

was completed, the solvent was evaporated and the product was collected, 2.70 g., m.p. 155–160°. Three crystallizations from petroleum ether (60–90°)–ethyl acetate (1:1) gave a product melting from 161–162°. The infrared spectrum showed no absorption in the C=N region, but did absorb at 1185 cm.<sup>-1</sup>. In addition to the aromatic protons, the n.m.r. spectrum showed a single peak (two protons, bridgehead) at  $\tau$  6.9 and a complex multiplet (six protons) from  $\tau$  7.6–8.7.

*Anal.* Calcd. for C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.57; H, 5.32; N, 5.78.

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## Unsaturated Neopentyl Compounds. The Acetolysis of 2,2-Dimethyl-3-buten-1-yl and 2,2,4-Trimethyl-3-penten-1-yl *p*-Bromobenzenesulfonates. $\pi$ -Electron Delocalization in the Absence of Steric Strain<sup>1</sup>

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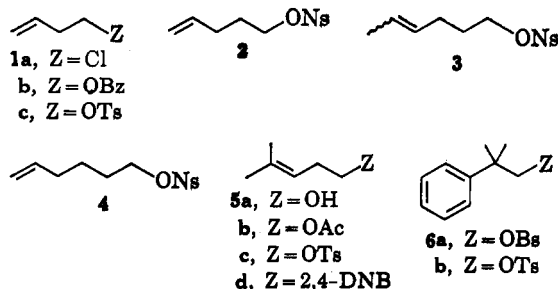
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The acetolysis of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate is about 60 times as rapid at 100° as that of 2,2-dimethylbutyl *p*-bromobenzenesulfonate, and yields a mixture of 2-methylpentadienes, 2-methyl-4-penten-2-yl acetate, and 4-methyl-3-penten-1-yl acetate. Evidence is presented that this rate enhancement is the result of  $\pi$ -electron delocalization in the absence of steric strain, and that vinyl is almost as good a "neighboring group" as phenyl. The anchimerically assisted solvolysis of 2,2,4-trimethyl-3-penten-1-yl *p*-bromobenzenesulfonate in anhydrous acetic acid at 25° yields a mixture of 2,5-dimethylhexadienes and 2,5-dimethyl-4-hexen-2-yl acetate. The nature of the transition state and intermediates in the acetolysis of these and other unsaturated primary arenesulfonates is discussed, and an explanation is offered for the *gem*-dimethyl effect in the solvolyses of homoallylically unsaturated neopentyl derivatives.

It is now a well established fact that the solvolytic displacement reactions of many cyclic and bicyclic esters may be markedly accelerated by an appropriately situated, nonconjugated double bond.<sup>2</sup> Winstein has provided the most generally accepted explanation of such rate enhancements by suggesting that they are the result of increased  $\pi$ -electron delocalization in the transition state of the rate-limiting step.<sup>2b,3</sup> Although there are ample theoretical reasons for suggesting such delocalization,<sup>4</sup> this experimental interpretation has recently been questioned by H. C. Brown<sup>5</sup> who points out that, in every unambiguous case of enhanced solvolysis by an isolated, nonconjugated double bond, this bond is either exocyclic to, or an integral part of, a cyclic or bicyclic ring. Such systems, he suggests, may derive their greater driving force from relief of steric strain in the transition state rather than from an electronic effect. Brown's interpretation, though certainly valid in many instances, would be rendered less generally condemning to the concept of  $\pi$ -electron delocalization if it could be shown that similar rate enhancements occur in systems where such steric effects are negligible.

Attempts to demonstrate solvolytic rate enhancements in the reactions of appropriately unsaturated acyclic derivatives have met with little success. The solvolysis of allylcarbinyl chloride (1a) in 50% aqueous ethanol at 100°<sup>6</sup> is only about one-third as rapid as that of *n*-propyl chloride,<sup>7</sup> while the ethanolysis of allylcarbinyl benzenesulfonate (1b) at 55°<sup>8</sup> is one-half as fast as that of *n*-butyl benzenesulfonate.<sup>9</sup> The acetolysis of 4-penten-1-yl (2) and 4-hexen-1-yl (3) *p*-nitrobenzenesulfonates are only seven-tenths as fast as that of the *n*-hexyl ester under the same conditions.<sup>2c,10</sup> Apparently in these cases the double bond provides little or no additional driving force, and, even in cases which do show a small rate enhancement, it is doubtful that electron delocalization is the cause. For example, the rate of acetolysis of 5-hexen-1-yl *p*-nitrobenzenesulfonate (4) is about one and one-half times that of the *n*-hexyl ester, but may not be a simple first-order reaction.<sup>2c,10</sup> Similarly, the acetolysis of allylcarbinyl *p*-toluenesulfonate (1c) is markedly accelerated by the addition of sodium acetate.<sup>11</sup>



(1) Portions of this work have been reported at the 36th Annual Meeting of the South Carolina Academy of Science, Columbia, S. C., April 1963 [*Bull. S. Carolina Acad. Sci.*, **25**, 28 (1963)] and at the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept. 1963, Abstracts, p. 6Q.

(2) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 153–157, 182–187; (b) S. Winstein, *Experientia, Suppl.*, **2**, 137 (1955); (c) P. D. Bartlett, *Ann.*, **653**, 45 (1962); (d) J. A. Berson, "Molecular Rearrangements," Part One, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 111 ff.

(3) S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).

(4) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 385–589; (b) M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954); (c) R. J. Piccolini and S. Winstein, *Tetrahedron Suppl.*, **2**, 423 (1963).

(5) (a) H. C. Brown and S. Nishida, Abstracts of the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961, p. 20; (b) H. C. Brown, Special Publication No. 16, The Chemical Society, London, 1962, p. 140ff.

(6) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

(7) C. A. Vernon, *J. Chem. Soc.*, 4462 (1954).

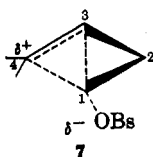
(8) C. G. Bergstrom and S. Siegel, *J. Am. Chem. Soc.*, **74**, 145 (1952).

(9) P. M. Laughton and R. E. Robertson, *Can. J. Chem.*, **33**, 1207 (1955).

(10) The temperature of these acetolyses was not specified.

(11) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

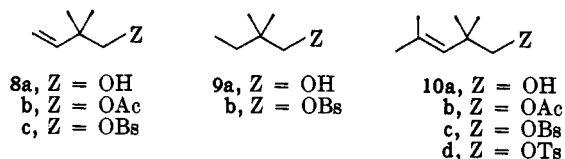
The only unequivocal case of solvolytic rate enhancement for an unsaturated, nonconjugated, aliphatic ester was reported recently by Rogan,<sup>12</sup> who found that at 45°, in the presence of sodium acetate, the acetolysis of 4-methyl-3-penten-1-yl *p*-toluenesulfonate (**5c**) is not complicated by competing bimolecular displacements<sup>13</sup> and occurs 1200 times as rapidly as the acetolysis of ethyl *p*-toluenesulfonate.<sup>14</sup> Since this result represents an example of rate enhancement in the absence of any conceivable steric driving force, Brown's arguments, at least as they apply to **5c**, would appear to be invalid. However, it might be suggested that the enhanced solvolytic reactivity of Rogan's tosylate **5c** is simply the result of the transfer of a substantial amount of the developing positive charge in the transition state from a less stable primary position, C-1, to a considerably more stable tertiary one, C-4.



Under such circumstances the transition state (7) would resemble electronically the  $\alpha,\alpha$ -dimethylcyclopropyl carbonium ion and the rate enhancement would be due less to  $\pi$ -electron delocalization than to charge localization. Some support for this view might be inferred from the fact that in absolute ethanol at 55° the solvolysis of *t*-butyl bromide is about 830 times as rapid as the unimolecular solvolysis of ethyl bromide in spite of greater nucleophilic participation by solvent in the latter case.<sup>17,18</sup> The ratio of the unimolecular acetolysis rates for the comparable tosylates, could it be measured, probably would not differ markedly from that of the bromides.<sup>20</sup>

Since none of the studies reported in the literature appeared to us to give a clear answer to the question of whether the accelerated solvolyses observed in the case of some unsaturated esters derive their additional driving force from the delocalization of the  $\pi$ -electrons or from another source, we decided to prepare and study a compound which could conceivably provide the desired test. Such a compound should contain an isolated, nonconjugated double bond appropriately situated with respect to a moderately good leaving group. This double bond should not be subject to steric crowding or strain of any kind. The unsaturated compound should solvolyze in a demonstrably unimolecular fashion with no competing bimolecular reaction with the solvent, and its solvolysis should not occur in a manner which places an appreciable

positive charge in the transition state at a single particularly stable position. We felt that the simplest compound which ought most nearly to fit these *a priori* criteria would be an arenanesulfonate of the simple, homoallylically unsaturated, neopentyl-type alcohol, 2,2-dimethyl-3-buten-1-ol (**8a**). Because of the ease with which it could be prepared and purified, we chose the brosylate **8c**. We report here its preparation and acetolysis, and a comparison of its reactivity to that of the saturated analogue 2,2-dimethylbutyl *p*-bromobenzenesulfonate (**9b**).



Prior to the appearance of our preliminary communications,<sup>1</sup> the chemical literature contained only a few scattered examples of unsaturated neopentyl-type esters, all of which are cyclic or bicyclic in nature.<sup>21</sup> Recently, however, both Wilcox and Nealy<sup>22b</sup> and V. A. Hoyle, Jr.,<sup>22a</sup> have reported studies similar to ours on the acetolysis of 2,2,4-trimethyl-3-penten-1-yl *p*-toluenesulfonate (**10d**). We will compare their results with ours in the Discussion section of this paper.

## Results

The rates of acetolysis of 2,2-dimethyl-3-buten-1-yl (**8c**) and 2,2-dimethylbutyl (**9b**) *p*-bromobenzenesulfonates have each been measured at several temperatures. The reactions, which are cleanly first order, could be followed to more than 90% completion with no appreciable deviation from linearity. The experimental infinity titers were consistently within 3% of the calculated values. By stopping the acetolysis of **8c** at about 50% reaction and diluting the reaction mixture with water, it is possible to recover the unchanged starting material uncontaminated by any rearranged brosylate. The activation parameters, calculated in the usual manner, are given together with the first-order rate constants in Table I.

Our kinetic data for the solvolysis of 2,2-dimethylbutyl *p*-bromobenzenesulfonate (**9b**) in buffered acetic acid containing ~1% acetic anhydride are in good agreement with those previously determined by McElrath and co-workers in the unbuffered solvent containing a trace of water.<sup>23</sup>

Product studies on the unsaturated ester were carried out as far as possible under conditions identical

(21) (a) A. Zürcher, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **37**, 2145 (1954); (b) J. W. Rowe, A. Melera, D. Arigoni, O. Jeger, and L. Ruzicka, *ibid.*, **40**, 1 (1957); (c) C. Djerassi, F. W. Donovan, S. Burstein, and R. Mauli, *J. Am. Chem. Soc.*, **80**, 1972 (1958); (d) R. S. Bly, Jr., and H. L. Dryden, Jr., *Chem. Ind. (London)*, 1287 (1959); (e) L. DeVries, *J. Am. Chem. Soc.*, **82**, 5242 (1960); (f) S. Winstein and M. Battiste, *ibid.*, **82**, 5244 (1960); (g) N. A. Nelson, J. H. Fassnacht, and J. U. Piper, *ibid.*, **83**, 206 (1961); (h) H. J. Dauben and D. J. Bertelli, *ibid.*, **83**, 4657 (1961); (i) S. Winstein, M. Battiste, and R. Pande, 6th Report on Research under the Sponsorship of the Petroleum Research Fund, 1961, p. 178; (j) C. F. Wilcox and S. S. Chibber, *J. Org. Chem.*, **27**, 2332 (1962); (k) S. Rakhit and M. Gut, *J. Am. Chem. Soc.*, **86**, 1432 (1964).

(22) (a) Reported at the 15th Annual Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov. 1963. We wish to thank Dr. Hoyle, Research Laboratories, Tennessee Eastman Co., Kingsport, Tenn., for communicating his results to us prior to their publication. (b) C. F. Wilcox, Jr., and D. L. Nealy, *J. Org. Chem.*, **28**, 3454 (1963).

(23) E. N. McElrath, R. M. Fritz, C. Brown, C. Y. LeGall, and R. B. Duke, *ibid.*, **25**, 2195 (1960).

(12) J. B. Rogan, *J. Org. Chem.*, **27**, 3910 (1962).

(13) See ref. 12, footnote 17.

(14) A better model might be *n*-butyl *p*-toluenesulfonate.<sup>15</sup> It may be estimated from the data of Glick, on *n*-butyl *p*-bromobenzenesulfonate,<sup>16</sup> Table III, that the acetolysis of **5c** is about 2200 times as rapid as that of *n*-butyl *p*-toluenesulfonate at 45°.

(15) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **78**, 4935 (1956).

(16) As quoted by R. Heck and S. Winstein, *ibid.*, **79**, 3105 (1957).

(17) See ref. 2a, p. 43, Table 22.

(18) The ratio of the unimolecular acetolysis rate of *t*-butyl bromide to that of ethyl bromide at 45° might well exceed 1200, since this ratio should be larger at this lower temperature and in this less nucleophilic but more solvolyzing solvent.<sup>19</sup>

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

(20) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

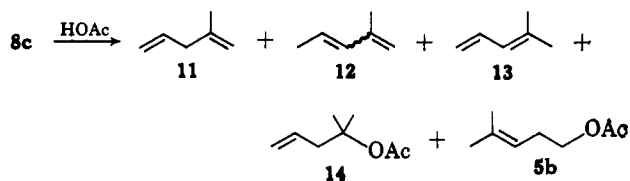
TABLE I  
 REACTION RATES<sup>a</sup>

Compd.	Temp., °C.	10 <sup>4</sup> k <sub>1</sub> sec. <sup>-1</sup>	ΔH*, kcal./mole	ΔS*, e.u.
2,2-Dimethyl-3-buten-1-yl OBs	70.53	4.03 ± 0.004	24.5	-7.5
	86.70	22.0 ± 0.03		
	100.32	77.7 ± 0.001		
2,2-Dimethylbutyl OBs	100.32	1.31 ± 0.005	29.4	-2.5
	129.20	24.4		
		23.8 <sup>c</sup>		

<sup>a</sup> 0.073–0.080 *M* compound in acetic acid containing ~1% acetic anhydride and 0.086–0.092 *M* sodium acetate. <sup>b</sup> 0.03814 *M* brosylate. <sup>c</sup> 0.03793 *M* brosylate.

with those used for the kinetic determinations. The cooled acetolysis solutions were extracted with either pentane or carbon tetrachloride, washed with aqueous sodium carbonate solution to remove the acetic acid, dried, and analyzed by gas chromatography. Because of the volatile nature of some of the products, no attempt was made either to concentrate the solvolysate extract or to separate the hydrocarbons from the esters prior to analysis. Instead, the entire solution, including the added solvent, was gas chromatographed under conditions for which all of the components were well resolved. When two components could not be separated on a single column, both were collected together and rechromatographed on a column which would resolve them completely. Each product mixture was analyzed on at least two different columns under several sets of conditions to assure that the observed proportions were independent of the analytical parameters. In order to determine that the products were stable to these gas chromatographic conditions, each component was collected and rechromatographed. The per cents reported here represent the relative peak areas determined by integration with a compensating polar planimeter and normalized to 100 (exclusive of solvent).<sup>24</sup> The individual components were identified as described in the Experimental section.

