tance reading recorded. By noting the direction of any drift and its magnitude, and assuming the drift to be constant throughout the run, the corrected infinity point was calculated. Rate constants were then calculated using the RATSOL2 computer program (see above). In several runs, we have plotted the concentrations of substrate from the computer output and found excellent first-order behavior over the 2 half-lifes examined.

Using the above procedure with the M-D Mini-Cell,[15] 30 ml of $10^{-3}$ *M* substrate solution is adequate to produce *duplicate* rate constants at *two* temperature and potentiometrically determined infinity titer checks at *both* temperatures.

**Registry No.**—Acetone, 67-64-1; acetic acid, 64-19-7; *p*-nitrobenzoic acid, 62-23-7; potassium acetate, 127-08-2; *exo*-bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate, 36740-22-4.

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# Preparation of 3-(Hydroxymethyl)-4,4-dimethylpentanoic Acid γ-Lactone

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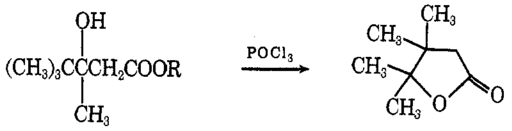
3-(Hydroxymethyl)-4,4-dimethylpentanoic acid γ-lactone can be prepared in 62% overall yield in four steps from ethyl 3-hydroxy-3,4,4-trimethylpentanoate. The latter was dehydrated to give a mixture of α,β- and β,γ-unsaturated esters which upon bromination with NBS yielded ethyl (*Z*)-3-(bromomethyl)-4,4-dimethyl-2-pentenoate. Thermal cyclization of the bromo ester produced 3-*tert*-butyl-2-buten-1,4-olide, which was hydrogenated to give the γ-lactone.

While preparing a number of conformationally biased compounds, 3-(hydroxymethyl)-4,4-dimethylpentanoic acid γ-lactone (**7**) was required as part of a synthetic scheme. It has been shown on several occasions[2a–c] that the material obtained from the dehydration of ethyl 3-hydroxy-3,4,4-trimethylpentanoate (**1c**) gives



$$(CH_3)_3CC(OH)(CH_3)CH_2COOR \xrightarrow{POCl_3} \mathbf{2}$$

**1a**, R = H
**b**, R = CH₃
**c**, R = C₂H₅

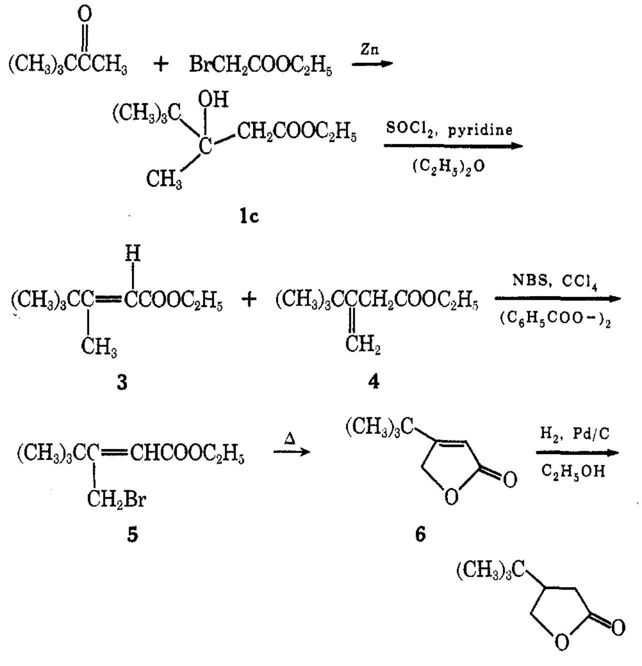
**2**

4-hydroxy-3,3,4-trimethylpentanoic acid γ-lactone (**2**) rather than **7** as originally thought.[2d] We have synthesized **7** in 62% yield from **1c** and now summarize our work.

The lactone **7** was prepared by the route shown in Scheme I. Using the procedure of Newman[2] and Heilman,[3] the hydroxy ester **1c** was dehydrated in good yield to give the two unsaturated esters **3** and **4** in equal amounts. After separation by preparative glc, ir, mass spectrum, and nmr analysis readily identified the compounds as **3** and **4**. This result agrees with the structural revision offered by Newman and Patrick[4] for the products which were obtained from the dehydration of **1b**.

