Preparation of 4-*tert*-Butyl-1,2,7,8-tetrahydroxydibenzofuran (29). To a solution of **24** (0.7 g, 2 mmol) in benzene (30 mL) was added a solution of BBr_3 (7.1 g, 28 mmol) in benzene (5 mL) at room temperature. After being stirred for 1 h, it was worked up as described above to give **29**: colorless needles (benzene); yield 435 mg (76%); mp 235–238 °C dec; IR (KBr) ν_{OH} 3400 cm^{-1}; NMR (Me_2SO-d_6) δ 1.43 (9 H, s), 6.70 (1 H, s), 6.91 (1 H, s), 7.38 (1 H, s), 8.78 (4 H, br); mass spectrum, m/e 288 (M^+).

Anal. Calcd for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.66; H, 5.63.

Preparation of 1,2,8-Trihydroxydibenzofuran (26). To a solution of **28** (500 mg, 1.8 mmol) in dry toluene (50 mL) was added finely powdered $AlCl_3$ (1.7 g, 12.7 mmol) at room temperature. After being stirred for 1 h, it was poured into a large amount of ice–water and extracted with ether. The ether solution was washed with water, dried over Na_2SO_4, and evaporated in vacuo to leave a residue, which was crystallized from hexane to give crude **26**: colorless needles (benzene); yield 190 mg (48%); mp 230–240.5 °C dec; IR (KBr) ν_{OH} 3400 cm^{-1}; NMR (Me_2SO-d_6) δ 6.77 (1 H, dd, J = 8.5, 2.5 Hz), 6.78 (1 H, d, J = 8.5 Hz), 6.88 (1 H, d, J = 8.5 Hz), 7.29 (1 H, d, J = 8.5 Hz), 7.39 (1 H, d, J = 2.5 Hz), 9.04 (1 H, br), 9.18 (1 H, s), 9.19 (1 H, br); mass spectrum, m/e 216 (M^+).

Preparation of 1,2,7,8-Tetrahydroxydibenzofuran (27). To a solution of **29** (290 mg, 1 mmol) in dry toluene (40 mL) was added finely powdered $AlCl_3$ (1.1 g, 8 mmol) at room temperature. After being stirred for 2 h, it was worked up as described above to give **27**: colorless needles (benzene); yield 137 mg (59%); mp ca. 250 °C dec; IR (KBr); 3320 cm^{-1}; NMR (Me_2SO-d_6) δ 6.75 (2 H, s), 6.88 (1 H, s), 7.35 (1 H, s), 8.89, 8.96, 9.02, 9.15 (each 1 H, s); mass spectrum, m/e 232 (M^+).

Acetylation of 19. Typical Procedure. A solution of **19** (500 mg, 2.5 mmol) in acetic anhydride (5 mL) was heated at 80 °C for 3 h. The reaction mixture was poured into ice–water, and the precipitate formed was filtered off and washed with water. The precipitate was recrystallized from hexane to give **30**: colorless needles; yield 560 mg (79%); mp 133.5–134.5 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1770–1750 cm^{-1}; NMR ($CDCl_3$) δ 2.32, 2.46 (each 3 H, s), 7.17–7.57 (5 H, m), 7.68–7.78 (1 H, m); mass spectrum, m/e 284 (M^+).

Anal. Calcd for $C_{16}H_{12}O_5$: C, 67.60; H, 4.26. Found: C, 67.69; H, 4.29.

31: colorless needles (hexane–benzene); yield 83%; mp 199–201 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1770–1745 cm^{-1}; NMR ($CDCl_3$) δ 2.31, 2.33, 2.46 (each 3 H, s), 7.05–7.56 (5 H, m); mass spectrum, m/e 342 (M^+).

Anal. Calcd for $C_{18}H_{14}O_7$: C, 63.16; H, 4.12. Found: C, 62.94; H, 4.15.

32: colorless needles (hexane–benzene); yield 82%; mp 203–204.5 °C; IR (KBr) ν_{OH} none, $\nu_{C=O}$ 1775–1760 cm^{-1}; NMR ($CDCl_3$) δ 2.33 (9 H, s), 2.46 (3 H, s), 7.24 (1 H, d, J = 8 Hz), 7.43 (1 H, d, J = 8 Hz), 7.44 (1 H, s), 7.56 (1 H, s); mass spectrum, m/e 400 (M^+).

Anal. Calcd for $C_{20}H_{16}O_9$: C, 60.00; H, 4.03. Found: C, 59.91; H, 3.98.

Registry No. **3**, 6390-69-8; **6a**, 77139-38-9; **6b**, 77139-39-0; **7a**, 19566-63-3; **14**, 86-77-1; **16**, 77139-41-4; **17**, 77139-40-3; **18**, 83025-50-7; **19**, 83025-51-8; **20**, 83025-52-9; **21**, 83025-53-0; **22**, 83025-54-1; **23**, 83025-55-2; **24**, 83025-56-3; **26**, 83025-59-6; **27**, 83025-60-9; **28**, 83025-57-4; **29**, 83025-58-5; **30**, 83025-61-0; **31**, 83025-62-1; **32**, 83025-63-2.

Synthesis and Chemistry of 2,2,5,5-Tetramethylthiolane-3,4-dione. A Route to Bicyclo[2.1.0]pentyl-1-sulfonium Intermediates

John M. Bolster and Richard M. Kellogg*

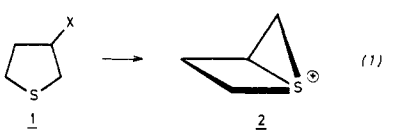
Department of Organic Chemistry, University of Groningen, Nijenborgh 16, 9747 AG Groningen, The Netherlands

Received April 30, 1982

The reaction of sodium sulfide with 2,5-dibromo-2,5-dimethylhexane-3,4-dione affords in good yield 2,2,5,5-tetramethylthiolane-3,4-dione (**3a**). This material has been converted to a variety of derivatives, including 2,2,5,5-tetramethyl-3-diazothiolane-4-one (**3b**) and the corresponding sulfone derivative. Compound **3b** on treatment with electrophiles undergoes rapid substitution by the electrophile at the diazo carbon. The reaction of **3b** with bromine was shown, however, to follow an indirect course involving the formation of a bicyclo[2.1.0]pentyl-1-sulfonium ion as probable intermediate; this is opened reversibly by attack of bromide at sulfur at lower temperature, whereas irreversible attack at carbon adjacent to carbonyl occurs at higher temperatures. Evidence for an ylidic variant of the 1-thiabicyclo[2.1.0]pentyl structure was obtained from the thermal decomposition of **3b**. No trace of a Wolff rearrangement product was obtained. In contrast, the sulfone **18**, derived from **3b** by oxidation, on thermolysis afforded 3,3-dimethyl-4-(2-propenyl)oxathiolan-5-one 2-oxide (**47**). This product was shown, by means of trapping experiments, to arise from the ketene derived by normal Wolff rearrangement of **18** without participation of sulfur. Various other transformations, including 1,3-dipolar cycloadditions, of **3b** and other derivatives, were investigated.

Introduction

Reorganizations of the carbon skeleton of a suitably functionalized thiolane (**1**) could be triggered through bicyclo[2.1.0]pentyl-1-sulfonium intermediates (**2**), obtained by sulfur participation in departure of a leaving group (eq 1). There have been, however, few synthetic



1 2 (1)

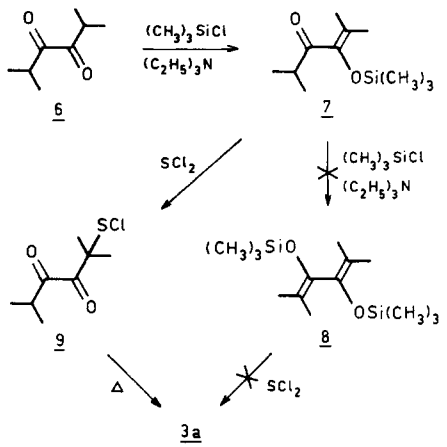
applications of the route shown in eq 1.[1] This is all the more remarkable because in other cyclic and alicyclic systems participation of sulfur β to a leaving group leading to a thiiranium ion is a common event.[2] The attractive-

(1) Such intermediates have been invoked in, for example, the solvolysis of the addition product of sulfur dichloride to 1,4-cyclohexadiene: Corey, E. J.; Block, E. *J. Org. Chem.* **1966**, *31*, 1663. Kinetic evidence for the generation of bicyclic thiiranium intermediates has also been obtained from solvolysis studies of some sulfur-containing steroids: Tsuji, T.; Komeno, K.; Itani, H.; Tanida, H. *J. Org. Chem.* **1971**, *36*, 1648. There is also evidence for a stable bicyclo[2.1.0]pentyl-1-sulfonium ion: Černý, J. V.; Poláček, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 1831. We thank a referee for this latter reference.

(2) Streitwieser, Jr., A. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962.

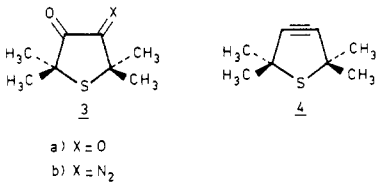
0022-3263/82/1947-4429$01.25/0

Scheme I



ness of **2** and its potential chemistry increase on realizing that thiolanes (**1**) are readily accessible by means of a variety of synthetic approaches.[3,4] Note also that the rationale of eq 1 applies either to loss of a single-bonded substituent X from a potential carbonium ion center, i.e., sp^3-bonded carbon in **1**, or from a potential carbene center, i.e., X is a double-bonded group such as nitrogen. In the latter case, the intermediate **2** will be an ylide.

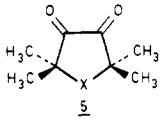
To examine the possibilities of generating examples of **2**, we chose the nonenolizable dione **3a** for investigation,



chiefly in the form of its α-diazo derivative **3b**. This entailed first the development of an efficient synthesis of **3a** and an investigation of various aspects of its chemistry. Deoxygenation of **3a** to the highly strained cyclic acetylene **4** has been communicated separately and will be reported on in detail in due course.[5]

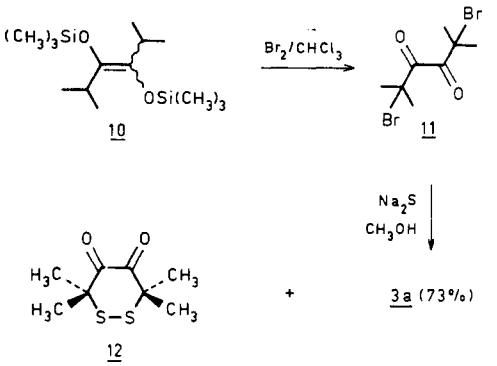
Results

A. Synthesis of Precursors. Previously described routes to the known diones **5a–d**[6-8] were not practical for

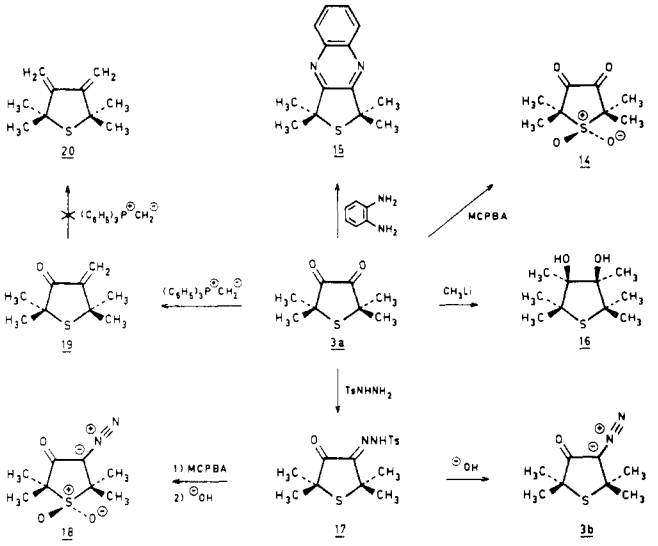


the preparation of **3a**. We therefore considered, as shown in Scheme I, an intramolecular version of a method for preparing α-thio-substituted ketones by addition of sulfenyl halides to trimethylsilyl ethers.[9] The conversion of **6** to **8** was envisaged, followed by cyclization with sulfur dichloride. In our hands, the silylation of **6** went no further than **7**. However, treatment of **7** with SCl_2 gave in about 90% yield sulfenyl chloride **9**, which on heating provided **2** in about 30% yield.

