

(300 mL) overlaid with ether (500 mL), and the layers were separated. The aqueous layer was extracted twice with ether, and the combined extracts were evaporated to leave 3.9 g of crude 3. Recrystallization from dichloromethane-hexane (100 mL/250 mL) gave 2.71 g (58%) of 3 in two crops: mp 194.5–195 °C and mp 188–189 °C; $[\alpha]_D^{20} +145^\circ$ (lit.¹ mp 192.5–194 °C and $[\alpha]_D^{23} +159^\circ$). The ¹H NMR spectrum was identical with that reported.

Methyl 4,6-O-Benzylidene-2-deoxy-3-C-[(trimethylsilyl)methyl]- α -D-ribo-hexopyranoside (5). In the same manner as above, 8.2 g (31 mmol) of ulose 4⁹ was allowed to react with the Grignard reagent derived from 92 mmol of (chloromethyl)trimethylsilane. Recrystallization of the crude product from pentane gave 9.48 g (87%) of 5: mp 85–86 °C; $[\alpha]_D^{19} +68.6^\circ$; ¹H NMR (CDCl₃) δ 7.26–7.60 (m, 5 H, arom), 5.53 (s, 1 H, C₆H₅CH), 4.73 (d, $J_{ax-eq} = 4$ Hz, 1 H, CHOCH₂), 3.50–4.43 (m, 4 H, H-4, H-5, H-6, H-6'), 3.38 (s, 3 H, OCH₃), 3.26 (m, 1 H, OH), 2.20 (dd, $J_{gem} = 13$ Hz, $J_{1,2} \leq 1$ Hz, 1 H, H-2_{eq}), 1.83 (dd, $J_{gem} = 13$ Hz, $J_{1,2} = 4$ Hz, H-2_{ax}), 0.80 and 1.36 (AB q, $J_{gem} = 15$ Hz, 1 H, SiCH₂), 0.10 (s, 9 H, CH₃Si). Anal. Calcd for C₁₈H₁₈O₅Si: C, 61.33; H, 8.01. Found: C, 61.17; H, 8.07.

Methyl 4-O-Benzoyl-6-bromo-6-deoxy-3-C-[(trimethylsilyl)methyl]- α -D-ribo-hexopyranoside (6). *N*-Bromosuccinimide (3.5 g, 15.6 mmol), barium carbonate (0.91 g), 5 (5.44 g, 15.4 mmol), and 380 mL of carbon tetrachloride were placed in a 500-mL, round-bottom flask equipped with a magnetic stirrer and a condenser. This mixture was heated (oil bath, 95 °C) and simultaneously irradiated with a 200-W flood lamp. The combination provided a very gentle reflux. When the solution began to turn red, the lamp was turned off. The color intensified and then began to disappear after 0.5 h. The lamp was again turned on to complete the reaction. After the solution became yellow, it was filtered (while still hot) and the succinimide was washed well with hot carbon tetrachloride. The solution was extracted with half-saturated sodium bisulfite (100 mL), saturated sodium bicarbonate (2 × 100 mL), and brine (100 mL) and dried (Na₂SO₄). Thin-layer chromatography (silica/chloroform) showed one spot (*R*_f 0.55). Concentration appeared to give rise to some decomposition overnight, but after column chromatography (230–400-mesh silica, 3:1 chloroform/pentane), 6 (4.81 g, 74%) was isolated as a syrup: ¹H NMR (CDCl₃) δ 8.06–8.20 (m, 2 H, arom), 7.33–7.73 (m, 3 H, arom), 4.83–5.00 (m, 2 H, H-4 and CHOCH₂), 4.06–4.40 (m, 1 H, H-5), 3.86 (br s, 1 H, OH), 3.46 (s, 3 H, OCH₃), 3.42 (2 H, CH₂Br), 2.26 (dd, $J_{gem} = 14$ Hz, $J_{eq-eq} \leq 1$ Hz, 1 H, H-2_{eq}), 1.87 (dd, $J_{gem} = 14$ Hz, $J_{ax-eq} = 4$ Hz, 1 H, H-2_{ax}), 0.73 and 1.13 (AB q, $J_{gem} = 15$ Hz, 2 H, SiCH₂), 0.07 (s, 9 H, SiCH₃). Anal. Calcd for C₁₈H₂₇BrO₅Si: C, 50.11; H, 6.31. Found: C, 49.02; H, 6.19.