The acetolysis of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate (**8c**) gives the products shown below in the proportions indicated in Table II. The product



mixture after 2.3 half-lives at 25° showed no components which were not also present in the 87° mixture.

The remaining 2% of the total product is made up of four components, a hydrocarbon (~0.9%) and three esters. Although their identities are not known, we have demonstrated by mixed gas chromatography with authentic samples that none of these components is 2,2-dimethyl-3-buten-1-yl acetate (**8b**), 3-methyl-1-penten-3-yl acetate (**15**), 3-methyl-*trans*-2-penten-

(24) Since the actual ratio of dienes to acetates is of secondary interest to us, we have made no attempt to correct for differences in thermal conductivity, even though it may be estimated that the response of a hot-wire detector on a weight-weight basis is probably about 1.2–1.3 times greater for the acetates than for the dienes.<sup>25</sup>

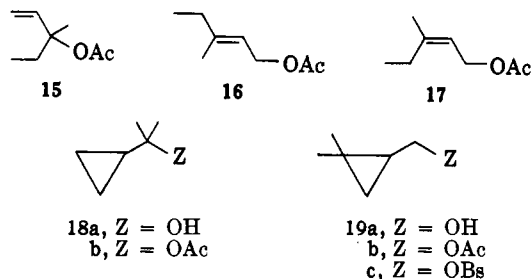
(25) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31**, 230 (1959).

 TABLE II  
 ACETOLYSIS PRODUCTS OF 2,2-DIMETHYL-3-BUTEN-1-YL  
*p*-BROMOBENZENESULFONATE

Product	%	
	87°	100°
2-Methyl-1,4-pentadiene ( <b>11</b> )	19	24
2-Methyl-1,3-pentadienes ( <b>12</b> )		11
	32 <sup>a</sup>	
2-Methyl-2,5-pentadiene ( <b>13</b> )		25
2-Methyl-4-penten-2-yl OAc ( <b>14</b> )	31	24
4-Methyl-3-penten-1-yl OAc ( <b>5b</b> )	16	14

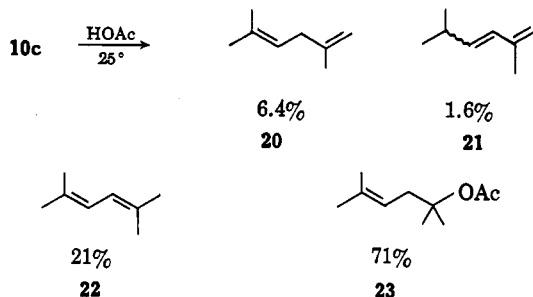
<sup>a</sup> Total of **12** and **13**.

1-yl acetate (**16**), 3-methyl-*cis*-2-penten-1-yl acetate (**17**),  $\alpha,\alpha$ -dimethylcyclopropylcarbinyl acetate (**18b**), or (2,2-dimethylcyclopropyl)carbinyl acetate (**19b**).



By subjecting an authentic sample of each to the acetolysis conditions at 87–88°, we have demonstrated that acetates **5b**, **8b**, **14**, and **19b** can be recovered unchanged after 9–14 half-lives, that **18b** yields only one acetate, **5b**, and that **15** yields a mixture of three hydrocarbons and the two acetates, **16** and **17**. Although we made several attempts to do so, we were never able to isolate (2,2-dimethylcyclopropyl)carbinyl *p*-bromobenzenesulfonate (**19c**). When decomposed in pyridine this brosylate yields a complex mixture the principal component of which is **11**.

In our hands, the acetolysis at 25° of 2,2,4-trimethyl-3-penten-1-yl *p*-bromobenzenesulfonate (**10c**) in buffered acetic acid containing ~1% acetic anhydride yields the products shown below. It may be estimated

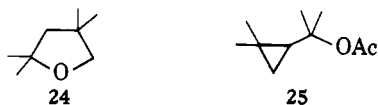


from the n.m.r. spectrum that the solvolysate extract prior to gas chromatography contains about 80 mole % of the tertiary acetate **23**. Although this is the largest proportion which we were able to measure, it seems likely to us that the amount of this ester produced in the actual acetolysis is even greater. We believe that the dienes **20** and **21** are true acetolysis products since we find that similar dienes are not isomerized when subjected separately to the acetolysis conditions.

Wilcox and Nealy<sup>22b</sup> report that the solvolysis of 2,2,4-trimethyl-3-penten-1-yl *p*-toluenesulfonate (**10d**) in buffered 99.8% acetic acid at 25° yields 40% 2,5-dimethyl-2,4-hexadiene (**22**), 40% 2,5-dimethyl-4-

hexen-2-yl acetate (23), 10% 2,2,4-trimethyl-3-penten-1-yl acetate (10b), and 10% 2,2,4,4-tetramethyltetrahydrofuran (24). These authors suggest that the unrearranged acetate 10b was probably formed from unchanged 2,2,4-trimethyl-3-penten-1-ol (10a) present in the starting tosylate (10d). Because this acetate was not present in our mixture even though it is stable to the conditions of the reaction, we conclude that it is not an acetolysis product of the brosylate 10c. Since the formation of 2,2,4,4-tetramethyltetrahydrofuran (24) in this acetolysis requires the presence of either water or 10a, we did not find this cyclic ether in our solvolysis carried out in anhydrous acetic acid. Wilcox and Nealy report a considerably higher proportion of diene 22 to tertiary acetate, 23, than we observed, but did not detect the presence of 20 and 21. We attribute this to their method of isolation and analysis rather than to any fundamental difference in the two acetolyses. No cyclic esters of hydrocarbons have been observed in this reaction.<sup>22</sup>

Each of our attempts to prepare (2,2-dimethylcyclopropyl)- $\alpha,\alpha$ -dimethylcarbinyl acetate (25) gave complex mixtures the principal constituents of which appeared to be 2,5-dimethyl-1,4-hexadiene (20), 2,5-dimethyl-2,4-hexadiene (21), and 2,5-dimethyl-4-hexen-2-yl acetate (23).



Although we have not investigated the nature of the acetolysis products of 9b, McElrath and her co-workers, who have done so, report them to be completely rearranged.<sup>23</sup>

### Discussion

**The Case for  $\pi$ -Electron Delocalization.**—The acetolysis of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate (8c) is about 60 times as rapid at 100° (300 times at 25°) as that of the saturated brosylate 9b. The reaction rate constants of these and some related arenesulfonates are collected in Table III. This increased reactivity is due to the more favorable enthalpy term of 8c which outweighs the less favorable entropy (Table I). We believe that the lower  $\Delta H^*$  is not due to a double bond induced destabilization of the starting material 8c with respect to its transition state for acetolysis,<sup>26</sup> but that it can only be due to increased stabilization of this transition state itself through  $\pi$ -electron delocalization. However, a nonconjugated double bond can also destabilize the transition state of a solvolysis by inductively retarding the departure of the incipient anion,<sup>2</sup> and, unless a correction can be applied for this inductive retardation, it is not possible to determine the extent to which the transition state

(26) We base this conclusion upon the following facts. As indicated by its heat of hydrogenation in the gas phase,<sup>27a</sup> the double bond of 3,3-dimethyl-1-butene is no less stable than that of propene,<sup>27b</sup> 1-butene,<sup>27b</sup> 1-heptene,<sup>27c</sup> or 3-methyl-1-butene<sup>27a</sup>; the relative heats of hydrogenation of alkyl-substituted ethylenes in acetic acid are not significantly different from those determined in the gas phase<sup>28</sup>; and the ultraviolet spectra of 8c and 9b in ethanol are virtually identical above 200 m $\mu$  (see Experimental section).

(27) (a) M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, and W. E. Vaughan, *J. Am. Chem. Soc.*, **59**, 831 (1937); (b) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **57**, 876 (1935); (c) *ibid.*, **58**, 137 (1936).

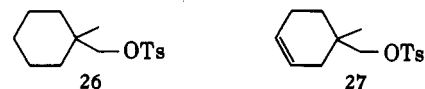
(28) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

TABLE III  
ACETOLYSIS RATES OF SOME NEOPENTYL AND OTHER  
PRIMARY ARENESULFONATES

Compd.	$k_1$ sec. <sup>-1</sup>	
	25°	100°
Neopentyl OBs	$1.4 \times 10^{-10a}$	$7.28 \times 10^{-6a}$
OTs	$3.1 \times 10^{-11b}$	$1.60 \pm 0.13 \times 10^{-6c}$
2,2-Dimethylbutyl OBs	$3.3 \times 10^{-10d}$	$1.21 \times 10^{-6d}$
	$5.0 \times 10^{-10e}$	$1.31 \pm 0.005 \times 10^{-6f}$
2,2-Dimethyl-3-buten-1-yl OBs	$1.5 \times 10^{-7g}$	$7.77 \pm 0.01 \times 10^{-4f}$
2,2,4-Trimethylpentyl OBs	$1.1 \times 10^{-9g}$	$1.74 \times 10^{-6g}$
OTs	$2.4 \times 10^{-10h}$	$3.9 \times 10^{-6h}$
2,2,4-Trimethyl-3-penten-1-yl OTs	$2.75 \times 10^{-4i}$	
<i>n</i> -Butyl OBs	$3.9 \times 10^{-9j}$	$1.55 \times 10^{-6j}$
OTs	$1.3 \times 10^{-9k}$	$5.2 \times 10^{-6k}$
4-Methyl-3-penten-1-yl OTs	$3.3 \times 10^{-8l}$	$8.6 \times 10^{-3l}$
Neophyl OBs	$1.4 \times 10^{-7m}$	$1.45 \times 10^{-3m}$
OTs	$3.9 \times 10^{-8n}$	$2.47 \pm 0.05 \times 10^{-4c}$

<sup>a</sup> Extrapolated from the data of McElrath, *et al.*,<sup>23</sup> using  $\Delta H^* = 31.2$  kcal./mole,  $\Delta S^* = +1.1$  e.u. <sup>b</sup> Extrapolated from the data of S. Winstein, *et al.* [*J. Am. Chem. Soc.*, **74**, 1113 (1952)], using  $\Delta H^* = 31.5$  kcal./mole,  $\Delta S^* = -1.0$  e.u. <sup>c</sup> Reported by Winstein, *et al.* (lit. b), at 99.58°. <sup>d</sup> Extrapolated from the data of McElrath, *et al.*,<sup>23</sup> using  $\Delta H^* = 30.3$  kcal./mole,  $\Delta S^* = -0.28$  e.u. <sup>e</sup> Extrapolated from our data at higher temperatures; see Table I. <sup>f</sup> At 100.32°; see Table I. <sup>g</sup> Extrapolated from the data of McElrath, *et al.*,<sup>23</sup> using  $\Delta H^* = 27.9$  kcal./mole,  $\Delta S^* = -6.0$  e.u. <sup>h</sup>  $k_1$  ROBs/4.5. <sup>i</sup> See ref. 22b. <sup>j</sup> Extrapolated from the data of R. Glick,<sup>16</sup> using a calculated  $\Delta H^*$  of 22.9 kcal./mole,  $\Delta S^* = -17.0$  e.u. <sup>k</sup>  $k_1$  ROBs/3.0.<sup>16</sup> <sup>l</sup> Extrapolated from the data of Rogan<sup>12</sup> using  $\Delta H^* = 22.6$  kcal./mole,  $\Delta S^* = -7.8$  e.u. <sup>m</sup> Extrapolated from the data of R. Heck and S. Winstein [*J. Am. Chem. Soc.*, **79**, 3432 (1957)] using  $\Delta H^* = 25.5$  kcal./mole,  $\Delta S^* = -4.6$  e.u. <sup>n</sup> Extrapolated from the data of Winstein, *et al.* (lit. b), using  $\Delta H^* = 25.7$  kcal./mole,  $\Delta S^* = -6.4$  e.u.

is stabilized by  $\pi$ -electron delocalization. Wilcox and Chibber<sup>21j</sup> have estimated that the acetolysis of 1-methyl-3-cyclohexen-1-ylcarbinyl *p*-toluenesulfonate (27) at 99.84° is inductively retarded by a factor of 3.1 compared with that of the saturated compound 26,



while Winstein, Battiste, and Pande report that the introduction of a second homoallylic double bond into the ring of 1-methyl-2-cyclohexen-1-ylcarbinyl *p*-bromobenzenesulfonate (28), *viz.* 29, reduces its rate of acetolysis at 25° by a factor of 8.<sup>21i</sup> Thus we suspect



that the rate of acetolysis of 8c is inductively retarded with respect to 9b by a factor of 5–10. On this basis we would conclude that the acetolysis of 8c is assisted by  $\pi$ -electron delocalization in the transition state of the rate-limiting step by 1500–3000 times at 25° or 300–600 times at 100°.

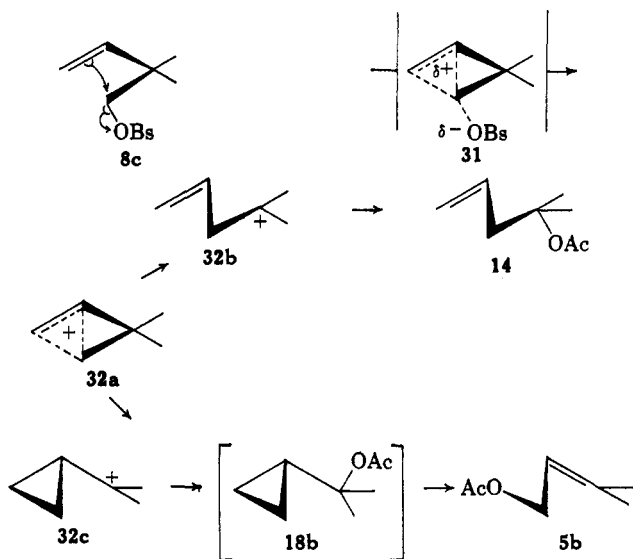
Although this estimate of anchimeric assistance is in line with those observed in other systems,<sup>2</sup> it is subject to several assumptions some of which may prove to be of dubious validity. Most of the uncertainty stems from the use of the saturated compound as a model for the unsaturated and from the estimation of the in-

ductive retardation in the unsaturated case.<sup>29</sup> These difficulties can be avoided and a minimum value for anchimeric assistance can be established if account is taken of the apparent absence of methyl migration during the acetolysis of **8c**. Each reacting molecule of unsaturated brosylate has a choice; it may undergo methyl migration or it may follow another path. The fact that there is another choice would in no way affect the absolute rate of methyl migration since the reaction paths are independent, mutually exclusive, and essentially irreversible. Since each of these reaction paths should be subject to approximately the same inductive retardation, the fact that no products of methyl migration have been observed must mean that the alternative reaction path is at least 200 times and probably 400 times more favorable. This represents a minimum estimate of anchimeric assistance by  $\pi$ -electron delocalization because the actual amount of methyl migration may be considerably less than the 0.5 to 1.0% that our experimental method would have detected, because methyl migration should itself be accelerated by charge delocalization if a substantial amount of positive charge were developed at an allylic position in the transition state,<sup>33,34</sup> and because the migratory aptitude of the methyl group is greater than that of the ethyl in the saturated compound **9b**.<sup>23</sup>

**Phenyl vs. Vinyl as a "Neighboring Group."**—Of all the substituents known for their ability to stabilize a positive charge at a nonconjugated position, *i.e.*, to act as a "neighboring group," phenyl is the classic example.<sup>2a,35</sup> How then does an isolated double bond, *i.e.*, vinyl group, compare in this respect with phenyl? As shown in Table III, the acetolysis of neophyl *p*-bromobenzenesulfonate (**6a**) is less than twice as rapid at 100° as that of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate (**8c**). At 25° the difference is almost nil. It can be calculated from the data of Saunders and Paine<sup>33</sup> that at ~120°, phenyl participation in the acetolysis of neophyl *p*-toluenesulfonate (**6b**) is about 600 times that of methyl, while our data indicate that at 100° vinyl participation is at least 200 to 400 times that of methyl. Since a phenyl group is only slightly more inductively negative than a vinyl,<sup>36</sup> we conclude that, in their ability to accelerate the acetolysis of a neopentyl derivative by delocali-

zation, the  $\pi$ -electrons of a homoallylic double bond are at most only slightly less, and possibly more effective than, the similarly situated  $\pi$ -electrons of an aromatic ring.<sup>39</sup>

**The Nature of the Intermediates.**—Having established that the transition state for the acetolysis of the unsaturated compound **8c** is stabilized effectively by  $\pi$ -electron delocalization, it is proper to ask how the over-all reaction sequence should be represented. Our experimental observations are insufficient to permit a unique formulation, but, after comparing them with the results of Rogan<sup>12</sup> and with those of Wilcox and Nealy,<sup>22b</sup> we feel that the following picture is most satisfactory.



