deoxycytidine, having been prepared in pyridine as previously described, was added 4-monomethoxytrityl chloride (1.015 equiv) at room temperature. The mixture became homogeneous within 1 h and was stirred overnight. Benzoyl chloride (0.5 mL/mmol) was then added dropwise, the mixture being stirred for 45 min and poured onto ice. The mixture was extracted with dichloromethane and the extract coevaporated with 1,2-dichloroethane until pyridine was no longer present. The remaining material was dissolved in dichloromethane[15] and ferric chloride (2 equiv) was added. The red mixture was stirred for 1 h (if necessary, an extra equivalent of ferric chloride was added) and then washed thoroughly with brine to eliminate the iron salts. After the solution was dried and the solvent evaporated, ethanol was added, the precipitate being pure **7**. Column chromatography of the mother liquors over 15% water-deactivated alumina, eluting with dichloromethane, gave additional **7**; the total yield was 60–70%. **7** has been compared with an authentic sample:[16] mp 223–226 °C (lit.[17] mp 222–224 °C); ^{1}H NMR (Me_2SO-d_6) δ 2.1–3.9 (m, $H_{2'}$ + $H_{4'}$ + $H_{5'}$), 5.4–5.6 (m, 1 H, $H_{3'}$), 6.25 (t, 1 H, $H_{1'}$), 6.9 (1 H, OH, exchangeable with D_2O), 7.2–8.15 (m, 11 H, aromatics and H_5), 8.4 (1 H, A part of an AB system, J_{AB} = 7.5, H_6); mass spectrum, *m/e* 435 ($M^{+}\cdot$), 105 (100).

Silylation of Preformed 3. To **3**, prepared from 2′-deoxycytidine (**1**, 114 mg, 0.5 mmol) and **2** (160 mg, 1.05 equiv) in dry DMF as described above, were added at room temperature *tert*-butyldimethylsilyl chloride[19] (165 mg, 1.1 mmol) and imidazole (150 mg, 2.2 mmol). After the mixture was stirred overnight and the solvent was evaporated, thick-layer chromatography on silica gel yielded **3** (120 mg) and **8** (65 mg). If more reagents were added after stirring overnight (*tert*-butyldimethylsilyl chloride, 165 mg, 1.1 mmol, and imidazole, 150 mg, 2.2 mmol) and the mixture was stirred for an addition 2 h, TLC indicated disappearance of **3** and formation of two silylated compounds which were isolated by thick-layer chromatography: **8** (110 mg, 49%) and **9** (84 mg, 30%), which were compared to samples prepared according to ref 18.

N^4-Benzoyl-$O^{5'}$-(*tert*-butyldimethylsilyl)-2′-deoxycytidine (8): mp 126–131 °C (lit.[18] mp 130–132 °C); ^{1}H NMR ($CDCl_3$) δ 0.15 [s, 6 H, $Si(CH_3)_2$], 0.95 [s, 3 H, $C(CH_3)_3$], 1.9–2.9 (2 H, $H_{2'}$), 3.5–4.5 (m, 4 H, $H_{3'}$ + $H_{4'}$ + $H_{5'}$), 6.35 (t, 1 H, $H_{1'}$), 7.6–8.4 (m, 6 H, aromatics + H_5), 8.5 (1 H, A part of an AB system, J_{AB} = 7.5, H_6); mass spectrum, *m/e* 435 ($M^{+}\cdot$), 105 (100).

N^4-Benzoyl-$O^{3'}$,$O^{5'}$-bis(*tert*-butyldimethylsilyl)-2′-deoxycytidine (9): mp fully melts at 134 °C (softens at ca. 100 °C) (lit.[18] mp 138–139 °C); ^{1}H NMR ($CDCl_3$) δ 0.05 and 0.1 [s, $O_{5'}$-$Si(CH_3)_2$ and $O_{3'}$-$Si(CH_3)_2$], 0.9 and 0.95 [s, 18 H, $O_{5'}$-$SiC(CH_3)_3$ and $O_{3'}$-$SiC(CH_3)_3$], 1.9–3.0 (m, 2 H, $H_{2'}$), 3.5–4.6 (m, 4 H, $H_{3'}$ + H_4' + $H_{5'}$), 6.25 (t, 1 H, $H_{1'}$), 7.3–8.2 (m, 6 H, aromatics + H_5), 8.4 (1 H, A part of an AB system, J_{AB} = 7.5, H_6); mass spectrum, *m/e* 559 ($M^{+}\cdot$), 370 (100).

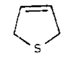
Registry No. 1, 951-77-9; 2, 14533-81-4; 3, 4836-13-9; 4, 67219-55-0; 5, 60920-99-2; 6, 75125-22-3; 7, 51549-49-6; 8, 51549-36-1; 9, 51549-38-3; 2,3,4,5,6-pentafluorophenol, 771-61-9; benzoic acid, 65-85-0; 4,4′-dimethoxytrityl chloride, 40615-36-9; 4-monomethoxytrityl chloride, 14470-28-1; benzoyl chloride, 98-88-4; *tert*-butyldimethylsilyl chloride, 18162-48-6.