Methyl 6-Bromo-3-C-methylene-2,3,6-trideoxy- α -D-erythro-hexopyranoside (7). The product just described 6 (2.98 g, 6.9 mmol) and freshly distilled anhydrous methanol (120 mL) were placed in a 200-mL, round-bottom flask under argon. Sodium (200 mg) in methanol (35 mL) was added portionwise, and the mixture was stirred for 14.5 h at room temperature. The loss of benzoate was monitored by TLC (silica, 2% methanol in chloroform). When starting material had disappeared, a large excess of analytical grade Dowex 50W-X8 cation-exchange resin that had been washed several times with methanol was added to the reaction mixture and the mixture stirred for 10 h at room temperature. The reaction was monitored by TLC (silica, chloroform). The resin was removed by filtration, and the methanol solution was concentrated to a small volume (20 mL). This was transferred to a separatory funnel with dichloromethane (75 mL) and extracted with saturated sodium bicarbonate (2 × 50 mL), water (50 mL), and brine (50 mL). It was dried (MgSO₄/K₂CO₃), and evaporated. Flash column chromatography (silica, 1% methanol in chloroform) gave 7 as a syrup (1.56 g, 95%): ¹H NMR (CDCl₃) δ 5.13 (s, 1 H, vinyl), 4.95 (s, 1 H, vinyl), 4.80 (t, $J = 3$ Hz, 1 H, CHOCH₂), 3.90–4.20 (m, 1 H, H-4), 3.40–3.90 (m, 3 H, H-5, CH₂Br), 3.37 (s, 3 H, OCH₃), 2.51 (br s, 2 H, H-2_{ax}, H-2_{eq}), 2.00 (br d, 1 H, OH). Anal. Calcd for C₈H₁₃BrO₃: C, 40.53; H, 5.53. Found: C, 40.38; H, 5.60.

Methyl 3-C-Methylene-2,3,6-trideoxy- α -D-erythro-hexopyranoside (8). A solution of dry benzene (6.7 mL) containing 500 mg (2.11 mmol) of 7 and 1.0 g (4.2 mmol) of tri-*n*-butyltin

hydride was refluxed for 3 h. A mercury vapor 200-W flood lamp was used as both a heat and light source. By the Jacobus workup,¹⁰ aqueous potassium fluoride was added, the mixture was stirred for 3 h at room temperature, and insoluble material was removed by filtration. The layers were separated, the aqueous layer was extracted with ether (5 mL), and the organic layers were combined, dried (MgSO₄), filtered, and evaporated to yield crude 8. Flash column chromatography (silica), using 1% methanol/chloroform, gave 326 mg (98%) of 8 as a colorless syrup: ¹H NMR (CDCl₃) δ 5.09 and 4.91 (2 br s, 2 H, vinyl H), 4.70 (br t, 1 H, H-1), 3.90–3.40 (m, 2 H, H-4, H-5), 3.31 (s, 3 H, OCH₃), 2.50 (br s, 2 H, H-2), 1.70 (br s, 1 H, OH), 1.32 (d, 3 H, $J = 6$ Hz, H-6); CI accurate mass measurement (C₈H₁₄O₃·NH₄⁺) calcd *m/e* 176.128, found *m/e* 176.126.

Preparation of Methyl α -D-Evermicoside (9) by Oxymercuration of 8. A solution of 8 (100 mg, 0.63 mmol), mercuric acetate (203 mg, 0.70 mmol), tetrahydrofuran (1.5 mL), and water (1.5 mL) was stirred at room temperature for 1 h. The flask was cooled to 0 °C, and 2 N sodium hydroxide was added until the solution was strongly basic, maintaining the temperature at 0–5 °C. A solution of 4 N sodium borohydride in 2 N sodium hydroxide was added dropwise maintaining the temperature at 0–10 °C until the reaction was no longer exothermic. Ether was added, and the flask was placed in a refrigerator overnight. The solution was decanted, leaving the coagulated mercury behind. Transfer was completed with ether, and the layers were separated. The aqueous layer was extracted with ether, and the organic layers were combined, washed with brine, dried (MgSO₄), filtered through a Celite pad, and concentrated to give a colorless oil (27.3 mg, 25%) identified as methyl evermicoside (methyl 2,6-di-deoxy-3-C-methyl- α -D-arabino-hexopyranoside, 9) by comparison of its ¹H NMR spectrum at 360 MHz with that reported for its enantiomer at 270 MHz.¹¹ The two spectra were identical.

