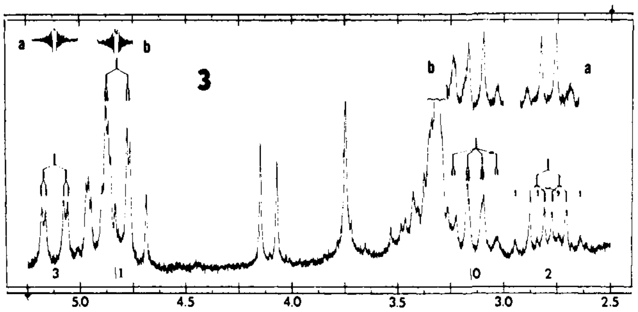

Figure 2. Partial nmr spectra of a $CDCl_3$ solution of triacetyldarcanolide (**3**). Inserts show the decoupled spectra arising from irradiation at a and b, respectively.

Irradiation of the doublet of doublets resonance at 5.00 ppm, assigned unequivocally to H-11, deshielded by the 11-acetyl group, results in sharpening of the 3.15-ppm quartet (H-10). The chemical shift of H-3 is located by the collapse of the resonance of H-2 when the doublet of doublets at 3.78 ppm is irradiated.

The partial nmr spectra of a $CDCl_3$ solution (Figure 2) of triacetyldarcanolide (**3**),[17] a tetraacetate, prepared from **2** by acetic anhydride–pyridine acetylation, also clearly shows the characteristic resonances of H-2 and H-10 at 2.79 and 3.13 ppm, respectively. Spin decoupling experiments (Figure 2, a and b) locate the chemical shifts of H-3 and H-11 at 5.12 and 4.82 ppm. The large paramagnetic shift of H-3 (−1.34 ppm), which can be accommodated only by acetylation of a geminal 3-hydroxyl group,[18] requires that the D-chalcose residue of **3** be bound at C-5. Since migration of a glycosidically bound sugar during acetylation or acid-catalyzed methanolysis is unlikely and has not been observed with other macrolide antibiotics, the D-chalcose residue must be at C-5 in **2** and **1**, thereby proving the alternate structure.

The glycosidic linkage of D-chalcose in **3** was shown to be β by the coupling constant[19] of the 4.11-ppm anomeric proton ($J_{1',2'} = 7.5$ Hz, Figure 2). The determination could not be made from the spectra of **1** or **2** since in these compounds H-1′ is also virtually coupled[20] to H-3′ due to the chemical shift proximity of H-2′ and H-3′ (Figure 1). Similarly, analysis of the 220-MHz nmr spectra[21] of **1** revealed an α-glycosidic linkage for 4-*O*-acetyl-L-arcanose ($J_{1'',2a''} = 4.5$ Hz, $J_{1'',2e''} = \sim 1$ Hz). These assignments corroborate previous molecular rotational difference determinations.[22]

The proposed structure is not unexpected in view of the suggested common biosynthetic origin of the various macrolide antibiotics.[23,24] The assignment of structure **1** to lankamycin removes the only discrepancy in the pattern of sugar substitution. All described 14-membered aglycone ring macrolide antibiotics, erythromycin A,[25] B,[26] and C,[27,28] oleandomycin,[29] lankamycin,[1] picromycin,[30,31] narbomycin,[32] and megalomicin A,[33] have now been shown to have a 4,6-dideoxy- or 3,4,6-trideoxy-3-dimethylamino-D-*xylo*-hexopyranose (D-desosamine[34,35] or D-chalose[6,7]) attached to the C-5 secondary hydroxyl *via* a β-glycoside bond;[22] a 2,6-dideoxy-L-hexopyranose of differing stereochemistry (L-cladinose,[36,37] L-mycarose,[37] L-oleandrose,[38] or 4-*O*-acetyl-L-arcanose[8]) is attached to the C-3 secondary hydroxyl, when present, *via* an α-glycoside bond.[22]

