quinones with *p*-toluidine the general amination procedure was followed except that air was not supplied, since oxidation of hydroquinone was not involved and it was found unnecessary to provide air for oxidation of the cerous chloride. When the alcoholic solution of 6-methoxy-5,8-quinolinequinone and *p*-toluidine was first boiled a short time, cooled under nitrogen, and then treated with 1 mole of catalyst, the reaction proceeded rapidly to completion in a nitrogen atmosphere (experiment 24).[16] In the other reactions of 6-methoxy-5,8-quinolinequinone and 2-methoxy-1,4-naphthoquinone with *p*-toluidine only 0.1 mmole of catalyst was used. The products obtained on the addition of water and acetic acid to the reaction mixture were fairly pure, contained no inorganic material and were not chromatographed.

6-*p*-Chloroaniline reacted much more slowly with 6-methoxy-5,8-quinolinequinone than did *p*-toluidine, giving only a 67% yield of desired product after 4 hr. at room temperature in the presence of 0.1 mole of cerouts chloride. When 2 moles of amine were used under the same conditions a high yield of crude aminoquinone was obtained. This material, like that obtained by adding *p*-chloroaniline to 5,8-quinolinequinone (I) (see above), contained cerium as shown by an ashing test. The inorganic material was removed by dissolving the crude product in acetic acid and precipitating with 2 or 3 volumes of water. The product thus obtained in 92% yield melted at 237.5–238.5°.

Addition of *p*-Nitroaniline to 1,4-Naphthoquinone.—A suspension of 1 mmole of 1,4-naphthoquinone in 6 ml. of absolute alcohol containing 1 mmole of *p*-nitroaniline and 0.1 mmole of cerous chloride heptahydrate was warmed slightly to dissolve the quinone. The clear solution was allowed to stand at room temperature in a stoppered flask and air was blown into the flask on alternate days. At intervals (given below) the reddish-orange precipitate was filtered off and washed well with absolute alcohol and then with a little hot alcohol. The combined filtrate and washings was evaporated in an air stream at room temperature under reduced pressure to the original volume of the reaction mixture and the reaction was allowed to continue. The solution was saturated with air twice a week. The following crops of crystals were obtained: after 6 days, 0.16 g. (55%); after 3 weeks, 0.055 g. (19%); after 5 weeks, 0.02 g. (7%); total yield, 81%. The melting point was 336.0–337.5°.

The experiment without cerous chloride was done simultaneously and under identical conditions except that the solution was saturated with air less frequently.

The Acetolysis of 4-Methyl-3-penten-1-yl *p*-Toluenesulfonate[1]

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4-Methyl-3-penten-1-yl tosylate was prepared and its acetolysis studied. The rate of acetolysis at 45° is approximately 1200 times that of ethyl tosylate. The products are 2-cyclopropylpropene and the acetate of 4-methyl-3-penten-1-ol. Both the rate and the products of solvolysis provide evidence that the reaction proceeds with participation of the olefinic bond.

Following the study of cholesteryl tosylate by Winstein and Adams,[3] participation of the carbon-carbon double bond during solvolysis reactions has become well established.[4] By far, the majority of authenticated cases of homoallylic participation has involved compounds in which the olefinic bond is strategically located in a ring system so as to favor interaction with the carbon undergoing solvolysis. An attempt to detect such interaction in the simplest homoallylic compound, allylcarbinyl chloride, yielded negative results[5] although nitrous acid deamination of allylcarbinylamine does lead to products resulting from homoallylic participation.[6] This report presents evidence that the acyclic compound, 4-methyl-3-penten-1-yl tosylate, undergoes acetolysis with participation of the olefinic bond.[7]

Synthesis.—Preparation of the required alcohol (I) by selective dehydration of 4-methyl-1,4-pentanediol has been reported.[8] The yield of the desired product is poor and on repeating this preparation the alcohol was found to exhibit weak absorption at 11.2 μ indicating contamination by the isomer, 4-methyl-4-penten-1-ol. The following synthesis was found to yield I in a high state of purity. Equilibration of 4-methyl-2-pentenoic acid (II) with the β,γ-unsaturated isomer (III) was carried out according to the published method.[9] Separation of the mixture of acids (20 α,β:80 β,γ) was not possible by careful fractional distillation nor was the mixture of alcohols resulting from hydride reduction separable in this way. Finally, it was found that methylation of the acid mixture under controlled conditions led to methyl 4-methyl-3-pentenoate of 99% purity. The separation takes advantage of the differing esterification rates

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

[4] For reviews and references, see A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," J. Wiley & Sons, Inc., New York, N. Y., 1961, pp. 385–389 and A. Streitwieser, Jr., *Chem. Rev.*, **56**, 725 (1956).