The mixture of unsaturated esters **3** and **4** obtained by the dehydration of **1c** gave only **5** upon free-radical bromination using NBS. Compounds similar to **5** have been converted into 2-buten-1,4-olides by treating them with concentrated HCl under reflux.[5] Our preliminary studies indicated that the allylic bromide **5** could be converted into the unsaturated lactone **6** simply by heating for a few minutes at 220°. In addition, 80% of the theoretical amount of bromoethane was isolated, but the volatile distillate from the pyrolysis reaction (see Experimental Section) fumed when exposed to the air, undoubtedly because of the HBr present. Ethene was not looked for in this reaction but presumably was also formed.

Scheme I



The bromo ester **5** was assigned the *Z* configuration. The structural assignment is by no means definitive, since it is possible that the conditions of the thermal reaction or the HBr produced could cause isomerization from (*E*)-**5** to (*Z*)-**5** before ring closure.

The thermal reaction then provided an excellent route to **5** and subsequently to **6**. The lactone **7** was finally obtained by low-pressure hydrogenation of **6**.

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[1] NSF Undergraduate Research Participant.

[2] (a) A. W. Burgstahler and D. E. Wetmore, *J. Org. Chem.*, **26**, 3516 (1961); (b) C. Metzger, D. Borrmann, and R. Wegler, *Chem. Ber.*, **100**, 1817 (1967); (c) T. B. Patrick and M. S. Newman, *J. Org. Chem.*, **34**, 3714 (1969); (d) M. S. Newman and R. Rosher, *J. Org. Chem.*, **9**, 221 (1944).

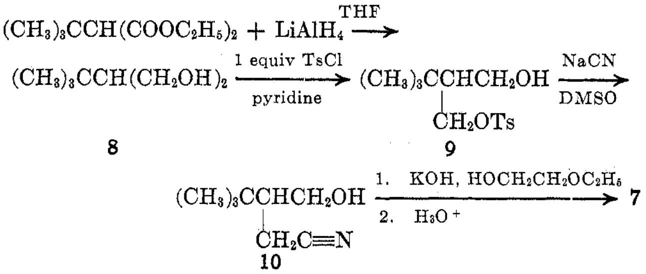
[3] R. Heilmann and R. Glenat, *Bull. Soc. Chim. Fr.*, 1586 (1955).

[4] M. S. Newman and T. B. Patrick, *J. Amer. Chem. Soc.*, **92**, 4312 (1970).

[5] M. U. S. Sultanbawa, P. Veeravagu, and T. Padmanathan, *J. Chem. Soc.*, 1262 (1960).

The lactone **7** was also prepared by the route shown in Scheme II. It is more laborious but does serve as a check on the proposed structure.

SCHEME II



$$(CH_3)_3CCH(COOC_2H_5)_2 + LiAlH_4 \xrightarrow{THF}$$

$$\underset{\mathbf{8}}{(CH_3)_3CCH(CH_2OH)_2} \xrightarrow[\text{pyridine}]{\text{1 equiv TsCl}} \underset{\mathbf{9}}{\underset{CH_2OTs}{(CH_3)_3CCHCH_2OH}} \xrightarrow[\text{DMSO}]{\text{NaCN}}$$

$$\underset{\mathbf{10}}{\underset{CH_2C{\equiv}N}{(CH_3)_3CCHCH_2OH}} \xrightarrow[\text{2. } H_3O^+]{\text{1. KOH, } HOCH_2CH_2OC_2H_5} \mathbf{7}$$

The lactone **7** was reduced with $LiAlH_4$ to give 2-*tert*-butyl-1,4-butanediol, which was identical in all respects with the product obtained by $LiAlH_4$ reduction of diethyl 2-*tert*-butylsuccinate.[6]

$$\mathbf{7} + LiAlH_4 \xrightarrow{THF}$$

$$HOCH_2\overset{+}{C}HCH_2CH_2OH \longleftarrow H_5C_2OOC\overset{+}{C}HCH_2COOCH_5$$

There have been several cases in which **7** has been postulated in addition to those already cited. In two instances **2** was actually isolated.[7]