Registry No. 1, 28642-65-1; 2, 82198-67-2; 3, 50827-20-8; 4, 6752-49-4; 5, 82190-42-9; 6, 82190-43-0; 7, 82190-44-1; 8, 82190-45-2; 9, 73712-09-1; (chloromethyl)trimethylsilane, 2344-80-1.

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Strain-Assisted α -Cleavage Reactions of Thioketones: Diphenylcyclopropenethione

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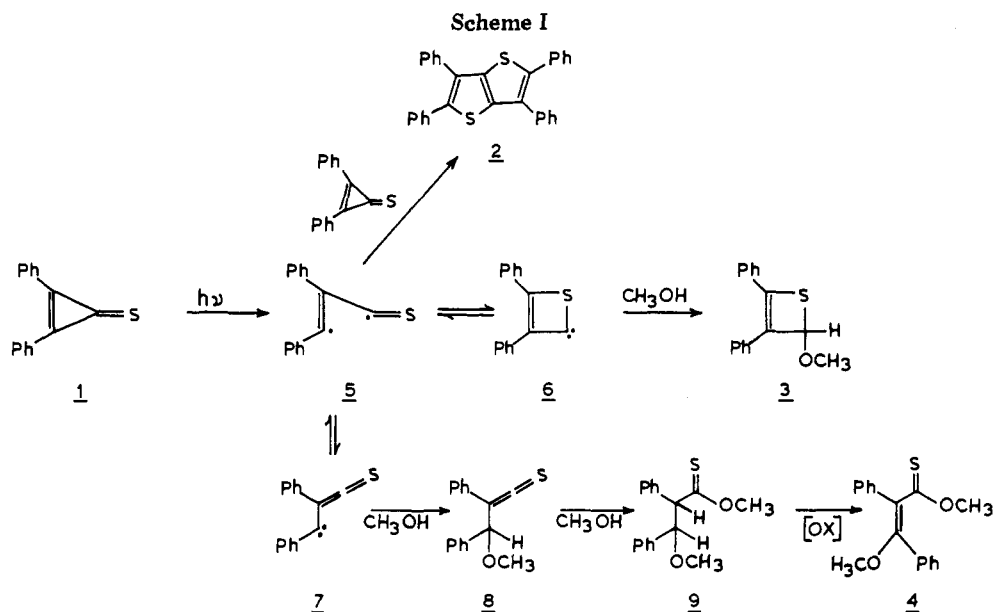
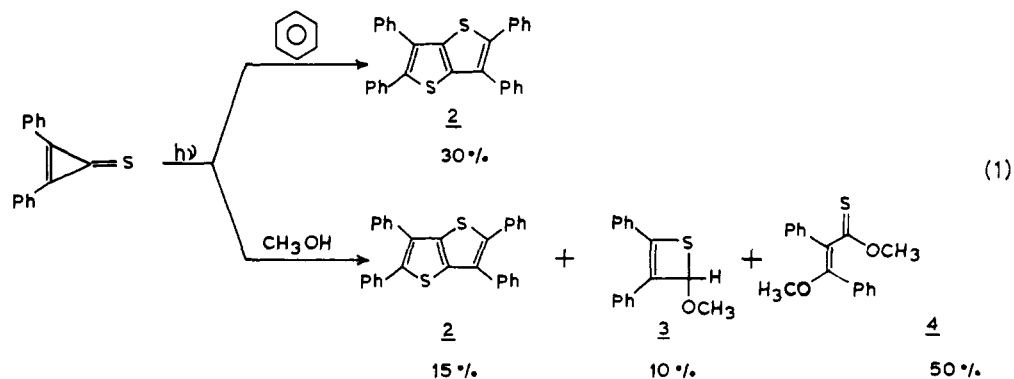
Photochemical α cleavage is characteristic of most alkanones¹ but is infrequently observed in thiocarbonyl systems.² Perhaps, because of the rarity of its occurrence, the photochemical Norrish type I α -cleavage process is one of the least studied excited-state transformations of thiocarbonyls. Nevertheless, it has been shown to occur in cyclobutanethiones.³ Recently, we have studied the effect of strain on the α -cleavage process and, of course, cyclopropene derivatives were suitable substrates. Prompted by the desire to explore the possibility of elimination of carbon monosulfide upon α cleavage and intrigued by the

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report that such a process does occur in diphenylcyclopropenethione (1),⁴ we undertook a careful photochemical investigation of 1. The results are presented below.