Scheme II



Scheme III



Subsequently, a more direct route was developed, as shown in Scheme II. Acyloin condensation of ethyl isobutyrate under conditions described by Rühlmann[10] afforded **10**, which was converted quantitatively to **11**. There is well-established precedent for direct substitution by nucleophiles at tertiary centers adjacent to carbonyl groups.[11,12] The mechanism of reaction of **11**, however, may well involve electron-transfer chemistry.[13]

The disulfide **12** is also formed as a side product in 5–20% yield in these reactions but is easily separated. The spectral behavior of **12** was sufficiently curious to raise our doubts about its structure. At −10 °C the ^1H NMR spectrum exhibits two singlets at δ 1.80 and 1.50. The singlets broaden on raising the temperature and coalesce at 30 °C; at 64 °C, the highest temperature used, the absorption line has become a narrow singlet. The $\Delta G^{\ddagger}$ value for this process is 15.4 kcal/mol. These spectral obser-

(3) Gronowitz, S. *Org. Cmpd. Sulphur, Selenium and Tellurium*, **1977**, *4*, 244. See also previous volumes of this series for a general coverage of synthetic methods leading to tetrahydrothiophenes, dihydrothiophenes, and thiophenes.

(4) For a 1,3-dipolar route to a number of thiolene derivatives, ee Buter, J.; Wassenaar, S.; Kellogg, R. M. *J. Org. Chem.* **1975**, *40*, 2573.

(5) (a) Bolster, J. M.; Kellogg, R. M.; *J. Am. Chem. Soc.* **1982**, *103*, 2868. (b) A portion of the present work appeared as a communication: Bolster, J., Kellogg, R. M. *J. Org. Chem.* **1980**, *45*, 4804.

(6) Rudenko, A. P.; Rodina, L. L.; Pragst, F.; Kutnevich, A. H. *Dokl. Akad. Nauk. SSSr* **1975**, 223, 883, and references cited therein.

(7) Saalfrank, R. W. *Angew. Chem.* **1974**, *86*, 162.

(8) Weiner, S. A.; Hamilton, E. J.; Monroe, B. M. *J. Am. Chem. Soc.* **1969**, *91*, 6350.

(9) Murai, S.; Kuroki, Y.; Hasegawa, I.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* **1972**, 946.

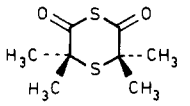
(10) Rühlman, K. *Synthesis* **1971**, 236.

(11) Mannich, C.; Budde, H. *Arch. Pharm. (Weinheim, Ger.)* **1933**, 271, 51.

(12) Föhlisch, B.; Gottstein, W. *Justus Liebig's Ann. Chem.* **1979**, 1768.

(13) (a) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647. (b) Kornblum, N.; Widmer, J. W.; Carlson, S. C. *Ibid.* **1979**, *101*, 658.

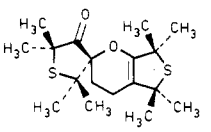
vations, as well as the molecular formula, are a priori consistent with either **12** or thioanhydride (**13**). Because of this ambiguity, an X-ray investigation was carried out. The correct structure was established to be the highly skewed disulfide (**12**).[14a-e]



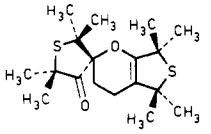
13

Some of the reactions carried out on **3a** are shown in Scheme III. Oxidation to sulfone **14** occurred on treatment with 2 equiv of *m*-chloroperbenzoic acid (MCPBA) at 0 °C in chloroform. This sulfone apparently decomposes or forms a water-soluble hydrate in the presence of the aqueous base normally used for workup to remove *m*-chlorobenzoic acid. A water-free workup procedure had to be devised to allow isolation of **14**. Quinoxaline **15** is obtained uneventfully from condensation of *o*-phenylenediamine with **3a** in acetic acid. The diol **16** was formed on addition of 2 equiv of methyllithium. A single geometrical isomer was isolated, which was assigned cis stereochemistry on the basis of the infrared (IR) spectrum, which showed a sharp OH absorption at 3600 cm^{-1} and a broader absorption at 3540 cm^{-1}. The relative intensities were unaffected on dilution in carbon tetrachloride solution.

Reaction of **3a** with methylenetriphenylphosphorane afforded in 46% yield the enone **19**. Attempts to carry out subsequent addition to obtain diene **20**, which has been prepared by another route,[15] failed. The enone **19** underwent dimerization on standing. The dimer is assigned structure **21** instead of **22** on the basis of the ^1H NMR



21

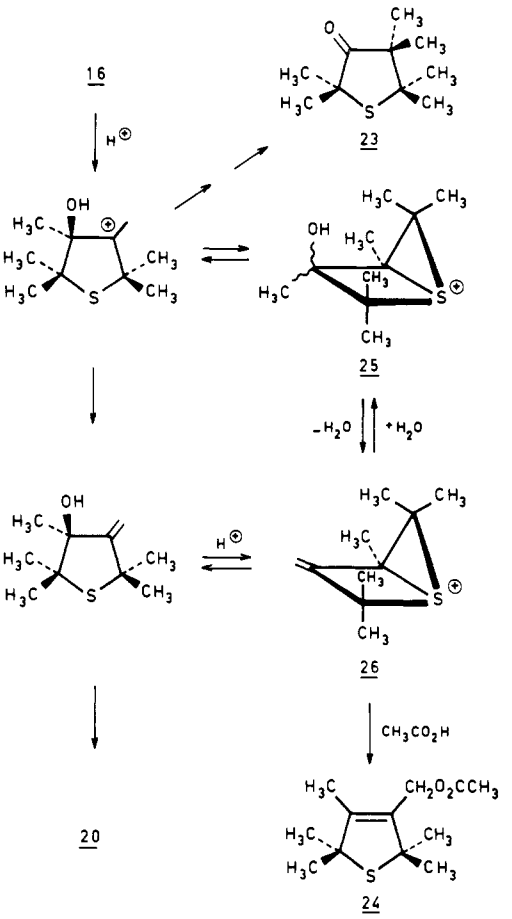


22

spectrum, in which the methylene absorptions are seen as broadened singlets at δ 2.00 and 1.29. In **22** the methylene adjacent to oxygen is expected at roughly δ 3.4. In **21** the dihydropyran ring is strongly twisted, resulting in a angle of roughly 90° between the vicinal hydrogens of the methylene groups and accounts for the virtual (and initially puzzling) absence of vicinal coupling.

The diene **20** could, however, be obtained in 43% yield by dehydration of **16** with *p*-toluenesulfonic acid in benzene. The product is accompanied by the rearranged ketone **23**. In the more nucleophilic solvent, acetic acid, the acetate **24** is formed, together with **23**. These observations are summarized schematically in Scheme IV. The bicyclic ions **25** and **26**, as specific examples of generalized **2**, are not obligate intermediates, although addition of acetate to **26** is an economical rationalization for the formation of **24**.[16] Stronger evidence for intermediates

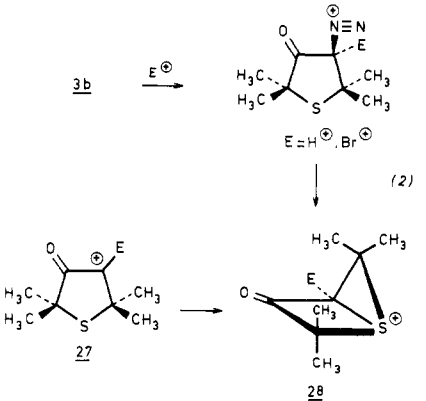
Scheme IV



structurally similar to **25** and **26** will come in the succeeding paragraphs.

The important compound **3b** was readily obtained in 78% overall yield by reaction of **3a** with *p*-toluenesulfonylhydrazine in methylene chloride, followed by treatment with base in a two-phase system.[17] The corresponding sulfone (**18**) was obtained by oxidizing **17** with MCPBA; during workup with aqueous base (compare with the behavior of **14**), spontaneous conversion to **18** occurred.

B. Electrophilic Reactions of α-Diazo Ketones 3b and 18. The reaction of **3b** with some electrophiles was first examined. The premise is encompassed in eq 2; addition of an electrophile to the diazo carbon generates a sp^3-hybridized center provided with an excellent leaving



(2)

(14) (a) Some selected bond lengths for **12** are: –S–S–, 1.99 Å; –S–C–$(CH_3)_2$, 1.83 Å; $(CH_3)_2$C–CO, 1.46 Å; OC–CO, 1.45 Å. Bond angles in the ring are S–S–C$(CH_3)_2$, 102.4°; S–C$(CH_3)_2$–CO, 100.4°; $(CH_3)_2$C–CO–CO, 122.7°. (b) Bond lengths are accurate to 0.01 Å and bond angles to 0.16°. (c) Jörgenson, F. S.; Snyder, J. P. *J. Org. Chem.* **1980**, *45*, 1015. (d) Gutterberger, H. G.; Bestmann, H. J.; Dickert, F. L.; Jörgenson, F. S.; Snyder, J. P. *J. Am. Chem. Soc.* **1981**, *103*, 159.

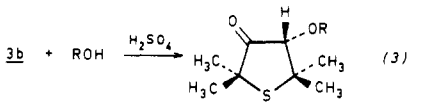
(15) Talma, A. G.; Goorhuis, J. G. M.; Kellogg, R. M. *J. Org. Chem.* **1980**, *45*, 2544.

(16) Somewhat related observations on a seven-membered ring diol containing sulfur have been made: de Groot, A.; Boerma, J. A.; Wynberg, H. *Tetrahedron Lett.* **1968**, *2365*.

(17) An excellent review of methods for the preparation and reactions of α-diazoketones is given in "The Chemistry of the Diazonium and Diazo Groups"; Patai, S., Ed.; Interscience: New York, 1978.

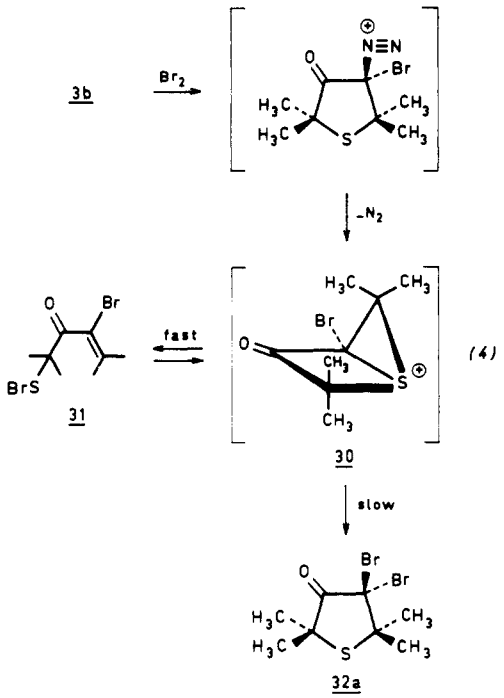
group. The bicyclic ion **28** (see also **26** and **27**) could arise either via **27** or by direct participation of sulfur during nitrogen loss.

