1212 *J. Org. Chem.* 1986, *51*, 1212-1216

Preparation and Reactions of Tetrakis(2-formyl-2-propyl)ethylene, an Acyclic Derivative of Tetra-*tert*-butylethylene[1]

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The preparation and reactions of tetrakis(2-formyl-2-propyl)ethylene (3) and 2,2-bis(2-formyl-2-propyl)-1,1-diphenylethylene (8) are described. Cleavage of the olefinic precursors 2 and 4 was carried out using osmium tetraoxide, followed by lead tetraacetate, affording 3 and 8. Attempted preparations of tetraol 15 and diol 13 via reductions of 3 and 8 led only to hemiacetals 16 and 12, presumably due to relief of steric strain. A facile thermal decarbonylation of 3 to a polycyclic trioxane 20 occurred, possibly due to enhanced diradical character in the olefinic bond of 3.

Recently, we and others have described the preparation of "tied-back" cyclic derivatives of tetra-*tert*-butylethylene (1).[2] These syntheses were designed to provide functionalizable intermediates which could be converted to acyclic derivatives of 1, and ultimately, to this long-sought-after compound. Bi-3,3,5,5-tetramethylcyclopentene-4-ylidene (2) was a key intermediate in this strategy. We assumed that the less sterically hindered endocyclic double bonds in 2 could be selectively oxidized, leaving the more hindered tetrasubstituted double bond intact, affording the desired tetrakis(2-formyl-2-propyl)ethylene (3). A series of reductions of 3 would then afford 1. We now report our investigations into the preparation and reactions of 3 and related compounds.

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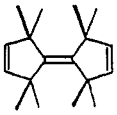

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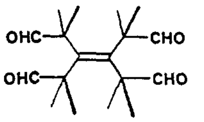

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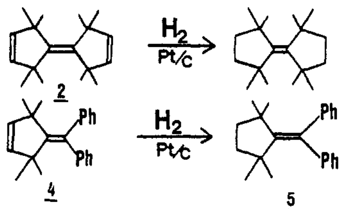
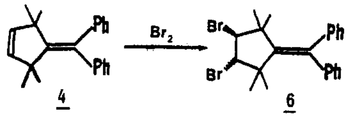
In our previous report, we noted that the endocyclic double bonds of 2 were remarkably inert toward oxidation by permanganate under a variety of reaction conditions.[2c] We also noted that 2 reacted in an anomalous manner with bromine, leading to a complex mixture of brominated products with liberation of hydrogen bromide. These difficulties in attempted functionalization of 2 led us to examine the less hindered 4-(diphenylmethylene)-3,3,5,5-tetramethylcyclopentene (4) as a model compound in such reactions, and compare the reactions of 2 and 4.

Olefin 4 could be easily prepared in a twofold extrusion reaction by the treatment of 2,2,5,5-tetramethylcyclopenteneselone[3] with diphenyldiazomethane. Hydrogenation of 4 cleanly afforded olefin 5, but this reduction was much slower than the corresponding reduction of 2. Under identical reaction conditions, catalytic hydrogenation of 2 over platinum was complete in 2 h,[2c] while the corresponding reduction of 4 was only 50% complete after 17 h. These differences in reactivity presumably are due either to the steric bulk of the phenyl moieties, or to the preferential coordination of the aromatic groups to the catalyst surface.



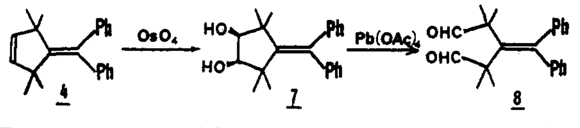
2 4 5

Bromination of 4 occurred slowly, affording the dibromo derivative 6. No liberation of hydrogen bromide was observed. Reaction of the dibromo compound with zinc dust led to greater than 89% recovery of olefin 4. Reexamination of the bromination of 2 showed that while a complex mixture was formed in this reaction, the major products were presumably the isomeric tetrabromo compounds. Zinc dust treatment of the bromination mixture led to recovery of 2 in 75% yield. Presumably, the hydrogen bromide liberation in this reaction occurs due to relief of steric strain by methyl migration after bromonium ion formation. The resulting triene is less strained and more reactive than 2, and can react further with bromine, affording a complex mixture of products (Scheme I).



4 6

As with olefin 2, attempted cleavage of the endocyclic double bond of 4 with permanganate was unsuccessful.[4] However, oxidation of 4 with one equivalent of osmium tetroxide afforded diol 7 in 75% yield. Cleavage of diol 7 could be carried out using lead tetraacetate in pyridine, affording the dialdehyde 8 in 92% yield.