This interpretation is similar to that developed by Roberts and co-workers to correlate the results of their extensive and elegant investigations into the reactions of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl arenesulfonates, amines, halides, and alcohols.<sup>40</sup> It recognizes that the acetolysis of **8c** is accelerated by  $\pi$ -electron delocalization in the transition state of the rate-limiting step and predicts that such assistance would be less than that observed by Rogan for the acetolysis of 4-methyl-3-penten-1-yl *p*-toluenesulfonate (**5c**)<sup>12</sup> and by Wilcox and Nealy for the acetolysis of 2,2,3-trimethyl-3-penten-1-yl *p*-toluenesulfonate (**10d**)<sup>22b</sup> (Table III). It is probably in accord with the lower activation entropy observed in the case of the unsaturated brosylate **8c** (Table I) and it agrees with the theoretical calculations of Howden and Roberts which predict a "bicyclobutonium" cation to be more stable than a "homoallyl."<sup>4b,41</sup> It suggests that the departing brosylate should shield the reactive side of the neopentyl carbon in **32a**, and hence prevent the

(29) Estimates of inductive retardation are best made by the use of the Taft equation,<sup>30</sup> but unfortunately the necessary data are not available in this case. The substituent constants,  $\sigma^*$ , for 2,2-dimethylbutyl and 2,2-dimethyl-3-buten-1-yl could easily be determined, but there is not presently available enough solvolytic rate data on suitably substituted, nonparticipating, neopentyl-type compounds to permit the evaluation of a meaningful  $\rho^*$ -value for this system. The series of tosylates recently reported by Stock,<sup>31</sup> for which good substituent values are known,<sup>32</sup> would be ideally suited for this purpose. Certainly one is not justified in using the  $\rho^*$  of Streitwieser, developed for the ethanolsis of primary tosylates,<sup>35</sup> to correlate data on the acetolysis of neopentyl arenesulfonates.

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

(31) H. D. Holtz and L. M. Stock, Abstracts of the 146th National Meeting of the American Chemical Society, Denver, Colo., Jan. 1964, p. 8C.

(32) J. D. Roberts and W. T. Moreland, Jr., *J. Am. Chem. Soc.*, **75**, 2167 (1953).

(33) W. H. Saunders, Jr., and R. H. Paine [*ibid.*, **83**, 882 (1961)] have demonstrated that the partial rate factor for methyl migration in the acetolysis of neophyl *p*-toluenesulfonate (**6b**) is approximately equal to that of neopentyl *p*-toluenesulfonate. They infer from this that little positive charge is developed at the benzyl carbon in the transition state of the path which leads to methyl migration.

(34) See ref. 40d, footnote 14.

(35) (a) W. Lwowski, *Angew. Chem.*, **70**, 483 (1958); (b) B. Capon, *Quart. Rev. (London)*, **18**, 45 (1964).

(36) As evidenced by the nearly equal acidities of benzoic ( $pK_a = 4.20$ )<sup>37</sup> and acrylic ( $pK_a = 4.25$ )<sup>38</sup> or of phenylacetic ( $pK_a = 4.31$ )<sup>37</sup> and vinylacetic ( $pK_a = 4.35$ )<sup>37</sup> acids.

(37) J. F. J. Dippy, *Chem. Rev.*, **25**, 151 (1939).

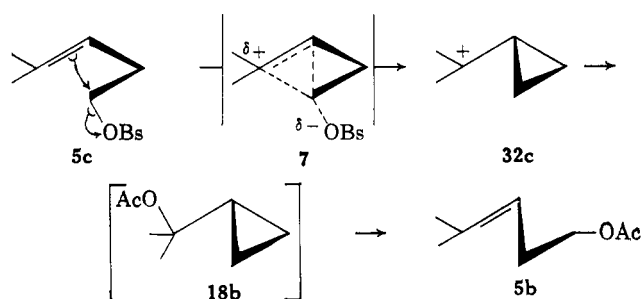
(38) M. Kilpatrick and J. G. Morse, *J. Am. Chem. Soc.*, **75**, 1854 (1953).

(39) W. Herz and G. Caple [*J. Org. Chem.*, **29**, 1691 (1964)] have recently presented evidence of a different nature that in some rearrangements to electron-deficient carbons, vinyl is a better migrating group than phenyl.

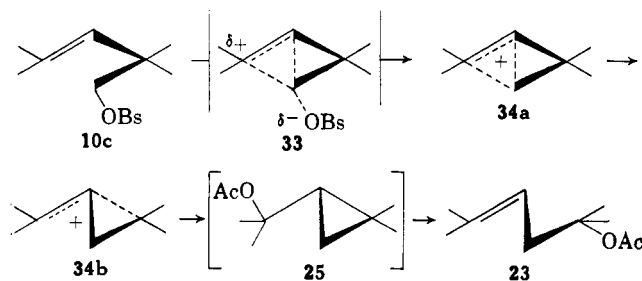
(40) (a) J. D. Roberts, Abstracts of the 16th National Organic Chemistry Symposium, Seattle, Wash., June 1959, p. 1; (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959), and references cited therein; (c) E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961); (d) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961); (e) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961).

formation of unrearranged acetate (**8b**), which, though stable to reaction conditions, was not observed. Theoretical considerations predict that the relative stabilities of the intermediates **32** would be  $32b > 32c > 32a$ .<sup>40d,41,42</sup> If it is assumed that attack by acetate on these intermediates is kinetically controlled and at the tertiary carbons, and that the primary acetate **5b** which we observe is formed in a subsequent step from the reactive intermediate,  $\alpha,\alpha$ -dimethylcyclopropylcarbinyl acetate, **18b**,<sup>44</sup> then this description will explain the predominance of the tertiary acetate **14** in the products of the solvolysis.

The fact that Rogan observed only the primary acetate **5b** from the acetolysis of **5c** and that the acetolysis of **18b** yields only this ester may be interpreted to mean that **32b** and **32c** represent discrete intermediates and that they are not equilibrated under these conditions. The course of the reaction may be represented as follows.<sup>42</sup>



Since our attempts to prepare (2,2-dimethylcyclopropyl)- $\alpha,\alpha$ -dimethylcarbinyl acetate (**25**) resulted in a mixture of dienes and the unsaturated ester **23**, similar in character to that formed in the acetolysis of **10c**, we suspect that this acetolysis may also yield the cyclic acetate **25** as an unstable intermediate.



**The gem-Dimethyl Effect.**—Until an accurate value for the unimolecular rate of acetolysis of allylcarbinyl brosylate **1b** is available,<sup>45</sup> we cannot know whether the two methyl groups actually increase the rate of unimolecular acetolysis of **8c** or whether they serve, by preventing bimolecular displacements, merely to render the first-order process observable. However, since the data of Wilcox and Nealy<sup>22b</sup> clearly show (Table III) that the methyl groups at C-2 in **10d** do increase its rate of unimolecular acetolysis, it seems reasonable that they do in the case of **8c** also.

(41) M. E. H. Howden and J. D. Roberts, *Tetrahedron Suppl.*, **2**, 403 (1963).

(42) Although we have represented the intermediates **32b** and **32c** in the classical manner to emphasize the preponderance of charge at the tertiary carbons, we do not intend to imply that this charge is completely localized or that these intermediates differ from those represented in the "non-classical" fashion by Roberts.<sup>42</sup>

(43) See ref. 40a, p. 9.

(44) See ref. 12, footnote 14, and the Results and Experimental sections of this paper.

(45) See ref. 12, footnote 17.

Since in neither compound (**8c** or **10d**) is significant charge developed at C-2 in the transition state of the rate-limiting step (**31** and **33**, respectively), it is appropriate to consider the manner in which the methyl groups at this position are able to accelerate these rates. In order for an acyclic homoallylically unsaturated compound such as **1**, **5**, **8**, or **10** to have its rate of acetolysis aided by the delocalization of its  $\pi$ -electrons, it is necessary that the C-1-C-2-C-3 bond angle decrease from its normal tetrahedral value.<sup>41</sup> This decrease is accompanied by a change in hybridization of the atomic orbitals at C-2 which confers more p-character to those which are utilized to form the C-1-C-2 and the C-2-C-3 "bent" bonds, and more s-character to the orbitals which form the  $\sigma$ -bonds with the substituents at C-2, *i.e.*, hydrogens in **1** and **5** and methyls in **8** and **10**.<sup>46</sup> The increased s-character at the C-2 end of the two  $\sigma$ -bonds results in a shift of electron density away from the substituents and toward this carbon.<sup>46,48</sup> This change in electron density along the bond is more easily accommodated by methyl (alkyl) groups, which use  $sp^3$  orbitals for bonding, than by hydrogens, which utilize  $1s$  orbitals for this purpose. Hence the function of the methyl groups at C-2 is to facilitate the hybridizational changes which occur at this position during the anchimerically assisted acetolysis of **8c** and **10d**.

### Experimental<sup>49</sup>

**2,2-Dimethyl-3-buten-1-ol (8a).**—A solution of 30 g. (0.21 mole) of ethyl 2,2-dimethyl-3-butenolate<sup>54</sup> in 200 ml. of anhy-

(46) The situation is analogous to that of cyclopropane,<sup>47</sup> as discussed in K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 123 ff.

(47) C. A. Coulson and W. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(48) A. D. Walsh, *Trans. Faraday Soc.*, **43**, 60 (1947).

(49) Melting and boiling points are uncorrected. Microanalyses were performed by either Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or Gailbraith Laboratories, Inc., Knoxville, Tenn. The infrared spectra were determined on a Perkin-Elmer grating spectrophotometer, Model 337, the nuclear magnetic resonance spectra on a Varian A-60 spectrometer at  $\sim 35^\circ$  using tetramethylsilane ( $\tau$  10.00)<sup>50</sup> and/or chloroform ( $\tau$  2.69) as internal standards in carbon tetrachloride. The ultraviolet spectra were determined on a nitrogen-flushed Cary Model 14M spectrophotometer. Spectral interpretations were made with the aid of standard reference works.<sup>51</sup> The gas chromatographic analyses were carried out on a Perkin-Elmer vapor fractometer, Model 154D, using a 0.25 in.  $\times$  6 ft. double hairpin copper tube packed with 15% Carbowax 20M on 80-100-mesh neutral firebrick or on an F and M Model 500 linear temperature-programmed gas chromatograph using 0.25 in.  $\times$  8 ft. coiled copper tubes packed with 20% Carbowax 20M on 100-140-mesh Gas-Chrom-S<sup>52</sup> or 60-80-mesh Chromasorb P,<sup>53</sup> 20% diethylene glycol saturated with silver nitrate on 80-100-mesh Chromasorb P,<sup>53</sup> 20% tris- $\beta$ -cyanoethoxypropane (TCEP) on 60-80-mesh Chromasorb P,<sup>53</sup> 20% silicone oil 200 on 60-80-mesh Chromasorb P,<sup>53</sup> or 20% diethylene glycol succinate (DEGS) on 60-80-mesh Chromasorb P.<sup>53</sup> Helium was used as a carrier gas at flow rates of 50-120 cc./min.

(50) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(51) (a) K. Nakaniishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962; (b) A. D. Cross, "An Introduction to Practical Infrared Spectroscopy," Butterworth and Co. (Publishers) Ltd., London, 1960; (c) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958; (d) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959; (e) J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961; (f) K. B. Wiberg and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962; (g) N. S. Bhacca, D. P. Hollis, L. F. Johnson, E. A. Pier, and J. N. Shoolery, "High Resolution NMR Spectra Catalog," Vol. I and II, Varian Associates, Palo Alto, Calif., 1962 and 1963; (h) A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry," Edward Arnold Ltd., London, 1958.

(52) Applied Science Laboratories, Inc., State College, Pa.

(53) Johns-Manville Products Corp.

(54) K. Folkers and H. Adkins, *J. Am. Chem. Soc.*, **53**, 1416 (1931).

drous ether was added, at a rate sufficient to maintain reflux, to a stirred slurry of 23 g. (0.58 mole) of lithium aluminum hydride and 200 ml. of anhydrous ether contained in a dry, nitrogen-flushed, 1-l., three-necked flask equipped with a dropping funnel, a stirrer, and a condenser. After the addition had been completed, the reaction mixture was heated at reflux for 1 hr. and cooled to about 5°; the complex was decomposed by the successive addition of 15 ml. of water, 20 ml. of 10% aqueous sodium hydroxide, and 50 ml. of water. The ethereal layer was separated, washed with three 25-ml. portions of water, and dried over anhydrous magnesium sulfate. The ether was removed by distillation at atmospheric pressure and the residue was distilled to yield 14 g. (67%) of 2,2-dimethyl-3-buten-1-ol, b.p. 128–131° (lit.<sup>54</sup> 128.5–131°),  $n_D^{20}$  1.4305. A gas chromatographic analysis on a Carbowax column at 125° showed the product to be greater than 99% pure.

Anal. Calcd. for  $C_6H_{12}O$ : C, 71.95; H, 12.08. Found: C, 71.76; H, 11.93.

Infrared:  $\nu_{\max}^{\text{film}}$  3355 (OH, bonded), 3093, 3020, 2980 sh 1840, 1420, 1290, 996, and 910 ( $\text{CH}=\text{CH}_2$ ), 2960 and 2870 ( $\text{CH}_2$ ), 2935 and 728 ( $\text{CH}_2$ ), 1645 ( $>\text{C}=\text{C}<$ ), 1390, 1370, and 1160 [ $>\text{C}(\text{CH}_3)_2$ ], and 1035  $\text{cm}^{-1}$  ( $\text{CH}_2\text{O}$ ). N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.20 quartet ( $\text{HHC}=\text{CHC} \leftarrow$ ), 5.01 octet ( $2\text{HHC}=\text{CH}$ ), 6.72 singlet, ( $2\text{-OCH}_2\text{C} \leftarrow$ ), 7.83 singlet (OH), 9.00 singlet [ $6 >\text{C}(\text{CH}_3)_2$ ]. The quartet at  $\tau$  4.20 and the octet at 5.01 together constitute the typical 12-line ABX pattern of a terminal vinyl group

$\text{H}_a$   
 $\text{H}_x >\text{C}=\text{C} < \text{H}_b$  for which the following coupling constants can be calculated:  $J_{ax} = 18.3$  c.p.s.,  $J_{bx} = 9.5$  c.p.s., and  $J_{ab} = 2.0$  c.p.s.

