha$  H), and 5.10–5.45 m (21 H) (pyridine- $d_5$ ). Nmr (100 MHz) of the product, as obtained from column chromatography, indicates the presence of **22** and **21** in a ratio of approximately 3:2. *Anal.* Calcd for  $\text{C}_{28}\text{H}_{38}\text{O}_2$ : C, 80.85; H, 10.18; mol wt, 356. Found: C, 80.79; H, 9.76; mol wt, 356 (ms).

b. To the  $\text{LiMe}_2\text{Cu}$  reagent prepared as above, 3 $\beta$ -acetoxy-17-(2'- $\beta$ -acetoxyethenylidene)-5 $\alpha$ -androstane (**24**) (0.58 g) was added. The reaction performed in the usual manner gave the crystalline product. The material has ir spectrum superimposable with the product obtained in procedure a. Similarly  $R_f$  values and nmr spectra (100 MHz, pyridine- $d_5$ ) of the products from both procedures are equal. The nmr spectrum indicates that **21** and **22** are present in approximately the same ratio as in the product obtained by procedure a.

**Acknowledgment.** The authors wish to thank Dr. J. H. Fried for stimulating discussions and valuable suggestions.

## Unsaturated Neopentyl Compounds. The Effect of Methyl Substitution on the Acetolysis Rates of Homoallenic Neopentyl-Type Brosylates

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**Abstract:** A series of 2,2-dimethyl-3,4-pentadienyl *p*-bromobenzenesulfonates with methyl substituents at C-3 and/or C-5 have been prepared and their solvolysis rates determined in buffered, anhydrous acetic acid. A Taft–Streitwieser treatment has been used to estimate that homoallenyl participation enhances the reaction rates by factors of 6200–170,000 times, and to deduce that the additional rate increases caused by 3-methyl substitution are due entirely to steric effects. It is suggested that the transition state of the rate-limiting step in each case is of the homoallyl–cyclopropylcarbinyl type with most of the charge concentrated at the vinyl position, C-4.

In a previous paper<sup>1</sup> we reported an example of homoallenyl participation in the solvolysis of a neopentyl-type brosylate, but were unable on the basis of our limited data to say much about the nature of the charge delocalization in the rate-limiting transition state. In order to be able to apply the technique of successive methyl substitution<sup>2</sup> to this problem we have prepared

and determined the acetolysis rates of several methyl substituted homoallenic neopentyl-type brosylates.

### Methods and Results

The required carboxylic acids and brosylates were prepared from the homoallenic aldehydes obtained *via* the Claisen–Cope rearrangement of propargyl vinyl ethers<sup>3</sup> derived from the *p*-toluenesulfonic acid catalyzed

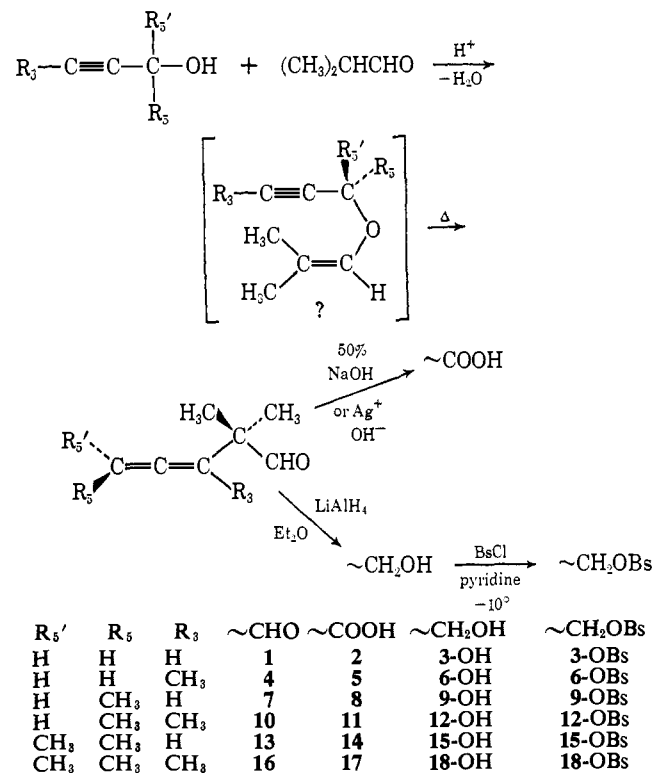
(1) R. S. Bly, A. R. Ballentine, and S. U. Koock, *J. Amer. Chem. Soc.*, **89**, 6993 (1967).

(2) (a) H. C. Brown and Min-Hon Rei, *ibid.*, **86**, 5004 (1964); (b) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); (c) P. D. Bartlett and G. D. Sargent, *ibid.*, **87**, 1297 (1965); (d) P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon, and G. H. Schmid, *ibid.*, **87**, 1314 (1965); (e) K. L. Servis and J. D. Roberts, *ibid.*, **87**, 1331

(1965); (f) J. A. Berson, A. W. McRowe, and R. G. Bergman, *ibid.*, **88**, 1067 (1966); (g) P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); (h) P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); (i) C. H. DePuy, L. G. Schnack, and J. W. Hauser, *ibid.*, **88**, 3343 (1966).

condensation of isobutyraldehyde and methyl-substituted propargyl alcohols (Scheme I). The over-all yield for the condensation and rearrangement steps ranged from 65% in the case of **10** to ~4% in the case of **16**.

Scheme I

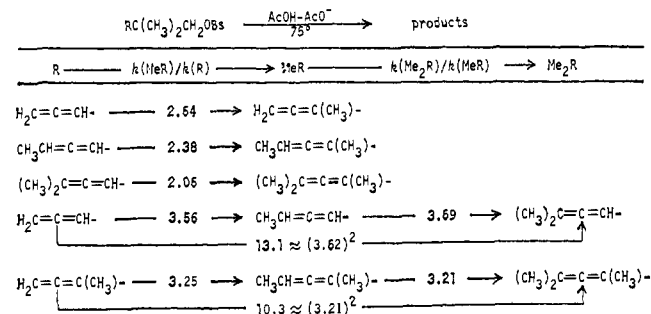


The apparent first-order acetolysis rates and activation parameters, determined as described in the Experimental Section and elsewhere,<sup>4</sup> are summarized in Table I.

## Discussion

**The Effect of Methyl Substitution on  $\pi$ -Electron Delocalization.** It is apparent from the data in Table I that each methyl substitution causes an increase in the over-all acetolysis rate of a homoallylic neopentyl-type brosylate. The effect of successive methyl substitution at 75° is summarized in Scheme II. Thus

Scheme II



3-methyl substitution causes an additional rate enhancement of 2.1–2.6 times, 5-methyl substitution of 3.2–3.7 times.

(3) (a) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 6784 (1965); (b) B. Thompson, U. S. Patent 3,236,869 (1965); (c) U. S. Patent 3,236,901 (1965).