4 7 8

Treatment of 2 with 2 equiv of osmium tetroxide afforded a single crystalline tetraol 9 in 60% yield. Treatment of 2 with 1 equiv of osmium tetroxide afforded crystalline diol 10 in 58% yield. In all cases, attempted oxidations using catalytic amounts of osmium tetroxide were unsuccessful. Cleavage of the tetraol 9 could be cleanly carried out by using lead tetraacetate, affording tetraaldehyde 3 in 85% yield. Cleavage of 10 could be carried out similarly, affording dialdehyde 11 in 85% yield.

The attempted reduction of dialdehyde 8 with excess lithium aluminum hydride in refluxing tetrahydrofuran

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(1) Presented at the 186th meeting of the American Chemical Society, Washington, DC, August 1983, ORGN 142.

(2) (a) Guziec, F. S., Jr.; Murphy, C. J.; Cullen, E. R. *J. Chem. Soc., Perkin Trans 1* 1985, 107; (b) Krebs, A.; Rüger, W.; Nickel, W.-U. *Tetrahedron Lett.* 1981, 4937. (c) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* 1982, *47*, 3563; (d) Krebs, A.; Born, W.; Kaletta, B.; Nickel, W.-U.; Rüger, W. *Tetrahedron Lett.* 1983, 4821.

(3) Guziec, F. S., Jr.; Moustakis, C. A. *J. Org. Chem.* 1984, *49*, 189.

(4) The X-ray crystal structure of 2 has been recently published.[5] The double bonds of the cyclopentene rings are remarkably compressed (1.289 Å), possibly accounting for this lack of reactivity.

(5) Pilati, T.; Simonetta, M. *Acta Crystallogr.* 1985, *C41*, 147.

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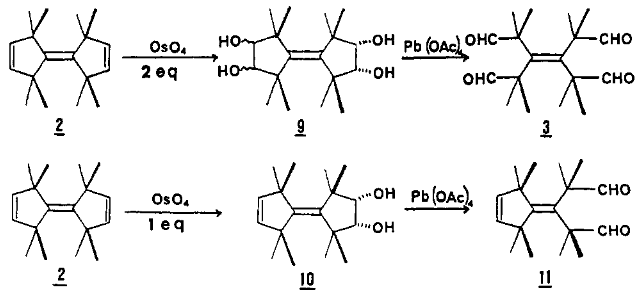
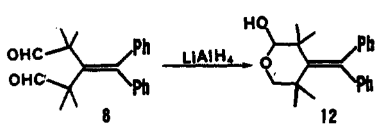
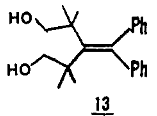


led only to formation of hemiacetal 12 in 70% yield. Even under forcing conditions, no acyclic diol 13 was obtained. Apparently, the six-membered hemiacetal is stable relative to the open-chain hydroxy aldehyde due to a "tying-back" of the methyl groups, relieving steric interactions across the central double bond. The carbocyclic analogue 14 of 12 can be easily prepared via a twofold extrusion reaction, suggesting there are no great steric repulsions in such a tied-back structure.[6]



8 12



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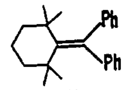

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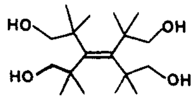
When tetraaldehyde 3 was treated with excess lithium aluminum hydride, mixtures of products resulted, with no observable tetraol 15. Presumably, the main products of this reaction are the isomeric dihemiacetals 16 (or 17) arising from a cyclization similar to that observed in the case of 8. It is interesting to note that the carbocyclic analogue of 16, olefin 18, could not be prepared via a twofold extrusion reaction, presumably due to extreme intramolecular steric interactions.[2a,6] Attempts to prepare either acetal or thioacetal derivatives of aldehyde 3 or hemiacetals 16, 17 led either to complete recovery of these compounds or to complex mixtures of products upon forcing conditions.



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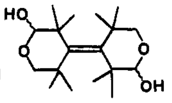

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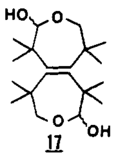

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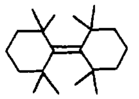

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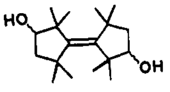

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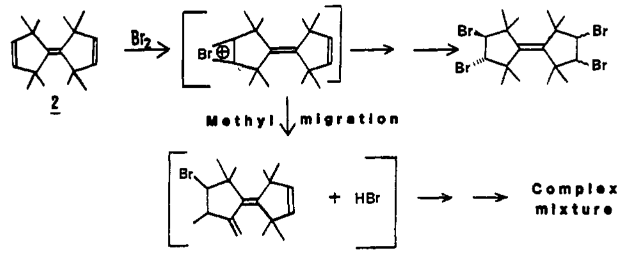
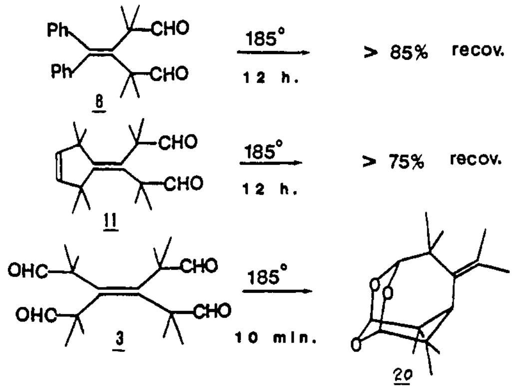
Attempted reduction of 3 with hydrazine in diethylene glycol led to a mixture containing isomeric diols 19. A similar reaction was observed in the attempted reduction of 1,2-bis(2-formyl-2-propyl)benzene to the corresponding diol when such a cyclization also occurred.[8]