Communications

Rearrangement Chemistry of the α-Diazo Ketone Derived from 2,2,5,5-Tetramethylthiolane-3,4-dione

Summary: The α-diazo ketone of 2,2,5,5-tetramethylthiolane-3,4-dione undergoes both thermally and photochemically induced rearrangement; the chief product, a thietanone derivative, undergoes smooth and rapid photochemically induced fragmentation.

Sir: The thiolane skeleton, readily available by various synthetic approaches, lends itself for many purposes. For example, derivatives of 2,5-dihydrothiophene (1) have found uses for such divergent purposes as the synthesis of dienes (stereocontrolled removal of the sulfur bridge being the synthetic key),[1-3] studies of σ-sulfurane chemistry,[4] syntheses of strained rings via photoinduced rearrangements,[5] generation of 2,2′-bisallyl radicals ("tetramethyleneethanes"),[6] and formation of organometallic complexes.[7,8] The fully saturated derivative is used as starting point for "chain growing reactions" involving rearrangement of allylic sulfonium ylides.[9,10]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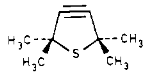
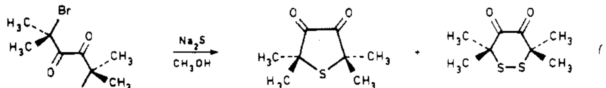


2

In conjunction with an approach to a highly strained acetylene, namely, the thiolane **2**,[11] we developed a route (eq 1) to the diketone **3**. This diketone, via the α-diazo derivative **5**, turns out to have a rich rearrangement chemistry, some of which is reported here.



3
4

The ring closure with Na_2S (eq 1) proceeds readily (73% yield of **3**)[12-14] possibly via radical anion intermediates.[15,16] A side product (**4**) is isolated in varying amounts, but its formation can be suppressed by adding the reagents slowly. The correct structure for **4** was established by an X-ray crystal structure determination.[17]

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(11) Bolster, J. M.; Kellogg, R. M., to be published.

(12) **3**: IR (film) 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.53 (s, 12 H, 4 CH_3's); UV (hexane) 321 nm (ϵ 208), 477 (49).

(13) Correct analytical or exact mass spectral data were obtained for all new compounds.

(14) During the course of this work a related ring closure of α,α′-dibromo ketones was reported: Föhlisch, B.; Gottstein, W. *Justus Liebigs Ann. Chem.* **1979**, 1768.

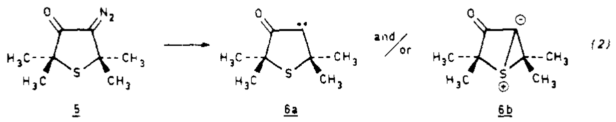
(15) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647.

(16) Kornblum, N.; Widmer, J. W.; Carlson, S. C. *J. Am. Chem. Soc.* **1979**, *101*, 658.

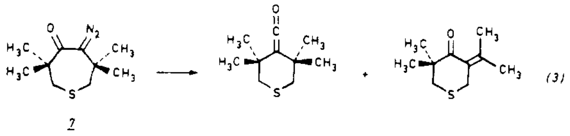
(17) **4**: IR (KBr) 1685 cm^{-1} (br); ^{1}H NMR ($CDCl_3$, −11 °C) δ 1.50 (s, 6, 2 CH_3's), 1.80 (s, 6, 2 CH_3's); NMR ($CDCl_3$, 60 °C) δ 1.65 (s, 12, 4 CH_3's); T_{coal} 30 °C (ΔG^* = 15.4 kcal/mol); UV (hexane) 294 nm (ϵ 300),

0022-3263/80/1945-4804$01.00/0

Reaction of **3** with tosylhydrazine (78% yield) followed by treatment with aqueous NaOH/pentane afforded **5**[18] in quantitative yield. There are in principle several rearrangement pathways open to the α-ketocarbene **6a** (perhaps to be formulated as **6b**) derived from **5** on loss of N_2 (eq 2). Analogues of **5** with, respectively, oxygen,[19,20] methylene,[21] and *N*-acetyl[22] in place of sulfur give only ring-contracted ketenes derived by Wolff rearrangement. On the other hand the addition of carbenes to sulfides to give ylides that subsequently rearrange is well-known.[23] Trapping, even intramolecularly, of an α-ketocarbene, however, is more problematical. The highly skewed α-diazo ketone **7** undergoes normal ring contractions (eq 3).[24]

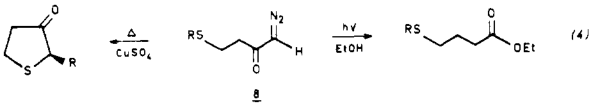


(2)