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

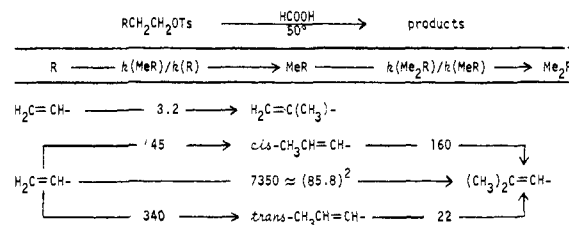
**Table I.** Apparent First-Order Rate Constants and Activation Parameters for the Acetolysis of Homoallylic Neopentyl-Type Brosylates<sup>a</sup>

Compd	Temp, °C <sup>b</sup>	10 <sup>6</sup> k, sec <sup>-1</sup> <sup>c</sup>	ΔH*, kcal/mole	ΔS*, eu
3-OBS <sup>d</sup>	75.00	81.5	23.0	-6.8
6-OBS	39.88	3.46 ± 0.03		
	57.25	31.7 ± 0.0	24.7	-0.18
	69.23	112 ± 1		
	75.00 <sup>e</sup>	215		
9-OBS <sup>f</sup>	39.89	6.47 ± 0.03		
	57.23	46.1 ± 0.2	22.8	-4.9
	69.23	164 ± 0.5		
	75.00 <sup>e</sup>	290		
12-OBS	24.94	2.41 ± 0.01		
	40.13	16.2 ± 0.0	22.7	-3.6
	54.95	87.7 ± 0.0		
	75.00 <sup>e</sup>	689		
15-OBS	24.91	3.14 ± 0.00		
	39.88	23.1 ± 0.65	23.3	-0.95
	55.37	131 ± 1		
	75.00 <sup>e</sup>	1070		
18-OBS	24.93	9.52 ± 0.01		
	40.13	56.5 ± 0.0	21.9	-3.6
	54.81	303 ± 0.5		
	75.00 <sup>e</sup>	2210		

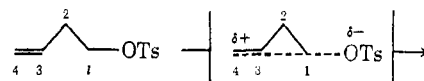
<sup>a</sup> As 0.04 M solutions in anhydrous acetic acid containing ~0.046 M sodium acetate and ~1% acetic anhydride. <sup>b</sup> Controlled to ±0.03°. <sup>c</sup> Mean of two determinations at each temperature. <sup>d</sup> Data from ref 1. <sup>e</sup> Extrapolated from data at lower temperatures. <sup>f</sup> Jacobs and Macomber<sup>5</sup> report k(40.0°) = 6.43 × 10<sup>-5</sup> sec<sup>-1</sup>, ΔH\* = 22.4 kcal/mole, ΔS\* = -6.3 eu.

The effects may be compared with those determined by Servis and Roberts<sup>2e</sup> for the formolysis of homoallylic nonneopentyl tosylates at 50° (Scheme III).

Scheme III



Their data do not extend to 5-methyl substitution but do indicate that 3- or 4-methyl substitutions cause rate enhancements of 3.2 or 22–340 times, respectively. Or the basis of these and other kinetic data, Servis and Roberts have suggested that most of the developing positive charge in the transition state of a solvolysis homoallyl derivative is concentrated at C-4, *i.e.*



with perhaps a much smaller amount at C-3.

Although the effect of 3-methyl substitution is similar in both the homoallyl and the homoallylic neopentyl-type systems it is probably not indicative in the latter cases of charge delocalization to C-3. McElrath and her coworkers<sup>6</sup> have examined the reactivity of a series of saturated neopentyl-type brosylates and find that 3-, 4-, and 5-methyl substitutions affect the acetolysis rates at 75° by factors of 1.9–4.9, 1.1–1.5, and 1.0 times,

(5) T. L. Jacobs and R. Macomber, *Tetrahedron Lett.*, 4877 (1967).

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

Table II. Estimation of Unassisted Acetolysis Rates at 75°

R'	p <i>K</i> <sub>a</sub> of R'COOH <sup>a</sup>	σ* of R' <sup>b</sup>	10 <sup>7</sup> <i>k</i> <sub>1</sub> of R'CH <sub>2</sub> OBS, <sup>c</sup> sec <sup>-1</sup>	Calcd <i>k</i> <sub>u</sub> / <i>k</i> <sub>s</sub> <sup>d</sup>
H <sub>2</sub> C=C=CHC(CH <sub>3</sub> ) <sub>2</sub> -	4.52	+0.093	0.14-0.97	0.14-0.020 <sup>e</sup>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> - H <sub>2</sub> C=C=C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> -	4.55	+0.071	7.0 0.50-3.4 <sup>f</sup>	0.15-0.021
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> - CH <sub>3</sub> CH=C=CHC(CH <sub>3</sub> ) <sub>2</sub> -	4.58	+0.050	23.3 <sup>g</sup> 0.20-1.2 <sup>f</sup>	0.17-0.029
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> - CH <sub>3</sub> CH=C=C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> -	~4.66 <sup>h</sup>	-0.007	7.0 <sup>g</sup> 0.98-4.7 <sup>f</sup>	0.20-0.043
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> - (CH <sub>3</sub> ) <sub>2</sub> C=C=CHC(CH <sub>3</sub> ) <sub>2</sub> -	4.70	-0.036	23 <sup>i</sup> 0.66-2.6 <sup>f</sup>	0.26-0.066
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> -			10 <sup>j</sup>	

<sup>a</sup> Determined in water at 25° as described in the Experimental Section. <sup>b</sup> Computed from the p*K*<sub>a</sub> of R'COOH as described in ref 7, using ρ\* = 1.4 for the ionization of R'COOH (where R' is tertiary) in water at 25°. We believe, on the basis of our fairly limited data<sup>1</sup> for the saturated acids, that this gives a slightly better correlation with neoacids than ρ\* = 1.72 suggested by Taft.<sup>7</sup> <sup>c</sup> In anhydrous acetic acid at 75°. <sup>d</sup> In the absence of π-electron participation. <sup>e</sup> Data from ref 1. <sup>f</sup> Estimated from the Taft equation,<sup>7</sup> using ρ\* = -2 to -4 for the acetolysis of R'CH<sub>2</sub>OBS (where R' is tertiary)<sup>8</sup> [J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *J. Amer. Chem. Soc.*, **88**, 4475 (1966)] and the *k*<sub>1</sub> of the saturated R'CH<sub>2</sub>OBS.<sup>8</sup> <sup>g</sup> Data from ref 6. <sup>h</sup> This determination is less precise because of solubility problems with this acid; cf. Experimental Section. <sup>i</sup> Estimated as *k*<sub>1</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OBS] ≈ *k*<sub>1</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OBS].<sup>8</sup> <sup>j</sup> Estimated as *k*<sub>1</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OBS] ≈ *k*<sub>1</sub>[(CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>OBS].<sup>8</sup>

Table III. Estimation of Acetolysis Rate Enhancements of 75° Due to π-Electron Participation

Compd	Found		Calcd <i>k</i> <sub>u</sub> / <i>k</i> <sub>s</sub> <sup>a</sup>	Estd rate enhancement, Δ
	10 <sup>7</sup> <i>k</i> <sub>1</sub> , sec <sup>-1</sup>	<i>k</i> <sub>u</sub> / <i>k</i> <sub>s</sub>		
H <sub>2</sub> C=C=CHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (3-OBS)	8,150 <sup>b</sup>	1,160	0.14-0.020	8,300-58,000
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS H <sub>2</sub> C=C=C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (6-OBS)	7.03 <sup>a</sup> 21,500 <sup>b</sup>	924	0.15-0.021	6,200-44,000
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> OBS CH <sub>3</sub> CH=C=CHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (9-OBS)	23.3 <sup>a</sup> 29,000 <sup>b</sup>	4,140	0.17-0.029	24,000-140,000
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS CH <sub>3</sub> CH=C=C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (12-OBS)	7.0 <sup>a</sup> 68,900 <sup>b</sup>	3,000	0.20-0.043	15,000-70,000
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (CH <sub>3</sub> ) <sub>2</sub> C=C=CHC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS (15-OBS)	~23 <sup>a</sup> 107,000 <sup>b</sup>	11,000	0.26-0.066	42,000-170,000
(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> OBS	~10 <sup>a</sup>			

<sup>a</sup> See Table II. <sup>b</sup> See Table I.

respectively. Since charge is not delocalized to these positions during solvolysis the effects are apparently steric in origin. The similar magnitude of the "3-methyl effect" in both the saturated and homounsaturated neopentyl-type systems suggests that the effect may be steric in the unsaturated compounds as well.