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The Stimulated Raman Effect. A New Source of Laser Temperature-Jump Heating[1]

Sir:

The temperature-jump technique is widely used for the study of rapid chemical reactions.[2] In this technique a capacitor is discharged through a cell containing the solution of interest, thereby raising its temperature 1–10° in about 10^{-6} sec. This type of heating can be employed only with solutions of moderately high ionic concentrations. It has been pointed out[3,4] that the use of optical heating with a Q-switched laser is not subject to this limitation. Moreover a laser temperature-jump apparatus can have a heating time of 10^{-8} sec or less by using a cavity-dumped[5] or mode-locked

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[1] Research performed at Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.

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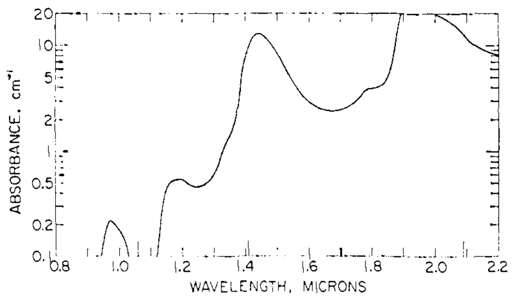

Figure 1. The absorption spectrum of H_2O measured against a carbon tetrachloride blank on a Cary 14 spectrophotometer at 25°.

laser.[6] The only lasers with enough power to produce a useful temperature jump are ruby and neodymium.[7] Unfortunately, ruby exhibits laser action at 0.694 μ, where water has negligible absorbance, while neodymium exhibits laser action at 1.06 μ, where the absorbance of water is only 0.067 cm^{-1}. It is apparent from Figure 1 that the absorbance of water is very large at wavelengths beyond 1.06 μ. In order to take advantage of this increased absorbance we have examined the possibility of using the stimulated Raman effect to shift the radiation emitted by a neodymium glass rod to longer wavelengths.[8]

A schematic diagram of the apparatus used in these studies is shown in Figure 2. The laser system consists of an oscillator–amplifier combination with a Pockels cell Q switch and an output of about 15 J in 25 nsec. The pulse from the laser is focused in the center of a 21-cm long dewar filled with liquid nitrogen. The choice of liquid nitrogen is dictated by three factors: (a) according to its Raman spectrum, it should shift 1.06–1.41 μ (and possibly 1.41–2.09 μ); (b) it has no absorbance at either of these wavelengths; and (c) it has a low threshold for stimulated Raman emission.[9] The output from the dewar is scattered by a magnesium oxide block, dispersed with a Bausch and Lomb monochromator with a reciprocal linear dispersion of 12.8 mμ mm^{-1}, and detected with a Kodak Ektron P-2 PbS detector. The signal is displayed on a Tektronix 453 oscilloscope which is triggered by the output of an EG&G photodiode (SGD-100A).

Two types of experiment were performed. In the first type of experiment, the incident laser beam was not focused (that is, the lens shown in Figure 1 was removed). Under these conditions the conversion efficiency, defined as $I_{1.41}/(I_{1.06} + I_{1.41})$, where I is the pulse height from the oscilloscope trace, was about 20% when the power density of the incident laser beam was 30 MW cm^{-2}. The conversion efficiency increased with the power density of the incident beam, and reached about 40% at power densities of 80 MW cm^{-2}. In the second type of experiment the laser beam was focused in the center of the dewar. Under these conditions, conversion efficiencies of about 50% were obtained at the higher power densities. The conversion efficiency can presumably be increased even further by increasing the path length of the dewar. No radiation was detected at intermediate wavelengths. It is apparent from Figure 1 that the absorbance of water is 1.5×10^2 times larger at 1.41 μ than it is at 1.06 μ.

