**2-(*tert*-Butyl Trithiocarbonato)acenaphthylenone (1i).** From 2-chloroacenaphthylenone, 3.0 g (90%) of trithiocarbonate was obtained after recrystallization from ethanol: mp 106–107 °C; IR (KBr) 2941, 2740, 1718, 1351, 1064, 995, 791, 772, 755 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 8.1–7.6 (m, 6 H), 6.3 (s, 1 H), 1.7 (s, 9 H).

Anal. Calcd for $C_{17}H_{16}OS_3$: C, 61.43; H, 4.81; S, 28.94. Found: C, 61.0; H, 4.5; S, 28.5.

**General Method for Preparation of 1,3-Dithiole-2-thiones (3).** The appropriate trithiocarbonate (1; 0.01 mol) was dissolved in a mixture of trifluoroacetic acid (10 mL), acetic acid (10 mL), and *p*-toluenesulfonic acid (0.1 g). The solution was warmed on a steam bath for 30 min and then refluxed for 30 min more. If the trithione **3** did not crystallize from the cooled solution, water (75 mL) was added, and the resulting oil was extracted with diethyl ether (75 mL), dried ($MgSO_4$), and evaporated under vacuum. The resulting oil was distilled under vacuum.

**4-Phenyl-1,3-dithiole-2-thione (3a).** From **1a**, 1.4 g (67%) of trithione was obtained: mp 116–117 °C (lit.[4] mp 117–118 °C); IR (KBr) 3100, 1486, 1446, 1055, 1045, 890, 740, 675 $cm^{-1}$.

**4-(Acetoxymethyl)-1,3-dithiole-2-thione (3b).** From **1b**, 2.0 g (98%) of trithione was obtained: bp 140–143 °C (0.05 torr); IR (neat) 2985, 1748, 1370, 1227, 1064, 1031 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.0 (t, $J$ = 2.1 Hz, 1 H), 4.9 (d, $J$ = 2.1 Hz, 2 H), 2.1 (s, 3 H).

Anal. Calcd for $C_6H_6O_2S_3$: C, 34.94; H, 2.91; S, 46.63. Found: C, 34.7; H, 2.8; S, 46.3.

**4-Methyl-1,3-dithiole-2-thione (3c).** From **1c**, 1.45 g (98%) of trithione was obtained and recrystallized from diethyl ether at −30 °C (60% yield); mp 30–31 °C (lit.[4,5] mp 32 °C); bp 90–93 °C (0.05 torr); NMR ($CDCl_3$) $\delta$ 6.7 (q, $J$ = 1.2 Hz, 1 H), 2.3 (d, $J$ = 1.2 Hz, 3 H).

**1,4-Phenylenebis(1,3-dithiole-2-thione) (3d).** From **1d**, 2.7 g (78%) of trithione was obtained, mp 345–347 °C (lit.[6] mp 347 °C).

**4,5-Dimethyl-1,3-dithiole-2-thione (3e).** From **1e**, 1.5 g (90%) of trithione was obtained after recrystallization from methanol, mp 95–96 °C (lit.[5] mp 96 °C).

**4,5-Trimethylene-1,3-dithiole-2-thione (3f).** From **1f**, 1.2 g (70%) of trithione was obtained after recrystallization from ethyl acetate, mp 107–108 °C (lit.[5] mp 109 °C).

**4,5-Dihydronaphtho[3,4-*d*]-1,3-dithiole-2-thione (3g).** From **1g**, 2.3 g (87%) of trithione was obtained after recrystallization from ethyl acetate: mp 114–116 °C (lit.[5] mp 116 °C); NMR ($CDCl_3$) $\delta$ 7.2 (m, 3 H), 7.0 (m, 1 H), 3.0 (m, 2 H), 2.8 (m, 2 H); mass spectrum, $m/e$ 236 ($M^+$), 203, 192, 160, 128, 115.

**Indeno[2,3-*d*]-1,3-dithiole-2-thione (3h).** From **1h**, 1.3 g (60%) of trithione was obtained: mp 127–129 °C (lit.[5] mp 131 °C); NMR ($CDCl_3$) $\delta$ 5–7.2 (m, 4 H), 4.7 (s, 2 H).

**4,5-(1,8-Naphtho)-1,3-dithiole-2-thione (3i).** From **1i**, 2.2 g (86%) of trithione was obtained after recrystallization from dioxane: mp 234–235 °C; IR (KBr) 1429, 1099, 1053, 800, 758 $cm^{-1}$; mass spectrum, $m/e$ 258 ($M^+$), 214, 170, 138, 126, 107, 93, 69.

