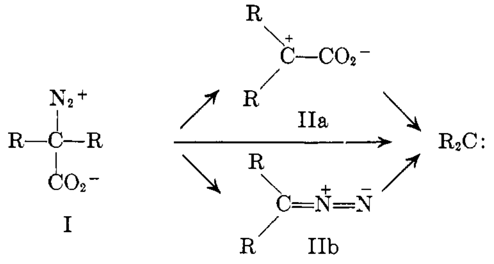

Although, the formation of cyclopropanes in these reactions might be due to carbene intermediates, formation of *cis*- and *trans*-2-butene from valine requires at least the simultaneous occurrence of an ionic path.[3] This might involve methyl or hydrogen migration in IIa to yield a carbonium ion β to the carboxylate group and subsequent decarboxylation to yield olefins. Alternatively, it has been suggested that protonation of IIb by unchanged amino acid or other reaction products could yield an alkyl diazonium ion.[4] Loss of nitrogen from the diazonium ion and subsequent established reactions of the resultant alkyl carbonium ion could account for the product distribution including the cyclopropanes.[5] If methylcyclopropane arises from carbenoid intermediates, its absence in the ethyl alcohol–water experiment might be explained by rapid trapping reactions. On the other hand this result could imply that only IIa is formed under these conditions and that it undergoes ionic rearrangements exclusively and then decarboxylation.[6]

Experimental

The amino acids used were optically inactive reagent grade materials (Matheson Coleman and Bell). Dimethylformamide was shaken with potassium hydroxide pellets and lump calcium oxide, and distilled from molecular sieves. *p*-Dioxane was shaken with potassium hydroxide pellets, refluxed for 50 hr. over sodium metal, and distilled. Isoamyl nitrite (Matheson Coleman and Bell) was used as commercially obtained.

Diazotization Reaction Conditions.—The method will be described for a typical reaction with valine. A heterogeneous mixture consisting of 0.1 g. (8.5×10^{-4} mole) of *dl*-valine, 1 ml. (7.5×10^{-3} mole) of isoamyl nitrite, and 25 ml. of anhydrous dioxane was heated with stirring under an atmosphere of prepurified nitrogen at 63° until gas evolution ceased (6–10 hr.). The reaction time is apparently a function of the rate of solution of amino acid in the solvent, since rates are strongly dependent on particle size. Approximately 25 ml. of gas was evolved and this was collected over mercury in a gas buret. The gas was analyzed by vapor phase chromatography yielding the composition: nitrogen[7] (82%), carbon dioxide (12%), nitrous oxide (5%), and hydrocarbon fraction (<1%). The presence of nitric oxide is inferred by the formation of traces of solid on the surface of the mercury in the gas buret, and the appearance of the characteristic nitrogen dioxide coloration (and solids) when the product gases were allowed to bubble through a mercury bubbler into the atmosphere in a separate experiment.

V.p.c. Analyses.—The hydrocarbon content of each gas sample was quantitatively analyzed using a 10 ft. × 0.125 in. 20% silicone SF-96 (60/80 firebrick) column (0°, nitrogen flow 20 ml./min.) in conjunction with an Aerograph (Wilkens Instrument Co.) electrometer and flame ionization detector. Retention times for the hydrocarbon gases under these conditions are methane (88 sec.), ethylene (111 sec.), ethane (125 sec.), propylene (227 sec.), propane (240 sec.), cyclopropane (375 sec.), isobutane (455 sec.), isobutene and 1-butene (600 sec.), *trans*-2-butene (745 sec.), methylcyclopropane (825 sec.), and *cis*-2-butene (865 sec.). The inorganic gases were identified using a 15 ft. × 0.25 in. silicone column in conjunction with an Aerograph A-90-C chromatograph equipped with a thermal conductivity detector. Proper and reproducible temperature was obtained in this latter instrument by placing Dry Ice in the oven.

Preliminary Analysis of Nonvolatile Products.—A reaction mixture from decomposition of valine in dioxane was distilled not quite to dryness and an infrared spectrum was taken of the liquid residue (reference pure dioxane). Bands were observed at 3420 (s), 1800 (w), 1780–1720 (s), 1640 (s), 1590 (sh), and 1555 cm.$^{-1}$ (s). The strong hydroxyl absorption is probably due to water and isoamyl alcohol, both anticipated reaction products. The infrared spectrum can also accomodate the presence of various esters and acids which might be expected and isovaleraldehyde (from isoamyl nitrite decomposition). An infrared spectrum of the distillate showed strong bands at 3420, 1640, and 1590 cm.$^{-1}$ (sh). The first is probably due to water, and the latter two are tentatively assigned to unchanged isoamyl nitrite.