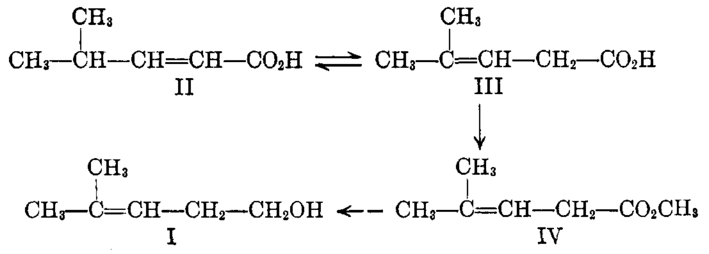
[5] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[6] E. Renk and J. D. Roberts, *ibid.*, **83**, 878 (1961).

[7] Early reports which pointed to the possibility of participation during solvolysis of derivatives of this compound have been noted by Roberts and Mazur. See footnote 4 of ref. 5.

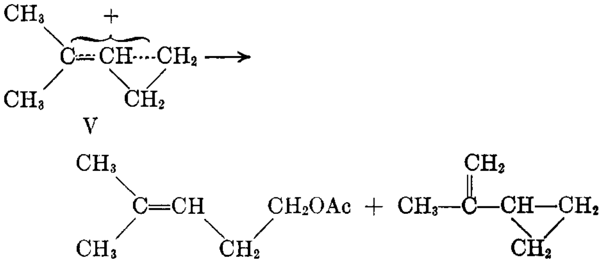
[8] L. Williams and H. Schinz, *Helv. Chim. Acta*, **35**, 2401 (1952).

[9] S. E. Boxer and R. P. Linstead, *J. Chem. Soc.*, 740 (1931); A. A. Goldberg and R. P. Linstead, *ibid.*, 2343 (1928).



of α,β- and β,γ-unsaturated acids.[10] Reduction of the ester to I was carried out by standard methods as was the preparation of the tosylate.

Solvolysis.—The tosylate of 4-methyl-3-penten-1-ol exhibited first-order kinetics in acetolysis. The rate constant at 45° (Table I) is approximately 1200 times greater than that calculated for ethyl tosylate. This rate enhancement is due to significant differences in both ΔH^* and ΔS^*. If the increased rate is due to intervention of the ion V, it might have been expected that ΔS^* for I-tosylate would have a larger negative value than that for ethyl tosylate. However, there is evidence that the large negative value for ethyl tosylate is due to oriented solvent molecule(s)[11] and inasmuch as V is internally "solvated," external solvation would be less important.


V

VI

VII

TABLE I

ACETOLYSIS RATES AND ACTIVATION PARAMETERS

Compound	$k(45°) \times 10^8$, sec.$^{-1}$	$k(60°) \times 10^8$, sec.$^{-1}$	ΔH^*, *k* cal./mole	ΔS^*, e.u.
Ethyl tosylate	2.6[a]	. . .	24.4[b]	−16.7[b]
I-tosylate	3160 ± 20	16,600 ± 100	22.6 ± 0.2	−7.8 ± 0.7

[a] Calculated value. [b] Ref. 11.

The major product isolated from the acetolysis is the acetate of 4-methyl-3-penten-1-ol, identified by its rapid reaction with neutral aqueous permanganate and saponification to the alcohol, I. A hydrocarbon product also was obtained and was shown to be 2-cyclopropylpropene (VII) by comparison of its physical properties and infrared spectrum with a sample prepared by the published method.[12]

The rate enhancement and the formation of 2-cyclopropylpropene both provide evidence that the solvolysis proceeds with anchimeric assistance to yield ion V.[13,14] Although a pronounced rate enhancement is not always the result of neighboring group participation,[16] the relatively low solvolysis rate of allylcarbinyl chloride[5] suggests that participation of the olefinic bond is not important during its solvolysis.[17] The intervention of ion V in the present case must therefore be the result of its stabilization through the presence of a tertiary carbon on which the positive charge may be delocalized. These results are comparable in a qualitative sense to the finding that 6-methylcholesteryl tosylate solvolyzes seventy-five times more rapidly than cholesteryl tosylate.[18]

Extensions of this study to higher homologs are in progress.

Experimental[19]

Methyl 4-Methyl-3-pentenoate.—The equilibrium mixture of acids III and IV was obtained by refluxing for 18 hr. an aqueous solution of 4-methyl-2-pentenoic acid (1 mole) and potassium hydroxide (12.3 moles).[9] Work-up in the usual manner yielded material with b.p. 99–110° (10 mm.).

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[10] For examples, see M. S. Newman in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1956, p. 210.

[11] S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

[12] R. V. Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *ibid.*, **71**, 172 (1949).