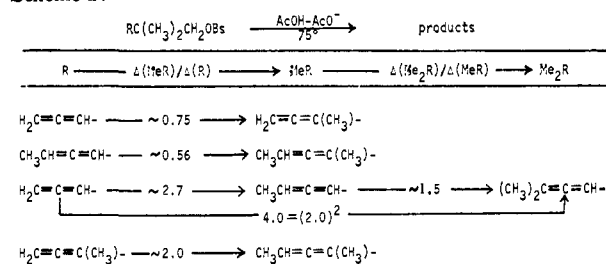
To test this we have estimated the effect of methyl substitution on the extent of π-electron delocalization in the following manner. As described previously,<sup>1</sup> the inductive substituent parameters (σ\*) of the unsaturated groups (R') were calculated from the Taft equation<sup>7</sup> and the measured ionization constants of the neocarboxylic acids (R'COOH) (Table II).

Using these inductive substituent parameters, an estimated reaction parameter of ρ\* = -2 to -4 for the acetolysis at 75° of a tertiary alkyl-substituted carbonyl brosylate,<sup>1</sup> and the measured acetolytic rate constants (*k*<sub>s</sub>) for the saturated neopentyl-type brosyl-

ates at 75°, the Taft-Streitwieser relation<sup>8</sup> was used to predict the ratio of the acetolysis rates of the corresponding unsaturated and saturated neopentyl-type brosylates, *k*<sub>u</sub>/*k*<sub>s</sub>, in the absence of π-electron delocalization; cf. Table III. The measured *k*<sub>u</sub>/*k*<sub>s</sub> ratio divided by the predicted one corresponds to the estimated rate enhancement (Δ) due to π-electron delocalization in each case (Table III).

The effect of methyl substitution on the extent of π-electron participation during the acetolysis of homoallylic neopentyl-type brosylates at 75°, computed from the data in Table III, is summarized in Scheme IV.

Scheme IV

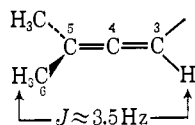


(7) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp 556 ff.

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

These methyl-substitution factors support the idea that the additional rate increases caused by 3-methyl substitution in the unsaturated neopentyl-type systems are steric in origin. Such substitution apparently decreases the extent of  $\pi$ -electron participation by a factor of 0.5–0.8 times. If these estimates are correct then the actual steric effect of a 3-methyl substituent causes a rate increase of about 3–5 times in these unsaturated neopentyl-type brosylates. This is comparable to the 1.9–4.9 times observed by McElrath, *et al.*,<sup>6</sup> in the saturated analogs.

In contrast to the effect of a 3-methyl substituent, methyl substitution at C-5 appears to increase slightly the extent of  $\pi$ -electron participation. As much as half of the over-all rate enhancement which results from substitution at this position may be due to an electronic effect. Since product studies<sup>9</sup> clearly indicate that it is the  $\Delta^3$  double bond which participates in the ionization, this effect, if real, is unexpected. Perhaps the increased polarizability of ethylidene and isopropylidene relative to methylidene provides some additional stabilization of the charge which develops at C-4 in the transition state (*vide infra*). Alternatively, the methyl-C-5  $\sigma$  bond may be slightly delocalized so that some charge actually develops at C-5 and/or C-6. Support for such "homo-hyperconjugation," which has been suggested previously by Jacobs and Macomber<sup>10</sup> to account for the direction of addition of 2,4-dinitrobenzenesulfonyl chloride to 3-methyl-1,2-butadiene, can be inferred from the appreciable long-range coupling between allenic methyl hydrogens and the hydrogen at C-3 which is apparent in the nmr spectra of such compounds<sup>11</sup> (*cf.* Experimental Section) and from the enhanced geminal coupling constants reported earlier for 1,1-dimethylallene.<sup>11b</sup>

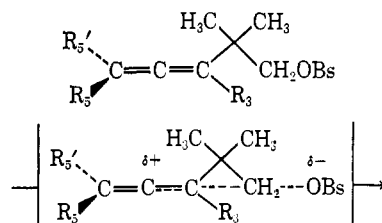


**The Nature of the Transition State.** From the large amount of  $\pi$ -electron participation which accompanies the acetolysis of these homoallenic neopentyl-type brosylates (Table III) it is evident that considerable charge delocalization is developed in the transition state of the rate-limiting step. The methyl-substituent effects indicate that little if any positive charge develops at C-3, C-5, or C-6. Hence most of this charge must appear at C-4. Unfortunately the structural limitations of the system prohibit our demonstrating this by the methyl-substitution technique which serves so well in the homoallyl cases.<sup>2e,12</sup> Nevertheless, it appears that the transition states for these acetolyses are probably best represented as homoallyl cyclopropylcarbinyll type with most of the charge concentrated at the vinyl position, *viz.*

As suggested previously<sup>1</sup> the greater driving forces associated with the solvolyses of homoallenic systems compared with those observed in the related homoallylic cases must derive in part from the enhanced ground-

(9) R. S. Bly and S. U. Koock, *J. Amer. Chem. Soc.*, **91**, 3299 (1969).  
 (10) T. L. Jacobs and R. Macomber, *J. Org. Chem.*, **33**, 2988 (1968).  
 (11) (a) R. K. Kullnig and F. C. Nachod, *J. Phys. Chem.*, **67**, 1361 (1963); (b) E. L. Allred, D. M. Grant, and W. Goodlett, *J. Amer. Chem. Soc.*, **87**, 673 (1965).

(12) *Cf.* ref 1, footnote 27.



state energies of the allenic double bonds, but the methyl-substitution effects revealed here indicate that homoallenic charge delocalization is also important.

### Experimental Section<sup>13</sup>

**2,2,3-Trimethyl-3,4-pentadien-1-al (4).** A solution of 54.5 g (0.778 mol) of 2-butyne-1-ol, 65.0 g (0.903 mol) of isobutyraldehyde, 0.05 g of hydroquinone, and 0.05 g of *p*-toluenesulfonic acid in 40 ml of benzene was heated under reflux for 27 hr in a 500-ml round-bottomed flask equipped with a Dean-Stark water separator. After 10.5 g (0.600 mol) of water had been removed, the reaction mixture was neutralized with 0.1 g of sodium acetate. After distillation of the solvent the residue was distilled under vacuum through a 10-in. wire-spiral-packed column to yield 54.0 g (0.433 mol, 57%) of aldehyde: bp 73–75° (60 mm); ir (CCl<sub>4</sub>) 2800, 2700 (–CHO), 1955 (>C=C=C<), 1740 (–HC=O), 1380, 1370 (>C(CH<sub>3</sub>)<sub>2</sub>), 1107 (–CHO), 850 cm<sup>–1</sup> (H<sub>2</sub>C=C=C<); nmr (CCl<sub>4</sub>)  $\delta$  9.38 (s, 1 >C=CHO), 4.78 (slightly perturbed 1:2:2:1 q,  $J = 3.0$  Hz, 2 CH<sub>2</sub>=C=C(CH<sub>3</sub>)–), 1.66 (slightly perturbed 1:2:1 t,  $J = 3.0$  Hz, 3 H<sub>2</sub>C=C=C(CH<sub>3</sub>)–), 1.18 (s, 6 >C(CH<sub>3</sub>)<sub>2</sub>).

*Anal.* Calcd for C<sub>8</sub>H<sub>12</sub>O: C, 77.37; H, 9.74. Found: C, 76.74; H, 9.85.