In each attempted reduction of tetraaldehyde 3 under forcing conditions, a byproduct was obtained which contained neither hydroxyl nor carbonyl functions. The same product was obtained after 3 was heated in refluxing cumene for 1 week. We also observed that 3 decomposed upon melting with liberation of a gas. When 3 was heated at 185 °C under argon for 10 min, it was quantitatively converted with loss of 1 mol of carbon monoxide to a material which again contained no observable carbonyl or hydroxyl groups. Under identical conditions, aldehydes 8 and 11 were stable for extended periods of time.

Scheme I





The structure of the decarbonylated product was determined spectroscopically to be 20. Compound 20 consists of tied-back six- and seven-membered rings in a rigid structure. A plane of symmetry bisects the trioxane ring coplanar with the olefinic bond. The ^{1}H NMR spectrum of 20 exhibits three pairs of equivalent methyl groups at 1.44, 1.31, and 0.96 ppm. The allylic methyl hydrogens appear at 1.89 and 1.73 ppm. The trioxane hydrogens appear as a one-proton singlet at 4.49 ppm and as a two-proton doublet at 4.62 ppm. The latter protons are coupled to the final allylic hydrogen, which appears as a broadened one proton doublet at 2.90 ppm via long range coupling through a W conformation in the rigid carbon framework.[9]

The ^{13}C spectra of 20 (broad band decoupled, off resonance decoupled, APT) show eleven distinct resonances, with only four methyl signals. Two methyl resonances appear to be superimposed, since five methyl signals are clearly resolved in the proton spectrum. Otherwise, the ^{13}C spectra, infrared spectra, and mass spectra are completely consistent with the proposed structure for 20.

Why should there be such a difference in thermal behavior between aldehyde 3 and the related compounds 8 and 11? Trioxane derivative 20 can arise from hydrogen transfer from an aldehyde function of 3 to an olefinic carbon, followed by decarbonylation and trimerization of the remaining aldehyde functions to the trioxane. Both radical abstraction of aldehydic hydrogens and decarbonylation of the resulting acyl radicals are well-documented;[10] however, uninitiated thermal reactions of this

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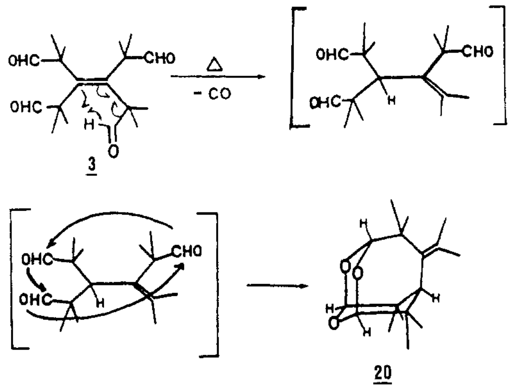
(6) The relative ease of formation of olefins via twofold extrusion reactions is a measure of intramolecular interactions in the resulting olefins.[2a,7]

(7) Guziec, F. S., Jr.; San Filippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, 4843.

(8) Burgstahler, A. W.; Abdel-Rahman, M. O. *J. Am. Chem. Soc.* **1963**, *85*, 173.

(9) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 4th ed.; Wiley: New York, 1981; p 209.

Scheme II



type occur at temperatures (~500 °C) much higher than those observed for the thermal transformation of 3 to 20.[11] We believe that greater steric interactions across the double bond of 3 relative to 8 and 11 account for this enhanced reactivity.

Calculations indicate that because of extreme steric interactions, tetra-*tert*-butylethylene (1) may exhibit significant diradical character in its olefinic bond.[12] Similar "steric strain" could lead to an enhanced diradical character in the olefinic bond of 3, especially at elevated temperatures, providing 20 via an intramolecular radical pathway (Scheme II).[13] Attempts to distinguish this mechanism from a purely concerted nonradical process are currently underway.