Decomposition of **3b** in water or methanol in the presence of a catalytic amount of sulfuric acid led to **29a,b** (eq 3) in high yields. Again it is not mandatory to invoke



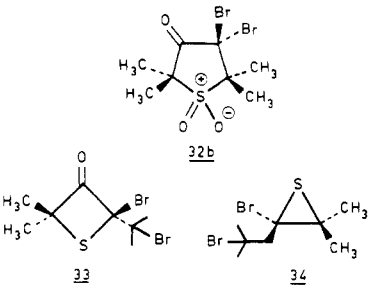
29
a) R = H
b) R = CH_3

bicyclic ions like **28** to explain the formation of these unrearranged products. This situation changes, however, for the case of an bromonium ion as electrophile. The behavior of **3b** with bromine is summarized in eq 4. At 30



31 **30** **32a**

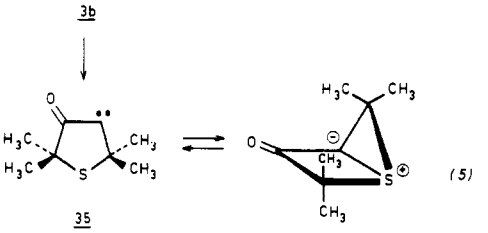
°C in chloroform solution, **32a** is formed rapidly in nearly quantitative yield. However, on following the reaction by ^{1}H NMR it is seen that an intermediate is first formed; this intermediate (**31**) is stable for several hours at −47 °C in deuteriochloroform. The assignment of structure **31** is based chiefly on consideration of various NMR data. The ^{1}H NMR spectrum [δ 1.75 (2 CH_3), 1.88 (1 CH_3), 1.98 (1 CH_3)] did not contain sufficient information for a structural assignment, but the ^{13}C NMR spectrum was more revealing in that it showed absorptions for quaternary carbons at δ 138.7, 108.4, and 51.6, in addition to readily assigned absorptions at δ 195 (quaternary carbon, carbonyl) and 24.5, 23.4, and 22.4, these absorptions coming from two identical and two nonidentical methyl groups. The low-field quaternary absorptions clearly arise from *vinylic* carbons and the higher-field quaternary carbon absorption must result from an isopropyl group to which a heteroatom substituent (SBr) is attached.[18] These data, together with the observed chemistry, are only consistent with **31** and not with the possible alternative structures **30**, **33**, or **34**,



32b **33** **34**

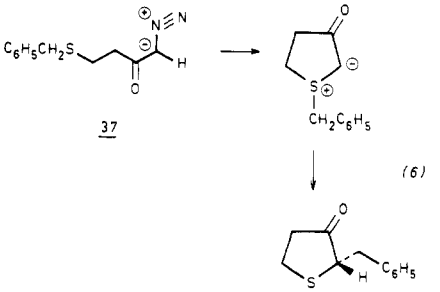
none of which contains vinylic carbons. We believe that a reasonable interpretation of the observations is that in a kinetically controlled reaction **30** is opened by attack of bromide at sulfonium sulfur to afford **31**. This reaction is reversible, and at higher temperatures the thermodynamic product (**32a**), formed by attack of bromide at the carbon adjacent to carbonyl, accumulates. This interpretation is supported by the observation that **18**, the sulfone derived from **3b**, gives no evidence of sulfur participation on reaction with bromine; **32b** is formed rapidly, and no intermediates were detected.

C. Thermally Induced Carbenoid Chemistry of α-Diazo Ketones. Considerable evidence for sulfur participation in an ylidic form of general structure **2** was obtained on examining the carbenoid chemistry of **3b**.[19] In this case, the key intermediate is **36**, which is formally an ylide formed on interaction of sulfur with the α-ketocarbene **35** (eq 5). Although the addition of carbenes to



35 **36**

sulfides to form ylides is well known,[20] there are few examples of *intra*molecular interactions of this nature. Some relevant cases can be found in, for example, the copper-catalyzed decomposition of **37** (eq 6)[21] and in the thermal



37

(18) The approximate chemical shifts for these three quaternary carbon atoms using simple increment tables are, respectively, for structure **31** δ 149 [$(CH_3)_2C$=C(Br)CO], 114.4 [COC(Br)=$C(CH_3)_2$], and 49.0 [$(CH_3)_2C$(SR)CO] using values from Hesse, M.; Meier, H.; Zeeh, B. "Spektroskopische Methoden in der Organischen Chemie"; Georg Thieme Verlag: Stuttgart, 1979.

(19) For discussions of the chemistry of α-diazoketones, see, for example, (a) Eistert, B.; Regitz, M.; Heck, G.; Schwall, H. *Methoden Org. Chem. (Houben-Weyl)*" **1968**, *4*, 473. (b) Kirmse, W. A. "Carbene Chemistry", 2nd ed.; Academic Press: New York; 1971; Vol. 1, p 425. (c) Baron, W. J.; de Camp, M. R.; Hendrick, M. E.; Jones, M., Jr.; Levin, R. H.; Sohn, M. B. "Carbenes"; Jones, M.; Moss, R. A., Eds.; Wiley: New York, 1973; Vol. 1, p 107. (d) Meier, H.; Zeller, K. P. *Angew. Chem.* **1975**, *87*, 52. (e) More O'Ferral, R. A. *Adv. Phys. Org. Chem.* **1967**, *5*, 331. (f) Smith, A. B.; Dieter, R. K.; *Tetrahedron* **1981**, *37*, 2407.

(20) See, for example, (a) Block, E. "Reactions of Organosulfur Compounds"; Academic Press, New York, 1978; pp 240–245. (b) Ando, W.; *Acc. Chem. Res.* **1977**, *10*, 179.

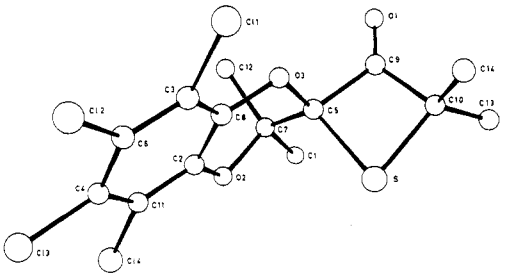
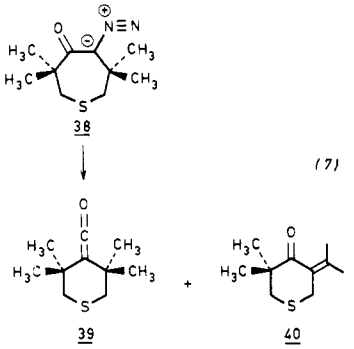


Figure 1. ORTEP projection of cycloadduct **46**.

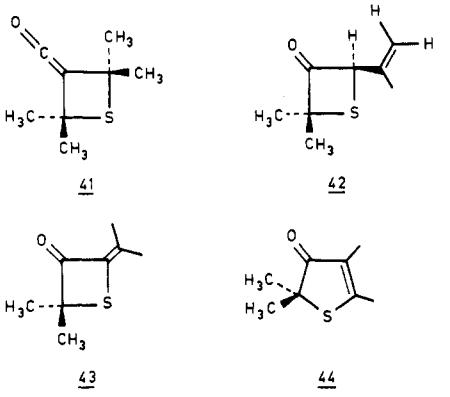
decomposition of **38**, which affords, in addition to the expected Wolff rearrangement product **39**, the rearranged structure **40** (eq 7).[22] The α-diazo ketones derived from



(7)

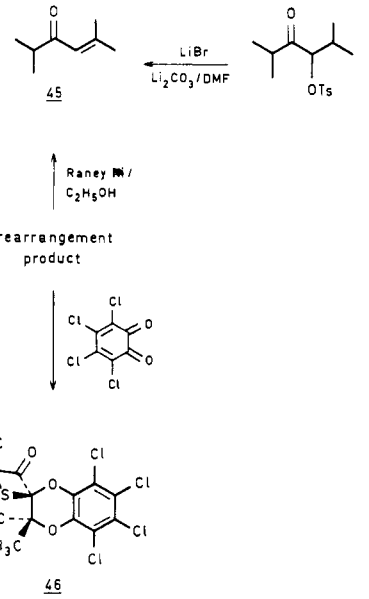
5a–c[6-8] also undergo uneventful Wolff rearrangements.

In boiling isooctane (99.3 °C), **3b** decomposed smoothly and afforded in quantitative yield a product with an elemental composition corresponding to the loss of nitrogen. Structural assignment was unexpectedly difficult, however. The spectroscopic data (Experimental Section), which, among other things, indicated the presence of two nonhydrogen bearing vinylic carbons, clearly were consistent neither with Wolff rearrangement product **41** nor **42**, which

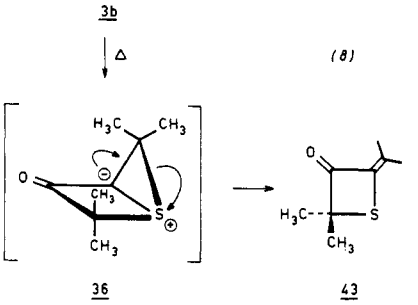


would be formed by hydrogen abstraction from methyl by an β-ketocarbene intermediate. However, either of the structures **43** or **44** could accommodate the spectral data. A clear choice between these possibilities could not be made on spectroscopic grounds. Desulfurization of the rearrangement product with Raney nickel gave in 5% yield **45**, which was prepared by independent synthesis (Scheme V). This observation is in accord with structure **43**, and this structural assignment was firmly established by determination by crystallographic methods of the structure of the cycloaddition product of **43** with tetrachloro-*o*-

Scheme V



quinone.[23] An ORTEP projection of the structure of cycloadduct **46** is given in Figure 1.[24] As shown in eq 8, the formation of **43** is readily accounted for by rearrangement of the bicyclo[2.1.0]pentyl-1-sulfonium intermediate (**36**).



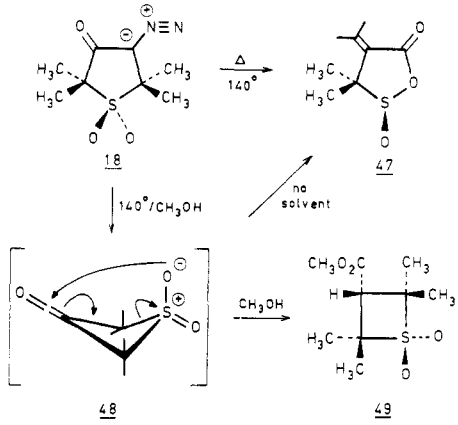
(8)

If the foregoing conclusions regarding the formation of bridged intermediates in the reactions of **3b** are correct, then a different course of reaction should be followed by the sulfone (**18**) derived by oxidation of **3b** (Scheme III). We expected that a ketene (**48**) formed by a Wolff rearrangement (Scheme VI) would be formed. The thermally induced reaction of **18** took, however, an unanticipated, indeed bizarre, course when **18** was heated without solvent to 140 °C. Nitrogen departed smoothly and there remained in 90% yield a product eventually identified as **47**. This structure was established chiefly from spectral data. The elementary formula ($C_8H_{12}O_3S$) confirmed that only nitrogen had been lost. The observation of *four* methyl singlets in the ^1H NMR spectrum ($CDCl_3$) at δ 2.23, 2.10, 1.66, and 1.45 (also seen as four separate absorptions in the ^{13}C NMR; see Experimental Section) can only be explained by the presence of a pyramidal heteroatom (sulfur) in the molecule. The strong IR absorptions at 1350 and 1150 cm^{-1} for **18** had been replaced by new bands at 1150 and 1090 cm^{-1}, readily assigned to a sulfoxide or sulfinate ester.[18] The presence of two fully substituted vinylidene

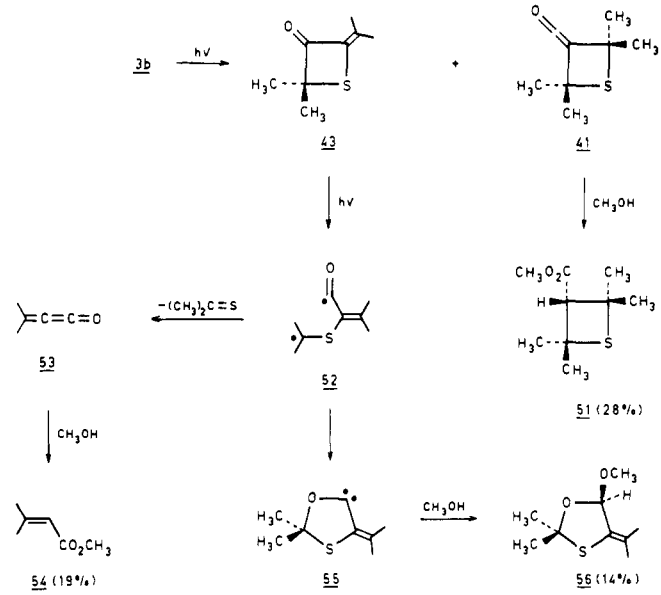
(21) Kondo, K.; Ojima, I. J. *J. Chem. Soc., Chem. Commun.* **1972**, 860.
(22) (a) de Groot, A.; Boerma, J. A.; de Valk, J.; Wynberg, H. *J. Org. Chem.* **1968**, *33*, 4025. (b) Krebs, A.; Kimling, H. *Justus Liebig's Ann. Chem.* **1974**, 2074.