**2,4-Dinitrophenylhydrazone**, mp 150–151°.

*Anal.* Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>4</sub>O<sub>4</sub>: C, 55.26; H, 5.30; N, 18.41. Found: C, 55.15; H, 5.48; N, 18.25.

**2,2,3-Trimethyl-3,4-pentadien-1-ol (6-OH).** To a stirred slurry of 1.45 g (0.0371 mol) of lithium aluminum hydride in 100 ml of anhydrous ether was added, at a rate sufficient to maintain reflux, 15.0 g (0.121 mol) of 2,2,3-trimethyl-3,4-pentadien-1-al (4) in 100 ml of anhydrous ether. After the addition was complete (75 min), the complex was refluxed for 1 hr, then decomposed by successive addition of 3 ml of water, 3 ml of 15% aqueous sodium hydroxide, and 3 ml of water.<sup>14</sup> The aqueous solution was extracted with three 25-ml portions of ether, and the combined ethereal solution was washed with water and dried over anhydrous magnesium sulfate. After removal of the solvent by distillation at atmospheric pressure, the residue was distilled under vacuum through a 10-in. wire-spiral-packed column to yield 10.5 g (0.084 mol) of alcohol: bp 82–84° (22 mm) or 48–50° (1 mm); ir (neat) 3390, 1045 (CH<sub>2</sub>OH), 1965 (>C=C=C<), 1480 (CH<sub>2</sub>), 1380, 1375 (>C(CH<sub>3</sub>)<sub>2</sub>), 845 cm<sup>–1</sup> (CH<sub>2</sub>=C=C<); nmr (CCl<sub>4</sub>)  $\delta$  4.62 (slightly perturbed 1:2:2:1 q,  $J = 3.0$  Hz, 2 H<sub>2</sub>C=C=C(CH<sub>3</sub>)–), 3.34 (s, 2 >CCH<sub>2</sub>OH), 2.57 (concentration-dependent s, 1OH), 1.68 (slightly perturbed 1:2:1 t,  $J = 3.0$  Hz, 3 H<sub>2</sub>C=C=C(CH<sub>3</sub>)–), 1.01 (s, 6 >C(CH<sub>3</sub>)<sub>2</sub>).

*Anal.* Calcd for C<sub>8</sub>H<sub>14</sub>O: C, 76.14; H, 11.18. Found: C, 75.81; H, 11.06.

**2,2,3-Trimethyl-3,4-pentadien-1-yl *p*-Bromobenzenesulfonate (6-OBs).** A solution of 3.6 g (0.028 mol) of 2,2,3-trimethyl-3,4-

(13) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalytisches Laboratorium, Germany, or Galbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nuclear magnetic resonance spectra at probe temperature in carbon tetrachloride using a Varian A-60 spectrometer equipped with a Model V-6058A spin decoupler with tetramethylsilane ( $\delta = 0.00$ ) and chloroform ( $\delta = 7.31$ ) as internal standards, the ultraviolet spectra on a Perkin-Elmer ultraviolet-visible spectrophotometer, Model 202, and the Raman spectra on a Cary Model 81 spectrometer equipped with a Spectra Physics Model 215 He-Ne Laser. The gas-liquid partition chromatographic (glpc) analyses were carried out on a F & M Model 500 linear temperature-programmed gas chromatograph using 0.25 in.  $\times$  8 ft, or 0.25 in.  $\times$  16 ft coiled copper tubes packed with 20% Carbowax 20M on 100–140 mesh Gas-Chrom S or 60–80 mesh Chromosorb P, or 20% diethylene glycol succinate (DEGS) on 60–80 mesh Chromosorb P. Helium was used as a carrier gas at flow rates of 70–200 ml/min. Preparative glpc collections employed  $\frac{3}{8}$  in.  $\times$  20 ft aluminum columns with similar packings in an Aerograph Autoprep, Model A-700.

(14) V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

pentadien-1-ol (6-OH) in 100 ml of anhydrous pyridine was cooled in an ice-salt mixture ( $\sim -15^\circ$ ) and mixed with 8.4 g (0.033 mol) of *p*-bromobenzenesulfonyl chloride. The reaction mixture was maintained at this temperature ( $\sim -15^\circ$ ) until pyridine hydrochloride began to precipitate (30 min), then maintained at  $-10^\circ$  for 49 hr. The cold solution was poured into 250 ml of ice-water and the resulting precipitate was separated by filtration, washed with cold water until the odor of pyridine was no longer apparent, and dried at 1 mm for 2 hr. The crude material, 5.2 g (0.015 mol, 54%), mp 45.0–46.0°, was recrystallized from *n*-hexane and dried at 1 mm for 2 hr to yield 4.7 g (0.014 mol, 50%) of brosylate: mp 46.0–46.5°; ir (CCl<sub>4</sub>) 3090, 3020, 1920, 1660, 1580 ( $>C=CH-$ , aromatic), 1960 ( $>C=C=C<$ ), 1480 (CH<sub>2</sub>), 1395, 1380 ( $>C(CH_3)_2$ ), 1180–1190 ( $-OSO_2-$ ), 850 cm<sup>-1</sup> (H<sub>2</sub>C=C=C<); nmr (CCl<sub>4</sub>)  $\delta$  7.74 (s, 4 aromatic hydrogens), 4.61 (slightly perturbed 1:2:2:1 q,  $J = 3.0$  Hz, 2 H<sub>2</sub>C=C=C(CH<sub>3</sub>)-), 3.83 (s, 2  $>CCH_2O-$ ), 1.64 (slightly perturbed 1:2:1 t,  $J = 3.0$  Hz, 3 H<sub>2</sub>C=C=C(CH<sub>3</sub>)-), 1.01 (s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for C<sub>14</sub>H<sub>17</sub>BrO<sub>3</sub>S: C, 48.70; H, 4.96; Br, 23.14; O, 13.90; S, 9.29. Found: C, 48.61; H, 4.96; Br, 23.13; O, 13.76; S, 9.54.

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

**2,2,3-Trimethyl-3,4-pentadienoic Acid (5).** A 25-g (0.062 mol) sample of sodium hydroxide was added slowly as a 60% aqueous solution to a solution of 25 g (0.20 mol) of 2,2,3-trimethyl-3,4-pentadien-1-ol (4) in 150 ml of methanol. After being stirred at 65–70° for 6 hr, the reaction mixture was poured into 300 ml of ice-cold water and the allenic alcohol was extracted with benzene. The aqueous solution which separated from the benzene layer, was acidified with 37 g (0.38 mol) of concentrated sulfuric acid. The solution was extracted with three, 80-ml portions of benzene, washed with water, and dried over anhydrous magnesium sulfate. After the solvent had been removed by distillation at atmospheric pressure, the residue was distilled under vacuum through a 10-in. wire-spiral-packed column to yield 2.01 g (0.014 mol, 14.6%) of acid: bp 94–96° (10 mm); ir (neat) 3000–2500 broad, 1705 (COOH), 1965 ( $>C=C=C<$ ), 1410, 2180 ((RCOOH)<sub>2</sub>), 1380, 1370 ( $>C(CH_3)_2$ ) 850 cm<sup>-1</sup> (CH<sub>2</sub>=C=C<); nmr (CCl<sub>4</sub>)  $\delta$  12.75 (broad s, 1, COOH), 4.64 (slightly perturbed 1:2:2:1 q,  $J = 3.0$  Hz, 2 H<sub>2</sub>C=C=C(CH<sub>3</sub>)-), 1.72 (slightly perturbed 1:2:1 t,  $J = 3.0$  Hz, 3 H<sub>2</sub>C=C=C(CH<sub>3</sub>)-), 1.31 (slightly perturbed s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.54; H, 8.63. Found: C, 68.83; H, 8.59.