Experimental Section

Melting points were determined using a Mel-Temp capillary block apparatus and are uncorrected. GLC analyses were performed with a Gow-Mac Series 550TCD gas chromatograph with a ($^1/_8$ in. × 6 ft) stainless steel column filled with OV-101 on Chromosorb W-80/100 mesh. ^{1}H NMR spectra were recorded with a JEOL PS 100 spectrometer; ^{13}C NMR spectra were recorded with a Varian XL 200 spectrometer. In both cases tetramethylsilane was used as an internal standard. IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Mass spectra were obtained with a Hitachi Perkin Elmer RMU-GL and a Hewlett-Packard 5995A gas chromatograph/mass spectrometer with a (2-mm i.d. × 6 ft) glass column filled with 3% SP 2100. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Tetrahydrofuran was dried by distillation from benzophenone–sodium. Diethylene glycol, pyridine, and hydrocarbon solvents were distilled from calcium hydride. Benzene was dried over sodium wire. Triethylamine was distilled from barium oxide. Solvents were removed by using a rotary evaporator under reduced pressure. Organic extracts were dried by washing first with saturated brine, and then the organic phase was treated with anhydrous sodium sulfate, unless otherwise stated.

4-(Diphenylmethylene)-3,3,5,5-tetramethylcyclopentene (4). A solution of diphenyldiazomethane (0.36 g, 2.0 mmol) in methylene chloride (5 mL) was added dropwise to a stirred solution of 2,2,5,5-tetramethylcyclopenteneselone[3] (0.41 g, 2.0 mmol) in dry ether (5 mL) under an atmosphere of nitrogen until the blue color of the selone was no longer observed. Removal of solvent under reduced pressure followed by heating to reflux overnight under nitrogen in carbon tetrachloride (20 mL) yielded a brown solid upon solvent evaporation. Column chromatography (silica, hexanes), followed by Kugelrohr distillation afforded olefin 4: 0.40 g, 68% yield, mp 156–157 °C; IR (KBr) 3045, 1428, 1358 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 7.3–7.1 (complex, 10 H), 5.24 (s, 2 H), 1.03 (s, 12 H); MS, *m/e* 288 (M$^+$), 273 (M$^+$ - CH$_3$). Anal. Calcd for $C_{22}H_{24}$: C, 91.61; H, 8.38. Found: C, 91.54; H, 8.43. Small amounts of symmetrical olefins (tetraphenylethylene and 2) were also isolated and characterized by their NMR spectra and melting points.

1-(Diphenylmethylene)-2,2,5,5-tetramethylcyclopentane (5). Olefin 4 (0.0211 g, 0.07 mmol) in ether (2 mL) and ethanol (5 mL) was hydrogenated at 1 atm pressure over platinum, 10% on charcoal (5 mg), under excess hydrogen (20.3 mL, 0.1 mmol) for 2 days. Filtration through Celite followed by evaporation of the solvent and Kugelrohr distillation afforded 0.0196 g (93% yield) of olefin 5; mp 108.5–110 °C; IR (KBr) 3080, 1480, 1365 cm^{-1}; MS, *m/e* 290 (M$^+$), 275 (M$^+$ - CH$_3$).

Reaction of 4 with Bromine. Bromine (96 mg) in carbon tetrachloride (2 mL) was slowly added to olefin 4 (166 mg) in CCl$_4$ (7 mL). No hydrogen bromide liberation was observed. After stirring for 3 h at room temperature, solvent was removed affording 226 mg (93%) of crude solid dibromide 6: NMR (CCl$_4$) δ 7.13 (s, 10 H), 4.11 (s, 2 H), 1.22 (s, 6 H), 0.82 (s, 6 H). Treatment of crude 6 with zinc dust (65 mg) in refluxing tetrahydrofuran (10 mL) containing a drop of acetic acid, filtration through Celite, concentration, and recrystallization from ethanol afforded starting 4, 148 mg, 89% recovery. A second crop afforded 25 mg of additional olefin (contaminated with zinc acetate).

4-(Diphenylmethylene)-3,3,5,5-tetramethylcyclopentane-*cis*-1,2-diol (7). To a solution of olefin 4 (1.05 g, 3.6 mmol) in pyridine (30 mL) and ether (10 mL), osmium tetroxide (1 g, 3.8 mmol) in pyridine (30 mL) was added with stirring. The mixture was stirred for 2 days at room temperature. Addition of water (30 mL) and NaHSO$_3$ (2.2 g) followed by extraction with chloroform (3 × 10 mL) yielded 1.1 g crude product. Kugelrohr distillation (170 °C, 0.1 torr) and recrystallization from methylene chloride–hexanes afforded the diol 7; 0.79 g, 75% yield; mp 175–176 °C; IR (KBr) 3420, 1595, 1360 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.3–7.1 (complex, 10 H), 3.7 (s, 2 H), 2.1 (s, 2 H), 1.03 (s, 6 H), 0.90 (s, 6 H); MS, *m/e* 322 (M$^+$), 307 (M$^+$ - CH$_3$).