**2,2-Dimethyl-3-buten-1-yl Acetate (8b).**—A 1.00-g. (0.0100-mole) sample of 2,2-dimethyl-3-buten-1-ol was mixed with 1.2 g. (0.012 mole) of acetic anhydride in 20 ml. of dry pyridine. The mixture was heated at reflux for 10 hr., cooled to 5°, and poured into 50 ml. of ice-water. The mixture was stirred until the ice had melted and the aqueous solution was extracted with 30 ml. of pentane. The pentane solution was washed successively with 10 ml. of 10% hydrochloric acid, 10 ml. of 10% aqueous sodium carbonate solution, and two 20-ml. portions of water, and was dried over anhydrous sodium sulfate. The pentane was distilled from the dried solution through a wire-spiral-packed column and the residue was distilled to give 0.98 g. (70%) of product, b.p. 147–150° (lit.<sup>55</sup> 149°),  $n_D^{26}$  1.4162.

A gas chromatographic analysis of this material on a Carbowax column at 100° showed the presence of three components whose relative retention times were 1.0, 1.2, and 1.5, respectively. The first peak (95%) was collected for spectra and analysis.

Anal. Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93; O, 22.49. Found: C, 67.71; H, 9.83; O, 22.39.

Infrared:  $\nu_{\max}^{\text{film}}$  3090, 1420, 997, and 917 ( $\text{CH}=\text{CH}_2$ ), 1740, 1240 and 1037 ( $\text{OCOCH}_3$ ), 1645 ( $>\text{C}=\text{C}<$ ), and 1390 and 1370  $\text{cm}^{-1}$  [ $>\text{C}(\text{CH}_3)_2$ ]. N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.19, quartet ( $\text{HHC}=\text{CHC} \leftarrow$ ), 5.04, octet ( $2\text{HHC}=\text{CH}$ ), 6.20, singlet ( $2\text{OCH}_2\text{C} \leftarrow$ ), 8.03, singlet ( $3\text{OCOCH}_3$ ), and 8.97, singlet [ $6 >\text{C}(\text{CH}_3)_2$ ]. The quartet at  $\tau$  4.19 and the octet at 5.04 together constitute the typical 12-line ABX pattern of a terminal vinyl group

$\text{H}_a$   
 $\text{H}_x >\text{C}=\text{C} < \text{H}_b$  for which the following coupling constants can be calculated:  $J_{ax} = 17.8$  c.p.s.,  $J_{bx} = 10.0$  c.p.s., and  $J_{ab} = 2.0$  c.p.s.

**2,2-Dimethyl-3-buten-1-yl *p*-Bromobenzenesulfonate (8c).**—A solution of 3.0 g. (0.030 mole) of 2,2-dimethyl-3-buten-1-ol in 75 ml. of pyridine was cooled to 5° and mixed with 8.40 g. (0.0330 mole) of *p*-bromobenzenesulfonyl chloride. The reaction mixture was maintained at –20° for 4 days, then poured on to 200 g. of ice. The resulting mixture was stirred until the ice had melted, and the crystalline product was recovered by filtration; yield 7–8 g. Recrystallization from pentane gave 6.3 g. (66%) of white plates, m.p. 43–43.5°.

Anal. Calcd. for  $C_{12}H_{18}BrO_3S$ : C, 45.14; H, 4.70; Br, 25.08. Found: C, 45.08; H, 4.54; Br, 25.86.

Infrared:  $\nu_{\max}^{\text{CCl}_4}$  3090, 987, and 918 ( $\text{CH}=\text{CH}_2$ ), 1915 and 957 (CO?), 1645 ( $>\text{C}=\text{C}<$ ), 1580 and 1460 (aromatic H), 1380 (?) and 1188 ( $\text{OSO}_2$ ), and 610  $\text{cm}^{-1}$  (CBr?). Ultraviolet:  $\lambda_{\max}^{\text{EtOH}}$  234  $\mu$  ( $\epsilon \approx 19,000$ ). N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  2.23, singlet (4 aromatic H), 4.24, quartet ( $1\text{HHC}=\text{CHC} \leftarrow$ ), 5.00, octet ( $2\text{HHC}=\text{CH}$ ), 6.24, singlet ( $2\text{OCH}_2\text{C} \leftarrow$ ), and 8.97, singlet [ $6 >\text{C}(\text{CH}_3)_2$ ].

(55) A. Courtot, *Bull. soc. chim. France*, **35**, 111 (1906).

The quartet at  $\tau$  4.24 and the octet at 5.00 together constitute the typical 12-line ABX pattern of a terminal vinyl group

$\text{H}_a$   
 $\text{H}_x >\text{C}=\text{C} < \text{H}_b$  for which the following coupling constants may be calculated:  $J_{ax} = 18.0$  c.p.s.,  $J_{bx} = 9.9$  c.p.s., and  $J_{ab} = 1.5$  c.p.s. This material was used for the solvolyses without further purification.

**2,2-Dimethylcyclopropanecarboxylic Acid.**—This material was prepared in three steps from neopentyl glycol (Eastman Chemical Products, Inc.)<sup>56</sup> in 49% over-all yield by the procedure of Nelson, *et al.*,<sup>57</sup> b.p. 80° at 4 mm. (lit.<sup>57</sup> 84° at 5 mm.),  $n_D^{25}$  1.4386.

Infrared:  $\nu_{\max}^{\text{film}}$  3500–2300 broad (CH stretches), 1690–1710 (COOH dimer), 1435 ( $\text{CH}_2$ ?), and 1380, 1365, and 1215 (?)  $\text{cm}^{-1}$  [ $>\text{C}(\text{CH}_3)_2$ ]. N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  –0.20, singlet (COOH), 8.28–9.30, a 14(?)–line multiplet ( $3 >\text{C}-\text{CHH}-\text{CH}-$ ) super-

imposed upon an 8.72 singlet ( $3\text{CH}_3$ ) and an 8.80 singlet ( $3\text{CH}_3$ ). The multiplet from  $\tau$  8.28–9.30 is apparently a typical ABC pattern of the three nonequivalent cyclopropane hydrogens.<sup>58</sup>

The purity of this acid was established by esterifying a 300-mg. sample with excess ethereal diazomethane and subjecting the product to gas chromatographic analysis. The esterified mixture showed two peaks on a Carbowax column at 115°. The second of these, which comprised about 95% of the total, was collected and shown by its infrared and n.m.r. spectra to be methyl 2,2-dimethylcyclopropanecarboxylate.

Infrared:  $\nu_{\max}^{\text{film}}$  3080 and 1007 (?) ( $>\text{C}-\text{CHH}-\text{CH}-$ ), 3005 ( $>\text{C}-\text{CHH}-\text{CH}-$ ), 2955, 2880, and 1460 ( $\text{CCH}_3$ ), 1740,

1260, and 1175 ( $\text{COOCH}_3$ ), and 1380 and 1370  $\text{cm}^{-1}$  [ $>\text{C}(\text{CH}_3)_2$ ]. N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  6.41, singlet ( $3\text{COOCH}_3$ ), 8.30–9.38, a 14(?)–line multiplet ( $3 >\text{C}-\text{CHH}-\text{CH}-$ ) superimposed upon an

8.82 singlet ( $3\text{CH}_3$ ) and an 8.84 singlet ( $3\text{CH}_3$ ). The multiplet from  $\tau$  8.30–9.38 is apparently a typical ABC pattern of the three nonequivalent cyclopropane hydrogens.

**(2,2-Dimethylcyclopropyl)carbinol (19a).**—A solution of 4.0 g. of 95% 2,2-dimethylcyclopropanecarboxylic acid (0.033 mole) in 35 ml. of anhydrous ether was added dropwise to a stirred slurry of 4.0 g. (0.11 mole) of lithium aluminum hydride in 35 ml. of ether. The mixture was refluxed for 1 hr. and then decomposed by the cautious addition of 5 ml. of water, 5 ml. of 10% aqueous sodium hydroxide, and 10 ml. of water. The ether layer was separated, washed with water, and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the residue was distilled to give 2.6 g. of alcohol (78%), b.p. 93–94° at 118 mm. (lit.<sup>59</sup> 95–96° at 120 mm.),  $n_D^{26}$  1.4318.

Gas chromatographic analysis on a Carbowax column at 125° showed two components whose relative retention times were 1.00 (3%) and 1.46 (97%). The second peak was collected for spectra and analysis.

Anal. Calcd. for  $C_6H_{12}O$ : C, 71.95; H, 12.08. Found: C, 71.83; H, 11.81.

Infrared:  $\nu_{\max}^{\text{film}}$  3340 broad and 1032 ( $\text{CH}_2\text{OH}$ , bonded), 3070 and 1007 ( $>\text{C}-\text{CHH}-\text{CH}-$ ), 3005 ( $>\text{C}-\text{CHH}-\text{CH}-$ ),

and 2955, 2880, 1460, and 1385  $\text{cm}^{-1}$  [ $>\text{C}(\text{CH}_3)_2$ ]. N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  6.49, septet ( $2 >\text{CHCHHOH}$ ), 6.98, singlet which moves with dilution (OH), 8.90, singlet ( $3\text{CH}_3$ ), 8.93, singlet ( $3\text{CH}_3$ ), and 8.90–10.05, complex multiplet ( $3 >\text{C}-\text{CHH}-\text{CH}-$

$-\text{CHH}-\text{O}-$ ). Comparison of this spectrum with that of (2,2-dimethylcyclopropyl)carbinyl acetate shows that the septet at  $\tau$  6.49 is actually formed by two overlapping quartets, centered at 6.42 and 6.53, respectively, which constitute the AB portion of an ABX pattern due to  $\text{H}_a$ ,  $\text{H}_b$ , and  $\text{H}_c$  of ( $>\text{C}-\text{CH}_a\text{H}_b-\text{CH}_c-$

$\text{CH}_b\text{H}_a-\text{O}-$ ). Even though the X portion of this pattern is superimposed on the complex ABC multiplet at  $\tau$  8.90–10.05 due to the three nonequivalent cyclopropane hydrogens  $\text{H}_c$ ,  $\text{H}_d$ , and  $\text{H}_e$ , the three coupling constants of the ABX

(56) We thank the supplier for a generous sample of this material.

(57) E. R. Nelson, M. Maienthal, L. A. Lane, and A. A. Benderly, *J. Am. Chem. Soc.*, **79**, 3467 (1957).

(58) This ABC pattern matched approximately the theoretical spectra 3E-72 and 3E-116 calculated by Wiberg and Nist.<sup>51f</sup>

(59) M. Julia, S. Julia, and J. A. du Chaffant, *Bull. soc. chim. France*, 1735 (1960).

system can be calculated. Comparison of these three coupling constants with the analogous ones for (2,2-dimethylcyclopropyl)carbinyl acetate (19b) and with the usual geminal-hydrogen coupling constant,<sup>51d</sup> leads us to conclude that  $J_{ab} = 16.9$  c.p.s.,  $J_{ac} = 11.2$  c.p.s., and  $J_{bc} = 7.3$  c.p.s.

(2,2-Dimethylcyclopropyl)carbinyl Acetate (19b).—A 300-mg. sample of 2,2-dimethylcyclopropylcarbinol (19a) was dissolved in 25 ml. of pyridine, and 2 ml. of acetic anhydride was added to the solution. The solution was heated under reflux overnight, cooled, and poured in 50 ml. of ice-water. The product was extracted with three 10-ml. portions of pentane. The pentane extract was washed with dilute hydrochloric acid to remove the pyridine and then washed to neutrality with 10% aqueous sodium carbonate and with water. The pentane solution was dried over anhydrous magnesium sulfate, filtered, and concentrated to a volume of about 2 ml. by distillation of the solvent through a 10-in. Widmer column. A gas chromatogram from a Carbowax column at 125° showed the presence of the solvent and only one other component. The product was collected from a Carbowax column for spectra and analysis.

Anal. Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93. Found: C, 67.51; H, 9.88.

Infrared:  $\nu_{\max}^{\text{film}}$  3080 and 1000 (?) ( $>C-CHH-CH-$ ); 3005

( $>C-CHH-CH-$ ); 2955, 2880, and 1460 ( $CH_3$ ); 1385 and 1380 ( $>C(CH_3)_2$ ); and 1745 and 1240  $cm^{-1}$ , broad ( $OCOCH_3$ ). N.m.r.:  $\nu_{\max}^{\text{CDCl}_3} \tau$  5.99, quartet (1  $>CHCHHO-$ ) superimposed upon another quartet at 6.12 (1  $>CHCHH-O-$ ), 8.05, singlet ( $3OCOCH_3$ ), 8.92, singlet [6  $>C(CH_3)_2$ ], and  $\sim 9.0-10.0$ , 15(?) -line multiplet (3  $>C-CHH-CH-CHH-O-$ ). The two

overlapping quartets, centered at  $\tau$  5.99 and 6.12, constitute the AB portion of the ABX pattern due to  $H_a$ ,  $H_b$ , and  $H_c$  of  $>C-CH_eH_d-CH_c-CH_bH_a-O-$ . By reasoning analogous to

that used in the case of (2,2-dimethylcyclopropyl)carbinol (19a) we conclude that  $J_{ab} = 20.4$  c.p.s.,  $J_{ac} = 11.2$  c.p.s., and  $J_{bc} = 7.1$  c.p.s. We note that the coupling constant most changed by the substitution of acetoxyl for hydroxyl is the constant which we have assigned to the geminal hydrogens, *i.e.*,  $J_{ab}$ . We take this to indicate that our assignment is probably correct.

The Attempted Isolation of (2,2-Dimethylcyclopropyl)carbinyl *p*-Bromobenzenesulfonate (19c). Method A.—To a solution of 0.50 g. (0.0050 mole) of (2,2-dimethylcyclopropyl)carbinol (19a) in 5 ml. of anhydrous pyridine maintained at 0° was added 1.40 g. (0.00550 mole) of *p*-bromobenzenesulfonyl chloride in one portion. The mixture was swirled until the crystals of the sulfonyl chloride had dissolved and was then maintained at  $-20^\circ$  for 24 hr. During this time needles of pyridine hydrochloride slowly precipitated. The cold heterogeneous mixture was then poured into 25 g. of an ice-water mixture and was extracted with 25 ml. of pentane. The pentane solution was washed with cold water until the odor of pyridine could no longer be detected, and was then dried over anhydrous magnesium sulfate. The solution was filtered to remove the drying agent, and the pentane was removed by evaporation in a rotary evaporator at room temperature. The oily residue was pumped at 0.5 mm. for 30 min. to remove traces of solvent and unchanged alcohol. An infrared spectrum of the residue was similar to that of *p*-bromobenzenesulfonic acid. No other nonvolatile materials could be detected.