Acknowledgment.—The invaluable assistance of Dr. Jerry A. Bell with the v.p.c. analyses is gratefully acknowledged. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.[8]

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[3] Rearrangement reactions of isobutylidene apparently do not yield *cis*- or *trans*-2-butene [L. Friedman and H. Shecter, *J. Am. Chem. Soc.*, **81**, 5512 (1959).

[4] L. Friedman, private communication.

[5] M. S. Silver, *J. Am. Chem. Soc.*, **82**, 2971 (1960); P. S. Skell, *et al.*, *ibid.*, **82**, 2971 (1960); **84**, 3962, 3963 (1962).

[6] We have no strong preference for the zwitterion IIa over an α-lactone intermediate. However, the diazonium ion origin of the intermediate implies that it would be more ionic than α-lactone intermediates which arise in nucleophilic substitution reactions of α-halocarboxylic acid salts.

[7] Corrected for the initial nitrogen present in the system.

[8] After these studies were completed, it was learned that Dr. Lester Friedman had obtained similar results with other amino acids. Helpful discussions with him are gratefully acknowledged.

A Convenient Spectrophotometric Method for Following the Reactions of Arenesulfonates[1]

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Received February 7, 1964

A convenient spectrophotometric method has been developed for following the reactions of methyl *p*-toluenesulfonate (tosylate). This should be of general interest in view of the widespread use of arenesulfonates for studies of organic reactions. The absorptions of methyl tosylate and tosylate anion are sufficiently different so that the reactions can be followed spectrophotometrically; at 261 mμ (in water) methyl tosylate has ε 671 and tosylate anion has ε 344. For reactions in transparent solvents, rate measurements are made by simply measuring the decrease in optical density (absorbance) with time. First-order rate constants determined by this method for the reactions of methyl tosylate in the presence of a large excess of various nucleophiles (conditions which preclude the use of titrimetric or conductometric methods) in methanol[2] were reproducible to 0.5 to 3%. The first-order rate constant for the hydrolysis of methyl tosylate in water at 25.00° of 7.98 ± 0.05 (average deviation from mean of three trials) $\times 10^{-6}$ sec.$^{-1}$, as determined by this

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[1] Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905 and by N.S.F. and N.I.H. predoctoral fellowships.

[2] C. G. Swain and W. D. Burrows, unpublished results.

method,[3] may be compared with that of 7.78×10^{-6} sec.$^{-1}$ at 24.85°, determined by conductivity.[4]

By suitable extraction techniques, this method may be used also for reactions in solvents that absorb in this region. Thus, reactions of methyl tosylate in benzene can be followed by extracting aliquots of the reaction mixture with water, back-extracting with cyclohexane, and measuring the absorbance of the water layer. In a number of runs in water, methyl tosylate was determined in cyclohexane after extraction. Similarly, extraction techniques may also be devised for following the reactions of an ester whose absorption is the same as that of the anion produced.

Experimental

The procedure used for the reactions in water is described below using the hydrolysis of methyl tosylate as a typical example.

Water was laboratory distilled water redistilled from sodium hydroxide–potassium permanganate in an all-Pyrex apparatus. It was degassed by bubbling carbon dioxide-free nitrogen through it for at least 20 min.

Methyl tosylate, Eastman White Label grade, was recrystallized from reagent grade cyclohexane–ether and dried in a desiccator over phosphorus pentoxide at 22° (1 mm.) for 3 days. The ester was allowed to melt, cooled, and a seed crystal was introduced. When approximately 75% of the material had crystallized, the solid ester was collected on a filter and then dried as before for 24 hr. The methyl tosylate, m.p. 28.4–29.4° (uncor.) lit.[5] m.p. 28–29°, was stored in a desiccator over Drierite (calcium sulfate).

Kinetics.—Temperature control was ± 0.02°. The temperature was determined using a thermometer calibrated by the National Bureau of Standards.

A 50-ml. volumetric flask was filled to the mark with water under an atmosphere of carbon dioxide-free nitrogen. Approximately 10 μl. of methyl tosylate was added and the resulting mixture was shaken vigorously to give the reaction solution, which was placed in the constant-temperature bath at 25°. After 10 min. (zero point), and at suitable times thereafter, a sample of reaction solution was transferred to a glass-stoppered 1-cm. silica cell and its absorbance was determined at 261 mμ at a slit width of 0.4 mm. using a Beckman DU spectrophotometer. A Beer's law plot (absorbance *vs.* fraction sodium tosylate) was linear for the change from methyl tosylate to tosylate anion. The concentration of methyl tosylate present initially was calculated from the infinity point, which was taken after the solution had been in the bath for 10 half-lives.