2,2-Bis(2-formyl-2-propyl)-1,1-diphenylethylene (8). Diol 7 (637 mg, 1.98 mmol) in dry pyridine (15 mL) was treated with lead tetracetate (85%, 975 mg, 1.98 mmol) in dry pyridine (15 mL) at 15 °C, and the mixture stirred for 1$^1/_2$ h. Saturated Na$_2$CO$_3$ solution (2 mL) was added, followed by K$_2$CO$_3$ (~1 g), and the mixture was filtered through Celite. Extraction with chloroform (3 × 25 mL) and concentration afforded a yellow solid. Kugelrohr distillation at ~60 °C (0.1 torr) afforded colorless crystals, mp 203–204 °C; IR (KBr) 2810, 2710, 1712, 1358 cm^{-1}; ^{1}H NMR (CCl$_4$) δ 9.14 (s, 2 H), 7.3–7.1 (complex, 10 H), 1.43 (s, 12 H); ^{13}C NMR (CDCl$_3$) δ 196.15, 146.52, 142.35, 147.17, 130.43, 128.48, 128.17, 53.16, 24.62; MS, *m/e* 320 (M$^+$), 292 (M$^+$ - CO); exact mass calcd for $C_{22}H_{24}O_2$ 320.17762; found 320.17732.

Reaction of Bi-3,3,5,5-tetramethylcyclopentene-4-ylidene (2) with Bromine. Bromine (40 mg, 0.25 mmol) in CDCl$_3$ (0.5 mL) was added dropwise at room temperature to a solution of olefin 2 (30 mg, 0.13 mmol) in CDCl$_3$. An exothermic reaction immediately occurred with liberation of an acidic gas. ^{1}H NMR showed a complex spectrum and TLC (silica, hexanes) showed a minimum of four components in the mixture. Treatment of this mixture with excess bromine simplified both TLC and NMR. Treatment of the resulting mixture with zinc dust as described for 6 led to recovered 2 in 75% yield.

Attempted Reactions of 2 with Permanganate Reagents. (a) A solution of potassium permanganate (153 mg, 1 mmol) and sodium hydroxide (300 mg, 10 mmol) in 40% aqueous *tert*-butyl alcohol (15 mL) was added to a solution of olefin 2 (367 mg, 1.5 mmol) in *tert*-butyl alcohol (10 mL). The mixture was heated with stirring to 75 °C for 2 days. Filtration through Celite and extraction with ether afforded starting olefin (327 mg, 89% recovery). Similar results were obtained using methylcyclohexane as the solvent.

(b) A solution of potassium permanganate (10 mg), potassium periodate (460 mg, 2.0 mmol), anhydrous magnesium sulfate (120 mg, 2.0 mmol), and olefin 2 (240 mg, 1.0 mmol) in 40% aqueous *tert*-butyl alcohol (10 mL) was stirred at room temperature for

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(10) March, J. "Advanced Organic Chemistry", 3rd ed.; Wiley: New York, 1985, pp 166, 655–656.

(11) Schubert, W. M.; Kintner, R. R. "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Wiley-Interscience: London, 1966; Vol. 1, pp 711–735.

(12) Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; *Academic: New York*, 1978; p 109.

(13) The X-ray structure of 3 has recently been published.[14] In this structure the aldehydic protons lie directly above and below the olefinic carbon to which hydrogen transfer occurs in our proposed mechanism.

(14) Krebs, A.; Nickel, W.-U.; Tikwe, L.; Kopf, J. *Tetrahedron Lett.* 1985, 1639.

3 days. Filtration through Celite followed by extraction with ether afforded unreacted olefin (180 mg, 70% recovery) as well as 50 mg of a complex mixture of more polar compounds.

(c) A solution of olefin **2** (198 mg, 0.80 mmol), potassium permanganate (830 mg, 5.3 mmol), and dicyclohexyl-18-crown-6 (5 mg) in benzene (10 mL) was stirred at room temperature for 2 weeks.[15] Filtration through Celite followed by extraction with ether afforded the unreacted olefin (174 mg, 88% recovery). Similar negative results were obtained with benzyltriethylammonium chloride in benzene with aqueous alkaline permanganate[16] and also with benzyltriethylammonium permanganate[17] in benzene.

Bi-*cis*-3,4-dihydroxy-2,2,5,5-tetramethylcyclopentanylidene (9). To a solution of bi-3,3,5,5-tetramethylcyclopentene-4-ylidene (**2**) (81.2 mg, 3.33 mmol) in pyridine (5 mL) and ether (0.5 mL) was added osmium tetraoxide (0.17 g, 0.7 mmol) and the solution stirred for 72 h. Water (6 mL), pyridine (7 mL), and $NaHSO_3$ (0.8 g) was then added and the mixture stirred for an additional hour. Extraction with chloroform (3 × 10 mL) followed by evaporation and Kugelrohr distillation (~185 °C, 1 torr) afforded the tetraol **9**; 62 mg, 60% yield: mp 220–221 °C; IR (KBr) 3550–3300 cm^{-1} (broad); ^1H NMR (acetone-d_6) δ 3.45 (s, 4 H), 1.75 (broad, 4 H), 1.40 (s, 6 H), 1.30 (s, 6 H); MS, *m/e* 312 (M^+), 294 ($M^+ - H_2O$). Anal. Calcd for $C_{18}H_{32}O_4$: C, 69.20; H, 10.32. Found: C, 69.27; H, 10.12.