[13] It is realized that other forms analogous to the bicyclobutonium ion[15] may contribute to the structure of V. However, the results presently available do not require that they be included.

[14] A referee has suggested that the acetate VI may have arisen from isomerization of an initially formed tertiary acetate having the cyclopropyl carbinyl structure. While this remains a possibility, recent evidence [J. L. Corbin, H. Hart, and C. R. Wagner, *J. Am. Chem. Soc.*, **84**, 1740 (1962)] indicates that nucleophilic attack on ion V can take place only at the primary carbon.

[15] E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, *ibid.*, **83**, 2719 (1961) and earlier papers.

[16] For example, S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961).

[17] During this work, an attempt was made to obtain a precise value for the rate of acetolysis of allylcarbinyl tosylate in the presence of sodium acetate. However, the kinetics indicated a competing second-order reaction, probably displacement by acetate ion. Kinetic and product studies in the absence of acetate ion were not made because of the probable isomerizations that would occur as strong acid was liberated. The data of J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5034 (1951), also suggest that displacement by acetate ion competes with acetolysis of allylcarbinyl tosylate. These workers found that increasing the concentration of acetate ion markedly affected the initial rate of consumption of acetate ion. No difficulties of this sort were encountered with the acetolysis of 4-methyl-3-penten-1-yl tosylate due to the large rate of the first-order reaction.

[18] R. A. Sneen, *ibid.*, **80**, 3982 (1958).

[19] Melting points are corrected; boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR-5 instrument. Analyses were determined by G. Weiler and F. B. Strauss, Microanalytical Laboratory, Oxford, England. An Aerograph Model A-110-C apparatus was used for gas chromatographic analyses.

A mixture of 94.8 g. (0.83 mole) of the acid mixture, 80.0 g. (2.50 moles) of methanol, 250 ml. ethylene dichloride, and 2.5 ml. of concentrated sulfuric acid was heated under reflux.[20] A few minutes after refluxing was begun, the solution became cloudy due to the appearance of a second liquid phase. Refluxing was continued 8 min. longer (640 mm. pressure), and the reaction mixture then was immediately cooled and poured over ice. The organic layer was separated, extracted with aqueous sodium bicarbonate, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed by distillation through a short column and the residue was distilled to yield 72.0 g. (68%) of the ester, b.p. 145–148 (640 mm.), $n^{25}\text{D}$ 1.4302. Gas chromatographic analysis (GLC) with a 5-ft. poly(diethyleneglycol succinate) column revealed the presence of 1.0% of methyl 4-methyl-2-pentenoate. A sample was redistilled for analysis.

Anal. Calcd. for $C_7H_{12}O_2$ (128.17): C, 65.59; H, 9.44. Found: C, 65.26; H, 9.63.

For purposes of comparison, a sample of methyl 4-methyl-2-pentenoate was prepared by the procedure above. The esterification mixture did not become cloudy until refluxing had continued approximately 6 hr. The product (64% yield), b.p. 74–75° (46 mm.), $n^{25}\text{D}$ 1.4305, contained 1.3% (GLC) of an impurity that could not be removed by distillation.

Anal. Found: C, 65.08; H, 9.45.

The structures assigned to both esters were supported by their infrared spectra.

4-Methyl-3-penten-1-ol.—Reduction of methyl 4-methyl-3-pentenoate to the alcohol was carried out in the usual way with lithium aluminum hydride. Distillation of the product through a 5-in. Vigreux column gave, after a small forerun, the product in 84% yield, b.p. 105–105.5° (110 mm.), $n^{25}\text{D}$ 1.4443. Gas chromatographic analysis with a 10-ft. poly(diethyleneglycol succinate) column indicated the presence of 1% (combined) of the *cis*- and *trans*-allylic alcohols resulting from reduction of the α,β-unsaturated ester. The allylic alcohols have the shorter retention times and were resolved from one another.

Anal. Calcd. for $C_6H_{12}O$ (100.16): C, 71.95; H, 12.08. Found: C, 72.05; H, 12.30.

The 3,5-dinitrobenzoate was prepared and after recrystallization from heptane melted at 70.9–71.6°.

Anal. Calcd. for $C_{13}H_{14}N_2O_6$ (294.26): C, 53.06; H, 4.80; N, 9.52. Found: C, 52.99; H, 4.89; N, 9.35.

Separation of the mixture of alcohols obtained by reduction of the equilibrium mixture of acids was not possible with a 60-plate Todd column.

