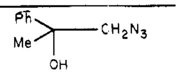
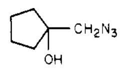
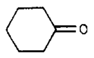
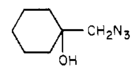
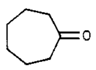
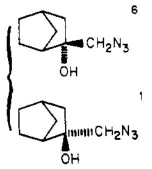
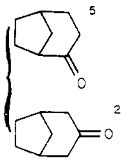
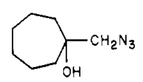
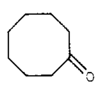
Table I. Reaction of β-Azido Alcohols with Nitrosonium Tetrafluoroborate in Acetonitrile at 0 °C

azido alcohol	product (yield, %)
 **1**	$PhCH_2COCH_3$, $PhCOCH_2CH_3$ (50) (trace)
 **2**	 (10)
 **3**	 (22)
 **4**	 (overall 38)[5]
 **5**	 (24)

reactions involve the same number of steps. Therefore, at present, the only difference between the two reactions lies in the protic (Tiffeneau[2]) vs. aprotic (our reaction) conditions. In fact, also in our reactions, from the present results, migratory aptitudes are typical of carbonium ion rearrangements, e.g., aryl migrates in preference to alkyl (1, Table I).

Experimental Section

General Methods. Solvents were purified and dried by standard procedures. ^1H NMR spectra were run in the indicated solvents on a Varian EM 360L spectrometer, and chemical shifts (δ) are measured from internal tetramethylsilane as reference. Infrared spectra were run on a Perkin-Elmer 337 spectrometer.

1-Azido-2-phenylpropan-2-ol (1). To a solution of 1-phenyl-1-methylethylene oxide[6] in 65 mL of dioxane at reflux (4.0 g, 30 mmol) was added dropwise sodium azide (40% molar excess) dissolved in 15 mL of water. The mixture was refluxed for an additional 23 h. The two layers were then separated, and the water layer was further extracted with dioxane. The combined dioxane extract was evaporated, and the residue was distilled in vacuo: yield 3.4 g (64%); bp 104–105 °C (6 torr); 55:45 mixture of 1 and 2-phenyl-2-azidopropan-1-ol. The two isomers were separated by column chromatography (silica gel; 1:1 petroleum ether–ethyl ether) whereby 1 was eluted first: ^1H NMR (CCl_4) δ 1.57 (s, 3 H, CH_3), 2.51 (s, 1 H, OH), 3.50 (AB system, 2 H, J_{AB} = 13 Hz, CH_2N_3), 7.59 (m, 5 H, C_6H_5); IR (CCl_4) 3430, 2105, 1275 cm^{-1}.

Anal. Calcd for $C_9H_{11}N_3O$: C, 61.00; H, 6.26. Found: C, 60.89; H, 6.18.

1-(Azidomethyl)cyclopentan-1-ol (2). The reaction was carried out as in the case of 1 with 3.4 g (35 mmol) of methylenecyclopentane oxide[7] for 16 h at reflux: yield 4.2 g (85%); bp 60–61 °C (8 torr); ^1H NMR (CCl_4) δ 1.60 (m, 8 H, cyclopentyl), 2.45 (br s, 1 H, OH), 3.32 (s, 2 H, CH_2N_3); IR (film) 3395, 2100, 1285 cm^{-1}.

Anal. Calcd for $C_6H_{11}N_3O$: C, 51.04; H, 7.85. Found: C, 51.20; H, 7.77.

1-(Azidomethyl)cyclohexan-1-ol (3). The reaction was carried out as in the case of 1 with 2.0 g (18 mmol) of methylenecyclohexane oxide[8] for 22 h at reflux: yield 1.2 g (43%); bp 69–70 °C (8 torr); ^1H NMR (CCl_4) δ 1.50 (m, 10 H, cyclohexyl), 1.98 (br s, 1 H, OH), 3.21 (s, 2 H, CH_2N_3); IR (film) 3410, 2100, 1285 cm^{-1}.

Anal. Calcd for $C_7H_{13}N_3O$: C, 54.17; H, 8.44. Found: C, 54.23; H, 8.19.

***exo*- and *endo*-2-(Azidomethyl)norbornan-2-ols (4).** The reaction was carried out as in the case of 1 with a 1:6 mixture of *exo*-2-methylene- and *endo*-2-methylenenorbornane oxide[9] for 23 h at reflux: yield 4.5 g (67%); bp 82–83 °C (6 torr); IR (CCl_4) 3410, 2100, 1280 cm^{-1}.

Anal. Calcd for $C_8H_{13}N_3O$: C, 57.47; H, 7.83. Found: C, 57.21; H, 7.96.