4-(*cis*-3,4-Dihydroxy-2,2,5,5-tetramethylcyclopentanylidene)-3,3,5,5-tetramethylcyclopentene (10). To a solution of olefin **2** (81.8 mg, 3.35 mmol) in pyridine (5 mL) and ether (0.5 mL), osmium tetroxide (0.08 g, 3.2 mmol) was added and the solution was stirred for 72 h. Workup as described for **9** followed by Kugelrohr distillation (~155 °C, 1 torr) afforded the diol **10** (54 mg, 58% yield), as a white powder: mp 165–166 °C; IR (KBr) 3480–3350 cm^{-1} (broad); ^1H NMR ($CDCl_3$) δ 5.1 (s, 2 H), 3.7 (s, 2 H), 1.85 (broad, 2 H), 1.50–1.38 (complex, 24 H); MS, *m/e* 278 (M^+), 260 ($M^+ - H_2O$). Anal. Calcd for $C_{18}H_{30}O_2$: C, 77.65; H, 10.87. Found: C, 77.90; H, 10.62.

A solution of the diol **10** (0.20 g, 73 mmol) in acetone (20 mL) and 1.5 N HCl (5 drops) was heated to reflux for 30 min followed by removal of the solvent. Evaporation under reduced pressure followed by sublimation afforded 4-[3,4-isopropylidenedioxy-2,2,5,5-tetramethylcyclopentanylidene]-3,3,5,5-tetramethylcyclopentene, 0.20 g, 88% yield: mp 91–93 °C; IR (KBr) 2940, 1375, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.10 (s, 2 H), 4.10 (s, 2 H), 1.52–1.36 (complex, 30 H); MS, *m/e* 303 ($M^+ - CH_3$).

Tetrakis(2-formyl-2-propyl)ethylene (3). To a solution of the tetraol **9** (359 mg, 1.15 mmol) in dry pyridine (10 mL), lead tetraacetate (85%, 1.2 g, 2.3 mmol) in dry pyridine (20 mL) was added and the mixture stirred for $1^1/_2$ h. Saturated Na_2CO_3 (2 mL) was added, followed by K_2CO_3 (~1 g), and the mixture was filtered through Celite. Extraction with chloroform (3 × 35 mL) followed by Kugelrohr distillation (~145 °C, 0.1 torr) afforded tetraaldehyde **3** which was recrystallized from ether–ethanol affording colorless crystals (306 mg, 85% yield): mp 183–185 °C; IR (KBr) 2730, 1735, 1395, 1360 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.37 (s, 4 H), 1.40 (s, 24 H); ^{13}C NMR ($CDCl_3$) δ 199.6, 149.9, 56.3, 25.6; MS, *m/e* 279 ($M^+ - 29$); CI, *m/e* 309 ($M^+ + 1$). Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.15. Found: C, 69.94; H, 9.30.

4-[Bis(2-formyl-2-propyl)methylene]-3,3,5,5-tetramethylcyclopentene (11). Treatment of the *cis*-diol **10** (346 mg, 1.24 mmol) with lead tetraacetate (600 mg, 1.24 mmol) in pyridine and workup as for **3** followed by Kugelrohr distillation (~90 °C, 0.1 torr) afforded dialdehyde **11** as a yellow oil (296 mg, 85% yield): IR (neat) 2710, 1725, 1375 cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.40 (s, 2 H), 5.15 (s, 2 H), 1.42 (s, 12 H), 1.23 (s, 12 H); MS, *m/e* 276 (M^+), 261 ($M^+ - CH_3$).

Reduction of Dialdehyde 8. (a) To a solution of dialdehyde **8** (90 mg, 0.28 mmol) in tetrahydrofuran (5 mL) was added lithium aluminum hydride (40 mg, 1.05 mmol) in small portions with stirring. The mixture was heated to reflux overnight under nitrogen. Addition of aqueous NaOH followed by neutralization with HCl (dilute), extraction with ether, and Kugelrohr distillation (~130 °C, 0.05 torr) afforded the hemiacetal **12** as a colorless solid (63 mg, 70% yield): mp 163–164 °C; IR (KBr) 3400, 1445, 1370 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.1 (complex, 10 H), 4.68 (d, $J \cong$ 5 Hz, 1 H), 3.72 (d, $J \cong$ 13 Hz, 1 Hz, 1 H), 3.34 (d, $J \cong$ 5 Hz, 1 H), 1.04–1.00 (complex, 12 H); ^{13}C NMR ($CDCl_3$) δ 146.8, 146.5, 146.2, 143.0, 129.0, 128.9, 128.7, 128.6, 128.0, 127.9, 125.8, 100.6, 74.3, 42.2, 37.2, 30.1, 29.7, 28.8, 26.3; MS, *m/e* 320 ($M^+ - 2$), 305 ($M^+ - 17$). Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.95; H, 8.13. Found: C, 81.82; H, 8.16.