Anal. Calcd for $C_{13}H_6S_3$: C, 60.44; H, 2.30; S, 37.23. Found: C, 60.8; H, 2.2; S, 37.2.

**3-Propynyl *tert*-Butyl Trithiocarbonate (4, R = H).** From 3-bromo-1-propyne, 2.0 g (100%) of trithiocarbonate was obtained and distilled at 0.1 torr: mp 78–80 °C (94% yield); IR (neat) 3330, 2857, 2128 (w), 1351, 1064, 800 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 4.0 (d, $J$ = 2.1 Hz, 2 H), 2.2 (t, $J$ = 2.1 Hz, 1 H), 1.6 (s, 9 H).

Anal. Calcd for $C_8H_{12}S_3$: C, 47.02; H, 5.92; S, 47.06. Found: C, 46.8; H, 5.7; S, 46.8.

**1-Phenyl-3-propynyl *tert*-Butyl Trithiocarbonate (4, R = $C_6H_5$).** From 3-bromo-1-phenyl-1-propyne,[7] 2.7 g of trithiocarbonate was obtained and used directly in the next syntheses: IR (neat) 2899, 2247 (w), 1508, 1355, 1163, 1064, 800, 758, 687 $cm^{-1}$; NMR ($CDCl_3$) $\delta$ 7.3 (m, 5 H), 4.3 (s, 2 H), 1.6 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}S_3$: C, 59.98; H, 5.71; S, 34.31. Found: C, 59.6; H, 5.8; S, 33.9.

**4-(Bromomethylene)-2-(*tert*-butylthio)-1,3-dithiolylium Bromide (5, R = H).** A solution of 2 g of 4 (R = H) in 25 mL of dichloromethane at −10 °C was treated dropwise with a solution of 1.6 g of bromine in 25 mL of dichloromethane. A precipitate formed immediately and was collected and air-dried. The yellow solid (3.5 g, 97%) was stable for a short time but began to lose isobutylene at room temperature: NMR (HOAc-$d_4$) $\delta$ 6.8 (t, $J$ = 2.5 Hz, 1 H), 4.9 (d, $J$ = 2.5 Hz, 2 H), 1.9 (s, 9 H); IR (KBr) 2899, 1412, 1227, 1072 (vs), 903, 779, 719 $cm^{-1}$.

**4-(Bromomethylene)-1,3-dithiolane-2-thione (6).** From **5**, when the mixture was allowed to stand overnight at room temperature, 2.2 g (100%) of trithione was obtained: NMR ($CDCl_3$) $\delta$ 6.2 (t, $J$ = 2.0 Hz, 1), 4.6 (d, $J$ = 2.0 Hz, 2 H); IR (KBr) 3030 (w), 1587 (w), 1379, 1258, 1055 (vs), 1042, 893, 781, 717 $cm^{-1}$.

Anal. Calcd for $C_4H_3BrS_3$: C, 21.15; H, 1.32; S, 42.35; Br, 35.18. Found: C, 20.8; H, 1.3; S, 42.0; Br, 34.8.

When the mixture was allowed to stand, a mixture of **7** and an insoluble polymer was formed. We detected **7** by its NMR spectrum when the mixture was extracted with deuteriochloroform: NMR ($CDCl_3$) $\delta$ 6.9 (t, $J$ = 0.9 Hz, 1 H), 4.4 (d, $J$ = 0.9 Hz, 2 H).[8] Yellow polymer slowly precipitated from the chloroform.

**4-(α-Bromobenzylidene)-1,3-dithiolane-2-thione (6, R = $C_6H_5$).** Compound **6** was prepared from **4** (R = $C_6H_5$) and bromine in a manner similar to that of the reaction of **4** (R = H) except aqueous $NaHCO_3$ (25 mL, saturated solution) was added, followed by solid $Na_2S_2O_5$ until the solution was colorless. The dichloromethane solution was separated, dried ($MgSO_4$), and evaporated. The yellow solid (2.8 g, 93%) was a mixture of cis and trans exo isomers in a ratio of 1.8:1: NMR ($CDCl_3$) $\delta$ 7.4 (m, 5 H), 4.8 (s, 1.3 H), 4.3 (s, 0.7 H). This mixture did not change on recrystallization from ethanol, nor did it isomerize to a compound like **7**.[9]

Anal. Calcd for $C_{10}H_7BrS_3$: C, 39.61; H, 2.31; S, 31.72, Br, 26.35. Found: C, 39.4; H, 2.2; S, 31.6; Br, 26.0.