(23) Horspool, W. M. *Q. Rev., Chem. Soc.* **1969**, *23*, 204.
(24) Bond lengths for the four-membered ring of **46** are: S–C_{10}, 1.87 Å; C_{10}–C_9, 1.53 Å; C_9–C_5, 1.57 Å; C_5–S, 1.87 Å, and C_5–C_7, 1.49 Å. Bond angles for the four-membered ring are: C_{10}–C–C_5, 79.3°; S–C_5–C_9, 88.4°; C_5–C_9–C_{10}, 100.4°; C_9–C_{10}–S, 89.6°. Bond distances are accurate to 0.01 Å and bond lengths to 0.16°. Note that the four-membered ring is badly distorted due to the combined effects of a carbonyl carbon, a bivalent sulfur, and a spiro carbon atom in the same ring. Data for **12** and **46** will be published separately by F. van Bolhuis and A. Vos.

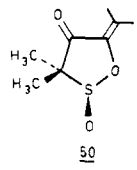
Scheme VI



Scheme VII



carbons was clear from absorptions at δ 161.5 and 120.0 in the ^{13}C NMR spectrum. In view of the molecular formula and the number of methyl groups, this means that an exocyclic isopropylidene group is attached to the molecule. Reasonable structural possibilities are either **47** or **50**. The latter structre is excluded, however, by the



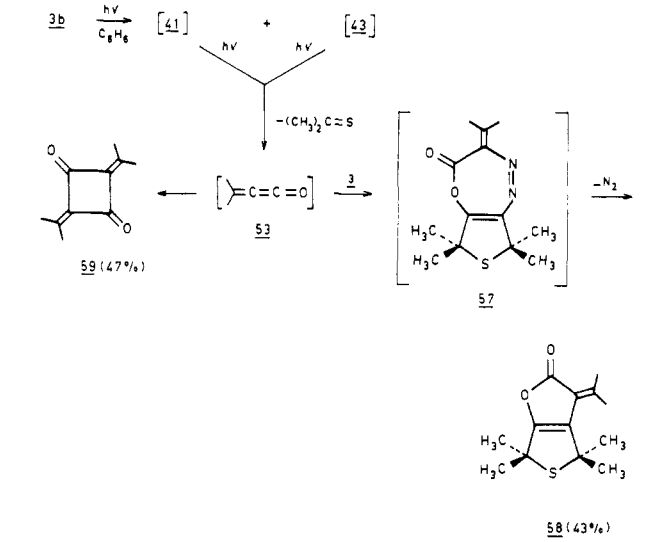
position of the ^{13}C NMR absorption for carbonyl carbon, which is found at δ 166.7 in good agreement with an *ester carbonyl* absorption rather than a *ketone* absorption (i.e., **50**) expected at 180 ppm or lower,[18,25] The presence of a γ-lactone ring system is verified further by the characteristic IR absorption for carbonyl at 1770 cm^{-1}. In contrast, an α,β-unsaturated cyclopentenone, even with an exocyclic double bond, will not absorb above ca. 1720 cm^{-1}.

The mysteries concerning the formation of **47** were resolved by carrying out the pyrolysis of **18** in methanol at 140 °C in a sealed tube; ester **49** was obtained as the product. Apparently, as shown in Scheme VI, Wolff rearrangement occurs to give ketene **48**, which in the absence of solvent undergoes an unusual sigmatropic rearrangement to **47**.

D. Photochemically Induced Carbenoid Chemistry of α-Diazo Ketones. The question of sulfur participation was also examined for the case of photolytically induced nitrogen loss from **3b**. Irradiation of **3b** with a high-pressure mercury lamp under nitrogen using a Pyrex filter led, for the case of methanol as solvent, to **51**, **54**, and **56** in the indicated yields (Scheme VII). The ketene **41** is clearly trapped by methanol to give **51**. That compounds **54** and **56** arise from secondary photolysis of **43** (probably via biradical **52** as indicated in Scheme VII)[26,27] was established by irradiation of **43** separately in methanol under the same irradiation conditions; **54** and **56** were formed rapidly in 28 and 22% yields, respectively, in addition to intractable material likely arising from thioacetone.

We thought that the Wolff rearrangement ketene (**41**) might be directly available by irradiation of **3b** in non-

Scheme VIII



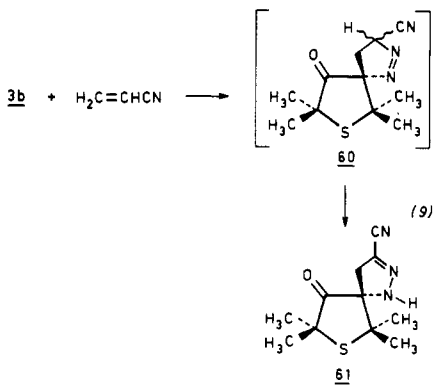
hydroxylic solvents. This turned out not to be the case, at least for high conversions of **3b**. Irradiation (benzene, nitrogen atmosphere, Pyrex filter) led to **58** as the only identified product. In Scheme VIII an interpretation, which includes the results from the direct irradiation of **41** in benzene, is given for the formation of these materials. No trace of **41** or **43** was found, but **43** was shown under these conditions to afford by loss of thioacetone, again the cumulene (**53**), which dimerized to **59**.[29] It is reasonable that **41** undergoes similar loss of thioacetone. Cycloaddition of **53** with unreacted α-diazo ketone (**3**), followed by loss of nitrogen, accounts for the formation of enol acetate (**58**).[30] This cycloaddition occurs more rapidly than dimerization to afford **59**.

On carrying out the irradiation of **3** in benzene or methanol with benzophenone as sensitizer, we obtained complicated mixtures, which were not investigated further. On the other hand, **18**, on photolysis in methanol, was cleanly converted to **49** (74% yield), derived by addition

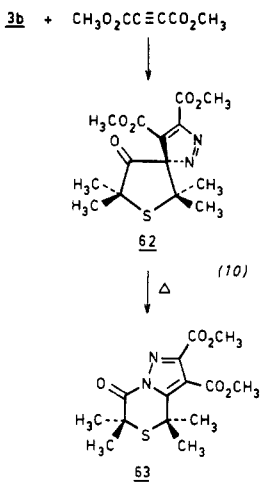
(25) Johnson, L. F.; Jankowski, W. C. "Carbon-13 NMR Spectra"; Wiley Interscience: New York, 1972.
(26) Morton, D. R.; Turro, N. J. *Adv. Photochem.* **1974**, *9*, 197.
(27) Turro, N. J.; Bauer, D.; Ramamurthy, V.; Warren, F. *Tetrahedron Lett.* **1981**, *22*, 611.
(28) Kellogg, R. M. "Photochemistry of Heterocyclic Compounds"; Buchart, O., Ed.; Wiley-Interscience: New York, 1976; pp 367–455.
(29) (a) Brown, R. F. G.; Eastwood, F. W.; Harrington, K. J. *Austr. J. Chem.* **1974**, *27*, 2373; (b) Arens, J. F. *Adv. Org. Chem.* **1960**, *2*, 197.
(30) Meier, H.; Zeller, K. P. *Angew. Chem.* **1975**, *87*, 52.

of methanol to ketene (48). This observation also provides indirect support for the postulation of 48 as an intermediate in the thermally induced rearrangement of 18, as shown in Scheme VI.

E. Cycloaddition of a α-Diazo Ketone. As a final point, the cycloaddition chemistry of **3b** was investigated briefly.[31] In pure acrylonitrile, **3b** underwent cycloaddition over a period of 3 weeks to give **62**, formed most likely from **61**, which undergoes a prototropic shift (eq 9). Cyclo-



addition with dimethyl acetylenedicarboxylate, again over a period of 3 weeks, gave in 93% yield **63**, the product of a 1,5 acyl shift in initial cycloadduct **62** (eq 10).



Conclusions

We believe that a plausible case has been established for the existence of 1-thiabicyclo[2.1.0]pentyl intermediates, either as sulfonium ions or ylides, the latter derived from sulfur participation with a carbene center. The ylides are formed most cleanly on thermally rather than photochemically induced decomposition of **3b**, which suggests that sulfur participates in the departure of nitrogen and that an α-ketocarbene intermediate may be bypassed completely. Major, synthetically useful, structural reorganizations are triggered from these ylidic structures. We note, for example, that Ando[32] has described recently the conversion of **43** to remarkably stable 2,3-di-2-propenylthiirane, this being formed most likely from a 1-thiabicyclo[1.1.0]butane ylidic intermediate.

Experimental Section

Melting points were recorded on a Mettler automatic FP-2 apparatus. UV spectra were taken with a Zeiss MPQII instrument, and infrared spectra were taken with a Perkin-Elmer 257 spectrometer. ^1H NMR spectrum (Me_4Si internal standard) were recorded on 60-MHZ Varian or JEOL instruments or on a Nicolet Model 1180 200-MHz unit; ^{13}C NMR spectra were taken with a Varian XL-100 instrument. Mass spectra were measured on a MS-9 instrument. Elemental analyses were carried out in the analytical division of these laboratories. Compounds cited without reference were either in stock or were prepared by standard laboratory techniques.

Synthesis of 2,5-Dimethyl-3-[(trimethylsilyl)oxy]hex-2-en-4-one (7). A mixture of chlorotrimethylsilane (8 g, 74 mmol), triethylamine (15 g, 148.5 mmol), diisopropyl diketone[33] (5 g, 35.2 mmol), and 25 mL of dry dimethylformamide was refluxed for 48 h. A yellow solid (according to House,[34] triethylamine hydrochloride) precipitated during the reaction. After cooling to room temperature, the reaction mixture was diluted with 100 mL of *n*-pentane and washed three times with cold aqueous $NaHCO_3$. The organic layer was subsequently rapidly washed with cold aqueous HCl (1.5 N) and cold aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated in vacuo to leave 5.5 g (25.7 mmol) of crude **47**. After distillation [bp 82–84 °C (15 mmHg)] pure **7** (4.1 g, 19.1 mmol) was isolated in 65% yield: ^1H NMR ($CDCl_3$) δ 0.18 (s 3 CH_3), 1.05 (d, J_{C-H} = 7 Hz, 2 CH_3), 1.75 (s, 1 CH_3), 1.85 (s, 1 CH_3), 3.10 (hept, J_{C-H} = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 207 (s, C=O), 142.4 (s, vinyl C), 124.4 (s, vinyl C), 35.9 (d, J_{C-H} = 132 Hz, tert-C), 19.3 (q, J_{C-H} = 130 Hz, 1 CH_3), 18.5 (q, J_{C-H} = 130 Hz, 1 CH_3), 17.5 (q, J_{C-H} = 130 Hz, 2 CH_3), 0.2 (q, J_{C-H} = 120 Hz, 3 CH_3). Exact mass calcd for $C_{11}H_{22}OSi$, *m/e* 214.137; found, 214.139.

Synthesis of 2,5-Dibromo-2,5-dimethylhexane-3,4-dione (11).[33c] A solution of 1,2-bis[(trimethylsilyl)oxy]-1,2-diisopropylethylene[10] (14.4 g, 50 mmol) and bromine (40 g, 0.25 mmol) in 50 mL of chloroform was stirred for 2 h under gentle warming. Quantitive formation of dibromide **11** had occurred as indicated by ^1H NMR spectroscopy. The HBr gas that evolved during the reaction was trapped by aqueous base. On evaporation of the solvent, 15 g (50 mmol, 100% yield) of NMR-pure dibromide **11** was obtained: ^1H NMR ($CDCl_3$) δ 2.00; ^{13}C NMR ($CDCl_3$) δ 197.4 (s, C=O), 60.2 (s, quaternary C), 30.1 (q, J_{C-H} = 132 Hz, CH_3); IR (neat) 1700 (broad) cm^{-1}.