A second fraction (15 mg) isolated by Kugelrohr distillation (~180 °C, 0.05 mmHg) was tentatively assigned as a mixture of diastereomeric dimers by the ^{13}C NMR spectrum. ^{13}C NMR ($CDCl_3$) δ 147.0, 146.8, 146.7, 146.6, 146.3, 142.2, 142.1, 129.1, 128.9, 128.8, 128.6, 129.5, 127.9, 127.8, 125.8, 125.7, 125.6, 107.5, 101.0, 74.2, 74.0, 42.8, 41.9, 37.0, 36.9, 30.4, 30.2, 30.1, 29.8, 29.3, 29.3, 28.4, 27.1.

1-(Diphenylmethylene)-2,2,6,6-tetramethylcyclohexane (14). To 2,2,6,6-tetramethylcyclohexaneselone[3] (60 mg, 0.28 mmol) in carbon tetrachloride (3 mL) was added dropwise diphenyldiazomethane (58 mg, 0.30 mmol) in dichloromethane (2 mL). The crimson color of the diazo compound was discharged initially and persisted when the addition was complete. Removal of solvent by a nitrogen stream afforded the colorless intermediate selenadiazoline. This was dissolved in carbon tetrachloride (3 mL) and heated to reflux under positive nitrogen pressure overnight. Removal of solvent and chromatography on silica (hexanes) afforded two major components: tetraphenylethylene (~65 mg) and crude **14** (~25 mg). Kugelrohr distillation at 85 °C (0.2 torr) afforded 15 mg (17%) pure olefin **14**: mp 133–134 °C; IR (KBr) 1598, 1492, 1467, 1443, 1363 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2–7.1 (10 H, m), 1.7–1.5 (6 H, m), 0.96 (12 H, s); MS, *m/e* 304 (M^+), 289 ($M^+ - CH_3$); exact mass calcd for $C_{23}H_{28}$ 304.21909, found 304.21909.

Attempted Reduction of Tetraaldehyde 3. (a) To a solution of **3** (37 mg, 0.12 mmol) in dry pyridine (2 mL) and ether (2 mL) was added lithium aluminum hydride (20 mg, 0.5 mmol) in small portions. After stirring overnight, dilute HCl was added and the solution was extracted with ether. Column chromatography on silica (0.5 g, chloroform–pyridine) afforded 33 mg of a white powder; mp 195–197 °C, IR (KBr) 3400, 2980, 1375, 1070 cm^{-1}; ^1H NMR (acetone-d_6) δ 4.6–4.2 (complex, 4 H; 2 H exchangeable with D_2O), 3.9–3.6 (complex, 4 H); 1.3–1.1 (complex, 24 H); the NMR signals varied depending on the temperature and the solvent used for the reduction.

(b) A mixture of **3** (70 mg, 0.22 mmol) in dry ether (5 mL), ethanol (5 mL) and 10% platinum on carbon (~5 mg) was stirred for 12 h under an excess atmosphere of hydrogen. Filtration through Celite afforded 58 mg of the unreacted tetraaldehyde.

(c) The tetraaldehyde **3** (75 mg, 0.25 mmol) and hydrazine (1 g, 30 mmol) in diethylene glycol (2 mL) were heated to reflux with stirring for 10 days. Extraction with ether (3 × 5 mL) followed by washing with water and drying yielded an oily material. Kugelrohr distillation (~120 °C, 0.1 torr) afforded 36 mg of an oily solid: IR (neat) 3400–3350 (broad) 2950, 1460, 1360, 1040 cm^{-1}; NMR ($CDCl_3$) δ 4.2–4.0 (broad, 2 H), 3.8–3.6 (complex, 2 H), 1.9–1.1 (complex, 28 H).