Method B.—A 53% suspension of sodium hydride in mineral oil (55 mg., 1.2 mmoles) was washed free of mineral oil with hexane. The hexane was decanted and the hydride was covered with 2 ml. of anhydrous ether. A solution containing 100 mg. (1.0 mmole) of (2,2-dimethylcyclopropyl)carbinol (19a) in 5 ml. of ether was added, and the suspension was stirred at reflux. When most of the sodium hydride had reacted and hydrogen evolution had virtually ceased (12 hr.), a solution of 260 mg. (1.1 mmoles) of *p*-bromobenzenesulfonyl chloride in 5 ml. of ether was added and the mixture was stirred at room temperature for an additional 5 hr. The ether was removed in a rotary evaporator at reduced pressure and the residue was pumped at 0.5 mm. for 2 hr. to remove any volatile products and unchanged alcohol. An n.m.r. spectrum, determined on the chloroform-soluble portion of the residue, showed only aromatic hydrogen absorptions, *i.e.*, had no absorptions in the region from  $\tau$  3 to 10. No other attempts were made to isolate this brosylate.

2-Methyl-4-penten-2-yl Acetate (14).—A solution of 60.5 g. (0.500 mole) of allyl bromide in 285 ml. of anhydrous ether was

added, at a rate sufficient to maintain a gentle reflux, to a rapidly stirred mixture of 36.5 g. (1.50 g.-atoms) of magnesium turnings and 100 ml. of anhydrous ether. The ethereal solution was decanted from the excess magnesium and cooled to  $-10^\circ$ . A solution of 43.5 g. (0.750 mole) of acetone in 100 ml. of anhydrous ether was added, during the course of 1 hr., to the cold solution. The resulting salt was decomposed by the cautious addition of a solution of 51 g. (0.50 mole) of acetic anhydride in 100 ml. of ether. The reaction mixture was poured into a separatory funnel and extracted with an equal volume of water. The layers were separated and the ether layer was washed with 10% aqueous sodium carbonate and with water until the washings were neutral. The solution was dried over anhydrous sodium sulfate and the solvent was removed by distillation through a 10-in. Widmer column. The remaining material was distilled at atmospheric pressure through a short Vigreux column. Distillation started at about  $90^\circ$ , and the boiling point rose gradually to  $138^\circ$ . Several fractions were collected, the total weight of which was 13 g. The final fraction, b.p.  $137-138^\circ$  (lit.<sup>60</sup>  $136^\circ$ ), which amounted to 2.0 g., was shown by gas chromatography to be approximately 90% pure. The pure acetate was isolated by collection from a Carbowax column at  $125^\circ$ .

Anal. Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93. Found: C, 67.82; H, 10.19.

Infrared:  $\nu_{\max}^{\text{film}}$  3085, 3020, 1840, 996, and 909 ( $CH=CH_2$ ), 2990 ( $CH_3$ ?), 2945 ( $CH_2$ ?), 1740, 1250, 1220 (?), and 1010 (?) ( $OCOCH_3$ ), 1645 ( $>C=C<$ ), and 1390, 1370, and 1195  $cm^{-1}$  ( $>C(CH_3)_2$ ). N.m.r.:  $\nu_{\max}^{\text{CDCl}_3} \tau$  3.83-4.62, complex multiplet ( $HHC=CHCH_2$ ), 4.75-5.20, complex multiplet ( $2HHC=CH$ ), 7.51, doublet (2  $=CH-CH_2C\leq$ ), 8.10, singlet ( $3OCOCH_3$ ), and 8.69, singlet ( $6C(CH_3)_2O$ ). The two complex multiplets between  $\tau$  3.82 and 5.20 constitute a typical pattern for the three vinyl hydrogens  $H_a$ ,  $H_b$ , and  $H_c$  of a terminal allyl group  $H_aH_bC=CH_c-CH_{d_1}-$ , see Varian Spectra No. 24, 26, 34, 38, 56, 134, and 136.<sup>51a</sup> It can be calculated from the doublet at  $\tau$  7.51 that  $J_{cd} = 7.3$  c.p.s.

4-Methyl-3-penten-1-ol (5a).—This material was prepared in three steps from 1-methyl-3,4-dihydrofuran in 8% over-all yield by the method of Ansell and Brown,<sup>61a</sup> b.p.  $156-157^\circ$  at 765 mm. and  $73.5-74.5$  at 26 mm. (lit.  $157-158^\circ$  and  $62-63^\circ$  at 13 mm.,<sup>61a</sup>  $98-100^\circ$  at 130 mm.,<sup>61b</sup>  $157^{(12)}$ ),  $n_D^{20}$  1.4440 (lit.  $n_D^{19}$  1.4452,<sup>61a</sup>  $n_D^{20}$  1.4455,<sup>61c</sup> and  $n_D^{20}$  1.4432<sup>61b</sup>).

Gas chromatographic analysis of this material on a Carbowax column at  $150^\circ$  showed only one component in addition to a trace of solvent. Samples were collected from this column for spectra and analysis.

Anal. Calcd. for  $C_6H_{12}O$ : C, 71.95; H, 12.08. Found: C, 71.95; H, 12.05.

Infrared:  $\nu_{\max}^{\text{film}}$  3335 (OH, bonded), 3110, 1682, and 890 ( $>C=CH_2$  ?), 3012, 1658, and 831 ( $>C=CH$  ?), 2994 and 1375 ( $CH_3$ ), 2928, 2882, and 1447 (?) ( $CH_2$ ), and 1049  $cm^{-1}$  ( $CH_2OH$ ). N.m.r.:  $\nu_{\max}^{\text{CDCl}_3} \tau$  4.89, triplet (0.74  $>C=CHCH_2$ ), 5.31, singlet (0.74  $>C=CH-C\leq$  or  $H_2C=C<$ ), 6.44, triplet superimposed upon a 6.48 triplet (2.0  $CH_2CH_2O$ ), 7.27, singlet which shifts with dilution (OH), 7.79, poorly resolved quartet superimposed upon a broad singlet at 8.03 (2.2  $=CHCH_2CH_2O + =CCH_2CH_2-CH_2O\leq$ ), and 8.27, perturbed singlet superimposed upon a perturbed singlet at 8.30 (5.4  $CH_3$ ).

These spectral data indicate that the alcohol is impure. The fact that the gas chromatogram showed only one peak must mean that the contaminant is closely related both structurally and chemically. The fact that the analysis agrees with the value calculated for 4-methyl-3-penten-1-ol must mean that the contaminant has the same molecular formula. From the infrared and n.m.r. spectra, the presence of both a terminal methylene group,  $>C=CH_2$ , and a trisubstituted double bond,  $>C=CH-$ , may be inferred. Hence a likely contaminant would be 4-methyl-4-penten-1-ol. It can be calculated on this basis from the vinyl hydrogen resonance at  $\tau$  4.89 and 5.31, that the products contain about 80% 4-methyl-3-penten-1-ol (5a) and 20% 4-methyl-4-penten-1-ol.

In order to confirm this we prepared, in the usual manner,<sup>62</sup>

(60) G. DuPont R. Dulou, and G. Christen, *Bull. soc. chim. France*, **21**, 820 (1954).

(61) (a) M. F. Ansell and S. S. Brown, *J. Chem. Soc.*, 1788 (1957); (b) L. Willmann and H. Schinz, *Helv. Chim. Acta*, **35**, 2401 (1952); (c) P. Bruylants and A. Dewael, *Bull. classe Sci. Acad. roy. Belg.*, [5] **14**, 140 (1928).

(62) R. L. Shiner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 212.



the 3,5-dinitrobenzoate from this material. After one recrystallization from heptane the melting point of this ester was 59–63°, and, after three recrystallizations from heptane, it was 67.5–68.5° (lit.<sup>12</sup> 70.9–71.6°).

Infrared:  $\nu_{\max}^{\text{KBr}}$  3120 and 1680 (?) ( $>C=CH_2?$ ), 3080, 1680 (?), 1640, 1605, 1600, 1078, and 725 (aromatic H), 3030 and 831 ( $>C=CH?$ ), 2985, 2870, 1460 (?), and 1375 ( $CH_3$ ), 2930 and 1450 (?) ( $CH_2$ ), 1720 (aromatic COO), and 1293 and 1175  $cm^{-1}$  (CO). N.m.r. of the crude 3,5-dinitrobenzoate:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  0.77–1.03, complex multiplet (3 aromatic H), 4.83, triplet (0.92  $>C=CHCH_2$ ), 5.25, singlet (0.58  $H_2C=C<$ ), 5.60, triplet (2.0  $CH_2O$ ), 7.48, quartet (1.9  $>C=CH-CH_2CH_2O$ ), 7.85, broad singlet (0.4  $CH_2CH_2$ ), and 8.25, poorly resolved doublet (5.8  $CH_3$ ). The n.m.r. of the thrice-recrystallized 3,5-dinitrobenzoate is similar except that the triplet at  $\tau$  4.83 now represents  $\sim 0.82$  hydrogens while the singlet at  $\tau$  5.25 represents  $\sim 0.12$  hydrogens. By making the same assumptions as before, it can be calculated that the crude ester mixture contains about 77% 4-methyl-3-penten-1-yl 3,5-dinitrobenzoate (5d) and 23% 4-methyl-4-penten-1-yl 3,5-dinitrobenzoate, while the thrice recrystallized material contains 93 and 7%, respectively, of these two esters.

**4-Methyl-3-penten-1-yl Acetate (5b).**—A 0.78-g. (7.8-mmmole) sample of impure 4-methyl-3-penten-1-ol (5a) (prepared as described previously) was dissolved in 10 ml. of anhydrous pyridine and 1 ml. of acetic anhydride was added to the solution. The mixture was heated at reflux overnight, allowed to cool to room temperature, and poured over 50 ml. of crushed ice. Pentane (20 ml.) was added and, after the ice had melted, the hydrocarbon layer was separated. The aqueous layer was washed with pentane and the pentane layers were combined, washed with 10 ml. of cold, dilute hydrochloric acid, 10 ml. of cold, 10% aqueous sodium carbonate solution, and finally with 10 ml. of cold water. The hydrocarbon layer was separated and dried over anhydrous sodium sulfate and the solvent was removed from the dried solution by distillation at atmospheric pressure. The residue was distilled to yield 0.68 g. (48%) of ester, b.p. 91–93° at 50 mm. (lit.<sup>12</sup> 92–93° at 50 mm.),  $n_D^{25}$  1.4311 (lit.<sup>12</sup>  $n_D^{25}$  1.4291).

A gas chromatographic analysis of this material on a Carbowax column at 125° showed only one component. A small sample was collected for the spectral determinations and analysis.

Anal. Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93. Found: C, 67.50; H, 9.91.

Infrared:  $\nu_{\max}^{\text{film}}$  3080,  $\sim 3035$  sh, 1650, and  $\sim 830$  ( $>C=CH$ ), 2975, 2860, 1450 (?), 1390, and 1370 [ $=C(CH_3)_2$ ], 2925 ( $CH_2$ ), and 1740,  $\sim 1240$ , and 1033  $cm^{-1}$  ( $OCOCH_3$ ). N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.92, triplet (0.84  $>C=CHCH_2$ ), 5.31, broad singlet (0.29  $H_2C=C<$ ), 6.00, a triplet superimposed upon a 6.03 triplet (2.0  $CH_2CH_2O + CH_2CH_2O$ , two types), 5.5 hydrogens which appear as a 7.73 quartet superimposed upon a broad singlet at 7.93 ( $=CH-CH_2CH_2O + CH_2CH_2$ ) superimposed upon a singlet at 8.03 ( $OCH_3$ ), and 8.29, singlet superimposed upon an 8.38 singlet (5.5  $CH_3$ , two types). We conclude that this material is a mixture containing 85% 4-methyl-3-penten-1-yl acetate (5b) and 15% 4-methyl-4-penten-1-yl acetate.

When this material was gas chromatographed on the silver nitrate–diethylene glycol column at 75°, two peaks were observed whose relative retention times were 1.0 (83%) and 1.26 (17%). The major peak was collected for an n.m.r.

N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.93, 1:2:1 triplet ( $>C=CHCH_2$ ), 6.03, 1:2:1 triplet (2  $CH_2CH_2O$ ), 7.73, 1:3:3:1 quartet (2  $=CHCH_2CH_2O$ ), 8.02, singlet (3  $OCOCH_3$ ), 8.29, singlet [3  $CH_3(CH_3)C=C<$ ], 8.36, singlet [3  $CH_3(CH_3)C=C<$ ]. It can be calculated from the triplets at  $\tau$  4.93 and 6.03 and from the quartet at 7.73 that for the system  $CH_3(CH_3)C=CH_a-CH_{b2}-CH_{c2}-O-$ ,  $J_{ab} \approx J_{bc} = 7.2$  c.p.s.

**3-Methyl-1-penten-3-yl Acetate (15).**—This compound was prepared in two steps (esterification and catalytic hydrogenation) from 3-methyl-1-pentyn-3-ol (Columbia Organic Chemicals) according to the procedure of Hennion, *et al.*<sup>63</sup> The product, b.p. 63–73° at 44–53 mm. (lit.<sup>14</sup> b.p. 70° at 50 mm.), was obtained in 42% over-all yield. When gas chromatographed on a Carbowax column at 95° this material gave two peaks whose relative retention times were 1.00 (16%) and 1.22 (86%). Samples were collected for spectra and analysis.

Since the n.m.r. of the first peak shows neither vinyl nor acetylenic hydrogen resonance, we assume that this material is

3-methylpent-3-yl acetate formed by complete saturation of the triple bond of the intermediate 3-methyl-1-pentyn-3-yl acetate.

Infrared of the second component:  $\nu_{\max}^{\text{film}}$  3100 and 920 ( $>C=CH_2$ ), 3020 and 996 ( $>C=CH$ ), 2980, 2890, 1470, and 1380 ( $CH_3$ ), 2945 and 1420 ( $CH_2$ ), 1740 ( $>C=O$ ), 1650 ( $>C=C<$ ), and 1247  $cm^{-1}$  ( $OCOCH_3$ ). N.m.r. of the second component:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.05, quartet ( $HHC=CHC<$ ), 4.91, octet (2  $HHC=CH$ ), 5 hydrogens which appear as a complex multiplet at 7.91–8.41 ( $CH_3CH_2C<$ ) superimposed upon a singlet at 8.05 ( $OCOCH_3$ ), 8.52, singlet (3  $CH_3C<$ ), 9.15, triplet,  $J \approx 7.5$  c.p.s. (3  $CH_2-CH_3$ ). The quartet at  $\tau$  4.05 and the octet at 4.91 together constitute the typical 12-line ABX pattern of a terminal vinyl

group  $>C=C<$  for which the following coupling constants  $H_a$   $H_b$   $H_x$   $H_y$  can be calculated<sup>61f</sup>:  $J_{ax} = 18.0$  c.p.s.,  $J_{bx} = 9.6$  c.p.s.,  $J_{ab} = 1.3$  c.p.s. The methylene hydrogens of the ethyl group do not appear as a clean quartet because they are not magnetically equivalent. This nonequivalence of the methylene hydrogens is also reflected as a perturbation of the methyl hydrogen triplet at  $\tau$  9.15.

**$\alpha,\alpha$ -Dimethylcyclopropylcarbinol (18a).**—An ethereal solution of methylmagnesium iodide was prepared under nitrogen in the usual manner from 2.4 g. (0.10 g.-atom) of magnesium, 20.0 g. (0.141 mole) of methyl iodide, and 25 ml. of anhydrous ether. This Grignard reagent was cooled to 0° and 5.18 g. (0.0615 mole) of methyl cyclopropyl ketone (Columbia Organic Chemicals) in 20 ml. of anhydrous ether was added dropwise with stirring to the cold solution. After the addition was complete the mixture was allowed to warm to room temperature and stand for 48 hr. The complex was decomposed by the addition of 20 ml. of a saturated aqueous ammonium chloride solution. The ethereal layer was separated, washed successively with 20 ml. of dilute sodium bisulfite solution and 50 ml. of water, and dried over anhydrous magnesium sulfate. The ether was removed and the residue was distilled to yield 4.0 g. (65%) of product, b.p. 122–124° (lit.<sup>64</sup> b.p. 124°).