Synthesis of 2,2,5,5-Tetramethylthiolane-3,4-dione (3a). Procedure I. A solution of **7** (500 mg, 2.34 mmol) and sulfur dichloride (275 mg, 2.67 mmol) in 25 mL of a mixture of 1,1,2,2-tetrachloroethane and carbon tetrachloride (4:1) was stirred at 40 °C for 15 min. The β-ketosulfenyl chloride **9** was formed in about 90% yield as indicated by the ^1H NMR spectrum in $CDCl_3$ [δ 1.60 (2 CH_3), 1.17 (1 CH_3), 1.02 (1 CH_3)]. The tertiary hydrogen was hidden by solvent absorptions in the crude reaction mixture. The reaction mixture was subsequently refluxed for 1.5 h, after which time diketone **3a** was present in about 50% yield as determined by ^1H NMR spectroscopy. After prolonged refluxing of the mixture, the yield of **3a** decreased. The reaction mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. Distillation [90 °C (16 mmHg)] of the dark-brown colored residue in a Kugelrohr apparatus afforded 125 mg (0.73 mmol, 31% yield) of NMR-pure diketone **3a** (for spectral and analytical data see following preparation).

Procedure II. To 52.8 g (0.176 mol) of dibromide **11** dissolved in 500 mL of methanol was added, with vigorous stirring during 2 h, a solution of Na_2S (22.9 g, 0.176 mol) in 400 mL of methanol. After the Na_2S had been added, the methanol was evaporated in vacuo. When almost all the solvent had been removed, the yellow-colored residue turned orange because of the decomposition of the hemiacetal of **3a** to the orange-red colored diketone (**3a**).[35]

(31) Some pertinent references on cycloaddition chemistry of α-diazoketones related to this work are: (a) Huisgen, R. *J. Org. Chem.* **1976**, *41*, 403. (b) Reference 19a, p 804. (c) Martin, M.; Regitz, M. *Justus Liebig's Ann. Chem.* **1974**, 1702. (d) Franck-Neumann, M.; Buchecker, C. *Tetrahedron Lett.* **1972**, 937. (e) Elzinga, J.; Hogeveen, H.; Schudde, E. P. *J. Org. Chem.* **1980**, *45*, 4337.

(32) Ando, W.; Haniu, Y.; Takata, T. *Tetrahedron Lett.* **1981**, *22*, 4815.

(33) (a) Snell, J. M.; McElvain, S. M. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 114. (b) Rigby, W. *J. Chem. Soc.* **1951**, 793; (c) Strating, J.; Reiffers, S.; Wynberg, H. *Synthesis* **1971**, 211.

(34) House, H.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

(35) Similar observations have been reported for the corresponding oxygen derivative by Sandris, C.; Ourisson, G. *Bull. Soc. Chim. Fr.* **1958**, 345; **1958**, 338.

Subsequently, 200 mL of ether was added, and the NaBr was filtered off. After evaporating the solvent, 28.6 g of crude reaction product remained. Distillation in vacuo [101–105 °C (22 mmHg)] afforded 22.2 g (129 mmol, 73% yield) of pure diketone **3a**. At the end of the distillation, 2.4 g (11.8 mmol, 7% yield) of disulfide **12** crystallized in the condenser. An analytically pure sample of **3a** was obtained by means of preparative GLC, using a glass column (6 ft × 0.25 in. SE 30, column temperature 110 °C): ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 4 CH_3); ^{13}C NMR ($CDCl_3$) δ 197.8 (s, C=O), 46.1 (s, quaternary C), 27.5 (q, J_{C-H} = 132 Hz, CH_3); IR (neat) 1732 (C=O) cm^{-1}; UV (isooctane) λ_{max} 321 nm (ϵ 207), 477 (49); UV (CH_2Cl_2) λ_{max} 329 nm (ϵ 170), 475 (45). Mass spectrum, m/e (parent) 172; calcd for $C_8H_{12}O_2S$, 172. Anal. Calcd. for $C_8H_{12}O_2S$: C, 55.79; H, 7.02; S, 18.61. Found: C, 55.57; H, 7.05; S, 18.57.

Analytically pure disulfide **12** was obtained after recrystallization from petroleum ether (40–60 °C): mp 108–109 °C; ^{1}H NMR ($C_2H_2Cl_4$ at −11 °C) δ 1.80 (s, 2 CH_3), 1.50 (s, 2, CH_3); ^{1}H NMR ($C_2H_2Cl_4$ at 60 °C) δ 1.65 (s, 4, CH_3); T_{coal} 30 °C; $\Delta G^{\ddagger}$ = 15.4 kcal/mol; ^{13}C NMR ($C_2H_2Cl_4$ at 60 °C) δ 200.1 (s, C=O), 64.5 (s, C=O), 64.5 (s, quaternary C), 21.8 (q, J_{C-H} = 132 Hz, 4 CH_3); IR (KBr); 1685 (broad, C=O) cm^{-1}. Anal. Calcd. for $C_8H_{12}O_2S_2$: C, 47.02; H, 5.92; S, 31.39. Found: C, 46.82; H, 5.83; S, 31.39.

Synthesis of 2,3-(1,1,3,3-Tetramethyl-2-thiatrimethylene)quinoxaline (15). A solution of **3a** (344 mg, 2 mmol) and *o*-phenylenediamine (540 mg, 5 mmol) in 5 mL of acetic acid was refluxed for 4 h. After the solution was cooled to room temperature, 100 mL of methylene chloride was added, and the resulting reaction mixture was washed with water until neutral and dried over $CaCl_2$. Evaporation the solvent in vacuo, followed by recrystallization from ethanol, afforded 360 mg (1.47 mmol, 74% yield) of pure **15**: mp 110–112 °C; ^{1}H NMR ($CDCl_3$) δ 1.82 (s, 4 CH_3), 7.68–8.18 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 161.0 (s), 141.1 (s), 129.0 (d, J_{C-H} = 157 Hz), 51.0 (s), 32.3 (q, J_{C-H} = 130 Hz). Anal. Calcd for $C_{14}H_{26}N_2S$: C, 68.81; H, 6.60; N, 11.46; S, 13.12. Found: C, 68.97; H, 6.69; N, 11.42; S, 13.12.

Synthesis of 2,2,5,5-Tetramethylthiolane-3,4-dione 1,1-Dioxide (14). To a solution of **3a** (450 mg, 2.61 mmol) in 20 mL of dichloromethane at 0 °C was added 2 equiv of *m*-chloroperbenzoic acid (1.06 g, 5.32 mmol). After the solution was stirred for 24 h, the precipitated *m*-chlorobenzoic acid was filtered off and the filtrate was concentrated in vacuo to about 8 mL. The remaining solution was cooled to 0 °C, and the obtained precipitate of *m*-chlorobenzoic acid was again filtered off. Evaporation in vacuo of the mother liquid afforded 340 mg (1.66 mmol, 63% yield) of almost (96%) pure **14**: mp 97–102 °C; ^{1}H NMR ($CDCl_3$) δ 1.62; ^{13}C NMR ($CDCl_3$) δ 193.4 (s, C=O), 65.1 (s, quaternary C), 20.0 (q, J_{C-H} = 132 Hz, CH_3); IR (KBr) 1760 (C=O), 1320 (SO_2), 1120 (SO_2) cm^{-1}. Exact mass calcd for $C_8H_{12}O_4S$, m/e 204.046; found, m/e 204.044. Due to the hygroscopic nature of **14**, a completely pure sample was not obtained.

Synthesis of 2,2,5,5-Tetramethyl-3-methylenethiolane-4-one (19). To a slurry of 1.25 g (3.5 mmol) of methyltriphenylphosphonium bromide in 75 mL of dry THF was added 2.2 mL (3.52 mmol) of a 15% *n*-BuLi solution in *n*-hexane under a nitrogen atmosphere at room temperature. After the solution was cooled to 0 °C, approximately 1 equiv of diketone **3a** (600 mg, 3.49 mmol) in 3 mL of THF was introduced, and the resulting reaction mixture was stirred for 20 min. Subsequently, the solvent was removed in vacuo, and the residue was extracted with *n*-hexane (3 times). After evaoration of the pentane in vacuo, there was obtained 276 mg (1.62 mmol, 46% yield) of NMR-pure enone **19**: ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 2 CH_3), 1.58 (s, 2 CH_3), 5.35 (s, 2 H), 6.03 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ 204.0 (s, C=O), 150.9 (s, vinyl C), 119.1 (t, J_{C-H} = 156 Hz, vinyl C), 53.0 (s, quaternary C), 45.1 (s, quaternary C), 33.1 (q, J_{C-H} = 132 Hz, CH_3), 28.5 (q, J_{C-H} = 132 Hz, CH_3). This material on standing was converted to dimer (**21**): ^{1}H NMR ($CDCl_3$) δ 2.00 (br s, 2 H), 1.58 (s, 1 CH_3), 1.53 (s, 2 CH_3), 1.47 (s, 2 CH_3), 1.42 (s, 1 CH_3), 1.40 (s, 1 CH_3), 1.35 (s, 1 CH_3), 1.29 (br s, 2 H). Exact mass calcd for $C_{18}H_{28}O_2S_2$, 340.151; found, 340.153. Due to a shortage of material, no attempts at further purification were carried out.

Attempted Conversion of 3a to 2,2,5,5-Tetramethyl-3,4-dimethylenethiolane (20). The same procedure as for the synthesis of enone **19** was followed (see above), except for the amount of **3a** added (300 mg, 1.75 mmol). A complex reaction product not containing any appreciable amount of **20** was obtained.

Synthesis of 2,2,3,4,5,5-Hexamethyl-*cis*-3,4-dihydroxythiolane (16). To a solution of **3a** (2.3 g, 13.37 mmol) in 50 mL of dry ether was introduced at −60 °C 17.5 mL (28 mmol) of a 5% solution of MeLi in *n*-hexane. After the solution was warmed to room temperature, 100 mL of water was added, and the ether layer was separated and dried over $MgSO_4$. After the solvent was evaporated in vacuo, there was obtained 2.4 g (11.7 mmol) of almost NMR-pure diol. After recrystallization from petroleum ether (40–60 °C), 1.8 g (8.82 mmol, 66% yield) of analytically pure diol **16** remained: mp 86–88 °C; ^{1}H NMR ($CDCl_3$) δ 1.26 (s, 2 CH_3), 1.36 (s, 2 CH_3), 1.46 (s, 2 CH_3), 2.77 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 85.7 (s), 53.6 (s), 29.6 (q, J_{C-H} = 123 Hz), 29.0 (q, J_{C-H} = 123 Hz), 21.1 (q, J_{C-H} = 123 Hz); IR (CCl_4) 3620 (sharp), 3550 (broad) cm^{-1}; mass spectrum (parent), m/e 204; calcd, 204. Anal. Calcd for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87; S, 15.69. Found: C, 58.50; H, 9.64; S, 15.57.

Synthesis of Tosylhydrazone (17). A solution of **3a** (20 g, 0.116 mol) and tosylhydrazine (23.5 g, 0.126 mol) in 1.25 L of methylene chloride was stirred for 4 h at room temperature. After evaporation of the solvent in vacuo, followed by recrystallization from methanol, there was obtained 31 g (0.112 mol, 97% yield) of tosylhydrazone **17**: mp 113–120 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 2 CH_3), 1.50 (s, 2 CH_3), 2.42 (s, CH_3), 7.29 and 7.79 (4 H, J = 7.8 Hz, AB system); ^{13}C NMR ($CDCl_3$) δ 201.3 (s), 146.1 (s), 144.4 (s), 134.9 (s), 129.4 (d, J_{C-H} = 158 Hz), 127.4 (d, J_{C-H} = 158 Hz), 50.2 (s), 44.6 (s), 31.8 (q, J_{C-H} = 132 Hz), 28.3 (q, J_{C-H} = 132 Hz), 21.3 (q, J_{C-H} = 128 Hz); IR (KBr) 3170 (NH), 1725 (C=O), 1680 (C=N), 1350 (SO_2), 1160 (SO_2) cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2OS$: C, 52.91; H, 5.92; N, 8.23; S, 18.84. Found: C, 52.79; H, 5.93; N, 8.29; S, 18.80.