1-(Azidomethyl)cycloheptan-1-ol (5). The reaction was carried out as in the case of 1 starting from 4.0 g (32 mmol) of methylenecycloheptane: yield 3.4 g (66%); bp 128–129 °C (22 torr); ^1H NMR (CCl_4) δ 1.56 (m, 12 H, cycloheptyl), 2.55 (br s, 1 H, OH), 3.20 (s, 2 H, CH_2N_3); IR (film) 3410, 2100, 1280 cm^{-1}.

Anal. Calcd for $C_8H_{15}N_3O$: C, 56.78; H, 8.93. Found: C, 56.23; H, 8.98.

General Procedure for the Treatment of β-Azido Alcohols with Nitrosonium Tetrafluoroborate. To a solution of the azido alcohol (ca. 0.5 M) in acetonitrile at 0 °C was added, with stirring, slightly less than the equimolar amount of crystalline nitrosonium tetrafluoroborate. After 5 min the mixture was analyzed by VPC to determine the yields (see Table I) of ketones which were then isolated by standard procedures. Physical data for the ketones exactly matched those for authentic samples either commercially available or prepared by literature methods. Yields of isolated ketones approach those given in Table I when the reactions were carried out on large quantities (several grams) of azido alcohols.

Acknowledgment. We are grateful to CNR, Roma, for financial support.

Registry No. 1, 1961-65-5; 2, 72939-17-4; 3, 57770-11-3; *exo*-4, 72939-18-5; *endo*-4, 72939-19-6; 5, 72939-20-9; $PhCH_2COCH_3$, 103-79-7; $PhCOCH_2CH_3$, 93-55-0; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; bicyclo[3.2.1]octan-2-one, 5019-82-9; bicyclo[3.2.1]octan-3-one, 14252-05-2; cyclooctanone, 502-49-8; 1-phenyl-1-methylethylene oxide, 2085-88-3; 2-phenyl-2-azidopropan-1-ol, 72939-21-0; methylenecyclopentane oxide, 185-60-4; methylenecyclohexane oxide, 185-70-6; *exo*-methylenenorbornane oxide, 16282-10-3; *endo*-methylenenorbornane oxide, 16282-11-4; methylenecycloheptane, 185-85-3.

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Raman Spectrum of a Malonic Anhydride

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Despite the simplicity of its molecular structure, malonic anhydride has been an elusive molecule for more than 70 years. Various substituted malonic anhydrides have been obtained, but these are polymeric.[1-4] More recently, a monomeric diethylmalonic anhydride was claimed,[5] on the

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(1) Einhorn, A.; von Diesbach, H. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1222–3; *Justus Liebigs Ann. Chem.* **1908**, *359*, 145–71.

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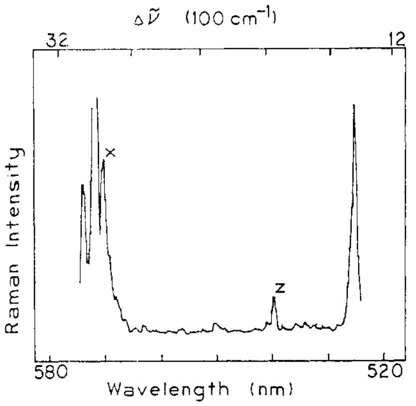
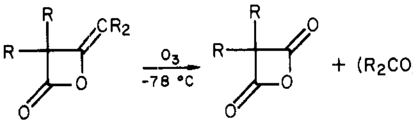


Figure 1. Direct tracing of the relevant portion of the Raman spectrum recorded for a solution of dimethylmalonic anhydride in dichloromethane with excitation of 488 nm. The features x and z at 570 and 539 nm are not observed in the scattering from the pure solvent.

basis of IR absorption at 1980 and 1900 cm^{-1}. However, extrapolation from the carbonyl frequencies of glutaric anhydride (1802, 1761 cm^{-1}) and succinic anhydride (1870, 1796 cm^{-1})[6] suggests that a four-membered-ring anhydride may be expected to absorb near 1940 and 1830 cm^{-1}. (A linear extrapolation is valid for malonic imides, which are known compounds.[7])

We recently reported[8] a new approach to malonic anhydrides, namely, ozonolysis of enol–lactone diketenes (eq 1, where R = H or CH_3), and we presented chemical and



(1)

NMR evidence[8] for the presence of monomeric malonic anhydride. However, the IR evidence was not in complete accord with the expected carbonyl frequencies. The anhydrides do show strong IR absorption at 1820 cm^{-1} (R = CH_3) or a doublet at 1820 and 1830 cm^{-1} (R = H), but there is no absorption from 1850 to 2000 cm^{-1}.