This material was used for the pK<sub>a</sub> determination without further purification.

**2,2-Dimethyl-3,4-hexadien-1-ol (7)** was prepared in a manner similar to that described for 4 from a solution of 33 g (0.47 mol) of 1-butyn-3-ol, 51 g (0.71 mol) of isobutyraldehyde, 0.1 g of *p*-toluenesulfonic acid, and 50 ml of toluene by refluxing the mixture until 6.1 g (0.33 mol) of water had separated (24 hr). The yield was 20 g (0.16 mol, 34%); bp 138–144° (760 mm) or 80–84° (90 mm) [lit.<sup>15</sup> 139–140° (760 mm)]; ir (CCl<sub>4</sub>) 2800, 2705, 1735 ( $-CHO$ ), 1960 ( $>C=C=C<$ ), 1470 (CH<sub>3</sub>), 1390, 1370 ( $>C(CH_3)_2$ ), 855 cm<sup>-1</sup> ( $-CH=C=CH-$ ); nmr (CCl<sub>4</sub>)  $\delta$  9.66 (s, 1  $>C-CHO$ ), 5.46–5.01 (m, 2 HC(CH<sub>3</sub>)=C=CHC<), 1.70 (q, 3 HC(CH<sub>3</sub>)=C=CH-), 1.13 (s, 6  $>C(CH_3)_2$ ).

**2,4-Dinitrophenylhydrazone**, mp 114–115° (lit.<sup>15</sup> 115.0–115.1°).

**2,2-Dimethyl-3,4-hexadien-1-ol (9-OH)** was prepared in a manner similar to that described for 6-OH from 10 g (0.079 mol) of 2,2-dimethyl-3,4-hexadien-1-ol (7) and 1.1 g (0.028 mol) of lithium aluminum hydride. The yield was 5.7 g (0.046 mol, 57%); bp 82–86° (22 mm) [lit.<sup>15</sup> 65–69° (13 mm)]; ir (neat) 3355, 1045 (CH<sub>2</sub>OH), 1960 ( $>C=C=C<$ ), 1480 (CH<sub>2</sub>), 1380, 1370 ( $>C(CH_3)_2$ ), 870 cm<sup>-1</sup> ( $-CH=C=CH-$ ); nmr (CCl<sub>4</sub>)  $\delta$  5.27–4.82 (m, 2 HC(CH<sub>3</sub>)=C=CHC<), 3.28 (s, 2  $>C-CHHO-$ ), 2.32 (sharp concentration-dependent s, 1 OH), 1.70 (q,  $J_{ab} = 7.0$  Hz,  $J_{ac} = 3.5$  Hz, 3 H<sub>b</sub>c-C(CH<sub>3</sub>)=C=CH-), 0.99 (s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for C<sub>8</sub>H<sub>14</sub>O: C, 76.14; H, 11.18. Found: C, 76.10; H, 11.30.

**2,2-Dimethyl-3,4-hexadien-1-yl *p*-bromobenzenesulfonate (9-OBs)** was obtained in a manner similar to that described for 6-OBs from 3.1 g (0.025 mol) of 2,2-dimethyl-3,4-hexadien-1-ol (9-OH) and 7.6 g (0.030 mol) of *p*-bromobenzenesulfonyl chloride in 100 ml of pyridine. The yield of crude brosylate, mp 28.5–29.0°, was 5.6 g (0.015 mol, 60%). The crude material was recrystallized from

*n*-hexane and dried at 1 mm for 30 min to yield 2.7 g (0.014 mol, 30%) of white needles: mp 29.5–30.0°; ir (CCl<sub>4</sub>) 3090 ( $>C=CH-$ ), 3020, 1930, 1660, 1580 (phenyl), 1965 ( $>C=C=C<$ ), 1480 (CH<sub>2</sub>), 1395, 1380 ( $>C(CH_3)_2$ ), 1185 cm<sup>-1</sup> ( $-OSO_2-$ ); nmr (CCl<sub>4</sub>)  $\delta$  7.74 (s, 4 aromatic hydrogens), 5.29–4.82 (perturbed m, 2 HC(CH<sub>3</sub>)=C=CHC<), 3.75 (s, 2  $>C-CHHO-$ ), 1.62 (q,  $J_{ab} = 7.0$  Hz,  $J_{ac} = 3.5$  Hz, 3 H<sub>b</sub>c-C(CH<sub>3</sub>)=C=CH-), 1.02 (s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for C<sub>14</sub>H<sub>17</sub>BrO<sub>3</sub>S: C, 48.70; H, 4.96; Br, 23.14; S, 9.29. Found: C, 48.66; H, 4.88; Br, 23.42; S, 9.38.

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

**2,2-Dimethyl-3,4-hexadienoic acid (8)** was prepared in a manner similar to that described for 5 from 24 g (0.60 mol) of sodium hydroxide as a 50% aqueous solution and a solution of 24 g (0.19 mol) of 2,2-dimethyl-3,4-hexadien-1-ol (7) in 125 ml of methanol. The yield was 4.6 g (0.033 mol, 34%); bp 138–140° (1 mm); ir (neat), 3000–2500 broad, 1705 (COOH), 1970 ( $>C=C=C<$ ), 1415, 1289 ((RCOOH)<sub>2</sub>), 1380, 1375 ( $>C(CH_3)_2$ ); nmr (CCl<sub>4</sub>)  $\delta$  13.48 (s, 1 COOH), 5.30–4.90 (complex m, 2 CH<sub>2</sub>CH=C=CHC<), 1.68 (q,  $J_{ab} = 7.0$  Hz,  $J_{ac} = 3.5$  Hz, 3 H<sub>b</sub>c-C(CH<sub>3</sub>)=C=CH-), 1.29 (s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.54; H, 8.63. Found: C, 68.47; H, 8.63.

This material was used for the pK<sub>a</sub> determination without further purification.

**3-Pentyn-2-ol.** To a nitrogen-blanketed, 24-g (1.0 g-atom) sample of magnesium turnings, covered with 50 ml of anhydrous ether, in a three-necked flask equipped with a sealed mechanical stirrer was added about 15 ml of ethyl bromide. When the reaction had started, an additional 350 ml of anhydrous ether and the rest of the ethyl bromide (total 127 g, 1.16 mol), dissolved in 100 ml of anhydrous ether, were added at a rate sufficient to maintain a moderate reflux. After the addition had been completed ( $\sim 4$  hr) an additional 350 ml of anhydrous ether was added. The dropping funnel was replaced by a gas inlet and gaseous methylacetylene (Matheson Co., Inc.) was passed into the ethereal solution of ethylmagnesium bromide. The rate of addition of the gas was controlled so that a gentle but steady reflux was maintained. The addition required  $\sim 4$  hr. The stirred solution of propynylmagnesium bromide was cooled to room temperature and acetaldehyde, which had been obtained by heating a mixture of 75 g (0.57 mol) of paraldehyde containing 0.5 g of *p*-toluenesulfonic acid, was introduced directly from a dropping funnel through an ice-water-cooled condenser. After the addition had been completed (3 hr), the mixture was stirred for 2 hr and allowed to stand overnight at room temperature. The reaction mixture was poured into 2 l. of ice-cooled, saturated, aqueous ammonium chloride solution and the resulting aqueous solution was extracted with three 150-ml portions of ether. The combined ethereal solution was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been removed by distillation at atmospheric pressure, the residue was distilled under vacuum through a 10-in. wire-spiral-packed column to yield 50 g (0.60 mol, 60%) of alcohol: bp 72–74° (70 mm) [lit.<sup>16</sup> bp 50–55° (16 mm)]; ir (neat) 3355 broad, 1075 ( $>CHOH$ ), 2252, 2220 ( $-C\equiv C-$ ), 1460, 1380 cm<sup>-1</sup> (CH<sub>3</sub>); nmr (CCl<sub>4</sub>)  $\delta$  4.50–4.18 (complex m, 1 CH<sub>2</sub>C=CCH(CH<sub>3</sub>)-), 3.61 (broad s, 1 OH), 1.79 (slightly perturbed 1:1 d,  $J_{ab} = 3$  Hz, 3 H<sub>a</sub>-CC=CCH<sub>b</sub>(-)), 1.35 (slightly perturbed 1:1 d,  $J_{ab} = 6.5$  Hz, 3  $\equiv CCH_b(CH_3)_a$ ).