First-order rate constants were obtained from a plot of per cent unchanged methyl tosylate *vs.* time on semilogarithmic paper by dividing 0.693 by the half-life. Data for a typical run are shown in Table I.

TABLE I
HYDROLYSIS OF 1.22×10^{-3} *M* METHYL TOSYLATE IN WATER AT 25°

Time, hr.	Absorbance	% unchanged
0.0	0.791	100.0
5.0	0.746	87.9
9.0	0.709	77.9
18.0	0.645	60.6
24.0	0.611	51.5
32.0	0.570	40.4
44.0	0.526	28.6
55.0	0.498	21.0
67.0	0.471	13.7
290.0	0.420	0.0

$k_1 = 7.91 \times 10^{-6}$ sec.$^{-1}$

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[3] C. R. Morgan, Ph.D. thesis in Organic Chemistry, Massachusetts Institute of Technology, May, 1963, p. 49.

[4] R. E. Robertson, *Can. J. Chem.*, **33**, 1536 (1955).

[5] F. Drahowzal and D. Klamann, *Monatsh.*, **82**, 460 (1951).

α-Pinene Oxide Reaction with Acetic Acid–Sodium Acetate

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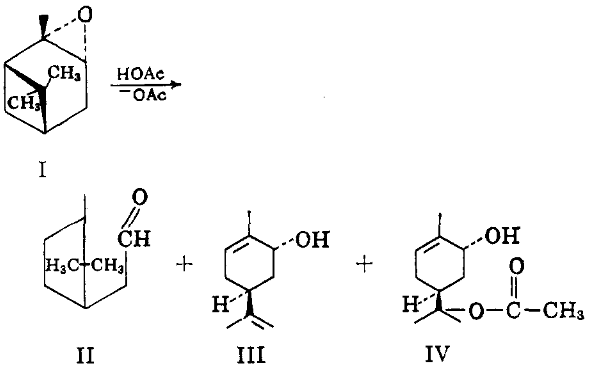
Received December 26, 1963

In a previous study,[3] the reaction of α-pinene oxide (I) with glacial acetic acid was reported to give campholenaldehyde (II) and a high boiling fraction which was apparently a crude hydroxyacetate. Arbuzow and Mikhailow[4] have reported the formation of a glycol monoacetate on treatment of α-pinene with peracetic acid in chloroform solution, and that a similar product was obtained on treatment of α-pinene oxide with acetic acid.

We have reinvestigated the reaction of *dl*-α-pinene oxide with a solution of sodium acetate in glacial acetic acid and found it to afford 39% campholenaldehyde, 19% *dl-trans*-carveol (III), and 23% *dl-trans*-8-acetoxy-6-hydroxy-1-*p*-menthene (IV). Identity of the latter product was established by saponification to *dl-trans*-sobrerol, and by pyrolysis to yield *dl-trans*-carveol (III) as the only product.

Inasmuch as the conversion of α-pinene oxide in this and previously reported work[4–7] to sobrerol or its derivatives has invariably afforded the *trans* isomers,[8] the stereochemistry of the epoxide must be as shown in I, the influence of steric hindrance playing a role similar to that observed for pinol.[9]

In view of the present results, the theoretical arguments of Brewster,[10] and the hydrogenation of the higher rotating carvotanacetol to the carvomenthols having the hydroxyl *trans* to the isopropyl group,[11] we must conclude that the generally accepted con-



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[1] Research Associate, Newport Industries Division, Heyden Newport Chemical Corp., Pensacola, Fla.

[2] National Defense Education Act Fellow, 1960–1963.

[3] E. E. Royals and L. L. Harrell, Jr., *J. Am. Chem. Soc.*, **77**, 3405 (1955); L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961).

[4] B. A. Arbuzow and B. M. Mikhailow, *J. prakt. Chem.*, **127**, 1 (1930).

[5] N. Prileschaev and V. Vershuk, *J. Russ. Phys. Chem. Soc.*, **67**, 473 (1929).

[6] A. J. Durbetaki and S. M. Linder, U. S. Patent 2,949,489 (1960); *Chem. Abstr.*, **55**, 608 (1961).

[7] E. A. Klein, U. S. Patent 2,815,378 (1957).

[8] H. Schmidt, *Ber.*, **86**, 1437 (1953).

[9] K. Piatkowski and H. Kuczynski, *Roczniki Chem.*, **35**, 1579 (1961).

[10] J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5493 (1959), and references therein.

[11] R. L. Kenney and G. S. Fisher, *J. Org. Chem.*, **28**, 3509 (1963).