A more recent reference suggests that **7** can be prepared by allowing allyl alcohol and *tert*-butyllithium to react and treating the adduct with $CO_2$.[8]

## Experimental Section

Boiling points are uncorrected and unless otherwise noted were observed at 580 mm. Melting points were determined using a Mel-Temp melting point apparatus and are corrected. Ir spectra were obtained using a Perkin-Elmer Model 621 spectrophotometer. The nmr spectra were run on a Varian HA-100 spectrometer using $CDCl_3$ or $CCl_4$ as solvents and tetramethylsilane as an internal standard. The nmr data are reported as chemical shifts in δ units followed by s = singlet, d = doublet, t = triplet, q = quartet, or m = multiplet, and the relative number of protons attributable to the particular signal is reported. Mass spectra were determined on a Varian-MAT CH-5 spectrometer. The mass spectral data are reported as *m/e* (for $M^+$ and major fragment ions) followed by per cent relative abundance. Varian Aerograph Models A90–P3 and 1200 were used for the glc analysis. Reagents were obtained from regular commercial sources unless otherwise noted. $MgSO_4$ was used as the drying agent.

**Ethyl 3-Hydroxy-3,4,4-trimethylpentanoate (1c).**—The synthesis was carried out in 77% yield according to the procedure of Newman and Rosher,[2] bp 47° (0.05 mm) [lit.[2] bp 104–107° (18 mm)].

**Dehydration of Ethyl 3-Hydroxy-3,4,4-trimethylpentanoate.**—The mixture of unsaturated esters **3** and **4** was prepared in 90% yield, bp 65–73° (6 mm) [lit.[3] bp 80–83° (12 mm)], by the $SOCl_2$–pyridine dehydration of **1c** using the method outlined by Heilman and Glenat.[3] The product mixture was analyzed on an 8 ft × 0.25 in. column packed with 15% SE-30 on 60/80 Chromosorb P at 150°. Compounds **3** and **4** were present in equal amounts with **4** having the shorter retention time. Preparative gc gave pure **3** and **4**. The spectral properties of **3** are as follows: ir, $\nu_{C=O}$ 1718, $\nu_{C=C}$ 1633 $cm^{-1}$ (liquid film); nmr δ 1.06 (s, 9 H), 1.21 (t, 3 H), 2.09 (d, 3 H, $J$ = 1.8 Hz), 4.00 (q, 2 H), 5.59 (q, 1 H, $J$ = 1.8 Hz); mass spectrum *m/e* (rel intensity) 170 (7), 128 (36), 126 (36), 109 (32), 97 (58), 81 (44), 47 (33), 55 (85), 43 (46), 41 (100), 39 (81), 29 (84). The spectral properties of **4** are as follows: ir $\nu_{C=O}$ 1740, $\nu_{C=C}$ 1638 $cm^{-1}$ (liquid film); nmr δ 1.02 (s, 9 H), 1.20 (t, 3 H), 2.90 (m, 2 H), 4.02 (q, 2 H), 4.78 (m, 1 H), 4.02 (m, 1 H); mass spectrum *m/e* (rel intensity) 170 (6), 109 (19), 96 (28), 83 (60), 82 (15), 81 (37), 69 (19), 67 (24), 57 (22), 55 (90), 43 (27), 41 (82), 39 (44), 29 (100). For ir and nmr data of the corresponding methyl esters see ref 4. Pure **3** can be prepared by the condensation of sodium diethyl carboethoxymethylphosphonate and pinacolone.[9]

**Ethyl (*Z*)-3-(Bromomethyl)-4,4-dimethyl-2-pentenoate (5).**—Both pure **3** and the mixture, **3** and **4**, gave **5** after reaction with NBS in the presence of $(C_6H_5COO-)_2$ in $CCl_4$ under reflux. A typical experiment is given. A mixture of **3** and **4** (41 g, 0.24 mol), NBS (43 g, 0.24 mol), and $(C_6H_5COO-)_2$ (1 g) in 250 ml of $CCl_4$ was heated under reflux for 48 hr. The succinimide was removed by filtration and the filtrate was concentrated by rotary evaporation to give crude **5**. Distillation of the crude product gave 49.5 g (82%) of **5**: bp 68° (0.04 mm); ir $\nu_{C=O}$ 1720 $cm^{-1}$ (liquid film); nmr δ 1.18 (s, 9 H), 1.26 (t, 3 H), 4.10 (q, 2 H), 4.49 (s, 2 H), 5.76 (s, 1 H); mass spectrum *m/e* (rel intensity) 250 (12), 248 (12), 205 (21), 203 (18), 155 (54), 127 (38), 123 (25), 109 (22), 95 (38), 57 (66), 55 (33), 43 (44), 41 (79), 39 (43), 29 (100), 27 (38).