**Registry No.** **1a**, 71988-71-1; **1b**, 72030-06-9; **1c**, 71988-72-2; **1d**, 71988-73-3; **1e**, 71988-74-4; **1f**, 71988-75-5; **1g**, 71988-76-6; **1h**, 71988-77-7; **1i**, 71988-78-8; **3a**, 2314-61-6; **3b**, 71988-79-9; **3c**, 3608-38-6; **3d**, 68144-36-5; **3e**, 17534-27-9; **3f**, 17534-29-1; **3g**, 17784-42-8; **3h**, 17534-42-8; **3i**, 71988-80-2; **4** (R = H), 71127-44-1; **4** (R = $C_6H_5$), 71127-45-2; **5** (R = H), 71988-81-3; **6** (R = H), 71988-82-4; *cis*-**6** (R = $C_6H_5$), 71988-83-5; *trans*-**6** (R = $C_6H_5$), 71988-84-6; **7**, 71988-85-7; sodium *tert*-butyltrithiocarbonate, 71127-42-9; *tert*-butylmercaptan, 75-66-1; carbon disulfide, 75-15-0; phenacyl bromide, 70-11-1; 1-acetoxy-3-chloroacetone, 40235-68-5; chloroacetone, 78-95-5; 1,4-bis(bromoacetyl)benzene, 946-03-2; 3-bromo-2-butanone, 814-75-5; 2-chlorocyclopentanone, 694-28-0; 2-bromo-α-tetralone, 13672-07-6; 2-bromo-1-indanone, 1775-27-5; 2-chloroacenaphthylenone, 16269-26-4; 3-bromo-1-propyne, 106-96-7; 3-bromo-1-phenyl-1-propyne, 1794-48-5.

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(8) The NMR spectrum of **7** is similar to that of 4-(bromomethyl)-1,3-dithiol-2-one prepared by an alternative unambiguous synthesis.
(9) The conjugative effect of the phenyl ring probably prevents the isomerization to an endo double bond.

## Photodimerization of Propellanones Involving a Cyclobutanone Moiety via an Oxacarbene Intermediate

Yoshihiro Fukuda,* Toshihiko Negoro, Koji Kimura, and Yoshinobu Odaira

*Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan*

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There has been remarkable interest recently in the chemistry of propellane systems, particularly in view of structure–reactivity relationships,[1] and the above relationships on various [*n*.3.2]propellanes have attracted our

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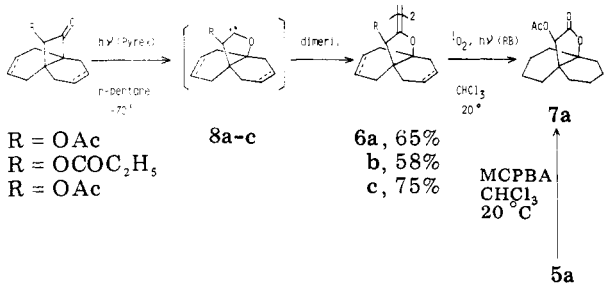
0022-3263/80/1945-0177$01.00/0 

Scheme I[a]




5a, R = OAc
b, R = $OCOC_2H_5$
c, R = OAc

8a-c

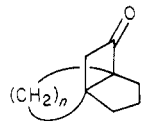
6a, 65%
b, 58%
c, 75%

7a

5a

[a] a and b, two saturated six-membered rings; c, two unsaturated six-membered rings.

attention.[2] In this connection, we have recently reported on the photochemical reaction of [*n*.3.2]propellanones **1–4** involving a cyclobutanone moiety in methanol.[2i]



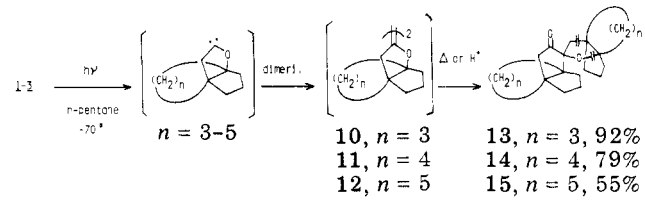
1, *n* = 3
2, *n* = 4
3, *n* = 5
4, *n* = 6

In this paper, we wish to report on the effective dimerization of oxacarbene intermediates generated by the photolysis of the cyclobutanones incorporated into propellane systems. Although the photochemistry of cyclobutanones has been widely investigated,[3] especially with respect to ring expansion, only one work has so far been reported on the dimerization of oxacarbene intermediates generated photochemically.[4]

Irradiation of 12-acetoxy[4.4.2]propellan-11-one (**5a**)[5] in *n*-pentane (0.03 M) in a degassed sealed Pyrex tube at −70 °C for 5 h with a high-pressure Hg lamp gave the oxacarbene dimer (**6a**) in 65% yield (see Scheme I).