7-Isopropylidene-6,6,9,9,11,11-hexamethyl-2,4,10-trioxatricyclo[3.3.2.1]undecane (20). (a) The tetraaldehyde (**3**) (50 mg, 0.16 mmol) was heated at 185 °C for 10 minutes under an argon atmosphere. Kugelrohr distillation (~100 °C, 0.1 torr) afforded **20**, 44 mg, 88% yield: mp 89–91 °C; IR ($CDCl_3$) 2980, 1425, 1395, 1380 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.62 (d, $J \sim 1$ Hz, 2H), 4.49 (s, 1 H), 2.90 (bd, 1 H), 1.89 (s, 3 H), 1.73 (s, 3 H), 1.44 (s, 6 H), 1.31 (s, 6 H), 0.96 (s, 6 H); ^{13}C NMR $CDCl_3$) δ 137.6 (s), 128.5 (s), 101.7 (d), 97.1 (d), 55.2 (d), 45.6 (s), 37.5 (s), 29.4 (q), 27.1 (q), 26.3 (q), 23.8 (q); MS, *m/e* 280 (M^+), 219; exact mass calcd for $C_{17}H_{28}O_3$ 280.20383, found 280.20437.

(b) The tetraaldehyde **3** (42 mg, 0.13 mmol) in distilled cumene (3 mL) was heated to reflux under positive nitrogen pressure for 7 days. The reaction was monitored by GC analysis. Adsorption onto silica (0.5 g) and elution with hexanes afforded 10 mg of bicumyl. Elution by chloroform afforded 25 mg, 68% yield of **20**, *which was identical with that formed by the neat pyrolysis* of the tetraaldehyde.

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Three-Electron-Bonded Sulfur-Centered Radical Cations and Possible Ylide Formation during the Oxidation of Various 1,3-Dithiacyclopentanes

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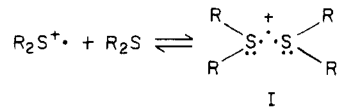
Transient radical cations with intramolecular S∴S three-electron bonds have been identified in the ·OH and Tl^{2+} induced oxidation of various 1,3-dithiacyclopentanes and 2,2-dimethyl-1,3-dithiacyclohexane. The stability of these three-electron-bonded species is greatly enhanced by dialkylation at C-2. This is attributed to the establishment of a conformation which favors sulfur–sulfur p-orbital interaction. The relative thermodynamic stability of the intramolecular S∴S bond is reflected in optical absorptions; λ_{max} increases with decreasing stability from 550 to 650 nm. Optical absorption spectra with λ_{max} ranging from 275 to 320 nm have been measured for neutral, predominantly carbon-centered radicals which are formed upon deprotonation of the radical cations. If C-2 centered, these radicals decay via second-order ionic disproportionation. The cationic products generated in this process and also via one-electron oxidation of the C-2 radicals are considered to stabilize by deprotonation to sulfur ylides and establishment of resonance structures.

Introduction

In a number of studies we have demonstrated that the optical absorption of three-electron-bonded radical cations of the general nature $(>S∴S<)^+$ obtained in the one-electron oxidation of organic sulfides are a sensitive probe for structural parameters.[1–6] The underlying rationale is that the unpaired p electron of an oxidized sulfur atom has a high tendency to coordinate with a free p-electron pair of a second sulfur. this leads to the establishment of an equilibrium,[7] e.g., as formulated for monosulfides (eq 1). Oxidation of di- (and poly-) thia compounds (except disulfides) may at low solute concentrations also lead to intramolecular stabilization as has been observed for open chain[3,4] and cyclic dithia[1–4,8,9] compounds in the equilibria (eq 2 and 3).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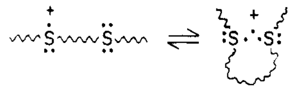
I

Three-electron bonds in I–III contain two bonding σ electrons and one antibonding, i.e., bond-weakening σ* electron.[4] The optical absorptions of these three-electron-bonded systems have experimentally been shown[1–6,10] and theoretically verified[11] to be attributable to a—in first approximation —σ→σ* transition[12] and thus to be a measure for the three-electron bond strength (at least for aliphatic $R_2S∴SR_2^+$). Generally, an increasing bond strength is associated with a blue shift in optical absorption and vice versa. Optimum conditions for the stabilization of an intramolecular radical cation of type III are given, for example, in 1,5-dithiacyclooctane, i.e., for a molecule which has three carbon atoms each located between the two interacting sulfur atoms. Such a configuration ensures an excellent p-orbital overlap, and λ_{max} = 400 nm has been observed.[3,4] Only a much weaker interaction of sulfur p orbitals (which are perpendicular to the carbon–sulfur–carbon plain) is possible in the corresponding species from 1,3-dithiacyclohexane, for example, for which a considerably red-shifted absorption maximum at 600 nm is observed.[2] No long-lived intramolecular S∴S bonded radical cation could finally be detected in the oxidation of the relatively planar 2-methyl-1,3-dithiacyclopentane.[3,4] In view of the flexibility which nevertheless appears to exist to a certain extent in five-membered rings[13–22] and which may assist some sulfur–sulfur interaction, we now con-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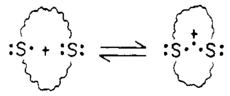
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III

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