**3-*tert*-Butyl-2-buten-1,4-olide (6).**—The bromo ester **5** (49.5 g, 0.198 mol) was placed in a 250-ml flask equipped with a reflux air condenser. A take-off head attached to a water-cooled condenser was placed on top of the air condenser. The water condenser was in turn connected to an adapter and flask which was cooled in an ice–water bath. The entire system was purged with $N_2$ and the reaction flask was then heated at 220° for 30 min. During the heating period the reaction was monitored by ir by periodically removing a drop and examining the C=O region of the ir spectrum. In addition, the rate at which $C_2H_5Br$ collected in the receiver flask was an indication of the progress of the reaction. After cooling the crude product, it was distilled to give 23.1 g (84%) of **6**: bp 60° (0.02 mm); ir $\nu_{C=O}$ 1789 and 1757 (characteristic of 2-buten-1,4-olides[10]), $\nu_{C=C}$ 1630 $cm^{-1}$ (liquid film); nmr δ 1.17 (s, 9 H), 4.71 (d, $J$ = 2 Hz, 2 H), 5.62 (t, $J$ = 2 Hz, 1 H); mass spectrum *m/e* (rel intensity) 140 (4), 125 (19), 110 (12), 96 (23), 95 (58), 81 (27), 67 (79), 57 (46), 41 (100), 39 (67).

**3-(Hydroxymethyl)-4,4-dimethylpentanoic Acid γ-Lactone (7).**—The butenolide **6** (10 g, 0.072 mol) was hydrogenated at 45 psi in 100 ml of ethanol using 1.5 g of 5% Pd/C as the catalyst. The reaction mixture was diluted with petroleum ether (bp 30–35°), the catalyst was removed by filtration, and the filtrate was diluted with $H_2O$ and continuously extracted with petroleum ether. The petroleum ether extract was dried and concentrated to give 11.2 g of crude product. Distillation gave 9.8 g (98%) of **7**: bp 45° (0.02 mm) (mp between 0 and 10°); ir $\nu_{C=O}$ 1785 $cm^{-1}$; nmr δ 0.88 (s, 9 H), 2.28 (m, 3 H), 4.06 (m, 2 H); mass spectrum *m/e* (rel intensity) 142 (8), 127 (7), 97 (4), 86 (100), 69 (28), 57 (87), 41(40).

**Reduction of 7 with $LiAlH_4$.**—A solution of the lactone (2.0 g, 0.0141 mol) in 2 ml of THF was added dropwise to a slurry of $LiAlH_4$ (0.402 g, 0.011 mol) in 10 ml of THF under an atmosphere of $N_2$ while keeping the reaction vessel immersed in an ice–water bath. After the addition had been completed, the reaction mixture was allowed to warm to room temperature and stirred for an additional 18 hr. Water was added to destroy excess $LiAlH_4$ followed by acidification with 10% $H_2SO_4$. The product was extracted with ether. The ether extract was dried and concentrated. The crude product was distilled to give 1.8 g (87%) of 2-*tert*-butyl-1,4-butanediol, bp 85° (0.02 mm), which was identical (ir and nmr) with material obtained from the $LiAlH_4$ reduction of diethyl 2-*tert*-butylsuccinate.[6]

**2-*tert*-Butyl-1,3-propanediol (8).**—Diethyl *tert*-butylmalonate[11] (25 g, 0.116 mol) in 60 ml of THF was added dropwise to a suspension of $LiAlH_4$ (5.3 g, 0.142 mol) in 100 ml of THF at 5° under $N_2$. After the addition had been completed, the reaction mixture was stirred at room temperature for 4 hr. The excess $LiAlH_4$ was destroyed by the addition of ethanol. Ether was added and the mixture was acidified with 10% aqueous $H_2SO_4$. NaCl was added and the layers were separated. The aqueous layer was extracted three times with ether. The organic solutions were combined,

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(6) V. K. Andersen and J. Munch-Petersen, *Acta Chem. Scand.*, **16**, 947 (1962).