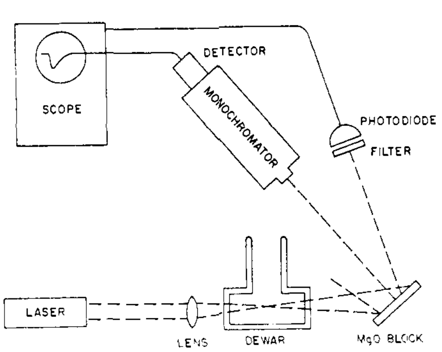

Figure 2. Schematic diagram of the apparatus used to study the stimulated Raman emission from liquid nitrogen.

The high conversion efficiencies found in this study are somewhat surprising in view of the fact that the width of the 1.06-μ line is about 50 Å, and it is generally believed that much narrower line widths are required for efficient operation of the stimulated Raman effect.[9] Another noteworthy feature is that the conversion efficiencies are high even at the high power densities used in this work.

The temperature jump that can be produced by this method depends upon the power of the laser, the efficiency of the stimulated Raman conversion, the absorbance of the sample, the amount of energy lost by scattering and reflections, geometrical considerations, etc. Estimates of these quantities indicate that temperature jumps of about 10° might be obtained under suitable conditions. Crude temperature measurements performed by inserting one junction of a thermocouple into a $10 \times 10 \times 2$ mm^3 sample of water after it had been irradiated indicate that the value of $(\Delta T)_0$, defined by $(\Delta T)_x/(\Delta T)_0 = \exp(-2.30Ax)$, where A is the absorbance of water at 1.41 μ and x is the distance from the front surface of the cell, is more than 6.5°.[10] This temperature rise, which is uncorrected for heat losses, is adequate for relaxation work and can be increased even further by focusing the beam and by decreasing the volume of the sample. The small volumes that can be heated make this technique eminently suitable for use with biological systems. The time required to produce the temperature jump is equal to the width of the laser pulse (25 nsec) plus the relaxation time of water, which is believed to be very rapid. This approach is, of course, not restricted to aqueous solutions, but by the proper selection of the substrate for the stimulated Raman effect it could be used also with a variety of nonaqueous systems.

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Rearrangement of Azidoquinones. VII. Thermal Cleavage of 2,5-Diazidoquinones to Cyanoketenes. Syntheses of *t*-Butylcyanoketene

Sir:

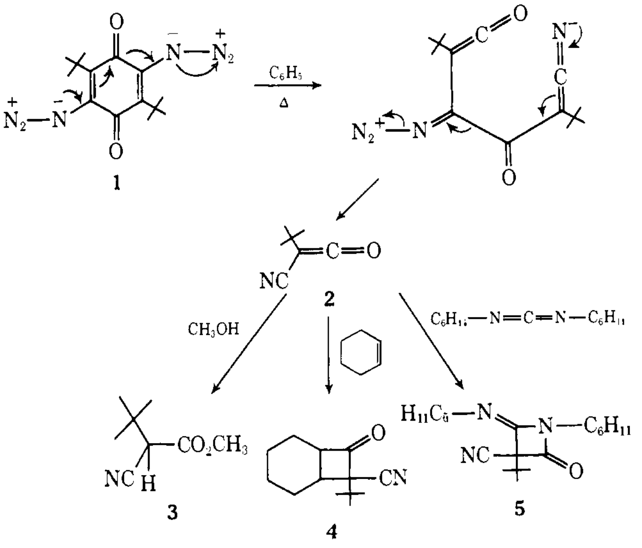
2,5-Diazido-3,6-di-*t*-butyl-1,4-benzoquinone (**1**)[1] undergoes a very facile thermal cleavage in refluxing benzene to give 2 mol of *t*-butylcyanoketene (**2**), a surprisingly stable yet very reactive ketene. This reaction constitutes a mild, noncatalytic entry into a previously unexplored class of ketenes.[2] To our knowledge, the only other reported members of this series are the parent, cyanoketene, and phenylcyanoketene, both of which have only been proposed as reactive intermediates.[3]