Excitation of diphenylcyclopropenethione⁵ into n, π^* or π, π^* excited states (500-W tungsten lamp or 450-W medium-pressure mercury lamp, Pyrex filter) in deaerated benzene gave a single crystalline product (30%), earlier identified to be 2,3,5,6-tetraphenylthieno[3,2-*b*]thiophene.⁶ On the other hand, irradiation of 1 in methanol gave two additional products (eq 1). On the basis of the spectral properties, 1:2 solvent-adduct has been identified to be methyl 1-methoxy-2-phenylthiocinnamate (4). Spectral properties of 1:1 solvent-adduct suggest that this might be 2-methoxy-3,4-diphenylthiete (3) and its properties are consistent with those of the closely related thietes.⁷ However, we are unable to confirm the structure owing to the difficulty in obtaining satisfactory elemental analysis and solid derivatives. Therefore, the structure of 3 is tentatively assigned to be 2-methoxy-3,4-diphenylthiete. The formation of both 3 and 4 is novel and unexpected. Thietes are a novel class of molecules and are established to be generally stable at room temperature.⁷ Since formation of the olefinic product 4 was most unexpected, the structure was confirmed by X-ray analysis (see experi-

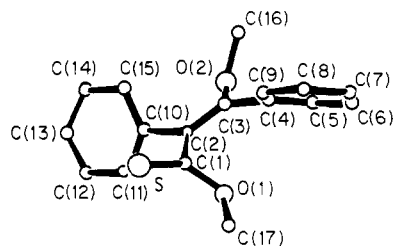


Figure 1. ORTEP drawing of 4.

mental Section). An ORTEP diagram for 4 is shown in Figure 1. As is evident from the figure, 4 has a *cis* geometry (*cis*-cinnamate) and is *s-transoid* with respect to α, β -unsaturated thiocarbonyl chromophore. Interestingly, the ^1H and ^{13}C spectra of 4 in CDCl_3 and C_6D_6 solution at ambient temperatures showed signals corresponding to four methoxy groups in almost equal amounts. On the basis of this, we initially believed that both *cis* and *trans* isomers of 4 are formed upon photolysis of 1 in methanol. However, attempts to separate these isomers using conventional chromatography (column and TLC) were not successful. This in addition to our X-ray results suggested⁸ that the isomers present at room temperature in solution are not geometrical but conformational. Indeed, ^1H NMR at temperatures above 120°C in $\text{Me}_2\text{SO}-d_6$ corresponded to a single isomer, i.e., four methoxy signals coalesced into

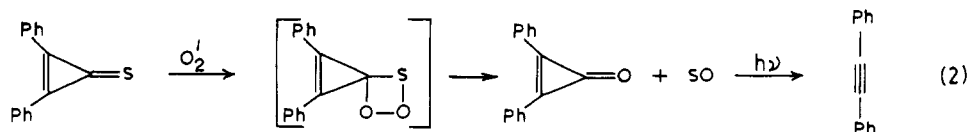
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two methoxy signals. Therefore, we believe that 4 is present in solution, at room temperature, in noninterconvertible *s*-transoid and *s*-cisoid conformations about α,β -unsaturated thiocarbonyl chromophore. High barrier for rotation around carbon-carbon single bonds having thiocarbonyl chromophore is precedented.⁹ Attempts to identify diphenylacetylene during benzene and methanol irradiation (deaerated solvents) did not reveal its presence.