The structure of **6a** was based on the elemental analysis and the spectral data (see Experimental Section). In particular, in the $^{13}C$ NMR spectrum of **6a**, the unusually high field positions of the olefinic carbon signals (δ 101.00 and 100.25) are due to the β oxygen atom.[6] Moreover, in order to make sure of the presence of a tetrasubstituted double bond in **6a**, dye-sensitized photooxygenation of **6a** was undertaken by using rose bengal as sensitizer in chloroform at 20 °C to afford propellane lactone (**7a**) in 48% yield. The spectral data and the GLC retention time of **7a** agreed with those of the authentic sample prepared independently by the Baeyer–Villiger oxiation of **5a** using *m*-chloroperbenzoic acid.

Scheme II



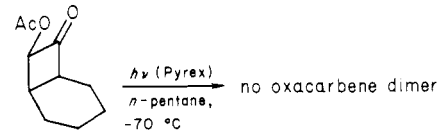

*n* = 3–5

10, *n* = 3
11, *n* = 4
12, *n* = 5

13, *n* = 3, 92%
14, *n* = 4, 79%
15, *n* = 5, 55%

On irradiation of 12-propionoxy derivative **5b** and 12-acetoxy[4.4.2]propella-3,8-dien-11-one (**5c**), the corresponding oxacarbene dimers **6b** and **6c** were likewise obtained in 58 and 75% yields, respectively.[7]

On the other hand, similar irradiation of a bicyclic homologue of **5a**, that is, 8-acetoxybicyclo[4.2.0]octan-7-one (**9**), afforded no oxacarbene dimers at all but a complex




9

mixture of products. From the above result, it may be considered that the propellane ring system plays a key role in the present dimerization of oxacarbene intermediates.

Furthermore, for the purpose of knowing the influence of 12-acyloxy substituents on the present dimerization, we have investigated the photochemical dimerization of [*n*.3.2]propellanones **1–3**. Similar irradiation of 0.05 M *n*-pentane solutions of **1–3** gave oxacarbene dimers **10–12** in 92, 79, and 55% yields, respectively.[8] Although the spectral data of crude oxacarbene dimers **10–12** before purification resembled closely those of **6a**, **10–12** isomerized readily by preparative GLC or column chromatography on silica gel (owing to their instability) to the isomeric dimers **13–15**, having the spirobispropellane structure.

The spectral data (IR, mass, and NMR) and the elemental analyses of **13–15** supported the structure illustrated in Scheme II. For example, the off-resonance $^{13}C$ NMR spectrum of sole product **13** suggested six quaternary carbon atoms and 14 secondary ones, and then, the single carbonyl peak (having a shift of δ 216.99) and the two singlet peaks (δ 104.95 and 93.51) are assignable to the cyclopentanone carbonyl carbon atom, the spiro one, and the bridgehead one adjacent to the oxygen atom in **13**, respectively.

To elucidate the thermal isomerization of the oxacarbene dimers **10–12**, we heated them in degassed sealed tubes. Heating the tube containing **10** for 5 min at 200 °C and also those of **11** and **12** (for 15 min at 220 °C and for 40 min at 240 °C, respectively) gave the isomeric dimers **13–15** exclusively. Particularly, the oxacarbene dimer **10**, even at room temperature, could be converted to **13** gradually, and after 5 days, **10** isomerized to **13** completely. The above process was monitored by measurement of the in-

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(6) It is too difficult to assign the peaks of its $^{13}C$ NMR spectrum to individual carbon atoms owing to complete mixing of two stereoisomers of **6a**.

(7) It is evidently reasonable that **6a–c** were formed by dimerization of oxacarbene intermediates (**8a–c**) generated by photochemical ring expansion of **5a–c**, because **8a–c** was trapped easily as a pair of acetals by methanol.

(8) Similar irradiation of **4** gave little dimer but a large amount of cycloelimination product, that is, bicyclo[6.3.0]oct-1(8)-ene.[2i]

frared and $^{13}C$ NMR spectra of the compounds. The carbonyl absorption at 1730 $cm^{-1}$ and the singlet peak ($\delta$ 104.95) assigned to the spiro carbon atom of **13** became larger in proportion to the disappearance of the two singlet peaks ($\delta$ 106.19 and 103.92), which may be assigned to the olefinic carbon atoms of two stereoisomers of **10**. Similar isomerization of **10** to **13** occurs on slightly acidic silica gel.