The ketene **2**, formed in nearly quantitative yield, is quite stable in solution. An anhydrous benzene solution of **2** which was kept at ambient temperature for 8 days showed (nmr) only minor decomposition. As yet, no attempts have been made to isolate the ketene since one can conveniently use benzene solutions of the compound for spectral and chemical investigations. The following procedure can be used for the preparation of benzene solutions of the ketene. A benzene solution consisting of 150 ml of anhydrous benzene and 5 g (0.0165 mol) of 2,5-diazido-3,6-di-*t*-butyl-1,4-benzoquinone (**1**), mp 89–90° dec, was refluxed for 45 min. During this time nitrogen evolved and the color of the reaction solution changed from bright orange to yellow. The ir and nmr spectra of such a solution indicated only the presence of the ketene. *t*-Butylcyanoketene (**2**) has a very simple ir spectrum showing characteristic absorptions at 2220 (w, CN), 2130 (s, C=C=O), and 1380, 1365 cm^{-1} (m, C(CH$_3$)$_3$). An nmr spectrum of a benzene solution of **2** shows only one sharp singlet at δ 0.75.

The ketene reacts instantaneously and nearly quantitatively with methanol to give methyl α-cyano-α-*t*-butylacetate (**3**). This colorless liquid shows the following characteristic spectral properties: ir 2270 (w, CN) and 1750 cm^{-1} (s, C=O); nmr (CDCl$_3$) δ 4.78 (3, s), 3.33 (1, s), 1.18 (9, s).

t-Butylcyanoketene (**2**) is *surprisingly* reactive in 2 + 2 cycloaddition reactions. For example, decomposition of the diazide (**1**) in cyclohexene (3 hr at reflux temperature) gives the cyclobutanone (**4**) in 63% isolated yield. Cyclohexene is normally quite unreactive in cycloaddition reactions with ketenes. For example, Staudinger and Suter[4] found that diphenylketene reacted with cyclohexene to give a 60% yield of the cyclobutanone after 10 days at 100°. Butylethylketene was shown by Martin and coworkers[5] to react with cyclohexene after 12 hr at 180° to give a 47% yield of the adduct. The white crystilline cyclobutanone (**4**) shows the following characteristic properties: mp, 68–69°; ir (Nujol) 2220 (w, CN) and 1775 cm^{-1} (s, C=O); nmr (CDCl$_3$) δ 3.89 (1, m, CH), 2.92 (1, m, CH), 1.55 (8, m, CH$_2$), 1.20 (9, s, C(CH$_3$)). *Anal.* Found: C, 76.17; H, 9.32; N, 6.85.

A benzene solution of the ketene (**2**) readily undergoes cycloaddition to dicyclohexylcarbodiimide giving the imino-β-lactam (**5**) in 84% isolated yield. The structure of this compound is based upon the following characteristic[6-8] properties: mp 111–112°; ir (Nujol) 2220 (w, CN), 1815 (s, C=O), and 1680 cm^{-1} (s, C=N); nmr (CDCl$_3$) δ 3.5 (2, m, CH), 1.1–2.1 (20, m, CH$_2$), 1.22 (9, s, C(CH$_3$)). *Anal.* Found: C, 72.88; N, 12.67; H, 9.43.



The above cycloaddition reactions of **2** are particularly interesting in view of De Selms'[3] recent report that phenylcyanoketene *does not* react with cyclopentadiene, cyclopentene, cyclohexene, diphenylacetylene, or benzalaniline.

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(1) This azidoquinone is readily available *via* the reaction of sodium azide with 2,5-di-*t*-butyl-3,6-dichloro-1,4-benzoquinone. For synthetic procedures to azidoquinones see H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, 92, 1675 (1970).

(2) This reaction has been applied to other 2,5-diazido-1,4-benzoquinones, *e.g.*, 2,5-diazido-3,6-dimethyl- and 2,5-diazido-3,6-diphenyl-1,4-benzoquinones. The ketenes resulting from the thermal decomposition of these diazides were trapped by ethanol to give the corresponding ethyl esters. These results will be detailed in a forthcoming paper.

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