aldehydic carbon. Oxidation of **2** with $KMnO_4$ in a water–ethyl acetate mixture also furnished **5**; however, contamination with unreacted starting material was present. Oxidation of the nitronate salt of **2** with $KMnO_4$ furnished the corresponding carboxylic acid **6**, the ^{13}C NMR spectrum of which shows a peak at δ 176.3 for the CO_2H.

Four-directional C-cores[12] with a variety of terminal functional groups may now be readily prepared, thus making tris(β-cyanoethyl)nitromethane a most attractive building block for cascade polymers.

Experimental Section

General Comments. All melting points were taken in capillary tubes and are uncorrected. The ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$, unless otherwise stated.

DMSO was dried and stored over 3A molecular sieves. Pyridine was dried over solid KOH, then distilled and stored over KOH. Unless specified, solvents were purified by simple distillation. Tris(β-cyanoethyl)nitromethane (Aldrich; **1**, 1 g) was recrystallized from MeCN/EtOH (6 mL; 1:5): mp 114–116 °C.

3-(Nitromethyl)-3-(2-cyanoethyl)-1,5-dicyanopentane (2). Freshly distilled CH_3NO_2 (10 g, 160 mmol) was carefully added to a stirred slurry of NaH (3.92 g, 163 mmol; 95%) in dry DMSO (350 mL) under an inert atmosphere. After the foaming had subsided, a solution of tris(β-cyanoethyl)nitromethane (8.8 g, 40 mmol) in DMSO (50 mL) was added and the mixture was irradiated (100-W incandescent lamp). The temperature was allowed to rise to 65 °C within a period of 35 min and maintained at 65 °C for an additional 25 min. The yellow solution was then cooled to 25 °C, treated with AcOH (18 mL), and then poured into water (4 L). After the aqueous solution was extracted with EtOAc (7 × 100 mL), the combined organic fraction was washed with brine and dried ($MgSO_4$). The residue was chromatographed (SiO_2), eluting with EtOAc/CH_2Cl_2 (3:7), to give the homologue **2** as colorless crystals: yield, 6 g (64%); mp 100.5–102 °C (MeOH); ^1H NMR (DMSO-d_6) δ 1.18–1.77 (m, $CH_2CH_2C{\equiv}N$, 6 H), 1.99–2.68 (m, $CH_2C{\equiv}N$, 6 H), 4.64 (s, CH_2NO_2, 2 H); ^{13}C NMR δ 10.8 ($CH_2C{\equiv}N$), 28.3 ($CH_2CH_2C{\equiv}N$), 40.4 (quat *C*), 78.2 (CH_2NO_2), 120.4 (*C*≡N); IR (KBr) 2225 (C≡N), 1558, 1383 (NO_2) cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_4O_2$: C, 56.39; H, 6.02; N, 23.91. Found: C, 56.43; H, 6.05; N, 23.99.

3,3-Bis(2-cyanoethyl)-4-nitro-1,6-dicyanohexane (3). To a solution of **2** (1.17 g, 5 mmol) and acrylonitrile (2.0 g, 37 mmol) in dimethoxyethane (DME; 20 mL) was added Triton-B (40% in water, 640 mg), and then the mixture was stirred at 25 °C for 48 h. Additional catalyst (650 mg) was added after 24 h. The catalyst was neutralized with dilute aqueous HCl, and the reaction mixture was concentrated in vacuo to afford a residue, which was stirred with EtOAc (50 mL) and water (10 mL). After the layers were separated, the combined organic phase was evaporated to dryness to give an oil. This was column chromatographed (SiO_2), eluting with EtOAc/CH_2Cl_2 (3:7) to furnish **3**, as colorless crystals: yield, 580 mg (40%); mp 114–116 °C (MeOH); ^1H NMR δ 1.72–1.82 (m, $CH_2CH_2C{\equiv}N$, 6 H), 2.45–2.50 (m, $CH_2C{\equiv}N$, 6 H), 4.72 (m, $CHNO_2$, 2 H); ^{13}C NMR δ 11.5 (3 × $CH_2C{\equiv}N$), 14.08 ($CH_2C{\equiv}N$), 23.8 ($CH_2CH_2C{\equiv}N$), 28.5 (3 × $CH_2CH_2C{\equiv}N$), 41.4 (quat *C*), 92.2 ($HCNO_2$), 119.16 (C≡N), 120.3 (3 × *C*≡N); IR (KBr) 2260 (C≡N), 1558 (NO_2) cm^{-1}. Anal. Calcd for $C_{14}H_{17}N_5O_2$: C, 58.52; H, 5.96; N, 24.38. Found: C, 58.59; H, 6.02; N, 24.32.