Such thermal or acidic isomerizations of enol ethers to carbonyl compounds via 1,3-alkyl shifts are known.[9]

Consequently, the obtainable result mentioned above may be explicable by the following account. Because of the steric requirement of the constrained propellane ring system, ring expansion proceeds smoothly to generate an oxacarbene intermediate. On the contrary, the reversion to the starting propellanone from the oxacarbene intermediate may be suppressed due to the increase of overall ring strain, and, as a result, dimerization occurs predominantly. When there are no acyloxyl substituents at the 12 position, the oxacarbene dimers **10–12** isomerize readily to the more stable isomeric dimers **13–15**. On the other hand, in the cases of **6a–c**, isomerization may be difficult, owing to the steric hindrance of the bulky acyloxyl substituents in addition to the constrained propellane ring systems facing each other.

## Experimental Section

**General Methods.** Melting points were measured in a sealed tube and are uncorrected. Infrared spectra were recorded on a JASCO IR-G spectrometer. $^1H$ NMR and $^{13}C$ NMR spectra were obtained on JEOL JNM-PS-100 and JEOL JNM-FX60S spectrometers, respectively, using $CCl_4$ or $CDCl_3$ as a solvent and $Me_4Si$ as an internal standard. Mass spectra were determined with a Hitachi RMU-6E spectrometer. UV spectra were recorded on a Hitachi 356 spectrometer. Analytical GLC was carried out on a Hitachi 163 gas chromatograph (1 m × 3 mm column: A, 10% FFAP; B, 5% SE-30; C, 5% OV-17), and preparative GLC separation was undertaken on a Varian Aerograph 90-P or 920 gas chromatograph (5 ft × 0.25 in. columns: D, 10% FFAP; E, 5% SE-30; F, 5% OV-17).

**[*n*.3.2]Propellanones 1–4.** [*n*.3.2]Propellanones **1–4** were prepared as described previously.[2i]

**12-Acyloxy[4.4.2]propellanones (5a–c) and *endo*-8-Acetoxybicyclo[4.2.0]octan-7-one (9).** Propellanones **5a–c** and bicyclic cyclobutanone **9** were prepared according to the procedures reported by Bloomfield[5,10] and Miller et al.[11]

**12-Acetoxy[4.4.2]propellan-11-one (5a):** mp 73–74 °C; IR (KBr) 1775, 1735, 1220 $cm^{-1}$; MS *m/e* 236 ($M^+$), 148 (base); $^1H$ NMR ($CCl_4$) $\delta$ 1.10–2.00 (m, 16 H), 2.12 (s, 3 H), 5.82 (s, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 20.21 (t), 20.40 (t), 20.80 (q), 22.09 (t), 23.33 (t), 26.57 (t), 27.48 (t), 29.95 (t), 31.19 (t), 36.00 (s), 54.58 (s), 80.44 (d), 169.84 (s), 204.66 (s); UV (MeOH) $\lambda_{max}$ 295 nm ($\epsilon$ 78). Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 70.86; H, 8.81.

**12-Propionoxy[4.4.2]propellan-11-one (5b):** IR (neat) 1775, 1735, 1160 $cm^{-1}$; MS *m/e* 250 ($M^+$), 165 (base); $^1H$ NMR ($CCl_4$) $\delta$ 1.10 (t, 3 H), 1.20–2.00 (m, 16 H), 2.34 (q, 2 H), 5.96 (s, 1 H); UV (MeOH) $\lambda_{max}$ 295 nm ($\epsilon$ 80). Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.97; H, 8.97.

**12-Acetoxy[4.4.2]propella-3,8-dien-11-one (5c):** mp 72–73 °C (lit.[10] 73.0–73.7 °C); IR (KBr) 3040, 1780, 1740, 1630, 1210 $cm^{-1}$; UV (MeOH) $\lambda_{max}$ 310 nm ($\epsilon$ 50).

***endo*-8-Acetoxybicyclo[4.2.0]octan-7-one (9):**[11] IR (neat) 1780, 1735, 1220 $cm^{-1}$; MS *m/e* 182 ($M^+$); $^1H$ NMR ($CCl_4$) $\delta$ 1.00–2.20 (m, 8 H), 2.05 (s, 3 H), 2.72 (m, 1 H), 3.00 (m, 1 H), 5.52 (dd, 1 H, *J* = 8, 1 Hz); UV (MeOH) $\lambda_{max}$ 290 nm ($\epsilon$ 57).