Synthesis of 3-Diazo-2,2,5,5-tetramethylthiolan-4-one (3b). To a solution of 1 g of NaOH in 150 mL of water was added **17** (6 g, 17.7 mmol), followed by 400 mL of *n*-hexane. The resulting two-phase system was stirred until the water layer was almost colorless. The organic layer was separated and washed twice with water, dried over $MgSO_4$, and evaporated in vacuo to yield 2.94 g (16 mmol, 90% yield) of pure diazo ketone **3b**: mp 37–38 °C; ^{1}H NMR ($CDCl_3$) δ 1.65 (s, 2 CH_3), 1.50 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 197.4 (s), 69.3 (s), 56.7 (s), 41.9 (s), 31.3 (q, J_{C-H} = 132 Hz), 28.9 (q, J_{C-H} = 132 Hz); IR 1645 (C=O), 2030 (C=N_2) cm^{-1}; mass spectrum, m/e (100 °C) 156, m/e (40 °C) 184; UV (isooctane) λ_{max} 257 nm (ϵ 11 300). Anal. Calcd for $C_8H_{12}N_2OS$: C, 52.15; H, 6.56; S, 17.40; N, 15.20. Found: C, 52.26; H, 6.59; N, 17.24; S, 15.25.

Synthesis of 3-Diazo-2,2,5,5-tetramethylthiolan-4-one 1,1-Dioxide (18). To a solution of **17** (3.4 g, 12.3 mmol) in 100 mL of methylene chloride at 0 °C was added 2 equiv of metachloroperbenzoic acid (85%, 405 mg). The reaction mixture was stirred at 0 °C for 24 h. After the solution was warmed to room temperature, the solvent was extracted with aqueous base (during which time the tosylhydrazone sulfone was transformed to the diazo ketone), washed with water, and dried over $CaCl_2$. After evaporation of the solvent in vacuo there remained 1.65 g (7.6 mmol, 62% yield) of NMR-pure α-diazo ketone **18**: mp 82–84 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (2 CH_3), 1.70 (2 CH_3); ^{13}C NMR ($CDCl_3$) δ 188.0 (s), 69.0 (s, C=N_2), 64.5 (s), 58.5 (s), 22.6 (q, J_{C-H} = 132 Hz), 20.0 (q, J_{C-H} = 132 Hz); IR (KBr) 2080 (C=N_2), 1660 (C=O), 1350 (SO_2), 1150 (SO_2) cm^{-1}; UV (isooctane) λ_{max} 215 nm (ϵ 3070), 267 (8700). Anal. Calcd for $C_8H_{12}N_2O_3S$: C, 44.44; H, 5.59; N, 12.96; S, 14.82. Found: C, 44.07; H, 5.58; N, 12.86; S, 14.55.

Synthesis of 4,4-Dimethyl-2-(2-propylidene)-3-thietanone (43). A solution of **3b** (368 mg, 2 mmol) in 25 mL of isooctane was refluxed for 15 min. After the solvent was evaporated in vacuo there was obtained 312 mg (20 mmol, 100% yield) of pure thietanone (**43**): ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 1 CH_3), 1.73 (s, 1 CH_3), 1.64 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 195.0 (s), 137.6 (s), 137.0 (s), 70.9 (s), 25.5 (q, J_{C-H} = 132 Hz), 22.1 (q, J_{C-H} = 126 Hz), 21.5 (q, J_{C-H} = 126 Hz); IR (neat) 1740 (C=O), 1642 (C=C) cm^{-1}; UV (*n*-hexane) λ_{max} 331 nm (ϵ 6560), 320 (5960), 221 (4200); mass spectrum (parent), m/e 156. Anal. Calcd for $C_8H_{12}OS$: C, 61.49; H, 7.74; S, 20.51. Found: C, 61.58; H, 7.72; S, 20.40.

Desulfurization of 43 with Raney Nickel. To a slurry of 2 g of Raney nickel (W5) in 25 mL of absolute ethanol was added

43 (200 mg, 1.28 mmol). The resulting reaction mixture was stirred and refluxed for 4 h. After the mixture was cooled to room temperature and filtered, 100 mL of *n*-pentane and water were added, and the organic layer was separated, washed with water, and dried over $MgSO_4$. After the solvent was evaporated in vacuo, there was obtained a brown-colored residue containing a small amount of **45** (5%, identified by its spectral characteristics, see below).

Synthesis of 2,5-Dimethyl-2-hexen-4-one (45). To a solution of 2,5-dimethyl-4-hydroxy-3-hexanone (2.5 g, 17.3 mmol) in 10 mL of dry pyridine was added 1 equiv (3.5 g) of tosyl chloride. The resulting reaction mixture was stirred overnight at room temperature. Subsequently, 250 mL of water and 150 mL of ether were added. The organic layer was separated and washed with dilute acid until neutral. This was dried over $CaCl_2$ and evaporated in vacuo to afford 2.9 g of crude product. Recrystallization from methanol afforded 2.2 g (7.3 mmol, 42% yield) of pure tosylate: ^1H NMR (CCl_4) δ 7.65 and 7.24 (AB quartet, J_{AB} = 8 Hz, 4 H), 4.58 (d, J_H = 5 Hz), 2.87 (h, J_H = 6 Hz, 1 H), 2.42 (s, 1 CH_3), 2.08 (m, 1 H), 1.00 (d, J = 6 Hz, 2 CH), 0.86 (d, J = 6 Hz, 1 CH_3), 0.77 (d, J = 6 Hz, 1 CH_3).

A solution of this tosylate (447 mg, 1.5 mmol), lithium bromide (320 mg, 3.0 mmol), and lithium carbonate (425 mg, 5.7 mmol) in 20 mL of dry dimethylformamide was refluxed for 1 h. After cooling to room temperature, the reaction mixture was poured into water, and 50 mL of *n*-pentane was added. The organic layer was separated, washed with water, dried over $CaCl_2$, and evaporated in vacuo to yield 95 mg (7.5 mmol, >100% yield) of NMR pure **45**: ^1H NMR ($CDCl_3$) δ 1.05 (d, J = 6 Hz, 2 CH_3), 1.88 (br s, 1 CH_3), 2.10 (br s, 1 CH_3), 2.50 (h, J = 6 Hz, 1 H), 6.05 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 204.3 (s), 155.1 (s), 122.3 (d, J_{C-H} = 156 Hz), 41.2 (d, J_{C-H} = 126 Hz), 27.4 (q, J_{C-H} = 128 Hz), 20.3 (q, J_{C-H} = 128 Hz), 18.0 (q, J_{C-H} = 130 Hz); IR 1690 (C=O), 1615 (C=C) cm^{-1}; mass spectrum (parent), m/e 126. This material was identical in all respect with the desulfurization product of **43**.

Synthesis of 3,3,4′,4′-Tetramethyl-3′-oxo-5,6,7,8-tetrachlorospiro[benzodioxin-2,2′-thietane] (46). A solution of thietanone **43** (181 mg, 1.16 mmol) and tetrachloro-*o*-quinone (285 mg, 1.16 mmol) in 5 mL of methylene chloride was stirred at room temperature for 1 h. After the solvent was evaporated in vacuo, a red-colored solid (355 mg) was obtained. After recrystallization from ether there was obtained 240 mg (0.6 mmol, 51% yield) of **45** as a white solid: mp 118–120 °C; ^1H NMR ($CDCl_3$) δ 1.92 (s, 1 CH_3), 1.65 (s, 1 CH_3), 1.38 (s, 1 CH_3), 1.30 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$) δ 195.0 (s, C=O), 138.8 (s, arom C), 136.4 (s, arom C), 126.2 (s, arom C), 124.4 (s, arom C), 121.0 (s, arom C), 120.6 and 106.3 (s, quat C), 77.2 (s, quat C), 73.4 (s, quat C), 28.4 (q, J_{C-H} = 132 Hz, CH_3), 25.1 (q, J_{C-H} = 132 Hz, CH_3), 23.9 (q, J_{C-H} = 132 Hz, CH_3), 22.7 (q, J_{C-H} = 132 Hz, CH_3). Anal. Calcd for $C_{14}H_{20}O_3Cl_4S$: C, 41.82; H, 3.01; Cl, 35.26; S, 7.97. Found: C, 41.80; H, 2.97; Cl, 35.26; S, 7.94.

Irradiation of α-Diazo Ketone (3b) in Methanol. A deoxygenated solution of **3b** in methanol (150 mL) was irradiated (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 12 h. Subsequently, 250 mL of *n*-pentane and 300 mL of water were added. The organic layer was separated and dried over $CaCl_2$. Removal of the solvent in vacuo at room temperature gave 859 mg of a yellow residue containing **51** (27.8%) **54** (19%), and **56** (14%). The yields were determined by ^1H NMR spectroscopy with dimethyl sulfone as internal standard. Separation of the reaction products was performed by preparative GLC using a glass column (10% SE 30 on Carbowax, 100 °C). **54**: ^1H NMR ($CDCl_3$) δ 1.87 (br s, 1 CH_3), 2.15 (br s, 1 CH_3), 3.60 (s, 1 CH_3), 5.57 (br s, 1 H); **56**: ^1H NMR ($CDCl_3$) δ 1.56 (s, 1 CH_3), 1.60 (s, 1.68 (br s, 2 CH_3), 3.35 (s, 1 CH_3), 5.48 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 132.1 (s), 123.0 (s), 106.6 (d, J_{C-H} = 170 Hz), 94.0 (s), 54.5 (q, J_{C-H} = 140 Hz), 33.2 (q, J_{C-H} = 130 Hz), 31.3 (q, J_{C-H} = 130 Hz), 24.2 (q, J_{C-H} = 130 Hz), 20.7 (q, J_{C-H} = 130 Hz). Exact mass calcd for $C_9H_{16}O_2S$, 188.087; found, 188.086. **51**: ^1H NMR ($CDCl_3$) δ 1.15 (s, 2 CH_3), 1.45 (s, 2 CH_3), 2.95 (s, 1 CH_3), 3.28 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 169.7 (s), 61.7 (d, J_{C-H} = 130 Hz), 50.4 (q, J_{C-H} = 145 Hz), 42.7 (s), 34.7 (q, J_{C-H} = 132 Hz), 28.6 (q, J_{C-H} = 132 Hz); IR (neat) 1740 (C=O) cm^{-1}. Exact mass calcd for $C_9H_{16}O_2S$, 188.087; found, 188.087.

Irradiation of Thietanone (43) in Methanol. A deoxygenated solution of **43** (721 mg, 4.62 mmol) in 120 mL of methanol was irradiated (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 3 h. Subsequently, 200 mL of *n*-pentane and 300 mL of water were added. The organic layer was separated and dried over $CaCl_2$. Removal of the solvent in vacuo at room temperature afforded 243 mg of a yellow-colored residue. On the basis of ^1H NMR (dimethyl sulfone as internal standard), 28% **54** and 22% **56** had been formed.

Irradiation of α-Diazo Ketone (3b) in Benzene. A deoxygenated solution of **3b** (340 mg, 1.85 mmol) in benzene was irradiated (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 4 h. After removal of the solvent in vacuo there was obtained 246 mg of crude reaction product. On basis of ^1H NMR spectroscopy (dimethyl sulfone as internal standard), **58** had been formed in 43% yield. An analytically pure sample of 6,6,8,8-tetramethyl-2-oxo-7-thia-4-(2-propenyl)bicyclo[3.3.0]oct-1(5)-en-3-one (**58**) was obtained by preparative HPLC (Alox T, 3% methylene chloride in *n*-hexane): mp 101–103 °C; ^1H NMR ($CDCl_3$) δ 1.70 (s, 2 CH_3), 1.80 (s, 2 CH_3), 2.08 (s, 1 CH_3), 2.22 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$): δ 163.0 (s), 146.6 (s), 139.5 (s), 129.2 (s), 125.8 (s), 45.5 (s), 45.0 (s), 33.7 (q, J_{C-H} = 132 Hz, 2 CH_3), 31.5 (q, J_{C-H} = 132 Hz, 2 CH_3), 22.5 (q, J_{C-H} = 128 Hz, 1 CH_3), 21.5 (q, J_{C-H} = 128 Jz, 1 CH_3); IR (Nujol) 1855 (C=O), 1705 (OC-H=CH_2), 1675 (C=C) cm^{-1}; mass spectrum (parent), m/e 238. Anal. Calcd for $C_{13}H_{18}O_2S$: C, 65.50; H, 7.61; S, 13.45. Found: C, 65.33; H, 7.59; S, 13.38.