**2,2,3-Trimethyl-3,4-hexadien-1-ol (10).** A solution of 40 g (0.48 mol) of 3-pentyn-2-ol, 45 g (0.63 mol) of isobutyraldehyde, 0.2 g of *p*-toluenesulfonic acid, 0.01 g of hydroquinone, and 60 ml of benzene was refluxed until 9.2 g (0.51 mol) of water had been collected (24 hr). The product, 45.5 g, bp 66–88° (45 mm), was isolated from the reaction mixture in a manner similar to that described for 4. A gas chromatographic analysis of this product on an 8-ft Carbowax column at 100° (helium flow 80 cc/min) showed three components whose relative abundance and retention times were 25.7% (12.3 min), 41.5% (15.6 min), and 36.7% (29 min). The first component was collected by preparative gas-liquid partition chromatography from 20-ft Carbowax or DEGS columns. The over-all yield of aldehyde ( $\sim 95\%$  pure) amounted to 9.3 g (0.067 mol, 14%); ir (CCl<sub>4</sub>), 2790, 2690, 1735 (CHO), 1960 ( $>C=C=C<$ ), 1395, 1375 cm<sup>-1</sup> ( $>C(CH_3)_2$ ); nmr (CCl<sub>4</sub>)  $\delta$  9.27 (s, 1  $>CCHO$ ), 5.13 (m, 1 CH<sub>2</sub>CH=C=C(CH<sub>3</sub>)-), 1.68 (slightly perturbed 1:1 d,  $J = 7$  Hz, 3 CH<sub>2</sub>CH=C=C(-)) superimposed on a d at 1.59 ( $J = 3$  Hz, 3  $-CH=C=C(CH_3)-$ ), 1.12 (s, 6  $>C(CH_3)_2$ ).

(15) T. L. Jacobs, R. Macomber, and D. Zunker, *J. Amer. Chem. Soc.*, **89**, 7001 (1967).

(16) C. D. Hurd and F. L. Cohen, *ibid.*, **53**, 1068 (1931).

**2,4-Dinitrophenylhydrazone**, mp 133–134°.

*Anal.* Calcd for  $C_{13}H_{13}N_3O_4$ : C, 56.59; H, 5.70; N, 17.60. Found: C, 56.45; H, 5.79; N, 17.60.

**2,2,3-Trimethyl-3,4-hexadien-1-ol (12-OH)** was prepared in a manner similar to that described for 6-OH from a solution of 5.6 g (0.041 mol) of 2,2,3-trimethyl-3,4-hexadien-1-al (10) in 40 ml of anhydrous ether and 0.84 g (0.022 mol) of lithium aluminum hydride in 75 ml of anhydrous ether. The yield of alcohol was 3.7 g (0.026 mol, 65%); bp 101–104° (35 mm); ir (neat) 3360, 1035 ( $CH_2OH$ ), 1960 w ( $>C=C=C<$ ), 1400, 1380  $cm^{-1}$  ( $>C(CH_3)_2$ ); Raman (neat)<sup>17</sup> 1965  $cm^{-1}$  ( $>C=C=C<$ ); nmr ( $CCl_4$ )  $\delta$  4.98 (m, 1  $CH_2CH=C=C(CH_3)-$ ), 3.30 (s, 2  $>CCHHO-$ ), 2.23 (concentration-dependent s, 1 OH), 1.66 (slightly perturbed 1:1 d,  $J \approx 3$  Hz, 3  $-CH=C=C(CH_3)-$ ) superimposed on a slightly perturbed 1:1 d at 1.63 ( $J \approx 7$  Hz, 3  $CH_2CH=C=C(-)$ ), 1.00 (6  $>C(CH_3)CH_3$ ).

*Anal.* Calcd for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 76.91; H, 11.33.

**2,2,3-Trimethyl-3,4-hexadien-1-yl *p*-bromobenzenesulfonate (12-OBs)** was prepared in a manner similar to that described for 6-OBs from 1.4 g (0.010 mol) of 2,2,3-trimethyl-3,4-hexadien-1-ol (12-OH) and 3.5 g (0.014 mol) of *p*-bromobenzenesulfonyl chloride in 50 ml of anhydrous pyridine. The yield of crude brosylate, mp 61.5–62.5°, was 3.1 g (0.0086 mol, 86%). The crude material was recrystallized from *n*-hexane and dried at 1 mm for 1 hr to yield 2.9 g (0.0081 mol, 81%) of white crystals: mp 62.0–62.2°; ir ( $CCl_4$ ) 3035, 1920, 1650, 1580, 735 ( $>C=CH-$ , aromatic), 1960 ( $>C=C<$ ), 1400, 1380  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  7.60 (s, 4 aromatic hydrogens), 4.88 (broad m, 1  $H_{3a}CCH_x=C=C(CH_3)_2-$ ) which collapses to a perturbed singlet when irradiated at +204 Hz (e.g., when decoupled from the nearly equivalent  $H_a$  and  $H_b$ ), 3.73 (s, 2  $>C-CHHO-$ ), 1.59 (slightly perturbed 1:1 d,  $J_{bx} = 3$  Hz, 3  $-CH_x=C=C(CH_3)_2-$ ) superimposed on a slightly perturbed doublet at 1.57 ( $J_{ax} \approx 7$  Hz, 3  $H_{3a}CCH_x=C=C(-)$ ) which collapses to a slightly perturbed singlet when irradiated at -202 Hz (e.g., when decoupled from  $H_a$ ), 1.01 (s, 6  $>C(CH_3)CH_3$ ).

*Anal.* Calcd for  $C_{13}H_{19}BrO_2S$ : C, 50.15; H, 5.33; Br, 22.24; S, 8.92. Found: C, 49.83; H, 5.30; Br, 22.09; S, 9.15.

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

**2,2,3-Trimethyl-3,4-hexadienoic Acid (11).** A suspension of silver oxide was prepared by precipitation from a mixture of 3.4 g (0.020 mol) of silver nitrate in 40 ml of water and 2.0 g of sodium hydroxide contained in a 100-ml, three-necked flask equipped with a mechanical stirrer. The alkalinity was adjusted to pH 11. A 1.0-g (0.0070 mol) sample of 2,2,3-trimethyl-3,4-hexadien-1-al (10) was slowly added to the slurry over a 10-min period while the temperature was maintained below 25° by external cooling. During this time the alkalinity of the slurry was controlled at pH 10–12 by the gradual addition of 5% aqueous sodium hydroxide solution. After the addition had been completed, the stirring was continued for 2 hr at room temperature. The precipitated silver was removed by filtration and the filtrate was extracted with three 30-ml portions of benzene to remove any organic by-products or impurities. The aqueous solution was then acidified using excess (5 g) concentrated sulfuric acid. This solution was extracted with three 30-ml portions of benzene and the combined benzene extract was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been removed in a rotary evaporator, the residue was cooled to -10° to yield 0.77 g (5.0 mmol, 69%) of yellowish solid, mp 24.0–25.5°. The solid was recrystallized from hexane to give 0.5 g (3 mmol, 44%) of white crystals: mp 25.0–26.0°; ir ( $CCl_4$ ) 3650–2500 broad, 1710 (COOH), 1970 ( $>C=C=C<$ ), 1410, 1280 ( $(RCOOH)_2$ ), 1375, 1370  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  4.96 (broad m, 1  $H_3CCH=C=C(CH_3)-$ ), 1.61 (slightly perturbed 1:1 d,  $J \approx 3$  Hz, 3  $-CH=C=C(CH_3)-$ ) superimposed upon a slightly perturbed 1:1 d at 1.56 ( $J \approx 7$  Hz, 3  $H_3CCH=C=C(-)$ ), 1.23 (s, 6  $>C(CH_3)CH_3$ ).