**General Irradiation Procedure.** *n*-Pentane solutions (0.03–0.05 M) of **1–3**, **5a–c**, and **9** in Pyrex tubes were degassed, sealed, and irradiated with a high-pressure Hg lamp (500 W) for 3–8 h at −70 °C (dry ice–ethanol bath). After evaporation of *n*-pentane, the residue was analyzed by GLC (columns A, B, and C), and products were purified by recrystallization or preparative GLC (columns D and E). Yields of the products were determined by GLC analyses based on the reacted cyclobutanones, except for **5a–c**.

**Irradiation of 5a.** Irradiation of **5a** (420 mg, 1.78 mmol) for 5 h (100% conversion) gave 403 mg of a white precipitate, which, upon recrystallization from benzene–*n*-hexane, yielded 272 mg (0.58 mmol) of **6a** (65%): mp 229–230 °C; IR (KBr) 1730, 1220, 1040, 950 $cm^{-1}$; MS *m/e* 472 ($M^+$, base), 430, 412, 388; $^1H$ NMR ($CCl_4$) $\delta$ 1.30–2.00 (m, 32 H), 2.08 (s, 6 H), 5.98 (s, 2 H). Anal. Calcd for $C_{28}H_{40}O_6$: C, 71.16; H, 8.53. Found: C, 70.93; H, 8.61.

**Irradiation of 5b.** Irradiation of **5b** (519 mg, 2.08 mmol) for 8 h (100% conversion) gave 464 mg of the product mixture, which, upon recrystallization from *n*-hexane, yielded 302 mg (0.60 mmol) of **6b** (58%): 106–107 °C; IR (KBr) 1730, 1170, 1070 $cm^{-1}$; MS *m/e* 500 ($M^+$, base), 443, 426, 388; $^1H$ NMR ($CCl_4$) $\delta$ 1.20 (t, 6 H), 1.34–2.10 (m, 32 H), 2.36 (q, 4 H), 6.04 (s, 2 H). Anal. Calcd for $C_{30}H_{44}O_6$: C, 71.97; H, 8.86. Found: C, 71.87; H, 8.88.

**Irradiation of 5c.** Irradiation of **5c** (317 mg, 1.37 mmol) for 4 h (98% conversion) gave 314 mg of a white precipitate, which, upon recrystallization from benzene, yielded 233 mg (0.50 mmol) of **6c** (75%): 122–123 °C; IR (KBr) 3030, 1730, 1630, 1220, 1060 $cm^{-1}$; MS *m/e* 464 ($M^+$, base), 404; $^1H$ NMR ($CCl_4$) $\delta$ 1.60–2.80 (m, 16 H), 1.90 (s, 3 H), 2.02 (s, 3 H), 5.42 and 5.54 (2 s, 2 H), 5.60–6.12 (m, 8 H). Anal. Calcd for $C_{28}H_{32}O_6$: C, 72.39; H, 6.94. Found: C, 72.50; H, 7.09.

**Irradiation of 9.** Irradiation of **9** (254 mg, 1.40 mmol) for 3 h (100% conversion) afforded 242 mg of the product mixture, the GLC analysis (columns A and C) of which showed more than 20 peaks. But the mass spectrum of the crude products indicated no dimeric mass number.

**Irradiation of 1.** Irradiation of **1** (229 mg, 1.53 mmol) for 3 h (98% conversion) gave 225 mg of the product mixture including **10** (92%). Although purification of **10** by preparative GLC (column D, column temperature 200 °C) or silica gel chromatography was unsuccessful, the isomeric dimer **13** was obtained almost quantitatively. **10**: IR (neat) 1640, 1180, 1040, 930 $cm^{-1}$; MS *m/e* 300 ($M^+$); $^1H$ NMR ($CCl_4$) $\delta$ 1.00–2.60 (m, 28 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 25.22 (t), 25.46 (t), 28.43 (t), 29.20 (t), 30.05 (t), 30.17 (t), 34.19 (t), 35.69 (t), 38.50 (t), 39.19 (t), 39.72 (t), 40.85 (t), 48.08 (s), 50.44 (s), 63.11 (t), 64.81 (t), 93.34 (s), 96.14 (s), 103.92 (s), 106.19 (s). **13**: mp 81–82 °C; IR (KBr) 1730, 1110, 1030, 960 $cm^{-1}$; MS *m/e* 300 ($M^+$), 272, 192, 80 (base); $^1H$ NMR ($CCl_4$) $\delta$ 0.96–2.14 (m, 24 H), 1.70 (d, 1 H, *J* = 14 Hz), 1.94 (d, 1 H, *J* = 16 Hz), 2.28 (d, 1 H, *J* = 14 Hz), 2.72 (d, 1 H, *J* = 16 Hz); $^{13}C$ NMR ($CDCl_3$) $\delta$ 24.82 (t), 25.17 (t), 25.51 (t), 27.00 (t), 34.14 (t), 37.46 (t), 37.69 (t), 39.01 (t), 41.01 (t), 41.58 (t), 41.81 (t), 42.82 (t), 48.27 (t), 52.73 (s), 60.34 (s), 61.31 (s), 93.51 (s), 104.95 (s), 216.99 (s). Anal. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.92; H, 9.20.