Formation of 3 and 4 can be mechanistically rationalized as illustrated in Scheme I, involving the Norrish type α -cleavage process.³ The resulting diradical 5 undergoes rearrangement to thiocarbene as observed in cyclobutane systems and to thioketene carbene 7, and these intermediates are trapped by methanol to give 3 and 4. Involvement of intermediate 7 is consistent with the excited-state behavior of cyclopropenes wherein vinylcarbenes have frequently been proposed as intermediates.¹⁰ Further, the diradical 5 is readily trapped by ground-state thione 1 to give thiophene 2 and in benzene this appears to be the only pathway.⁶ It is interesting to note that 9 undergoes facile oxidation to 4; attempts to seek evidence for the presence of 9 were not successful; however, this appears to be the most reasonable pathway for the formation of 4. On the basis of the photobehavior of cyclopropenes¹¹ which readily eliminate carbon monoxide to give acetylenes and resist ring expansion to oxacarbene, the excited state behavior of 1 is most unexpected and is truly unique. It is indeed interesting to note that the two systems investigated, namely, cyclobutanethiones³ and cyclopropenethione, show similarity in their photobehavior. They undergo α cleavage and the resulting diradicals ring expand to thiocarbene. Surprisingly, in both systems elimination of carbon monosulfide is lacking.

The above results are not in agreement with the earlier report wherein diphenylacetylene was obtained upon photolysis of 1.⁴ For probing the reasons for this difference, a careful investigation, under various conditions, of the photolysis of 1 seemed appropriate. To our surprise, irradiation of 1 (benzene, ethanol, acetonitrile) in an unpurified nitrogen atmosphere gave diphenylacetylene as the only product (yield, about 80%) and 2 was not present in the product mixture. However, an action plot reveals that the precursor for diphenylacetylene is diphenylcyclopropenone and not diphenylcyclopropenethione. Indeed, with the use of appropriate filters, the reaction could be stopped at the stage of diphenylcyclopropenone. We believe that diphenylcyclopropenone has arisen through self-sensitized singlet-oxygen oxidation of 1,¹² oxygen being present as an impurity in the nitrogen used. It is interesting to note that oxidation is much faster compared to α -cleavage process. Confirming the above rational is the observation that singlet oxygen, generated by dye sensitization (methylene blue, rose bengal) and by

thermal decomposition of triphenylphosphite ozonide, readily reacted with 1 to yield diphenylcyclopropenone (eq 2). No diphenylacetylene is obtained during the above oxidation. Singlet oxygen appears to selectively react with the thiocarbonyl chromophore of 1. Although the detailed mechanism of the oxidation is still a subject of investigation,¹² we speculate that this might involve the 1,2,3-dioxathietane intermediate. Interestingly, the decomposition of such an intermediate, if involved, is not a chemiluminescent process as no diphenylacetylene, the expected product from the excited state of diphenylcyclopropenone, is detected during singlet-oxygen oxidation.¹³

We have thus demonstrated the occurrence of α cleavage in yet another strained system. An earlier report of elimination of carbon monosulfide upon photoexcitation of 1 suggests involvement of the oxidation of 1 through a self-sensitized process. It is apparent that the photobehavior of 1 cannot be extrapolated from that of cyclopropenones. Little is known about the generality of α cleavage in thiocarbonyl systems and much synthetic and mechanistic work remains to be done.

Experimental Section

Diphenylcyclopropenethione was prepared following the reported procedure⁵ and was purified by column chromatography (silica gel, hexane/benzene). Solvents for irradiation were distilled once prior to use. A 450-W Hanovia medium-pressure mercury lamp was used as the source of UV radiation and was contained in a water-cooled Pyrex immersion well. The 450-mL irradiation vessel had the provision for gas inlet. Irradiation was conducted while oxygen-free (freed using alkaline solution of pyrogallol) nitrogen was bubbled through. Irradiation in the visible region (oxidation experiments) was conducted with 500-W tungsten lamps as external sources. The sample to be irradiated was contained in a water-cooled irradiation vessel containing a gas inlet. All irradiations were monitored by tlc and were run until essential disappearance of the starting material.