*Anal.* Calcd for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.32; H, 9.24.

This material was used for the  $pK_a$  determination without further purification.

**2,2,5-Trimethyl-3,4-hexadien-1-al (13)** was prepared in a manner similar to that described for 4 from 84 g (1.0 mol) of 2-methyl-3-

butyn-2-ol, 72 g (1.0 mol) of isobutyraldehyde, 0.1 g of *p*-toluenesulfonic acid, and 50 ml of benzene. The mixture was refluxed until 17 g (0.95 mol) of water had been removed (24 hr). The yield of aldehyde was 52 g (0.38 mol, 38%); bp 96–99° (104 mm) or 152–155° (760 mm) [lit.<sup>3b</sup> 99° (104 mm)]; ir ( $CCl_4$ ) 2805, 2710, 1735 ( $CHO$ ), 1970 ( $>C=C=C<$ ), 1390, 1375  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  9.32 (s, 1  $>CCHO$ ), 4.87 (slightly perturbed septet,  $J \approx 3$  Hz, 1 ( $CH_3)_2C=C=CHC<$ ), 1.76 (slightly perturbed 1:1 d,  $J \approx 3$  Hz, 6 ( $CH_3)_2C=C=CH-$ ), 1.13 (s, 6  $>C(CH_3)_2$ ).

**2,4-Dinitrophenylhydrazone**, mp 97–98° (lit.<sup>3a</sup> 98–99°).

**2,2,5-Trimethyl-3,4-hexadien-1-ol (15-OH)** was obtained in a manner similar to that described for 6-OH from 25 g (0.18 mol) of 2,2,5-trimethyl-3,4-hexadien-1-al (13) in 150 ml of anhydrous ether and 2.4 g (0.063 mol) of lithium aluminum hydride in 100 ml of anhydrous ether. The yield of alcohol was 18 g (0.13 mol, 70%); bp 90–94° (22 mm); ir (neat) 3350, 1055 ( $CH_2OH$ ), 1960 ( $>C=C=C<$ ), 1475 ( $>CH_2$ ), 1390, 1380  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  4.86 (slightly perturbed septet,  $J \approx 3$  Hz, 1 ( $H_3C)_2C=C=CHC<$ ), 3.26 (s, 2  $>CCH_2O-$ ), 2.58 (concentration-dependent s, 1 OH), 1.68 (slightly perturbed d,  $J \approx 3$  Hz, 6 ( $CH_3)_2C=C=CH-$ ), 0.99 (s, 6  $>C=C=CHC(CH_3)_2-$ ).

*Anal.* Calcd for  $C_9H_{16}O$ : C, 77.09; H, 11.50. Found: C, 76.98; H, 11.15.

**2,2,5-Trimethyl-3,4-hexadien-1-yl *p*-bromobenzenesulfonate (15-OBs)** was prepared in a manner similar to that described for 6-OBs from 8.4 g (0.060 mol) of 2,2,5-trimethyl-3,4-hexadien-1-ol (15-OH) and 16 g (0.066 mol) of *p*-bromobenzenesulfonyl chloride in 150 ml of anhydrous pyridine. The yield of crude brosylate, mp 47.0–48.5°, was 19 g (0.054 mol, 90%). The crude material was recrystallized from *n*-hexane and dried at 1 mm for 90 min at room temperature to yield 18 g (0.051 mol, 83%) of white needles: mp 48.5–49.0°; ir ( $CCl_4$ ) 3090, 3020, 1580 ( $>C=CH-$ , aromatic), 1970 ( $>C=C=C<$ ), 1480 ( $CH_2$ ), 1385, 1375 ( $>C(CH_3)_2$ ), 1183  $cm^{-1}$  ( $-OSO_2-$ ); nmr ( $CCl_4$ )  $\delta$  7.73 (s, 4 aromatic hydrogens), 4.91 (slightly perturbed septet, 1 ( $CH_3)_2C=C=CHC<$ ), 3.75 (slightly perturbed s, 2  $>CCH_2O-$ ), 1.68 (slightly perturbed d,  $J \approx 3$  Hz, 6 ( $CH_3)_2C=C=CH-$ ), 1.00 (slightly perturbed s, 6  $>C(CH_3)_2$ ).

*Anal.* Calcd for  $C_{13}H_{19}BrO_2S$ : C, 50.15; H, 5.33; Br, 22.24; S, 8.92. Found: C, 49.98; H, 5.39; Br, 21.99; S, 9.08.

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

**2,2,5-Trimethyl-3,4-hexadienoic acid (14)** was prepared in a manner similar to that described for 5 from 19 g (0.14 mol) of 2,2,5-trimethyl-3,4-hexadien-1-al (13) in 120 ml of methanol and 17 g (0.42 mol) of sodium hydroxide as a 50% aqueous solution. The yield of crude acid, mp 39–41°, was 4.0 g (0.026 mol, 38%). The crude material was recrystallized from water and dried at 1 mm for 24 hr at room temperature yielding 3.5 g (0.023 mol, 33%) of white crystals: mp 44.0–44.5°; ir ( $CCl_4$ ) 3000–2500, 1705 (COOH), 1970 ( $>C=C=C<$ ), 1415, 1285 ( $(RCOOH)_2$ ), 1380, 1370  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  13.2 (broad s, 1 COOH), 5.10 (broad m, 1 ( $H_3C)_2C=C=CHC<$ ), 1.79 (slightly perturbed d,  $J \approx 3$  Hz, 6 ( $CH_3)_2C=C=CH-$ ), 1.26 (slightly perturbed s, 6  $>C(CH_3)_2$ ).

*Anal.* Calcd for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.30; H, 9.15.

This material was used for the  $pK_a$  determination without further purification.

**2-Methyl-3-pentyn-2-ol** was prepared in a manner similar to that described for 3-pentyn-2-ol from 290 g (2.66 mol) of ethyl bromide, 55 g (2.3 g-atom) of magnesium turnings, 120 g (3.00 mol) of methylacetylene (Matheson Co., Inc.), and 174 g (3.00 mol) of acetone in 1200 ml of anhydrous ether. The yield of alcohol was 156 g (1.59 mol, 73%); bp 71–73° (15 mm) [lit.<sup>18</sup> 73.5–74.5° (15 mm)]; ir (neat) 3360 (OH), 2245 ( $C\equiv C$ ), 1375, 1365 ( $>C(CH_3)_2$ ), 1160  $cm^{-1}$  ( $>COH$ ); nmr ( $CCl_4$ )  $\delta$  2.88 (s, 1 OH), 1.77 (s, 3  $CH_3C\equiv C-$ ), 1.40 (s, 6  $-C(CH_3)_2O-$ ).