**Irradiation of 2.** Irradiation of **2** (159 mg, 0.97 mmol) for 3 h (100% conversion) gave 139 mg of the product mixture including **11** (79%). Attempted isolation of **11** by preparative GLC (column F, column temperature 220 °C) afforded **14** (a mixture of two stereoisomers). **11**: IR (neat) 1640, 1180, 1030 $cm^{-1}$; MS *m/e* 328 ($M^+$); $^1H$ NMR ($CCl_4$) $\delta$ 0.98–2.40 (m, 32 H). **14**: IR (neat) 1730, 1120, 1000 $cm^{-1}$; MS *m/e* 328 ($M^+$), 300, 179, 121 (base); $^1H$ NMR ($CCl_4$) $\delta$ 0.92–2.60 (m, 32 H). Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83. Found: C, 80.23; H, 9.74.

**Irradiation of 3.** Irradiation of **3** (101 mg, 0.57 mmol) for 3 h (100% conversion) gave 98 mg of the product mixture including **12** (55%). Attempted isolation of **12** by preparative GLC (column F, column temperature 240 °C) afforded **15** (a mixture of three stereoisomers). **12**: IR (neat) 1650, 1190, 1070 $cm^{-1}$; MS *m/e* 356 ($M^+$); $^1H$ NMR ($CCl_4$) $\delta$ 1.00–2.30 (m, 36 H). **15**: IR (neat) 1730, 1100, 1010, 950 $cm^{-1}$; MS *m/e* 356 ($M^+$), 220, 136, 93 (base); $^1H$ NMR ($CCl_4$) $\delta$ 0.94–2.54 (m, 36 H). Anal. Calcd for $C_{24}H_{36}O_2$: C, 80.85; H, 10.18. Found: C, 80.71; H, 10.36.

**Photooxygenation of 6a and Baeyer–Villiger Oxidation of 5a.** **6a** (48 mg, 0.1 mmol) in 10 mL of $CHCl_3$ containing rose

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bengal ($2.0 \times 10^{-3}$ M) was irradiated under a current of oxygen for 30 min at 20 °C in the standard manner.[12] After removal of the solvent under reduced pressure, the GLC analysis (columns A and C) of the product mixture showed that the major product was **7a** (48%) by comparing its retention time of GLC with that of the authentic sample prepared independently. **7a** was isolated by preparative GLC (column F, column temperature 200 °C), and its spectral data agreed with those of the authentic sample described below.

A 400-mg (1.69 mmol) sample of **5a** and 600 mg (3.48 mmol) of 85% *m*-chloroperbenzoic acid (MCPBA) were dissolved in 50 mL of $CHCl_3$, and the resultant solution was stirred at 20 °C for 2 days. The solution was washed sequentially with sodium sulfite solution, aqueous $NaHCO_3$, and water, dried ($Na_2SO_4$), and evaporated in vacuo to afford 425 mg of two isomers (4:1) of propellane lactone in 98% yield. The two isomers were separated by preparative GLC (columns E and F, column temperature 200 °C), and the major isomer was **7a**: mp 103–104 °C; IR (KBr) 1775, 1740, 1210, 1080, 950 $cm^{-1}$; MS *m/e* 252 ($M^+$), 208, 166, 148 (base); $^1H$ NMR ($CCl_4$) δ 1.12–2.00 (m, 16 H), 2.16 (s, 3 H), 5.84 (s, 1 H); $^{13}C$ NMR ($CDCl_3$) δ 20.01 (t), 20.34 (t), 20.79 (t and q), 22.94 (t), 27.48 (t), 29.37 (t), 30.08 (t), 36.39 (t), 43.79 (s), 72.77 (d), 83.82 (s), 169.90 (s), 172.20 (s). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.66; H, 8.30.