4-Methyl-3-penten-1-yl Tosylate.—To 2.10 g. (11.0 mmoles) of recrystallized *p*-toluenesulfonyl chloride dissolved in 10 ml. of purified pyridine was added 1.00 g. (10.0 mmoles) 4-methyl-3-penten-1-ol. The mixture was allowed to stand in an ice bath for 60 min. and then poured into a mixture of water and petroleum ether (b.p. 60–71°). The organic layer was washed with dilute hydrochloric acid and water and then was dried over anhydrous magnesium sulfate. On cooling the solution in a Dry Ice bath, the tosylate first separated as an oil which then solidified. The solvent was decanted and the residue exposed to full pump vacuum (0.1 mm.) for 30 min. at room temperature. The tosylate obtained in this way was a colorless oil, 2.25 g. (89%), $n^{25}\text{D}$ 1.5127. The product discolored on standing.

Anal. Calcd. for $C_{13}H_{18}O_3S$ (254.34): C, 61.38; H, 7.13; S, 12.61. Found: C, 61.44; H, 7.37; S, 12.35.

Preparations carried out on a larger scale gave the tosylate in yields of 70–80%.

Kinetics.—Anhydrous acetic acid was prepared by distillation of reagent grade acetic acid (0.5% water) from triacetyl borate.[21] Five milliter aliquots of a solution of the tosylate (approx. 0.1 *M*) and anhydrous sodium acetate (approx. 0.1 *M*) were placed in a constant temperature bath. At intervals, an aliquot was removed, rapidly cooled, and then titrated with standard *p*-toluenesulfonic acid (approx. 0.05 *M*) in anhydrous acetic acid using bromphenol blue as an indicator.[22] The data for one run are given in Table II.

TABLE II

ACETOLYSIS OF 4-METHYL-3-PENTENE-1-YL TOSYLATE, 45.0°

Time, sec.	Titer, ml.	10^5 *k*, sec.$^{-1}$
0	9.19	. . .
3600	8.36	3.02
7200	7.56	3.17
10,800	6.88	3.19
15,600	6.11	3.16
21,600	5.28	3.14
27,600	4.58	3.15
35,700	3.85	3.13
	Average	3.16 ± 0.02

Acetolysis (for Product Analysis).—A solution of 36.2 g. (0.142 mole) of I-tosylate and 21.1 g. (0.157 mole) of sodium acetate dissolved in 450 ml. of anhydrous acetic acid was heated at 60° for 15 hr. (13 half-lives). The solution was distilled at 120 mm. using an 8-in. column packed with glass helices and a receiver containing 25 ml. of pentane cooled in a Dry Ice bath. Approximately 20 ml. of distillate was collected at which point the head temperature was 67°.

The distillate was washed with water, aqueous sodium bicarbonate and then dried over anhydrous magnesium sulfate. Fractionation of this material in a Todd distillation assembly cleanly separated the pentane from a fraction with b.p. 63.5–65.5° (640 mm.), $n^{25}\text{D}$ 1.4230, 1.56 g. (13.4%). Gas chromatographic analysis (5-ft. silicone column) revealed the presence of 5% of impurities that were not identified. The infrared spectrum of this material is identical with a sample of 2-cyclopropylpropene prepared by the published method.[12] Reported for 2-cyclopropylpropene, b.p. 70.33° (760 mm.), $n^{20}\text{D}$ 1.4255.[23]

The residual acetic acid solution was poured into 1000 ml. of cold water and the mixture extracted three times with pentane. The combined extracts were washed with sodium bicarbonate solution and saturated sodium chloride solution and then were dried over anhydrous magnesium sulfate. Distillation of the residue after removing the pentane yielded 8.45 g. (42%) of crude I-acetate, b.p. 84–93° (36 mm.), and 1.51 g. of a dark, partially solid residue. The acetate was taken up in pentane, washed with aqueous sodium bicarbonate, and dried. Distillation through a 5-in. Vigreux column yielded 7.61 g. of material, b.p. 92–93° (50 mm.), $n^{25}\text{D}$ 1.4291, which reacted rapidly with neutral aqueous permanganate.

Anal. Calcd. for $C_8H_{14}O_2$ (142.19): C, 67.57; H, 9.93. Found: C, 67.10, 68.24; H, 9.63, 10.11.

A 1.42-g. (10 mmoles) sample of the acetate was saponified with aqueous sodium hydroxide. This yielded 0.90 g. (90%) of an alcohol, $n^{25}\text{D}$ 1.4438, the infrared spectrum of which was identical with that of authentic 4-methyl-3-penten-1-ol.

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(20) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

(21) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1957, p. 281. Preparation of triacetyl borate by the method described in this reference (warming a mixture of boric acid and acetic anhydride) resulted in a highly exothermic reaction. A controlled reaction rate was possible by adding boric acid in small portions to acetic anhydride maintained at 70–90°.

(22) S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).

(23) V. A. Slabey and P. H. Wise, *ibid.*, **74**, 1473 (1952).