This material, when gas chromatographed on a Carbowax column, was resolved into two components whose relative retention times were 1.00 (19%) and 18.2 (81%). When the second component was collected and rechromatographed, the first component reappeared. We suspect that the  $\alpha,\alpha$ -dimethylcyclopropylcarbinol (18a) dehydrates under the conditions of the analysis. A sample of the second component was collected.

Infrared:  $\nu_{\max}^{\text{film}}$  3390 (OH, bonded), 3080 and 1005 (?), 3010 ( $HHC-CHH-CH-$ ), 2955 and 2880 ( $CH_3$ ), 2935 and 1470

(?) ( $CH_2$ ), 1380 and 1370 [ $>C(CH_3)_2$ ], and 1155  $cm^{-1}$  ( $\geq COH$ ).

N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  8.30, singlet which is shifted slightly by dilution (1  $HOC<$ ), 8.83, singlet (6  $CH_3$ ), 9.0–9.4, a poorly resolved complex multiplet ( $HHC-CHH-CH-$ ),  $\sim 9.7$ , 4(?)–line multiplet (4  $HHC-CHH-CH-$ ).

**$\alpha,\alpha$ -Dimethylcyclopropylcarbinyl Acetate (18b).**—A mixture of 2.0 g. (0.020 mole) of  $\alpha,\alpha$ -dimethylcyclopropylcarbinol (18a), 15 ml. of anhydrous pyridine, and 2.5 ml. (0.034 mole) of acetic anhydride was heated under reflux for 15 hr., allowed to cool, and poured with stirring into a mixture of 15 ml. of ice-water and 20 ml. of pentane. After the ice had melted, the pentane layer was separated, the aqueous portion was washed with 5 ml. of pentane, and the pentane-containing portions were combined. These combined pentane extracts were washed in sequence with 5 ml. of dilute hydrochloric acid, 5 ml. of 10% aqueous sodium carbonate solution and three 5-ml. portions of cold water. After the pentane-containing solution had been dried over anhydrous magnesium sulfate, the major portion of the solvent was removed by distillation, and the residue was analyzed by gas chromatography on a Carbowax column at 115°. Three major nonsolvent peaks were evident, whose retention times relative to air were 1.0 (4.7%), 1.56 (16.8%), and 1.87 (78.5%). The major peak was collected.

Anal. Calcd. for  $C_8H_{14}O_2$ : C, 67.57; H, 9.93. Found: C, 67.37; H, 9.77.

Infrared:  $\nu_{\max}^{\text{film}}$  3085 and 1005 ( $HHC-CHH-CH-$ ), 3005 ( $HHC-CHH-CH-$ ), 2975 and 2880 ( $CH_3$ ), 2940 and 1470

(63) G. F. Hennion, W. A. Schroeder, R. P. Lu, and W. B. Scanlon, *J. Org. Chem.*, **21**, 1142 (1956).

(64) P. Bruylants, *Rec. trav. chim.*, **28**, 180 (1909)

(CH<sub>2</sub>), 1733 (>C=O), 1389 [ $\nu_{\text{max}}$  >C(CH<sub>3</sub>)<sub>2</sub>], and 1240 cm.<sup>-1</sup> (OCOCH<sub>3</sub>).

N.m.r.:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  8.10, singlet ( $\sim 3\text{OCOCH}_3$ ), a complex multiplet ( $\sim 1\text{HHC}-\text{CHH}-\text{CH}$ ) superimposed upon an 8.67 singlet [ $\sim 6 >C(\text{CH}_3)_2$ ], 9.62, perturbed doublet ( $\sim 4\text{HHC}-\text{CHH}-\text{CH}$ ). This material was apparently contaminated

with an impurity, which showed small resonances at  $\tau$  5.40 and 7.98 and which served to obscure the integral values.

The second largest peak in the gas chromatogram was identified as unchanged  $\alpha,\alpha$ -dimethylcyclopropylcarbinol (18a) by comparison of its retention time with that of an authentic sample.

**2,2-Dimethylbutyl *p*-Bromobenzenesulfonate (9b).**—This material was prepared in the manner described previously for the unsaturated brosylate 8c using 5.1 g. (0.050 mole) of 2,2-dimethylbutan-1-ol (9a) (Eastman Chemical Products Incorporated).<sup>56</sup> The yield of brosylate after two recrystallizations from pentane was 7.6 g. (50%), m.p. 34–35° (lit.<sup>23</sup> 35°). This material, which was shown by infrared and n.m.r. analysis to contain no unreacted alcohol, was used for the rate studies without further purification.

Ultraviolet:  $\lambda_{\text{max}}^{\text{EtOH}}$  234 m $\mu$  ( $\epsilon$  15,600).

**Acetolysis of 2,2-Dimethyl-3-butene-1-yl *p*-Bromobenzenesulfonate (8c).**—A solution of 2.0 g. (6.2 mmoles) of this ester (0.096 *M*) in 67 ml. of acetic acid containing sodium acetate (0.15 *M*) and acetic anhydride (0.1 *M*) was heated at 100° for 3.5 hr. ( $\sim 14$  half-lives), cooled, and poured into 50 ml. of an ice-water mixture. The aqueous solution was extracted with 10 ml. of carbon tetrachloride in several portions and the combined extracts were washed with dilute aqueous sodium carbonate solution and with water until the washings were neutral to pHydriion paper. The resulting solution of the solvolysate in carbon tetrachloride was dried over anhydrous magnesium sulfate, filtered, and analyzed by gas chromatography on a temperature-programmed (isothermal at 60° for 4.0 min., heated from 60 to 160° at a constant 7.9°/min., isothermal at 160° for 10 min.) Carbowax column using an initial helium flow of 95 ml./min. The resulting gas chromatogram showed eight components, all of which were clearly separated from the carbon tetrachloride. Samples of each of the major components were collected and identified as described below.

**First Component.**—Retention time, 0.72 min.; relative abundance,<sup>24</sup> 0.9%. This material was not identified but was probably a hydrocarbon.

**Second Component.**—Retention time, 1.12 min.; relative abundance,<sup>24</sup> 24%.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>: C, 87.73; H, 12.27. Found: C, 83.10; H, 11.67.

Infrared:  $\nu_{\text{max}}^{\text{CCl}_4}$  3093 and 2980 (=CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 3020 sh (=CH—, C—H stretch), 2940 and 2885 (CH<sub>3</sub>, C—H stretch), 2940 and 2885 (CH<sub>3</sub>, C—H stretch), 2920 and 2850 sh (CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 2740 (CH<sub>3</sub>, overtone of symmetric C—H bending), 1840 (—CH=CH<sub>2</sub>, overtone of C—H out-of-plane bending), 1790 (>C=CH<sub>2</sub>, overtone of C—H out-of-plane bending), 1655 sh (>C=CH<sub>2</sub>, C=C stretch), 1645 (CH=CH<sub>2</sub>, C=C stretch), 1460 and 1380 (CH<sub>3</sub>, asymmetric and symmetric C—H bending, respectively), 1430 (C=CCH<sub>2</sub>C=C, CH<sub>2</sub> bending), 1420 (CH<sub>2</sub>, in-plane C—H bending), 992 and 915 (CH=CH<sub>2</sub>, out-of-plane C—H bending), and 890 cm.<sup>-1</sup> (>C=CH<sub>2</sub>, out-of-plane C—H bending). In addition there are maxima at 1268, 1213, 629, and 503 cm.<sup>-1</sup> which we are unable to assign.

Ultraviolet:  $\lambda_{\text{max}}^{\text{cyclohexane}}$  no measurable maximum; end absorption starting at 215 m $\mu$  ( $\epsilon \approx 0$ ) and rising to  $\epsilon \approx 2900$  at 200 m $\mu$ .

N.m.r.:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  3.96–4.57 >16-line multiplet (HHC=CHCH<sub>2</sub>), 5.48–5.22 a complex, perturbed doublet made up of an 8-line multiplet centered at 4.89 and an 8-line multiplet centered at 5.13 (2HHC=CH—CH<sub>2</sub>); 5.32, a perturbed singlet (2HHC=C<); 7.29, a perturbed doublet,  $J = 6.4$  c.p.s. (2HHC=CH—CH<sub>2</sub>C<); 8.31, singlet (3CH<sub>2</sub>C<). The complex pattern of absorptions from  $\tau$  3.96–4.57, 5.48–5.22, and 7.29 are typical of a terminal allyl group. This portion of the spectrum bears a close similarity in these regions to the spectrum of allyl sulfide, Varian Spectrum No. 136.<sup>51a</sup>

We conclude that this component can only be 2-methyl-1,4-pentadiene (11).

**Third Component.**—Retention time, 2.48 min.; relative abundance,<sup>24</sup> 36%.

*Anal.* Calcd. for C<sub>6</sub>H<sub>10</sub>: C, 87.73; H, 12.27. Found: C, 82.78; H, 11.41.

Infrared:  $\nu_{\text{max}}^{\text{CCl}_4}$  3093 and 2980 (=CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively); 3040 sh, 3020 and 3000 sh (=CH—, C—H stretch); 2940 and 2885 (CH<sub>3</sub>, asymmetric and symmetric C—H stretch, respectively); 2920 and 2855 (CH<sub>3</sub>, overtone of symmetric C—H bending); 1805 (CH=CH<sub>2</sub>, overtone of out-of-plane C—H bending); 1780 sh (>C=CH<sub>2</sub>, overtone of out-of-plane C—H bending); 1660 (CH=CH<sub>2</sub>, C=C stretch); 1620 and 1610 (>C=CC=C<, C=C stretch); 1455, 1445 sh, and 1385 (CH<sub>3</sub>, asymmetric and symmetric C—H bending, respectively); 1420 (=CH— in-plane C—H bending); 1218 [=C(CH<sub>3</sub>)<sub>2</sub> skeletal?]; 993 and 898 (CH=CH<sub>2</sub>, out-of-plane C—H bending); 965 (*trans* CH=CH, asymmetric out-of-plane C—H bending); and 882 cm.<sup>-1</sup> (>C=CH<sub>2</sub>, out-of-plane C—H bending).

Ultraviolet:  $\lambda_{\text{max}}^{\text{cyclohexane}}$  227–229 m $\mu$  ( $\epsilon \approx 20,000$ ) and 232–234 m $\mu$  ( $\epsilon \approx 20,000$ ).

N.m.r.:  $\tau$  3.16–4.42, >12-line multiplet (2 =CH); 4.81–5.28, poorly resolved, asymmetric triplet (2 =CHH); an 8.21 singlet (?) (3CH<sub>3</sub>) superimposed upon an 8.22 singlet (?) (3CH<sub>3</sub>).

Collected samples of this component polymerized when allowed to stand for a couple of days at room temperature. On the basis of the chemical and spectral evidence we suspected that this component has a dimethyl-1,3-butadiene skeleton. However, since we could not satisfactorily explain the complex splittings in the n.m.r., the double maxima in the ultraviolet, or the out-of-plane C—H deformations and the two conjugated C=C stretches in the infrared on the basis of a single structure; we were forced to conclude that this third component is a mixture of dimethyl-1,3-butadienes. In order to test this, the collected third component from a Carbowax column was rechromatographed on the TCEP column at 4° using a helium flow of 40 ml./min. Two peaks, 3A and 3B, appeared whose relative retention times were 22.0 (30%) and 26.2 min. (70%), respectively. Samples of each of these components were collected from the column.

Infrared of component 3A:  $\nu_{\text{max}}^{\text{CCl}_4}$  3093 and 2982 (=CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 3040 and 3005 (two types of =CH—, C—H stretches), 2958 and 2890 (?) (CH<sub>3</sub>, asymmetric and symmetric C—H stretch, respectively), 2930 and 2862 (?) (CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 2745 (CH<sub>3</sub>, overtone of symmetric C—H bending), 1787 (>C=CH<sub>2</sub>, overtone of C—H out-of-plane bending), 1663 (C=C stretch), 1625 (C=CC=C stretch), 1460 and 1450 (two types of CCH<sub>3</sub>, asymmetric C—H bendings), weak 1415 (>C=CH<sub>2</sub>, in-plane C—H bending), 1390 (CCH<sub>3</sub>, symmetric C—H bending), 967 (*trans*—CH=CH, asymmetric out-of-plane C—H bending), and 886 cm.<sup>-1</sup> (CH<sub>2</sub>, asymmetric out-of-plane C—H bending). We were unable to satisfactorily assign absorptions at 1745, 1018, 937, and 497 and a shoulder at 1725 cm.<sup>-1</sup>.

Ultraviolet of component 3A:  $\lambda_{\text{max}}^{\text{cyclohexane}}$  222 m $\mu$  ( $\epsilon \approx 19,500$ ) sh, 228.5 (21,700), and 236 ( $\approx 14,700$ ) sh.

N.m.r. of component 3A:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  3.88, a perturbed asymmetric doublet,  $J \approx 15$  c.p.s. ( $\sim 1 >C-\text{CH}=\text{CH}$ ), overlapping an 8 (?) -line multiplet (two quartets?) at  $\sim 4.0$ – $4.6$  ( $\sim 1-\text{CH}=\text{CH}-\text{CH}_3$ ), 5.20, perturbed singlet (2 >CHH), 8.20, a singlet (3 >CCH<sub>3</sub>) superimposed upon a slightly perturbed doublet,  $J \approx 5.0$  c.p.s., and 8.22 (3 >CHCH<sub>3</sub>).

We conclude, on the basis of these spectra and the analysis, that component 3A is 2-methyl-1,3-pentadiene (12) [(lit.<sup>65</sup>  $\lambda_{\text{max}}^{\text{heptane}}$  2.28 m $\mu$  ( $\epsilon$  22,400)]. This material must constitute  $\sim 11\%$  of the total solvolysis products. It is obvious from the presence of the out-of-plane, C—H deformation at 967 cm.<sup>-1</sup> that the material is wholly or largely the *trans* isomer; however, the n.m.r. spectrum may be interpreted to indicate the presence of a small amount of the *cis* isomer also. Since the *cis* out-of-plane, C—H deformation would probably be obscured by the solvent, this question cannot be decided on the basis of the infrared spectrum in carbon tetrachloride.

Infrared of component 3B:  $\nu_{\text{max}}^{\text{CCl}_4}$  3093 and 2980 (=CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 3045 and 3020 (two types of =CH—, C—H stretch), 2940 and 2885 (?) (CH<sub>3</sub>, asymmetric and symmetric C—H stretch, respectively), 2958 (?) and 2920 (CH<sub>2</sub>, asymmetric and symmetric C—H stretch, respectively), 2745 (CH<sub>3</sub>, overtone of symmetric C—H bending), 1808 (CH=CH<sub>2</sub>, overtone of C—H out-of-plane

(65) J. P. Phillips and F. C. Nachod, "Organic Electronic Spectral Data," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1963, p. 89.

bending), 1660 (C=C stretch), 1608 (C=CC=C stretch), 1455 (CCH<sub>3</sub>, asymmetric C—H bending), 1420 (CH=CH<sub>2</sub>, in-plane C—H bending), 1382 (CCH<sub>3</sub>, symmetric C—H bending), 1215 [=C(CH<sub>3</sub>)<sub>2</sub>, skeletal], and 993 and 898 cm.<sup>-1</sup> (CH=CH<sub>2</sub>, C—H out-of-plane bendings). We were unable to assign absorptions at 1340, 1060, 655 and 438 cm.<sup>-1</sup>.