Irradiation of Thietanone (43) in Benzene. A deoxygenated solution of **43** (178 mg, 1.14 mmol) in benzene was irradiated (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 70 min. After evaporation of the solvent in vacuo there was obtained 94 mg of an orange-colored semisolid. The ^1H NMR spectrum indicated the formation of 2,3-di-2-propenyl-1,3-cyclobutadienone (**59**; 47% yield, dimethyl sulfone used as internal standard). The dione **5a** is a known compound:[29] ^1H NMR ($CDCl_3$) δ 2.18 (s); mass spectrum (parent), m/e 164 (calcd for $C_{10}H_{12}O_2$ 164). In some experiments a small amount of material was obtained, which is tentatively believed to be 5-methyl-2-(2-propenyl)thiolan-4-en-3-one: ^1H NMR (C_6D_6) δ 1.42 (br s, 1 CH_3), 1.68 (br s, 1 CH_3), 1.97 (br s, 1 CH_3), 5.55 (br s, 1 H); mass spectrum (parent), m/e 154 (calcd for $C_8H_{10}OS$ 154).

Sensitized Irradiation of 3b. A deoxygenated solution of **3b** (55 mg, 0.30 mmol) and benzophenone (52 mg, 0.29 mmol) in 4 mL of benzene was irradiated for 4 h. The solvent was removed in vacuo and there remained a complex reaction mixture in which no products could be identified. A deoxygenated solution of α-diazo ketone **42** (100 mg, 0.54 mmol) and benzophenone (109 mg, 0.6 mmol) in 7 mL of methanol was irradiated for 5 h. The solvent was removed in vacuo and again a complex unidentifiable reaction mixture was obtained.

$AgClO_4$-Catalyzed Decomposition of α-Diazo Ketone 3b in Methanol, Vinyl Acetate, and Acrylonitrile. To a stirred suspension of $AgClO_4$ (42 mg, 0.2 mmol) and Na_2CO_3 (212 mg, 2 mmol) in 5 mL of methanol was added **3b** (200 mg, 1.09 mmol). The reaction mixture was stirred overnight. After 50 mL of *n*-pentane was added, the resulting suspension was filtered, and the solvent was evaporated in vacuo. There was obtained 160 mg (0.98 mmol, 98% yield) of NMR-pure thietanone **43**. The same result was obtained when vinyl acetate or acrylonitrile was used as solvent.

$CuSO_4$-Catalyzed Decomposition of 3b in Methanol. To a solution of $CuSO_4 \cdot 5H_2O$ (125 mg, 0.05 mmol) in 5 mL of methanol was added **3b** (80 mg, 0.43 mmol). After the solution was stirred for a few minutes at room temperature, a white precipitate was obtained. Stirring of the suspension was continued for 4 days at room temperature. Subsequently, 100 mL of ether and 100 mL of water was added. The organic layer was separated, dried over $CaCl_2$, and evaporated in vacuo to afford 78 mg (0.45 mmol, 100% yield) of NMR-pure α-methoxy ketone **29b**. (For spectral data, see "Acid-Catalyzed Decomposition of **3b** in Methanol".)

$CuSO_4$-Catalyzed Decomposition of 3b in Vinyl Acetate. To a slurry of $CuSO_4 \cdot 5H_2O$ (125 mg, 0.5 mmol) in 5 mL of vinyl acetate was added **3b** (80 mg, 0.43 mmol). After the solution was stirred for 1 night at room temperature, a white precipitate had formed. Stirring was continued for 1 week at room temperature. Ether (100 mL) was added, and the resulting suspension was filtered. Evaporating the solvent in vacuo afforded 70 mg (0.45

mmol, 100% yield) of NMR-pure thietanone (**43**).

Acid-Catalyzed Decomposition of 3b in Water. To a slurry of **3b** (350 mg, 1.9 mmol) in 25 mL of water was added a catalytic amount of sulfuric acid. After stirring for 1 h at room temperature, the mixture was extracted with 50 mL of *n*-pentane. The pentane layer was washed with aqueous base and water and dried over $MgSO_4$. Evaporation of the solvent in vacuo afforded 278 mg (1.6 mmol, 84% yield) of pure hydroxy ketone **29a**: mp 45–47 °C; ^1H NMR ($CDCl_3$) δ 1.18 (1 CH_3), 1.57 (3 CH_3), 3.0 and 4.45 (AB quartet, J_{AB} = 4 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 215.0 (s), 81.5 (d, J_{C-H} = 144 Hz), 49.4 (s), 46.5 (s), 30.5 (q, J_{C-H} = 132 Hz), 28.5 (q, J_{C-H} = 132 Hz), 27.5 (q, J_{C-H} = 132 Hz), 24.6 (q, J_{C-H} = 132 Hz). Anal. Calcd for $C_8H_{14}O_2S$: C, 55.14; H, 8.10; S, 18.39. Found: C, 54.99; H, 8.04; S, 18.29.

Acid-Catalyzed Decomposition of 3b in Methanol. To a solution of 3b (200 mg, 1.23 mmol) in 10 mL of absolute methanol was added a catalytic amount of sulfuric acid. Nitrogen evolved immediately. After the evolution of nitrogen had stopped, 100 mL of ether was added. The resulting mixture was washed with water (3 times), dried over $MgSO_4$, and evaporated in vacuo to yield 250 mg (1.33 mmol, 100% yield) of pure **29b**: ^1H NMR ($CDCl_3$) δ 3.92 (s, 1 H), 3.55 (s, 3 CH_3), 1.43 (s, 3 CH_3), 1.22 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$): δ 213.5 (s), 90.3 (d, J_{C-H} = 140 Hz), 59.4 (q, J_{C-H} = 144 Hz), 48.8 (s), 45.0 (s), 30.7 (q, J_{C-H} = 132 Hz), 28.9 (q, J_{C-H} = 132 Hz), 28.0 (q, J_{C-H} = 132 Hz), 25.3 (q, J_{C-H} = 132 Hz); IR (neat) 1740 (C=O), 1115 (CO) cm^{-1}. Exact mass calcd for $C_9H_{16}O_2S$, 188.087; found, 188.086.

Reaction of 3b with Bromine. To a solution of **3b** (25 mg, 0.136 mmol) in 1.5 mL of $CDCl_3$ in an NMR tube was slowly added at 0 °C bromine (22 mg, 0.138 mmol) in 0.6 mL of $CDCl_3$. Nitrogen evolved immediately. Intermediate (**31**) was formed almost quantitatively as indicated by ^1H NMR spectroscopy. It is stable for several hours at −47 °C but rearranges rapidly to dibromide **32a** at 30 °C (90% yield). For **31**: ^1H NMR ($CDCl_3$) δ 1.75 (s, 2, CH_3), 1.88 (s, 1 CH_3), 1.98 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$, −47 °C) δ 195 (s, C=O), 138.7 (s, vinyl C), 108.4 (s, vinyl C), 56.1 (quat C), 24.5 (q, J_{C-H} = 132 Hz, 2 CH_3), 23.4 (q, J_{C-H} = 130 Hz, 1 CH_3), 22.4 (q, J_{C-H} = 130 Hz, 1 CH_3). For **32a**: ^1H NMR ($CDCl_3$) 1.68 (s, 2 CH_3), 1.62 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 203.6 (s, C=O), 77.5 (s, quat C), 52.4 (s, quat C), 50.6 (s, quat C), 31.8 (q, J_{C-H} = 132 Hz, 2 CH_3), 27.9 (q, J_{C-H} = 132 Hz, 2 CH_3); IR (neat) 1735 (C=O), 1715 (CBr), 660 (CBr) cm^{-1}. Exact mass calcd for $C_8H_{12}OSBr_2$, 313.898; found, 313.896.

Reaction of 18 with Bromine. The α-diazo ketone **18** (400 mg, 1.85 mmol) was dissolved in 4 mL of $CHCl_3$ and cooled to −50 °C. To the magnetically stirred solution was added dropwise bromine (385 mg, 2.41 mmol) dissolved in 1 mL of $CHCl_3$. Gas evolution occurred immediately. After the solution was warmed to room temperature and the solvent was removed, there remained 620 mg (1.78 mmol, 96% yield) of **32b**: mp 168° dec (after recrystallization from ether); IR (KBr) 1745 (C=O), 1310 and 1110 (SO_2), 742 and 620 (CBr) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77 (s, 4 CH_3), ^1H NMR (C_6D_6) 1.32 (s, 2 CH_3), 1.38 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 77.12 (s, C=O), 68.11 (s, quat C), 67.21 (s, quat C), 61.83 (s, quat C), 24.97 (q, J_{CH} = 132 Hz, 2 CH_3), 21.40 (q, J_{CH} = 132 Hz, 2CH_3). A satisfactory elemental analysis could not be obtained. On the following the reaction at −50 °C by ^1H NMR, as done for **3b**, only absorptions for **32b** were seen after consumption of **18**; no extraneous short-lived absorptions could be detected.

Reaction of 3b with Dimethyl Acetylenedicarboxylate. A solution of **3b** (350 mg, 1.9 mmol) in 2 mL of dimethyl acetylenedicarboxylate was stirred for 21 days at room temperature. Quantitative formation of adduct **63** had occurred as indicated by ^1H NMR spectroscopy. After evaporation (80 °C, 0.1 mmHg) of the solvent, 580 mg (1.8 mmol, 93% yield) of **63** was obtained. An analytically pure sample was obtained after thin-layer chromatography (Al_2O_3, ether): mp 71–72 °C; ^1H NMR ($CDCl_3$) δ 1.67 (2 CH_3), 1.87 (2 CH_3), 3.83 (1 CH_3)e, 3.93 (1 CH_3); ^{13}C NMR ($CDCl_3$) 178.0 (s), 165.0 (s), 160.1 (s), 149.7 (s), 138.8 (s), 114.8 (s), 52.4 (q, J_{C-H} = 145 Hz), 52.1 (q, J_{C-H} = 145 Hz), 49.6 (s), 45.5 (s), 30.2 (q, J_{C-H} = 130 Hz), 27.2 (q, J_{C-H} = 130 Hz); IR (neat) 1775 (C=O), 1576 (broad, C=N) cm^{-1}. Anal. Calcd for $C_{14}H_{18}ON_2O_5S$: C, 51.52; H, 5.56; N, 8.58; S, 9.83. Found: C, 51.38; H, 5.56; N, 8.59; S, 9.82.

Reaction of 3b with Arylonitrile. A solution of **3b** (850 mg, 4.62 mmol) in 3 mL of acrylonitrile was stirred at room temperature for 27 days. After evaporation of the solvent in vacuo there was obtained crude adduct **61** as a yellow-colored semisolid (900 mg). After recrystallization from *n*-pentane, 620 mg (2.62 mmol, 57% yield) of pure **61** was obtained: mp 103–104 °C; ^1H NMR (C_6D_6) δ 0.60 (1 CH_3), 0.65 (1 CH_3), 1.15 (1 CH_3), 1.22 (1 CH_3), 2.07 and 2.85 (AB quartet, J = 18 Hz, 2 H), 6.32 (NH); ^{13}C NMR ($CDCl_3$) δ 209.6 (s), 121.6 (s), 113.4 (s), 81.6 (s), 51.7 (s), 47.8 (s), 35.5 (t, J_{C-H} = 138 Hz), 30.1 (q, J_{C-H} = 132 Hz), 25.7 (q, J_{C-H} = 132 Hz), 22.4 (q, J_{C-H} = 132 Hz); IR (KBr) 3310 (NH), 2220 (C≡N), 1725 (C=O), 1550 (C=N) cm^{-1}. Anal. Calcd for $C_{11}H_{15}N_3OS$: C, 55.65; H, 6.37; N, 17.70; S, 13.51. Found: C, 55.64; H, 6.35; N, 17.76; S, 13.35.

Irradiation of α-Diazo Ketone (18) in Methanol. A deoxygenated solution of **18** (100 mg, 0.46 mmol) in 10 mL of methanol was irradiated (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) for 4 h. After evaporation of the solvent in vacuo there was obtained 90 mg of a semisolid. On the basis of ^1H NMR spectroscopy, 74% ester **49** had been formed. A pure sample was obtained after recrystallization from ether: mp 94.5–96.5 °C; ^1H NMR ($CDCl_3$) δ 1.60 (s, 2 CH_3), 1.68 (s, 2 CH_3), 2.90 (s, 1 H), 3.77 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$) δ 167.7 (s), 78.2 (s), 51.9 (q, J_{C-H} = 140 Hz), 30.8 (d, J_{C-H} = 144 Hz), 24.5 (q, J_{C-H} = 130 Hz, 2 CH_3), 20.2 (q, J_{C-H} = 130 Hz, 2 CH_3); IR (KBr) 1740 (C=O), 1350 (SO_2), 1170 (SO_2) cm^{-1}; spectrum, m/e 189 (M − OCH_3). Exact mass (for M − OCH_3) calcd for $C_8H_{13}O_3S$: 189.059; found 189.060. Anal. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32; S, 14.55. Found: C, 49.19; H, 7.28; S, 14.61.