The absence of the band expected near 1940 cm^{-1} was rationalized by assuming it was too weak to see. This band corresponds to the symmetric, in-phase mode. Since the carbonyls are opposed, this mode does not change the dipole moment appreciably, so it may be expected to be weak. Indeed, it is well established that although the high-frequency carbonyl band is the more intense one in acyclic anhydrides, it is the less intense one in cyclic anhydrides.[9] Tetramethyl-1,3-cyclobutanedione, where the carbonyls are opposed, shows no detectable high-frequency absorption.[10] However, since malonic anhydride lacks a center of inversion, the weakness of the high-frequency carbonyl is not a strict forbiddenness that is required by the symmetry of the molecule. Given the elusiveness of the molecule, a conclusive structure proof requires verification of the high-frequency band. Fortunately, Raman spectroscopy is subject to different selection rules, such that the high-frequency band ought not be weakened by the opposition of the carbonyl dipoles.

We now report that the Raman spectrum of dimethylmalonic anhydride is fully in accord with that expected for a four-membered-ring anhydride. Ozonolysis of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone produces a solution containing dimethylmalonic anhydride. Owing to the instability of the anhydride, it is necessary to keep this solution cold. The only prominent lines in the Raman spectrum (Figure 1) not due to solvent appear at 2937 ± 7 and 1947 ± 7 cm^{-1}, with relative areas in the ratio 3:1. This ratio is similar to that for the corresponding peaks of acetone, and their intensity is comparable to that of a 1 M solution of acetone in dichloromethane. Therefore, the 1947-cm^{-1} peak is not merely due to a minor byproduct of the ozonolysis. Moreover, the frequency, 1947 cm^{-1}, is in admirable agreement with the predicted[8] frequency, 1940 cm^{-1}. This observed frequency is so high and so unique[11] that it constitutes excellent confirmation for a malonic anhydride.

Experimental Section

A solution of 0.67 g of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone (Aldrich) in 6 mL of CH_2Cl_2 was ozonized (OREC Model 03V5-O ozonator) at −78 °C until a blue color appeared. The excess ozone was removed with a stream of oxygen.

The supernatant (**Caution**: at these high concentrations peroxidic material precipitates from the reaction mixture) was then transferred to a stoppered, cylindrical, Suprasil tube, inserted into the cold finger of an evacuated cryostat cooled with dry ice.

The Raman spectrometer assembled for this study was conventional. An argon laser (Spectra Physics Model 164) was used for excitation, and spectra were recorded at both 488 and 514.5 nm. A feedback loop maintained constant optical power. Approximately 300 mW was incident upon the sample, focused into a vertical sheet by a cylindrical lens.

Scattered light was collected at 90° and dispersed by a pair of J-Y H-20 monochromators arranged in tandem. Simple dc amplification was followed by strip-chart recording. Resolution was 0.5 nm for the narrowest slits employed; spectra were also taken with wider slits. Signal-to-noise performance may be inferred from Figure 1. Several runs were made at each of the two exciting wavelengths in order to verify the reproducibility of the features of interest and also to search for evidence of photodegradation or other systematic deficiencies; no such problems were encountered.

The Raman spectrum of the solvent dichloromethane was recorded to test the apparatus; it was found to agree with previous results.[13] Also, a solution of acetone in dichloromethane showed prominent and well-resolved lines at 2930 and 1708 cm^{-1}, with the expected amplitude ratio.[14] However, the very strong line at 785 cm^{-1} appeared only as a shoulder obscured by the dichloromethane solvent.

A Raman spectrum of the dimethylmalonic anhydride is shown in Figure 1. In replicate spectral scans, two characteristic lines were measured at 2937 ± 7 and 1947 ± 7 cm^{-1} (mean plus or minus standard deviation). One other detectable feature not due to solvent appeared near 860 cm^{-1}. This may be due to the peroxide that is a byproduct of the ozonolysis.

Acknowledgment. This research was supported in part by the National Science Foundation and by the Academic Senate of UCSD. We thank Professor S. Lee for the use of his laser.

Registry No. 3-Hydroxy-2,2,4-trimethyl-3-pentenoic acid β-lactone, 3173-79-3; dimethylmalonic anhydride, 22922-58-3.

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[9] Dauben, W. G.; Epstein, W. W. *J. Org. Chem.* **1959**, *24*, 1595–6.

[10] "Sadtler Standard Infrared Prism Spectra"; Sadtler Research Laboratories, Inc.: Philadelphia, PA, 1976; No. 16350.

[11] To the best of our knowledge the only other sp^2 carbonyl compound with such a high frequency is β,β-bis(trifluoromethyl)-β-propiolactone, which is reported[12] to show a doublet at 1890 and 1949 cm^{-1}. We are indebted to a referee for bringing this to our attention.

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