**Thermal Isomerization of 10–12 to 13–15.** After compounds **10–12** were heated in degassed sealed capillaries at 200, 220, and 240 °C for 5, 15, and 40 min, respectively, their IR spectra showed the carbonyl absorption at 1730 $cm^{-1}$ in each case.

**Registry No.** 1, 71734-13-9; 2, 71734-14-0; 3, 71734-15-1; **5a**, 71987-75-2; **5b**, 71987-76-3; **5c**, 7176-87-6; **6a**, 71987-77-4; **6b**, 71987-78-5; **6c**, 71987-79-6; **7a**, 71987-80-9; **9**, 71987-81-0; **10**, 71987-82-1; **11**, 71987-83-2; **12**, 71987-84-3; **13**, 71987-85-4; **14**, 71987-86-5; **15**, 71987-87-6.

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## Carbon-13 Nuclear Magnetic Resonance Spectra of *trans*-1-Thiadecalin, *trans*-1,4-Dithiadecalin, *trans*-1,4-Oxathiadecalin, and the Corresponding Sulfoxides and Sulfones

Robert P. Rooney and Slayton A. Evans, Jr.*

*The William Rand Kenan, Jr. Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514*

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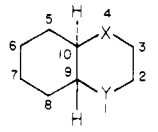
During the course of our research dealing with the quantitative conformational aspects of heterosubstituted *trans*-decalins,[1] it became apparent that an examination of the $^{13}C$ NMR shifts of these molecules might provide useful information about interactions of sulfinyl and sulfonyl groups with neighboring carbons. Although a number of reports are available describing the influence of sulfinyl and sulfonyl groups on the shifts of proximal carbons,[2] much of the information is difficult to correlate in a useful way because of uncertainties in conformational distribution in acyclic systems and the lack of a large number of systematic studies on conformationally homogeneous compounds. The compounds described below are of the *trans*-decalin structure which ensures conformational rigidity as well as stereochemical similarity.



X = O, S, $CH_2$
Y = S, SO(ax), SO(eq), $SO_2$

## Results and Discussion

**Syntheses.** The preparations of *trans*-1,4-oxathiadecalin (**1**), the isomeric sulfoxides (**2α**, **2β**), and the sulfone (**3**), as well as *trans*-1-thiadecalin (**4**) and *trans*-1,4-dithiadecalin (**7**), have been previously described.[1,3,6]

Oxidation of thiadecalin **4** with 1 equiv of *m*-chloroperoxybenzoic acid (mCPBA) gave sulfoxides **5α** and **5β** in 55% yield. Thiadecalin 1,1-dioxide **6** was obtained by exhaustive oxidation of **4** with hydrogen peroxide in acetic acid.[5] The diastereoisomeric dithiadecalin sulfoxides, **8α** and **8β**, were prepared from oxidation of **7** with a 0.5 equiv of hydrogen peroxide in acetic acid[7] while sulfone **9** was obtained from potassium permanganate oxidation of **8**.[8]

**Stereochemical Assignments.** The trans stereochemistry about the C9,C10 ring junction for oxathiadecalin **1**, thiadecalin **4**, and dithiadecalin **7** has been determined from the methods of syntheses.[1,3b,6] Establishment of the axial and equatorial configuration of the isomeric sulfoxides was based primarily on the expected differences in $^{13}C$ shifts of Cβ and Cγ carbons. For example, the isomer of the pair with the larger upfield Cγ shifts and smaller downfield Cβ shifts was assigned the β (axial) configuration.

**$^{13}C$ NMR Spectral Data.** The $^{13}C$ NMR shift assignments were based on anticipated shifts due to the inductive/field effects[9] of oxygen and sulfur atoms in the ring and particularly the effects of sulfinyl and sulfonyl moieties in conjunction with the multiplicity of the carbon signals during coherent proton off-resonance decoupling experiments.[10] The data are discussed in terms of β and γ effects as oxygen substitution on sulfur is altered. Thus, the β carbons are *adjacent* to the sulfur atom and β to the substituent on the sulfur atom (e.g., lone pair electrons or oxygen atom).

**$^{13}C$ NMR Spectra of Sulfides.** The $^{13}C$ NMR chemical shifts of thiadecalin **4** have been previously assigned,[11] while only the assignments of C2, C3, C9, and C10 of oxathiadecalin **1** have been made.[1] The chemical shift of C2 in **1**[12] previously assigned as δ 32.74 is now reassigned as

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