Ultraviolet of component 3B:  $\lambda_{\text{max}}^{\text{cyclohexane}}$  228–230 m $\mu$  ( $\epsilon \approx 22,000$ ) sh, 234.8 (23,600), and 242–243 ( $\approx 17,000$ ) sh.

N.m.r. of component 3B:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  3.53, 1:2:1:1:2:1 sextet (1 HHC=CH—CH=), 4.23, broad, asymmetric doublet (1 =CH—CH=C<), 4.83–5.24, asymmetric, perturbed triplet (2HHC=CH), 8.22, broad singlet (6CH<sub>3</sub>C<).

We conclude, on the basis of these spectra and on the analysis that component 3B is 2-methyl-2,4-pentadiene (13) [lit.<sup>65</sup>  $\lambda_{\text{max}}^{\text{pentane}}$  234 m $\mu$  ( $\epsilon$  29,900)], and that it constitutes  $\sim 25\%$  of the total solvolysis products.

**Fourth Component.**—Retention time, 15.1 min.; relative abundance,<sup>24</sup> 24%. The infrared and n.m.r. spectra of this compound are identical with those of authentic 2-methyl-4-penten-2-yl acetate (14). When a pure, authentic sample of this acetate was mixed with the solvolysate and rechromatographed on a Carbowax column, no new peaks were evident, but the relative amount of the fourth component had increased.

**Fifth, Sixth, and Seventh Components.**—Retention times, 17.5, 18.2, and 19.6 minutes, respectively; relative abundance,<sup>24</sup> <0.2, <0.2, and 0.3%, respectively. No attempt was made to identify these components.

**Eighth Component.**—Retention time, 20.9 min.; relative abundance,<sup>24</sup> 14%. The infrared and n.m.r. spectra of this material are identical with those of authentic 4-methyl-3-penten-1-yl acetate (5b). When the solvolysate was mixed with this ester and rechromatographed on a Carbowax column, the relative area of the eighth peak was greater than for the solvolysate alone; no new peaks appeared.

When a 0.09 *M* solution of 2,2-dimethyl-3-buten-1-yl *p*-bromobenzenesulfonate (8c) in acetic acid containing 0.15 *M* sodium acetate and 0.1 *M* acetic anhydride was heated at 87–88.5° for 10 hr. (8.7 half-lives), worked up, and analyzed in a similar manner, the solvolysate had the following composition<sup>24</sup>: 2-methyl-1,4-pentadiene (11), 19%; dimethyl-1,3-butadienes (12 + 13), 32%; 2-methyl-4-penten-2-yl acetate (14), 31%; 4-methyl-3-penten-1-yl acetate (5b), 16%. The remaining 2% of the product appeared on the gas chromatogram as a single component whose retention time corresponded most nearly to that of the unidentified sixth component in the acetolysis carried out at 100°. When a solution of similar concentration was solvolysed at room temperature (25°) for 2.3 half-lives (120 days), the ratio of tertiary to primary ester (14/5b) in the products was 5.5. When the solvolysis was carried out at 60° for 24 hr. ( $\sim 0.4$  half-life) this ratio was 4.2.

In order to demonstrate that an additional solvolysis product(s) was not being obscured by the large carbon tetrachloride peak in these gas chromatograms, a portion of the acetolysis mixture (87°) was extracted with pentane instead of with carbon tetrachloride. When gas chromatographed on the same Carbowax column (isothermal at 135°, helium flow of 85 ml./min.), the large pentane peak completely obscured the 2-methyl-1,4-pentadiene 11 and partially overlapped the dimethyl-1,3-butadienes 12 and 13. The remaining components, *i.e.* 2-methyl-4-penten-2-yl acetate (14), the unidentified sixth (?) component, and the 4-methyl-3-penten-1-yl acetate, had retention times of 6.7, 9.9, and 18.6 min., respectively, under these conditions. The relative areas of these latter three peaks was essentially unchanged, *i.e.*, 31:3:16. The fact that no peaks appeared in this gas chromatogram between that of the dimethyl-1,3-butadienes and that of 2-methyl-4-penten-2-yl acetate indicates that no components were obscured by the carbon tetrachloride in the earlier chromatograms. The same analytical results could be obtained using either the DEGS or the silicone oil columns (although the hydrocarbons were not resolved on this latter column) and appeared also to be independent of flow rate, temperature, and rate of heating.

In order to ascertain that our analytical technique would have detected them had they constituted more than  $\sim 0.5\%$  of the solvolysate, a pure authentic sample of each of the following acetates was added to the pentane solution of solvolysis products, and the mixture was rechromatographed under the same conditions (Carbowax column, 135° isothermal, helium flow of 85 ml./min.): 2,2-dimethyl-3-buten-1-yl acetate (8b), 3-methyl-1-penten-3-yl acetate (15), 3-methyl-*trans*-2-penten-1-yl acetate

(16), 3-methyl-*cis*-2-penten-1-yl acetate (17),  $\alpha,\alpha$ -dimethylcyclopropylcarbinyl acetate (18b), or (2,2-dimethylcyclopropyl)carbinyl acetate (19b). Since, in each case, a new peak appeared in the gas chromatogram, we conclude that none of these esters is present in appreciable quantity in the solvolysis mixture after 10 half-lives.

**Stability Studies of Observed and Potential Products. Hydrocarbons.**—In order to determine whether dienes similar to those we had observed as acetolysis products of 8c were stable under the reaction conditions, 100-mg. ( $\sim 0.1$  *M*) samples of 1,4-pentadiene, 1,3-pentadiene, and 2,5-dimethyl-2,4-hexadiene (Eastman Chemical Products Incorporated)<sup>66</sup> were dissolved in acetic acid containing 0.15 *M* sodium acetate and  $\sim 0.1$  *M* acetic anhydride and heated for 7–10 hr. at 85–88°. In each case, the n.m.r. spectrum of a carbon tetrachloride solution of the solvolysate, worked up in the manner of the original acetolysis, clearly showed that no isomerization had occurred. Hence, we conclude that the dienes 11, 12, and 13 are probably true acetolysis products.

**Acetates.**—Solutions of the appropriate acetates were treated in the same fashion and analyzed by gas chromatography. In this manner it was determined that 4-methyl-3-penten-1-yl acetate (5b), 2,2-dimethyl-3-buten-1-yl acetate (8b), 2-methyl-4-penten-2-yl acetate (14), and (2,2-dimethylcyclopropyl)carbinyl acetate (19b) were completely stable to the reaction conditions, and that  $\alpha,\alpha$ -dimethylcyclopropylcarbinyl acetate (18b) was converted completely and exclusively to 4-methyl-3-penten-1-yl acetate (5b).

The solvolysate of 3-methyl-1-penten-3-yl acetate (15) when analyzed on the DEGS column at 75° (helium flow 75 ml./min.) showed three hydrocarbons and three esters. A sample of each of the esters was collected.

**First Ester.**—Retention time, 8.3 min.; relative abundance, 2%. The retention time and infrared spectrum of this material matched exactly those of the starting material, 3-methyl-1-penten-3-yl acetate (15).

**Second Ester.**—Retention time, 28.5 min.; relative abundance, 35%.<sup>24</sup>

Infrared:  $\nu_{\text{max}}^{\text{CCl}_4}$  3035 and 1675 (>C=CH); 2980, 2880, 1455, 1380, and 1370 (CCH<sub>3</sub>); 2940, 2925, 2870 sh, and 1460 (CH<sub>2</sub>); and 1745, 1230, and 1026 cm.<sup>-1</sup> (OCOCH<sub>3</sub>).

N.m.r.:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  4.76, poorly defined triplet,  $J \approx 7.0$  c.p.s. (1 >C=CH—CH<sub>2</sub>); 5.53, doublet,  $J \approx 7.0$  c.p.s. (2 =CH—CH<sub>2</sub>O); 7.62–8.13, a perturbed quartet (?),  $J \approx 7$  c.p.s. [2 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>] superimposed upon a sharp singlet at 8.03 (3OCOCH<sub>3</sub>); 8.27, slightly split doublet [3 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>]; 8.99, an asymmetric, perturbed triplet,  $J \approx 7.7$  c.p.s. [3 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>].

**Third Ester.**—Retention time, 31.2 min.; relative abundance, 63%.<sup>24</sup>

Infrared:  $\nu_{\text{max}}^{\text{CCl}_4}$  3030 and 1675 (>C=CH); 2980, 2885, 1450, 1380, and 1370 (CCH<sub>3</sub>); 2945, 2925 sh, 2865, and 1460 (CH<sub>2</sub>); and 1745 and 1028 cm.<sup>-1</sup> (OCOCH<sub>3</sub>).

N.m.r.:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  4.72, poorly defined triplet,  $J \approx 7.3$  c.p.s. (1 >C=CHCH<sub>2</sub>); 5.50, doublet,  $J \approx 7.3$  c.p.s. (2 =CHCH<sub>2</sub>O); 7.70–8.20, a quartet,  $J \approx 7.5$  c.p.s. [2 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>] superimposed upon a sharp singlet at 8.02 (3OCOCH<sub>3</sub>); 8.28, a perturbed singlet [3 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>]; 8.98, an asymmetric, perturbed triplet,  $J \approx 7.5$  c.p.s. [3 =C(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>].

We interpret these spectral data to indicate that these latter two esters are the geometric isomers of 3-methyl-2-penten-1-yl acetate, 16 and 17, respectively.

**Preparation and Decomposition of (2,2-Dimethylcyclopropyl)carbinyl *p*-Bromobenzenesulfonate (19c).**—A solution of 100 mg. (1.00 mmole) of (2,2-dimethylcyclopropyl)carbinol in 2 ml. of anhydrous pyridine was cooled to  $-10^\circ$  in an ice-salt bath and 260 mg. (1.02 mmoles) of *p*-bromobenzenesulfonyl chloride was added in one portion. The reaction mixture was maintained at  $-20^\circ$  for 7 days during which time a precipitate of pyridine hydrochloride formed. The entire mixture was then poured into 5 ml. of cold water. The resulting solution was slightly turbid, but no crystalline material separated. The cloudy solution was extracted with three 2-ml. portions of carbon tetrachloride which were combined, washed with three 1-ml. portions of cold water, and dried over anhydrous sodium sulfate. A gas chromatographic analysis on a Carbowax column (isothermal at 75° for 4.0 min., programmed from 75 to 200° at 6°/min.) revealed the presence of seven components in addition to carbon tetrachloride, pyridine, and unreacted carbinol. The first two of these constituted about one-third of the product mixture and had retention times less than that of carbon tetrachloride. The first and major

peak was collected and identified as 2-methyl-1,4-pentadiene by comparison of its infrared spectra with an authentic sample. The remaining components were not identified.

**2,2,4-Trimethyl-3-penten-1-yl *p*-Bromobenzenesulfonate (10c).**—To a solution of 1.28 g. (0.0100 mole) of 2,2,4-trimethyl-3-penten-1-ol (Eastman Chemical Products, Inc.)<sup>66</sup> in 20 ml. of dry pyridine was added 2.80 g. (0.0110 mole) of *p*-bromobenzenesulfonyl chloride. The mixture was swirled until the sulfonyl chloride had dissolved, maintained at  $-20^\circ$  for 2 days, and then poured into 50 ml. of an ice-water mixture. After the ice had melted, the resulting crystals were separated by filtration, washed with 20 ml. of cold water, and dissolved in pentane. The pentane solution was dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The crude *p*-bromobenzenesulfonate was recrystallized from cold pentane to yield 2.5 g. (72%) of white plates, m.p.  $23-26^\circ$ . Although this ester was unstable and decomposed on standing at room temperature, we were able, by working rapidly, to obtain fairly good infrared and n.m.r. spectra.

Infrared:  $\nu_{\max}^{\text{CCl}_4}$  3095 (weak), 1665, and 842 (?) ( $=\text{CH}$ ); 2965, 2870, 1390, 1385, 1220, and 1185 (?) [ $>\text{C}(\text{CH}_3)_2$ ]; 2935 and 1470 ( $\text{CH}_2$ ); 1910, 1575, and 790 (aromatic H); 1370 (?) and 1162 (?) ( $\text{SO}_2\text{O}$ ); 950 ( $\text{CO}$  ?); and 610  $\text{cm}^{-1}$  ( $\text{CBr}$  ?). The presence of a small peak at  $2325 \text{ cm}^{-1}$  is probably due to pyridine hydrochloride.

N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  2.30, singlet (4 aromatic H); 5.04, sextet (1  $>\text{C}=\text{CHC}$  <); 6.22, singlet (2  $\geq \text{CCH}_2\text{O}$ ); 8.34, singlet superimposed upon a singlet at 8.36 (6  $-\text{HC}=\text{C}(\text{CH}_3)\text{CH}_3$ ); and 8.90, singlet [6  $>\text{C}(\text{CH}_3)_2$ ].

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

**Acetolysis of 2,2,4-Trimethyl-3-penten-1-yl *p*-Bromobenzenesulfonate (10c).**—A solution of 2.4 g. (6.9 mmoles) of this ester (0.096 *M*) in 72 ml. of acetic acid containing sodium acetate (0.15 *M*) and acetic anhydride (0.1 *M*) was allowed to stand at room temperature for 24 hr., poured into 100 ml. of an ice-water mixture, and extracted with two 5-ml. portions of pentane. These extracts were combined, washed successively with 5 ml. of 10% aqueous sodium carbonate and 20 ml. of cold water, and dried over anhydrous sodium sulfate.

For purposes of product identification, the pentane solution of solvolysate was analyzed by gas chromatography on a temperature-programmed (isothermal at  $75^\circ$  for 9.8 min., heated from  $75$  to  $110^\circ$  at a constant  $5.6^\circ/\text{min}.$ , isothermal at  $110^\circ$  for 10 min.) Carbowax column using an initial helium flow of 90 ml./min. Four major, nonsolvent peaks were observed which comprised  $\sim 99\%$  of the total reaction products. The same four components were also evident on a temperature-programmed (isothermal at  $65^\circ$  for 15.8 min., programmed from  $65$  to  $110^\circ$  at a constant  $5.6^\circ/\text{min}.$ , isothermal at  $110^\circ$ ) silicone rubber column, although their relative peak areas were different. Samples were collected for identification from the Carbowax column.

**First Component.**—Retention time: Carbowax, 2.5 min.; silicone rubber, 7.7 min.

Since both the infrared and n.m.r. spectra of this component indicated a mixture of hydrocarbons rather than a pure compound, the first component collected from the Carbowax column was rechromatographed on the TCEP column (isothermal at  $9^\circ$ , helium flow of 50 ml./min.). Two peaks, 1A and 1B, appeared whose retention times were 37 and 39 min. and whose relative areas were 80 to 20%, respectively. These two components were collected for identification.