Thermally Induced Decomposition of α-Diazo Ketone 18 in Methanol. A solution containing **18** (316 mg, 1.46 mmol) in 150 mL of dry methanol was placed in a well-sealed pressure cell and heated for ca. 30 min to 180 °C. After removal of the solvent and recrystallization there was obtained 286 mg (1.30 mmol, 89% yield) of **49**, pure by ^1H NMR spectroscopy. For characterization of **49**, see the foregoing experiment.

Thermally Induced Decomposition of α-Diazo Ketone 18 in the Absence of Solvent. Pure **18** (126 mg, 0.58 mmol) was warmed to 140 °C. Nitrogen was evolved from the melt, yielding 108 mg (0.57 mmol, 98% yield) of almost pure 3,3-dimethyl-4-(2-propenyl)-1,2-oxathiolan-5-one 2-oxide (**47**): ^1H NMR ($CDCl_3$) δ 2.23 (s, 1 CH_3), 2.10 (s, 1 CH_3), 1.66 (s, 1 CH_3), 1.45 (s, 1 CH_3); ^{13}C NMR ($CDCl_3$) δ 166.7 (s, C=O), 161.5 (s, vinyl C), 120.0 (s, vinyl C), 64.2 (s, quat C), 23.8 (q, J_{C-H} = 130 Hz, CH_3), 21.1 (q, J_{C-H} = 130 Hz, CH_3), 21.4 (q, J_{C-H} = 130 Hz), 20.4 (q, J_{C-H} = 130 Hz, CH_3); IR 1770 (C=O), 1624 (C=C), 1150 (SO), 1090 (SO) cm^{-1}. Exact mass calcd for $C_8H_{12}O_3S$, 188.051; found, 188.053.

Reaction of Diol 16 in the Presence of a Catalytic Amount of Acid. A mixture of diol **16** (250 mg, 1.23 mmol) and *p*-toluenesulfonic acid (100 mg, 0.58 mmol) in 50 mL of benzene was refluxed for 3 h. The water liberated during the reaction was removed by means of a Dean–Stark trap. On the basis of ^1H NMR spectroscopy, ca. 40g of diene **20**[15] and 14% 2,2,4,4,5,5-hexamethylthiolan-3-one (**23**) had been formed. After prolonged heating, the yield of **20** decreased. The reaction mixture was washed with water, and the solvent was evaporated in vacuo to yield 120 mg of crude reaction product, which contained only **20** and **23**. No attempts were made to purify these materials. For **20**: ^1H NMR (CCl_4) δ 1.54 (s, 4 CH_3), 4.72 (2 H), 5.16 (s, 2 H). Spectral and analytical data for **23** are given in the following paragraph.

A solution of **16** (200 mg, 1 mmol) and a catalytic amount of concentrated sulfuric acid in 10 mL of acetic acid was refluxed for 45 min. The solution became purple immediately. After the solution was cooled to room temperature, water and 150 mL of *n*-pentane were added. The organic layer was separated, washed with water (3 times), and dried over $MgSO_4$. Evaporation of the solvent in vacuo yielded 229 mg of a yellow liquid consisting of 2,2,4,5,5-pentamethyl-3-[(methoxycarbonyl)methyl]thiol-3-ene (**24**; 62%) and ketone **23** (18%). Purification of both products was performed by preparative GLC (SE 30 column, 140 °C). For **24**: ^1H NMR ($CDCl_3$) δ 4.63 (s, 2 H), 2.05 (s, 3 H), 1.72 (s, 3 H), 1.48 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 170.3 (s, C=O), 144.7 (s, vinyl C), 134.0 (s, vinyl C), 58.2 (t, J_{C-H} = 147 Hz), 57.2 (s, quat C), 56.7 (s, quat C), 31.6 (q, J_{C-H} = 130 Hz), 30.7 (q, J_{C-H} = 128 Hz); IR 1760 (C=O) cm^{-1}; Exact mass calcd for $C_{12}H_{20}O_2S$, 228.117; 117; found, 228.118. For **23**: ^1H NMR ($CDCl_3$) δ 1.47 (s, 2 CH_3), 1.35 (s, 2 CH_3), 1.21 (s, 2 CH_3); ^{13}C NMR ($CDCl_3$): δ 221.9 (s, C=O),

54.5 (s, quat C), 53.1 (s, quat C), 50.6 (s, quat C), 30.5 (q, J_{C-H} = 132 Hz), 27.0 (q, J_{C-H} = 132 Hz), 21.2 (q, J_{C-H} = 132 Hz); IR 1730 (C=O) cm^{-1}. Exact mass calcd for $C_{10}H_{18}OS$, 186.108; found, 186.107.

Acknowledgment. We are indebted to F. Van Bolhuis of the Department of Chemical Physics of this university for carrying out the X-ray structural determinations cited in this article.

Registry No. 3a, 74966-44-2; **3b**, 74966-46-4; **6**, 4388-87-8; **7**, 83044-60-4; **9**, 83044-61-5; **10**, 6838-61-5; **11**, 74966-57-7; **12**, 74966-45-3; **14**, 83044-62-6; **15**, 83044-63-7; **16**, 83044-64-8; **17**, 83044-65-9; **18**, 83044-66-0; **19**, 83044-67-1; **20**, 73368-55-5; **21**, 83044-68-2; **23**, 83044-69-3; **24**, 83044-70-6; **29** (R = H), 83044-71-7; **29** (R = Me), 83044-72-8; **31**, 83044-73-9; **32a**, 83044-74-0; **32b**, 83044-75-1; **43**, 74966-50-0; **45**, 13905-13-0; **46**, 83044-76-2; **47**, 83044-77-3; **49**, 83044-78-4; **50**, 83044-79-5; **51**, 74966-52-2; **53**, 598-26-5; **54**, 924-50-5; **56**, 74966-53-3; **58**, 74966-51-1; **59**, 53942-65-7; **62**, 83044-80-8; **63**, 83044-81-9; ethyl isobutyrate, 97-62-1.

2-Cyano-Δ^3-piperidines. 5.[1] Toward the Synthesis of Corynanthe-Type Indole Alkaloids. Computer-Assisted Study of the Conformations of an "Inside" Indoloquinolizidine Series[2]

David S. Grierson, Marc Vuilhorgne, and Henri-Philippe Husson*

Institut de Chimie des Substances Naturelles, F-91190 Gif-sur-Yvette, France

Guy Lemoine

Centre de Recherche Roussel-Uclaf, 93230 Romainville, France

Received February 2, 1982

1-[β-[N_a-(Phenylsulfonyl)indol-3-yl]ethyl]-2-cyano-Δ^3-piperidines **21** and **26** have been used to mimic the two-step reaction sequence **7** → **8** (Scheme I) in which a 5,6-dihydropyridinium salt, **7**, acts as a potential precursor of the tetracyclic corynanthe-type indole alkaloids. The required amino nitriles **21** and **26** were prepared by an established four-step procedure from the corresponding pyridinium salts.[10,11] Amino nitrile **21** was successfully condensed with sodium dimethyl malonate, giving the enamine **27** which in certain experiments was reacted with KCN to give the corresponding amino nitriles **32** and **34**. The benzenesulfonyl protecting group of **27**, **32**, and **34** was efficiently removed by using *t*-BuOK in THF and the C ring subsequently closed by reaction with HCl in MeOH. Three tetracyclic indoles (**29**–**31**) were obtained on cyclization of the deprotected enamine **28** (51% overall yield from **21**). In accord with this mechanism, on cyclization of deprotected amino nitrile **33**, indoles **30** and **31** were formed, and on ring closure of amino nitrile **35**, indole **29** only was formed. Because **30** and **31** were observed a priori to adopt unfavorable conformations where the malonyl and ethyl substituents were axial, a detailed analysis of the relative energies of the conformational possibilities for these products were undertaken with the aid of the computer program SCRIPT.[13] Similarly, the unsubstituted amino nitrile **26** was sequentially reacted with sodium dimethyl malonate and KCN, giving compound **37** in 75% yield. Removal of the benzenesulfonyl protecting group with *t*-BuOK in THF and cyclization by using a two-step "one pot" procedure ($AgBF_4$, HCl/MeOH) led to the formation of two tetracyclic indoles, **39** and **40**. The predominant product **40** was shown to possess the trans H-3,15 configuration typical of the alkaloid antirhine **6**.

In terms of their biogenetic origin the corynanthe-type indole alkaloids are the first of the three main families to be formed from tryptamine and secologanin.[3] Despite the considerable diversity of structural types observed within this family of alkaloids, the greater majority of these natural products display several common features,[4] i.e., an indoloquinolizidine system wherein the piperidine or D ring is further substituted at C-15 (biogenetic numbering system;[5] see **1**) by a β-dicarbonyl functionality (or modified form thereof) and at C-20 by a two-carbon unit. These features are present, for example, in the tetracyclic corynanthe alkaloids geissoschizine (**1**), corynantheine (**2**), and hirsuteine (**3**) (as well as their dihydro forms) where a formyl acetic ester unit is found at C-15 and in the pentacyclic yohimbine (**4**) and heteroyohimbine (**5**) alkaloids where the fifth or E ring has been formed by condensation of one of the carbonyl units with the appropriate fragment at C-20.

Our interest in this alkaloid series originated from the desire to develop a new, general approach toward its synthesis based upon the recognition that a similarly substituted piperidine moiety is present in each of its members.[4] An approach whereby the C-15-substituted tetracyclic system could be constructed in two steps from a 5,6-dihydropyridinium salt, **7**, is illustrated by the retrosynthetic analysis in Scheme I. The required C–C bonds would be formed by (a) condensation of a malonate anion at C-15 of the dihydropyridinium precursor **7** followed by (b) closure of the C ring. The key intermediate **8** could then be further elaborated in one of four directions, depending upon the nature of the C-20 substituents R and R′, to the yohimbine (**4**) or heteroyohimbine (**5**) systems (for which efficient methodology has been developed[6]), to

(1) For part 4 see: Harris, M.; Grierson, D. S.; Husson, H.-P. *Tetrahedron Lett.* **1981**, *22*, 1511–4.

(2) This work was presented as a preliminary communication at the 2nd European Society of Chemistry (ESOC II) meeting at Stresa, Italy, June 1981.

(3) Cordell, G. A. *Llyodia* **1974**, *37*, 219–98.

(4) Corynanthe alkaloids such as echitamine and the vobasine family do not possess the indoloquinolizidine ring system; however, their ring systems are derived from it biogenetically, and synthetic routes have been devised for rearrangement of suitable indoloquinolizidine precursors to them.

(5) Le Men, J.; Taylor, W. I. *Experientia* **1965**, *21*, 508–10. By use of this biogenetic numbering system, the α-aminonitrile carbon corresponds to C-3 since this center becomes C-3 of the tetracyclic structures.

(6) (a) Wenkert, E.; Reynolds, G. D. *Synth. Commun.* **1973**, *3*, 241–3. (b) Wenkert, E. Chang, C. J.; Chawla, H. P. S.; Cochran, D. W.; Hagaman, E. W.; King, J. C.; Orito, K. *J. Am. Chem. Soc.* **1976**, *98*, 3645–55. (c) Wenkert, E.; Kunesch, G.; Orito, K.; Temple, W. A.; Yadar, J. S. *Ibid.* **1979**, *101*, 4894–5. (d) Wenkert, E.; Halls, T. D. J.; Kunesch, G.; Orito, K.; Stephens, R. L.; Temple, W. A.; Yadav, J. S. *Ibid.* **1979**, *101*, 5370–6. (e) Wenkert, E.; Vankar, Y. D.; Yadav, J. S. *Ibid.* **1980**, *102*, 7971–3.

0022-3263/82/1947-4439$01.25/0