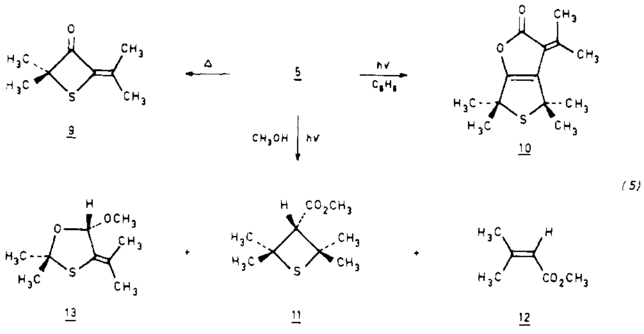
(3)

The α-diazo ketone **8** also yields a Wolff rearrangement product on photochemically induced decomposition, but sulfur participation leading to a different rearrangement product occurs on Cu(II)-catalyzed decomposition (eq 4).[25]



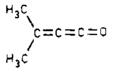
(4)

We found that on thermally induced (99.3 °C) decomposition of **5** in isooctane the thietanone **9**[26] is formed quantitatively (eq 5). In sharp contrast on irradiation of **5** in benzene (high-pressure Hg lamp, Pyrex filter, N_2 atmosphere) only the enol acetate **10**[27] is found (43% yield). On changing the solvent to methanol, **5** provided on photochemically induced decomposition a mixture of **11**[28] (28% yield), **12** (19% yield), and **13**[29] (14% yield).



(5)

The thermal reaction of **5** clearly proceeds through a variant of the Wolff rearrangement involving a selective shift of the sulfur bridge to provide **9**. The best clue to understanding the photochemical reactions is obtained from the results in CH_3OH. The ester **11** must be a trapping product of a ring-contracted ketene (normal Wolff rearrangement product) and **12** is a trapping product of cumulene **14**.[30] The unusual structure **13** is likely derived by methanol addition to α-oxa carbene **15**, which could be formed from secondary photolysis of **9** (see below) via biradial **16**. The enol acetate **10** formed *in benzene* could arise if **5** is converted to **9**, which undergoes *rapid* secondary photolysis to give cumulene **14**, which cycloadds with α-diazo ketone **5**, with subsequent loss of N_2 providing **10**.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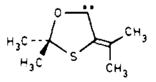
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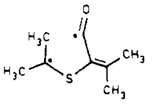
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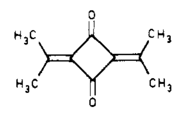
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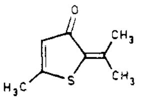
18

9 was irradiated (same conditions as for **5**) separately in CH_3OH to test this interpretation; **13** (22% yield) and **12** (28% yield) were rapidly formed in addition to intractable materials likely arising from thioacetone. On irradiation in benzene **9** afforded **17**,[31] likely formed by dimerization of cumulene **14**, in 47% yield. In some cases a small amount of a side product, tentatively identified as **18**, was obtained.

It is obvious that the ketocarbenes (**6a**,**b**) derived from **5** (or from structurally related compounds) are effective precursors of a variety of otherwise difficultly accessible sulfur-containing small-ring systems.

Registry No. 3, 74966-44-2; 4, 74966-45-3; 5, 74966-46-4; 6a, 74966-47-5; 6b, 74966-48-6; 7, 74966-49-7; 9, 74966-50-0; 10, 74966-51-1; 11, 74966-52-2; 12, 924-50-5; 13, 74966-53-3; 14, 63364-70-5.

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306 (280); mp 108–109 °C. The X-ray structure (determined by Mr. F. van Bolhuis, Department of Chemical Physics, of these laboratories) reveals that **4** has a highly skewed conformation; the carbonyl–carbonyl dihedral angle is 88° and the S–S dihedral angle is 68° (80–85° is normal for disulfides; see: Jørgensen, F. S.; Snyder, J. P. *J. Org. Chem.* **1980**, *45*, 1015).

(18) **5**: IR (Nujol) 1645, 2030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 2 CH_3's), 1.65 (s, 2 CH_3's); UV (hexane) 257 nm (ϵ 11 130); mp 37–38 °C.

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(26) **9**: IR 1642, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.14 (s, 3, CH_3), 1.73 (s, 3, CH_3), 1.64 (s, 6, 2 CH_3's); UV (hexane) 221 nm (ϵ 4200), 320 (5960), 331 (6560). **9** was desulfurized with deactivated Raney nickel to give 2,5-dimethyl-4-oxo-2-hexene, prepared independently for comparison purposes.

(27) **10**: IR (KBr) 1675, 1705, 1855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70 (s, 6, 2 CH_3's), 1.80 (s, 6, 2 CH_3's), 2.08 (s, 3, CH_3), 2.22 (s, 3, CH_3); mp 101–103 °C.

(28) **11**: ^{1}H NMR (C_6D_6) δ 1.15 (s, 6, 2 CH_3's), 1.45 (s, 6, 2 CH_3's), 2.95 (s, 3, OCH_3), 3.28 (s, 1, tertiary H).

(29) **13**: ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 3, CH_3), 1.60 (s, 3, CH_3), 1.68 (br s, 6, 2 CH_3's), 3.35 (s, 3, OCH_3), 5.48 (br s, 1, tertiary H).

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