(7) (a) Y. Maroni-Barnaud and J. E. DuBois, *Bull. Soc. Chim. Fr.*, C-27 (1953); (b) W. J. Hickinbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 2529 (1954).

(8) J. K. Crandall and A. C. Clark, *Tetrahedron Lett.*, 325 (1969).

(9) M. J. Jorgenson and T. Leung, *J. Amer. Chem. Soc.*, **90**, 3769 (1968).

(10) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 45.

(11) (a) H. F. Van Woerden, *Recl. Trav. Chim. Pays-Bas*, **82**, 920 (1963); (b) E. L. Eliel, R. O. Hutchins, and M. Knoeber, *Org. Syn.*, **50**, 38 (1970).

washed with saturated NaCl solution, dried, and concentrated on the rotary evaporator to give 12.5 g (80%) of white crystals. Recrystallization from $CCl_4$ gave 7.0 g of **8**, mp 58–58.5° (lit.[11a] mp 58–59°). A second crop was obtained from the mother liquors.

**2-*tert*-Butyl-3-*p*-toluenesulfonoxy-1-propanol (9).**—The diol **8** (7 g, 0.053 mol) and *p*-toluenesulfonyl chloride (10.05 g, 0.053 mol) were dissolved in 100 ml of pyridine. The solution was placed in the refrigerator for 3 days. The reaction mixture was poured onto ice–water and the product was extracted with ether. The ether extract was washed successively with dilute HCl, saturated $NaHCO_3$, and $H_2O$. The ether solution was dried and concentrated on the rotary evaporator to give 14 g (92%) of crude monotosylate **9**, which contains some ditosylate: nmr of **9**, $\delta$ 0.86 (s, 9 H), 2.44 (m, 1 H), 2.40 (s, 3 H), 3.60 (m, 2 H), 4.04 (m, 2 H), 7.26 (m, 2 H), 7.66 (m, 2 H).

**3-*tert*-Butyl-4-hydroxybutyronitrile (10).**—Sodium cyanide (2.9 g, 0.059 mol) was added to a solution of the crude monotosylate **9** (14 g) in 50 ml of DMSO. The mixture was stirred at room temperature for 6 days and was then poured on ice–water. The product was extracted with ether. Concentration of the ether extract yielded 6.1 g (88%, assuming that the 14 g of crude tosylate was all **9**) of crude **10**, which was distilled to give 4.9 g of product: bp 72° (0.08 mm); ir $\nu_{OH}$ 3500, $\nu_{C\equiv N}$ 2255 $cm^{-1}$ (liquid film); nmr of **10**, $\delta$ 0.95 (s, 9 H), 1.6 (m, 1 H), 2.46 (m, 2 H), 3.00 (s, OH), 3.68 (m, 2 H). The nmr spectrum suggests the presence of about 20% of 3-*tert*-butylglutaronitrile. The dinitrile undoubtedly arose from the ditosylate impurity in **9**. The presence of the ditosylate in **9** could not be unequivocally established from the nmr spectrum of crude **9**. 3-*tert*-Butyl-1,5-pentanedioic acid is, however, isolated from the hydrolysis of the nitrile mixture, confirming the presence of the dinitrile in the hydroxynitrile **10**. See the preparation of **7** from **10** which follows.

**3-(Hydroxymethyl)-4,4-dimethylpentanoic Acid $\gamma$-Lactone (7) from 3-*tert*-Butyl-4-hydroxybutyronitrile (10).**—The procedure for the basic hydrolysis of nitriles outlined by Sandler and Karo[12] was used. The product was isolated by extraction with ether. The ether extract was washed with $H_2O$ and then dried and the ether was removed on the rotary evaporator. The crude product was dissolved in ether–pentane and cooled. 3-*tert*-Butyl-1,5-pentanedioic acid (1 g) precipitated and was removed by filtration. The mother liquors were concentrated to give 2.5 g of **7** which had physical properties, *i.e.*, boiling point and ir and nmr spectra, identical with those obtained for **7** synthesized by another route (*vide supra*).