1. Irradiation of Diphenylcyclopropenethione in Benzene. Diphenylcyclopropenethione (1.8 g, 0.02 mol; 400 mL) was irradiated (450-W medium-pressure mercury lamp) for 60 h, while N_2 was continuously bubbled through. Evaporation of the solvent and purification of the product mixture by column chromatography (silica gel, hexane/benzene) and recrystallization of the first fraction in chloroform gave 2,3,5,6-tetraphenylthieno[3,2-*b*]thiophene as a white crystalline solid⁶ (yield 30%, 540 mg, mp 274 °C). Solubility of 2 is very low in most organic solvents. Although the following spectral properties correspond to the structure proposed, attempts to confirm it by X-ray analysis could not be realized as no good single crystals of 2 could be obtained. Spectral data of 2 are summarized below: UV ($CHCl_3$) λ_{max} 245 nm ($\epsilon \sim 70000$); IR ($CHCl_3$) 2900, 1480, 1240, 1120, m; cm^{-1} ; 1H NMR ($CDCl_3$) δ 7.2 (8 H, m), 7.3 (8 H, m), 7.5 (4 H, m) ^{13}C NMR ($CDCl_3$) δ 149, 139, 134, 129.4, 129.18, 128.82, 128.54, 127.70; MS (250 °C, 70 eV), *m/e* 444, 312; exact mass 444.1006 \pm 0.0017. Anal. Calcd for $C_{30}H_{20}S_2$: C, 81.07; H, 4.54. Found: C, 80.70; H, 4.50.

2. Irradiation of Diphenylcyclopropenethione in Methanol. Diphenylcyclopropenethione (0.02 mol, 1.8 g; 400 mL) was irradiated as above in methanol for 9 h (the reaction is comparatively faster in methanol). Column chromatography of the product mixture gave 2 (yield, 270 mg, 15%), 3 (250 mg, 10%), and 4 (1.27 g, 50%). Compound 3 had the following spectral properties: UV ($CHCl_3$) δ_{max} 330 nm ($\epsilon \sim 900$); 244 (~ 70000);

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IR (neat) 1690, 1440, 1100–1250 (br) cm^{-1} ; $^1\text{H NMR}$ (CDCl_3) δ 4.1 (3 H, s), 6.15 (1 H, s), 7.3–8.1 (10 H, m); $^{13}\text{C NMR}$ (CDCl_3) δ 134.79, 133.30, 129.98, 129.77, 128.99, 128.74, 128.13, 70.1 (d), 59.5 (q); MS (70 eV), m/e 254, 178, 165, 121, 105, 77. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{SO}$: C, 75.58; H, 5.55. Found: C, 74.22; H, 5.32. The spectral data for 4 (mp 86–89 °C) are reported below ($^1\text{H NMR}$ and $^{13}\text{C NMR}$ data were collected at room temperature): UV (cyclohexane) λ_{max} 418 nm ($\epsilon \sim 600$), 314 (8300), 233 (14000); IR (CHCl_3) 1600, 1460, 1320, 1220, 1100 cm^{-1} ; $^1\text{H NMR}$ δ 3.2 (s), 3.3 (s), 3.6 (s), 4.0 (s), 7.0–7.4 (m) [singlets at δ 3.2 and 3.6 and δ 3.3 and 3.4 are of the same intensity]; $^{13}\text{C NMR}$ (CDCl_3) δ 216.37 (s), 216.05 (s), 159.55 (s), 156.43 (s), 138.17 (s), 137.25 (s), 135.07 (s), 133.29 (s), 130.3–126.98 (8 peaks), 58.62 (q), 58.38 (q), 58.18 (q), 58.06 (q); MS (70 eV), m/e 284, 151, 105, 77. Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{SO}_2$: C, 71.82; H, 5.67. Found: C, 71.55; H, 5.74.

Both ^{13}C and $^1\text{H NMR}$ spectra indicate the presence of two isomers at room temperature. However, attempts to separate these isomers using column (silica gel) and thin-layer (silica gel and alumina) chromatography were not successful. Therefore, it was thought that these are conformational and not geometrical isomers.

$^1\text{H NMR}$ spectra were run at variable temperatures (–60–150 °C) in $\text{Me}_2\text{SO}-d_6$. Spectra remained unaltered in the temperature range –60–100 °C. However, broadening and coalescing of four OCH_3 peaks (δ 3.2, 3.3, 3.6, 4.0) were observed in the range 100–120 °C and above 120 °C only two peaks (δ 3.2 and 3.8) corresponding to OCH_3 groups, expected for a single isomer of 4 was observed. No attempts were made to record $^{13}\text{C NMR}$ spectra at different temperatures. We suggest that 4 exists in solution at room temperature as noninterconvertible conformational isomers. Such hindrance for rotation around C–C single bonds carrying thio-carbonyl as opposed to carbonyl is known and can be attributed to the larger size of the sulfur atom.⁹