**2,2,3,5-Tetramethyl-3,4-hexadien-1-al (16)** was prepared in a manner similar to that described for 4 from 55 g (0.56 mol) of 2-methyl-3-pentyn-2-ol, 56 g (0.77 mol) of isobutyraldehyde, 50 ml of toluene, 0.15 g of *p*-toluenesulfonic acid, and 0.15 g of hydroquinone by refluxing the mixture until 10 g (0.55 mol) of water had separated. Of the 10 g of product mixture, bp 72–80° (57 mm), which was obtained by distillation, a glpc analysis on a 16-ft Carbowax column at 95° (helium flow, 150 cc/min) revealed that 35% was the desired aldehyde (retention time, 17 min). A 1.60-g (0.0100 mol) sample of the aldehyde was collected by preparative glpc using a 20-ft

(17) Because the symmetric double-bond stretching of tri- and tetra-substituted alkenes is accompanied by small changes in molecular moment but larger changes in polarizability, the absorption at  $\sim 1960$   $cm^{-1}$  is often stronger and more easily identified in the Raman than in the infrared.

(18) T. L. Jacobs and R. A. Meyers, *ibid.*, 86, 5244 (1964).

DEGS column: ir (neat) 2785, 2685 (CHO), 1970 very weak ( $>C=C<$ ), 1735 (CHO), 1450 ( $CH_2$ ), 1395, 1370  $cm^{-1}$  ( $>C(CH_3)_2$ ); nmr ( $CCl_4$ )  $\delta$  9.24 (s, 1  $>CCHO$ ), 1.71 (a slightly perturbed s, 6  $(CH_3)_2C=C=C(-)$ ), 1.57 (a slightly perturbed s, 3  $>C=C=C(CH_3)-$ ), 1.11 (s, 6  $>C(CH_3)_2$ ).

All attempts to increase the yield of this compound by changing the solvent, benzene or cumene instead of toluene, reaction time, or amount of acid failed. The pyrolysis<sup>8a,16</sup> of isobutenyl-1-methyl-2-butenyl ether, which was obtained from the reaction of 1-chloroisobutyl-1-methyl-2-butenyl ether and N,N-dimethylaniline at 75°, did not give the desired aldehyde.

**2,2,3,5-Tetramethyl-3,4-hexadien-1-ol (18-OH)** was prepared in a manner similar to that described for 6-OH from 1.6 g (1.1 mmol) of 2,2,3,5-tetramethyl-3,4-hexadien-1-al (16) in 20 ml of anhydrous ether and 0.35 g (7.5 mmol) of lithium aluminum hydride in 30 ml of anhydrous ether. The yield of alcohol was 1.3 g (8.4 mmol, 80%); bp 110–113° (25 mm); ir (neat) 3360 (OH), 1965 very weak ( $>C=C=C<$ ), 1450 ( $CH_2$ ), 1380, 1365 ( $>C(CH_3)_2$ ), 1030  $cm^{-1}$  ( $CH_2OH$ ); Raman (neat)<sup>17</sup> 1970  $cm^{-1}$  ( $>C=C=C<$ ); nmr ( $CCl_4$ )  $\delta$  3.27 (s, 2  $>CCH_2O-$ ), 1.68 (slightly perturbed s, 6  $(CH_3)_2C=C=C<$ ) superimposed on a singlet at 1.62 (3  $>C=C=C(CH_3)-$ ), 1.14 (broad, slightly perturbed concentration-dependent s, 1 OH), 0.97 (slightly perturbed s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for  $C_{10}H_{18}O$ : C, 77.86; H, 11.76. Found: C, 77.76; H, 11.75.

**2,2,3,5-Tetramethyl-3,4-hexadien-1-yl p-bromobenzenesulfonate (18-OBs)** was prepared in a manner similar to that described for 6-OBs from 1.2 g (7.7 mmol) of 2,2,3,5-tetramethyl-3,4-hexadien-1-ol (18-OH) and 2.5 g (9.8 mmol) of p-bromobenzenesulfonyl chloride in 50 ml of anhydrous pyridine. After 122 hr at  $-10^\circ$ , the yield of crude brosylate was 1.4 g (3.8 mmol, 50%), mp 49.5–50.5°. Recrystallization from n-hexane followed by drying at 1 mm for 2 hr yielded 1.2 g (3.2 mmol, 42%) of pure material: mp 54.0°; ir ( $CCl_4$ ) 3090, 1920, 1655, 1585 ( $>C=CH-$ , aromatic), 1970 weak ( $>C=C=C<$ ), 1480 ( $CH_2$ ), 1450 ( $CH_3$ ), 1400, 1380 ( $>C(CH_3)_2$ ), 1175  $cm^{-1}$  ( $-OSO_2-$ ); nmr ( $CCl_4$ )  $\delta$  7.72 (s, 4 aromatic hydrogens), 3.77 (s, 2  $>CCH_2O-$ ), 1.62 (s, 6  $(CH_3)_2C=C=C<$ ), 1.57 (s, 3  $>C=C=C(CH_3)-$ ), 1.01 (s, 6  $>C(CH_3)_2$ ).

Anal. Calcd for  $C_{18}H_{22}BrO_2S$ : C, 51.48; H, 5.67; Br, 21.41; S, 8.59. Found: C, 51.40; H, 5.78; Br, 21.52; S, 8.79.

The material was used for the rate studies without further purification.

**Determination of Acetolysis Rates.** Anhydrous acetic acid was prepared by mixing Baker and Adamson analytical reagent acetic acid with 1% by volume acetic anhydride, refluxing overnight, and distilling through a 3-ft helix-packed column. To the center cut,

bp 118.0–118.3°, was added 1% by volume analytical reagent acetic anhydride and enough freshly fused reagent grade sodium acetate to make a 0.1 M solution. A weighed sample of the brosylate, sufficient to yield a 0.04 M solution, contained in a 10-ml or 25-ml volumetric flask was dissolved in this solution and diluted to the mark at 25°. Aliquots (1 or 2 ml) of this solution were sealed in test tubes and placed in a thermostated bath maintained to  $\pm 0.03^\circ$ . At measured intervals, tubes were removed and dropped into a Dry Ice-acetone bath to quench the reaction. Tubes were washed, cracked, and titrated immediately with standard perchloric acid to a crystal violet end point. An Ultra-Buret Model 200 (Scientific Industries, Inc., Springfield, Mass.) was used to carry out the titrations. Standard solutions were protected from moisture at all times.

Rate determinations were made at several temperatures. Duplicate runs were made in each case, and the rate constants reported (Table I) are the mean of duplicate determinations at each temperature. The first-order plot in each case was linear to  $>90\%$  reaction and the infinity titers were consistently within 3% of the calculated values. In each case, the brosylate recovered after 0.5–1 half-life was identical with the starting material. The apparent first-order titrimetric acetolysis constants are summarized in Table I, the activation parameters, computed as described previously,<sup>4</sup> in Table II.

**The Ionization Constants of Methyl-Substituted Homoallenic Neopentyl-Type Acids.** The ionization constants of 2,2,3-trimethyl-3,4-pentadienoic acid (5), 2,2-dimethyl-3,4-hexadienoic acid (8), 2,2,3-trimethyl-3,4-hexadienoic acid (11), and 2,2,5-trimethyl-3,4-hexadienoic acid (14) were determined by potentiometric titration according to the procedure of Albert and Sergeant.<sup>19</sup> Standard aqueous solutions of the carboxylic acids,  $\sim 0.01 M$  in acid except in the case of 11 where solubility problems made it necessary to use a 0.004 M solution, were titrated with 0.1 N standard sodium hydroxide solution using a glass vs. standard calomel electrode in conjunction with a Beckman Research pH meter. The  $pK_a$  values recorded in Table II represent averages of six to ten readings from two separate determinations for each acid.

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(19) A. Albert and E. P. Sergeant, "Ionization Constants of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1962, pp 16 ff.