Infrared of component 1A:  $\nu_{\max}^{\text{sil}} 3080$  and  $2985 \text{ sh}$  ( $=\text{CH}_2$ , asymmetric and symmetric C—H stretch, respectively);  $3030$  ( $=\text{CH}-$ , C—H stretch);  $2975$  and  $2885$  ( $\text{CH}_3$ , asymmetric and symmetric C—H stretch, respectively);  $2935$ ,  $2920$  and  $2860$  ( $\text{CH}_2$  asymmetric and symmetric C—H stretch, respectively);  $2735$  ( $\text{CH}_3$ , overtone of symmetric C—H bending);  $1780$  ( $>\text{C}=\text{CH}_2$ , overtone of out-of-plane C—H bending);  $1680 \text{ sh}$  ( $>\text{C}=\text{CH}$ , C=C stretch);  $1655$  ( $>\text{C}=\text{CH}_2$ , C=C stretch);  $1470 \text{ sh}$  ( $\text{CH}_2$ , scissor);  $1455$ ,  $1385$  and  $1350 \text{ sh}$  (?) [ $=\text{C}(\text{CH}_3)_2$ , asymmetric and symmetric C—H bending, respectively];  $1445$  ( $\text{C}=\text{CCH}_2-\text{C}=\text{C}$ ,  $\text{CH}_2$  bending?);  $888$  ( $=\text{CH}_2$ , out-of-plane C—H bending); and  $856 \text{ cm}^{-1}$  ( $>\text{C}=\text{CH}$ , out-of-plane C—H bending). In addition, there are maxima at  $1268$ ,  $1222$ ,  $1104$ ,  $1028$ ,  $800$ , and  $776 \text{ cm}^{-1}$  which we are unable to assign.

Ultraviolet of component 1A:  $\lambda_{\max}^{\text{cyclohexane}}$  no measurable maximum; end absorption starting at  $220 \text{ m}\mu$  ( $\epsilon \approx 0$ ) and rising to  $\epsilon \approx 6000$  at  $205 \text{ m}\mu$ .

N.m.r. of component 1A:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.87, perturbed triplet,  $J \approx 1.8 \text{ c.p.s.}$  (1  $>\text{C}=\text{CHCH}_2$ ); 5.38, perturbed singlet (2  $>\text{C}=\text{CH}_2$ ); 7.37, doublet,  $J \approx 1.8 \text{ c.p.s.}$  (2  $=\text{CHCH}_2\text{C}$  <); 8.29, perturbed singlet [ $3\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}_2-$ ] and ( $3_{\text{H}}>\text{C}=\text{C}< \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$  ?); 8.40, singlet ( $3_{\text{H}}>\text{C}=\text{C}< \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$  ?).

We conclude that this component, which represents about 8% of the total solvolysis products, is 2,5-dimethyl-1,4-hexadiene (20).

Infrared of component 1B:  $\nu_{\max}^{\text{CCl}_4}$  3085, 2990 sh ( $=\text{CH}_2$ , asymmetric and symmetric C—H stretch, respectively); 3025 sh and 3010 sh ( $=\text{CH}-$ , C—H stretches); 2965 and 2930 (?) ( $\text{CH}_3$ , symmetric C—H stretch); 2725 ( $\text{CH}_3$ , overtone of symmetric C—H bending); 1778 ( $\text{CH}_2$ , overtone of C—H out-of-plane bending); 1650 and 1615 (C=CC=C stretch); 1465 and 1445 ( $\text{CH}_2$ , asymmetric CH bendings ?); 1385, 1375, and 1365 ( $\text{CH}_3$ , symmetric C—H bendings ?); 1435 (H—C < bending ?); 1415 ( $=\text{CH}$ , C—H in-plane bending ?); 1172 [ $\text{CH}(\text{CH}_3)_2$ , skeletal]; 965 (*trans*-HC=CH—, out-of-plane bending); 883 ( $>\text{C}=\text{CH}_2$ , out-of-plane C—H bending); and  $715 \text{ cm}^{-1}$  (*cis*-HC=CH—, out-of-plane bending ?). In addition there are maxima at  $\sim 1250$ ,  $1115$ ,  $1098$ , and  $945 \text{ sh cm}^{-1}$  which we are unable to assign.

Ultraviolet of component 1B:  $\lambda_{\max}^{\text{cyclohexane}}$  224  $\text{m}\mu$  (relative  $\epsilon$  0.894), 230.5 (1.00), and 237.5 (0.652). Since this spectrum was determined with  $\sim 0.5 \text{ mg.}$  of compound, we are unable to calculate accurate molar extinction coefficients.

N.m.r. component 1B:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$ , 3.8–4.8, complex multiplet ( $\sim 2 = \text{CCH}=\text{CHCH}$ ); 5.20, perturbed (?) singlet ( $2\text{H}_2\text{C}=\text{C}$  <);

8.21, triplet,  $J \approx 0.5 \text{ c.p.s.}$  [ $3\text{H}_2\text{C}=\text{C}(\text{CH}_3)$ ]; 8.45, perturbed asymmetric quartet [ $\sim 1 = \text{CHCH}(\text{CH}_3)_2$ ]; 8.97, doublet,  $J = 6.7 \text{ c.p.s.}$  [ $6\text{CH}(\text{CH}_3)_2$ ].

We conclude that this compound is 2,5-dimethyl-1-*trans*-3-hexadiene (21) perhaps contaminated with a small quantity of the *cis* isomer. Woodward's Rule<sup>66</sup> would predict a  $\lambda_{\max}$  of 227  $\text{m}\mu$  for this material.

**Second Component.**—Retention time: Carbowax, 6.0 min.; silicone rubber, 14.2 min.

Infrared:  $\nu_{\max}^{\text{sil}} 3030$  ( $=\text{CH}-$ , stretch); 2975 and 2925 ( $\text{CH}_3$ , asymmetric C—H stretches ?); 2880 and 2815 ( $\text{CH}_3$ , symmetric C—H stretches ?); 2735 (overtone of symmetric C—H bending); 1700 ( $>\text{C}=\text{CH}$ , C=C stretch ?); 1625 ( $>\text{C}=\text{CC}=\text{C}$  stretch); 1450, 1390, and 1375 [ $=\text{C}(\text{CH}_3)_2$ , asymmetric and symmetric C—H stretch]; and  $838 \text{ cm}^{-1}$  ( $>\text{C}=\text{CH}$ , out-of-plane C—H bending). There are additional maxima at  $1258$ ,  $1168$ ,  $1052$ ,  $1019$ ,  $983$ , and  $812 \text{ cm}^{-1}$  which we are unable to assign. This spectrum is similar to, but of considerably higher resolution than, the published infrared spectrum of 2,5-dimethyl-2,4-hexadiene.<sup>67a</sup>

Ultraviolet:  $\lambda_{\max}^{\text{cyclohexane}}$  237  $\text{m}\mu$  (relative  $\epsilon$  0.917) sh, 244 (1.00), and 252.5 (0.738) sh. Since this spectrum was determined on 5 mg. of compound, we are unable to calculate accurate molar extinction coefficients. The published spectrum of 2,5-dimethyl-2,4-hexadiene<sup>67a</sup> shows a  $\lambda_{\max}$  242.5  $\text{m}\mu$ . Wilcox and Nealy<sup>22b</sup> report  $\lambda_{\max}$  242  $\text{m}\mu$  ( $\epsilon$  25,900).

N.m.r.:  $\nu_{\max}^{\text{CCl}_4}$   $\tau$  4.02, singlet (2  $>\text{C}=\text{CHCH}=\text{C}$  <); 8.21, singlet [ $6\text{CH}_3(\text{CH}_3)\text{C}=\text{CH}-$ ]; and 8.26, singlet [ $6\text{CH}_3(\text{CH}_3)\text{C}=\text{CH}-$ ]. This spectrum is identical with that of 2,5-dimethyl-2,4-hexadiene (22) (Varian Spectrum No. 515).<sup>51g</sup>

**Third Component.**—This material, which constituted less than 10% of the total solvolysis product on the Carbowax column, appeared as a shoulder on the much larger peak of the fourth component. We have not been able to separate it in a pure form, or to identify it from the infrared and n.m.r. spectra of the impure material. Since this component is not present when the mixture is analyzed on a DEGS or silver nitrate-diethylene glycol column at a lower temperature, we do not believe it to be a primary solvolysis product.

**Fourth Component.**—Retention time: Carbowax, 22.4 min.; silicone oil, 33.4 min. When this component is collected from either the Carbowax or the silicone oil column at  $100-125^\circ$ , the n.m.r. spectrum indicates the presence of a small amount of component three. Pure component four could be obtained by

(66) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).

(67) Sadler Research Laboratories, Philadelphia 2, Pa.: (a) Infrared Spectrum No. 5715. (b) Ultraviolet Spectrum No. 5715.

collection at a lower temperature (50–65°) from the DEGS or the silver nitrate–diethylene glycol column.

Infrared:  $\nu_{\text{max}}^{\text{CCl}_4}$  3015 sh (=CH—, C—H stretch); 2980 and 2860 sh (?) (CH<sub>3</sub>, asymmetric and symmetric C—H stretch, respectively); 2935 and 2925 sh (?) (CH<sub>2</sub>, asymmetric C—H stretches); 2740 (CH<sub>3</sub>, overtone of symmetric C—H bending); 1743, 1240 and 1040 sh (OCOCH<sub>3</sub>); 1470 (CH<sub>2</sub> bending); 1460 (—CH<sub>3</sub>, asymmetric C—H bending); and 1390 and 1375 cm.<sup>-1</sup> [ $>C(CH_3)_2$ , symmetric C—H bending]. In addition to these, there are several other maxima between 1300 and 700 cm.<sup>-1</sup> which we are unable to assign.

N.m.r.:  $\nu_{\text{max}}^{\text{CCl}_4}$   $\tau$  4.90, triplet,  $J = 7.2$  c.p.s. (1  $>C=CH-CH_2$ ); 7.58, doublet,  $J = 7.2$  c.p.s. (2  $=CHCH_2C<$ ); 8.09, singlet (3OCOCH<sub>3</sub>); 8.27, slightly perturbed singlet,  $J \approx 0.5$  c.p.s. (3  $\begin{matrix} CH_3 \\ >C=C< \\ CH_3 \end{matrix}$ ); 8.38, singlet (3  $\begin{matrix} CH_3 \\ >C=C< \\ CH_3 \end{matrix}$ ); and 8.61, singlet [6C(CH<sub>3</sub>)<sub>2</sub>O].

These data are consistent with the structure 2,5-dimethyl-4-hexen-2-yl acetate (23) for this fourth component. The double bond stretch at  $\sim 1670$  cm.<sup>-1</sup> and the out-of-plane bending of the vinyl hydrogen at  $\sim 840$ –800 cm.<sup>-1</sup>, which should be visible in the infrared spectrum of this material, are probably obscured by the solvent, CCl<sub>4</sub>, absorptions at these frequencies.

We find that because the tertiary acetate 23 readily eliminates acetic acid to yield a mixture of the dienes 20–22, the apparent composition of this acetolysis mixture is quite dependent upon the analytical conditions. The ratio of acetate 23 to dienes 20–22 depends upon the nature of the gas chromatographic column employed for the analysis. With any single column the ratio 23/(20 + 21 + 22) is decreased if the acetolysis is allowed to proceed for 20 half-lives instead of being stopped after nine, if the solvolysate extract in either pentane or carbon tetrachloride is allowed to stand at room temperature for 1 hr. or so before being analyzed, if any attempt is made to concentrate the extract by distillation of the solvent at atmospheric pressure, (provided diene is not actually lost in this process), if the temperature of the gas chromatographic column is raised, or if the flow rate at a given temperature is decreased. We also note that the ratio of conjugated to nonconjugated diene, *i.e.* (21 + 22)/20, observed under any single set of analytical conditions, is decreased if the solvolysate extract is allowed to stand at room temperature for even 30 min., or if an attempt is made to remove some of the solvent by distillation, prior to gas chromatography. This decrease in the relative amount of conjugated dienes is accompanied by the precipitation of a waxy white, apparently polymeric, solid<sup>22b</sup> which we assume to be a mixture of poly-2,5-dimethylhexadienes. The best estimate of the composition of this mixture, which we could obtain was from the unconcentrated pentane extract of an acetolysis run at room temperature for nine half-lives (90 min.) and analyzed isothermally on the DEGS column at 75° with a helium flow of 100 ml./min. The figures for the abundance of 20 and 21 are calculated from the proportion obtained when the collected first component was rechromatographed on the TCEP column. The composition of the acetolysis mixture obtained in this manner shows 6.4% 2,5-dimethyl-1,4-hexadiene (20), 1.0% 2,5-dimethyl-1,3-hexadiene(s) (21), 21% 2,5-dimethyl-2,4-hexadiene (22), and 71% 2,5-dimethyl-4-hexen-2-yl acetate (23). An n.m.r. spectrum, taken of a carbon tetrachloride extract of this same solvolysis mixture prior to gas chromatographic analysis, indicates that the tertiary acetate 23 constitutes about 80 mole % of the total product.

**The Attempted Preparation of (2,2-Dimethylcyclopropyl)- $\alpha,\alpha$ -dimethylcarbinyl Acetate (25).**—Two slightly different attempts were made to prepare this compound by reaction of methyl 2,2-dimethylcyclopropanecarboxylate with methylmagnesium iodide.

**First Attempt.**—A solution of methyl 2,2-dimethylcyclopropanecarboxylate (5.76 g., 0.045 mole) in 50 ml. of anhydrous ether was added dropwise with stirring to a solution of methylmagnesium iodide prepared from 14.2 g. (0.100 mole) of methyl iodide and 2.43 g. (0.100 g.-atom) of magnesium in 50 ml. of anhydrous ether. After the addition was complete, the mixture was stirred at reflux temperature for 1 hr. The mixture was then poured over 75 ml. of chopped ice, and 30 ml. of dilute hydrochloric acid was added. The ether layer was quickly separated and washed successively with 10% aqueous sodium carbonate solution and with cold water. The ether was removed by distillation at atmospheric pressure from the dried solution. A mixture of 25 ml. of pyridine and 4.1 g. of acetic anhydride was added to the residue, and the whole was heated under reflux for 12 hr. The mixture was cooled, poured into 50 ml. of an ice-water mixture, and extracted with pentane. After having been washed with cold water and dried over magnesium sulfate, the pentane solution was analyzed by gas chromatography on a Carbowax column. Five components were apparent, three of which constituted greater than 90% of the total products. These components were collected and identified as 2,5-dimethyl-1,4-hexadiene (20), 2,5-dimethyl-2,4-hexadiene (22), and 2,5-dimethyl-4-hexen-2-yl acetate (23) by comparison of their n.m.r. spectra with those of samples obtained from the acetolysis of 2,2,4-trimethyl-3-penten-1-yl *p*-bromobenzenesulfonate (10c).

**Second Attempt.**—This differed from the former only in the treatment of the Grignard adduct.

The reaction mixture, after the addition of the methylmagnesium iodide, was mixed with a slight excess of acetyl chloride in ether and stirred overnight. The solution was poured over ice and the ethereal layer was separated, washed successively with dilute sodium thiosulfate solution, 10% aqueous sodium carbonate solution, and cold water. A gas chromatogram of the dried, ethereal solution showed evidence of several hydrocarbons, the principal one of which was 2,5-dimethyl-2,4-hexadiene (22).

**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, b.p. 118.0–118.3°, was added 1% by volume analytical reagent acetic anhydride and enough freshly fused reagent grade sodium acetate to make an  $\sim 0.1$  M solution. A weighed sample of the brosylate contained in a 100-ml. volumetric flask was dissolved in this solution and diluted to the mark at 25°. Aliquots (5 ml.) of this solution were sealed in test tubes and placed in a thermostatted bath. 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. Standard solutions were protected from moisture at all times.

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