X-ray Analysis of 4. Slow evaporation of the benzene-chloroform solution of 4 gave platelike crystals: $a = 8.729$ (1) Å, $b = 20.227$ (3) Å, $c = 9.523$ (1) Å, $\beta = 114.69$ (1)°, $V = 1527.7$ Å³, molecular formula $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}$, $Z = 4$, d_{measd} (floatation in aqueous KI) = 1.24 g/cm^3 , d_{calcd} = 1.239 g/cm^3 , space group $P2_1/n$. Intensity data were collected on a Enraf-Nonius CAD-4 diffractometer using monochromated $\text{Cu K}\alpha$ radiation in $\omega/2\theta$ scan mode for a crystal of dimensions $1.0 \times 0.8 \times 0.3$ mm³. A total of 2510 reflections were collected out of which 2002 were significant [$|F_0| \geq 3\sigma(|F_0|)$]. The structure was solved by direct methods (MULTAN 80).¹⁴ The full-matrix least-squares refinement of the positional and anisotropic thermal parameters of 20 non-hydrogen atoms and positional and isotropic thermal parameters of 16 hydrogen atoms (kept fixed in the final cycles) using the weighting scheme $w = 1/[\sigma^2(F) + 0.18|F|^2]$ has led to a final R value of 7.0% for significant reflections.

3. Oxidation of Diphenylcyclopropenethione. a. Direct Excitation. Diphenylcyclopropenethione (0.01 M) in chloroform, acetonitrile, or ethanol was irradiated (450-W mercury lamp or 500-W tungsten lamp) while nitrogen, without passing through alkaline pyrogallol, was bubbled through. After 48 h of irradiation, diphenylacetylene was isolated in 80% yield. The reaction was followed by TLC and the primary product was identified to be diphenylcyclopropenone. By an independent control experiment we showed that diphenylcyclopropenone could be converted to diphenylacetylene in the above solvents with either of the above irradiations.⁸ Surprisingly, formation of 2 was not detected under these conditions.

b. Dye Sensitization. Dye-sensitized irradiation of 1 was conducted by irradiating aerated solutions of 1 (0.01 M) in the presence of appropriate dyes (10^{-4} M, methylene blue, or 100 mg of polymer-bound rose bengal). Selective excitation of the dye was achieved with Corning glass filter CS-2.58. Diphenylcyclopropenone was the only isolated product (65%).

c. Singlet Oxygen Generated by the Decomposition of Triphenyl Phosphite Ozonide. Triphenyl phosphite ozonide was prepared at –78 °C in dichloromethane by following the reported procedure.¹⁵ The above solution was warmed to –10 °C at which time oxygen evolution was visible and at this stage

1 was added. Upon keeping the reaction mixture at room temperature for about an hour, diphenylcyclopropenone was isolated as the only product (75%).

4. Control Experiments. Refluxing 1 in benzene and methanol for more than 24 h did not yield products 2–4. 1 is stable under these conditions.

Diphenylcyclopropenone failed to react with singlet oxygen generated by dye sensitization or by thermal decomposition of triphenyl phosphite ozonide.

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Registry No. 1, 2570-01-6; 2, 35093-32-4; 3, 82246-85-3; (E)-4, 82246-86-4; oxygen, 7782-44-7.

Supplementary Material Available: Atomic coordinate and thermal parameter tables for 4 (6 pages). Ordering information is given on any current masthead page.

Reactions of Alkoxyppyrylium Salts with Dimethylsulfonium Methylide and Nitromethane Anion

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The nucleophilic reactions of certain pyrylium salts have been studied in detail and are the subject of extensive reviews.¹ Apparently, 2- or 4-alkoxyppyrylium salts have not been examined in this context. These salts, prepared by the O-alkylation of common pyrones,^{2,3} would yield specific polysubstituted benzenes when treated with a heteroatom-stabilized nucleophile. Few alternative methods permit construction of benzene rings, containing several substituents, from nonbenzenoid precursors.⁴ In this note, we report that the reaction of four pyrylium salts with dimethylsulfonium methylide⁵ and with the anion of nitromethane does yield benzenoids.

The reactions of pyrylium salts with ylides have been the subject of four brief reports. 2,4,6-Triphenylpyrylium perchlorate (15) with triphenylphosphonium methylide⁶ and 5 with a carboalkoxyphosphonate⁷ provided the expected benzene derivatives. The two reports of sulfur ylide reactions describe unprecedented ylide products. Tamura⁸

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