**Registry No.**—**3**, 16812-82-1; **4**, 36976-64-4; **5**, 36976-65-5; **6**, 36976-66-6; **7**, 22530-95-6; **9**, 36976-68-8; **10**, 36976-69-9; 2-*tert*-butyl-1,4-butanediol, 36976-70-2.

**Acknowledgments.**—The support of the University of Wyoming Division of Basic Research and the Research Coordinating Committee is appreciated. Our thanks to Mr. R. Mendoza for assistance in obtaining many of the mass and nmr spectra.

[12] S. R. Sandler and W. Karo, "Organic Functional Group Preparation," Vol. I, Academic Press, New York, N. Y., 1968, p 229.

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# Rearrangement of Dihalocyclopropanes Derived from Some 6,7-Dihydrobenzo[*b*]thiophenes

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*Received July 11, 1972*

1,1-Dihalocyclopropanes **10** have been prepared from 6,7-dihydrobenzo[*b*]thiophenes **4** derived from 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**2**) through formation of either enol ethers **4a** and **4b** or dehydration of the tertiary alcohols **5**. These alcohols were obtained by reduction of **2** with sodium borohydride or Grignard reagents. The dihalocarbene adducts **10** rearranged with or without an organic base to afford 8*H*-cyclohepta[*b*]thiophenes **11**.

The 1-thiaazulenium cation (the thienotropylium cation **1**, Scheme I) was reported[2a] to possess unusual stability relative to tropylium and the isoelectronic benzotropylium cations.[2b] Since this discovery, the expected publications describing other representatives of **1** have not appeared.[3] These two factors led us to consider the synthesis of substituted 1-thiaazulenium cations. The preparation of some 8*H*-cyclohepta[*b*]thiophenes as possible precursors of such cations constitutes the subject of this report.

The 4,4-dialkoxy-4,5,6,7-tetrahydrobenzo[*b*]thiophenes **3a** and **3b** (Scheme I) were obtained by heating 4-oxo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**2**)[4] under reflux with the appropriate alcohol, a twofold molar excess of trialkyl orthoformate, and a catalytic amount of *p*-toluenesulfonic acid (TsOH). These ketals, unstable in air at room temperature, slowly eliminated alcohol to produce the respective 4-alkoxy-6,7-dihydrobenzo[*b*]thiophenes, **4a** and **4b**. The rate of conversion of **3a,b** to **4a,b** was enhanced by heating **3a,b** with TsOH for 10 min. The enol ethers **4a,b** required refrigeration under nitrogen to prevent reversion to the ketone **2**.

Treatment of **2** with sodium borohydride in ethanol gave an 81% yield of the alcohol **5a**, which readily underwent acid-catalyzed dehydration to 6,7-dihydrobenzo[*b*]thiophene (**4c**). Alkenyl-substituted thiophenes are known to exhibit instability leading to polymerization.[5] Likewise, **4c** polymerized so rapidly that a correct elemental analysis was prevented. The initial report[6] on the reduction of **2** with methylmagnesium bromide stated that only 4-methyl-6,7-dihydrobenzo[*b*]thiophene (**4d**) or the exocyclic isomer, 4-methylene-4,5,6,7-tetrahydrobenzo[*b*]thiophene (**6**) were produced. Subsequent publications[7,8a] described

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[1] Taken, in part, from the doctoral dissertation of V. G. G., St. John's University, 1971.

[2] (a) R. G. Turnbo, D. L. Sullivan, and R. Pettit, *J. Amer. Chem. Soc.*, **86**, 5630 (1964); see also D. L. Sullivan and R. Pettit, *Tetrahedron Lett.*, 401 (1963); (b) H. H. Rennhard, G. Modica, W. Simon, E. Heilbronner, and E. Eschenmoser, *Helv. Chim. Acta*, **40**, 957 (1957).

[3] Derivatives of the isomeric 2-thiaazulenium cation have been prepared by M. Winn and F. G. Bordwell, *J. Org. Chem.*, **32**, 1610 (1967), from the precursor, 2-thiaazulen-6-ones, and were found to be more stable than **1**.

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