3-(2-Cyanoethyl)-1,3,5-tricyanopentane (4). A solution of **2** (468 mg, 2 mmol), pyridine (5 mL), and PCl_3 (430 mg, 3 mmol) was maintained at 25 °C for 35 h, diluted with water (80 mL), and acidified with concentrated HCl (5 mL). The aqueous solution was extracted with EtOAc (3 × 50 mL), and the combined extract was dried ($MgSO_4$). Evaporation of the solvent afforded the tetranitrile as colorless crystals: yield, 270 mg (69%); mp 128–130 °C (MeOH); ^1H NMR β 1.16–1.73 (m, $CH_2CH_2C{\equiv}N$, 6 H), 2.01–2.69 (m, $CH_2C{\equiv}N$, 6 H); ^{13}C NMR δ 12.0 ($CH_2C{\equiv}N$), 29.4 ($CH_2CH_2C{\equiv}N$), 39.0 (quat *C*), 119.6 (*C*≡N), 120.3 (3 × *C*≡N); IR (KBr) 2260 (C≡N) cm^{-1}. Anal. Calcd for $C_{11}H_{12}N_4$: C, 65.97; H, 6.04; N, 27.98. Found: C, 65.80; H, 5.85; N, 28.11.

3-Formyl-3-(2-cyanoethyl)-1,5-dicyanopentane (5). A solution of **2** (468 mg, 2 mmol) in MeOH was added to LiOMe (80 mg, 2.1 mmol) in MeOH (15 mL) at 0 °C. After concentration in vacuo, the remaining salt was dissolved in saturated aqueous $K_2B_4O_7$ (25 mL). A solution of $KMnO_4$ (316 mg, 2 mmol) in saturated aqueous $K_2B_4O_7$ (25 mL) was added dropwise. After addition, the solution was stirred for an additional 30 min and then decolorized with aqueous $Na_2S_2O_4$ and dilute H_2SO_4. The solution was extracted with EtOAc (2 × 30 mL), and then the combined extract was washed with water (5 mL), dried ($MgSO_4$), and concentrated in vacuo to give aldehyde **5** as colorless crystals: yield, 330 mg (82%); mp 108–110 °C (MeOH); ^1H NMR δ 1.18–1.76 (m, $CH_2CH_2C{\equiv}N$, 6 H), 1.98–2.62 (m, $CH_2C{\equiv}N$, 6 H), 9.71 (s, *CHO*, 1 H); ^{13}C NMR δ 11.13 ($CH_2C{\equiv}N$), 25.9 ($CH_2CH_2C{\equiv}N$), 50.4 (quat *C*), 120.4 (*C*≡N), 204.6 (*CHO*); IR (KBr) 2823, 2726 (CH stretch), 2250 (C≡N), 1720 (CHO) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.00; H, 6.45; N, 20.68. Found: C, 64.84; H, 6.52; N, 20.61.

2,2-Bis(2-cyanoethyl)-4-cyanobutanoic Acid (6). To a stirred solution of MeOLi (60 mg, 1.65 mmol) in water (20 mL) was added **2** (350 mg, 1.5 mmol) followed by aqueous $KMnO_4$ (340 mg, 2 mmol; 30 mL of H_2O). The MnO_2 was dissolved by adding $Na_2S_2O_4$ and dilute H_2SO_4. Repeated extraction with Et_2O (5 × 30 mL) then concentration in vacuo of the combined organic extract gave acid **6** as colorless crystals: yield, 250 mg (65%); mp 126–127 °C (MeOH/H_2O); ^1H NMR δ 1.18–1.77 (m, $CH_2CH_2C{\equiv}N$, 6 H), 1.97–2.63 (m, $CH_2C{\equiv}N$, 6 H); ^{13}C NMR δ 13.00 ($CH_2C{\equiv}N$), 29.96 ($CH_2CH_2C{\equiv}N$), 48.1 (quat *C*), 121.7 (*C*≡N), 176.3 (CO_2H); IR (KBr) 2260 (C≡N), 1705 (CO_2H) cm^{-1}. Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.25; H, 5.98; N, 19.17. Found: C, 60.26; H, 6.01; N, 19.30.

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Registry No. **1**, 1466-48-4; **2**, 133887-78-2; **3**, 133909-48-5; **4**, 133887-79-3; **5**, 36394-40-8; **6**, 133887-80-6; $CH_2{=}CHCN$, 107-13-1; nitromethane sodium salt, 25854-38-0.

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Chemistry of Cyclic Phosphorous Compounds. 4. Syntheses of the Sex Pheromone from the Pedal Gland of Bontebok and Some 1,4-Diketones by Use of 1,1-Diphenylphospholanium Perchlorate

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The Wittig reactions of the ylides generated from cyclic phosphonium salts afford the phosphine oxides[1] which have a newly formed carbon–carbon double bond. Further olefination of the phosphine oxides by the Horner–Wittig reaction results in the formation of a diene.[2] These tandem Wittig reactions with the same phosphorous atom from a cyclic phosphonium salt provide a versatile procedure for synthesis of unconjugated dienes. We have previously reported the synthesis of 1,6-dienes[3] by the

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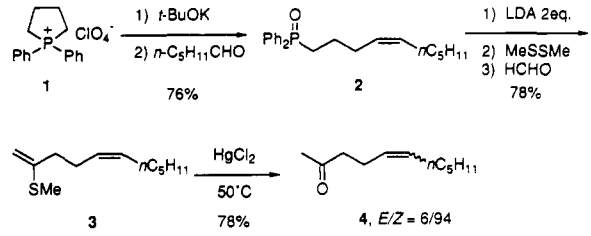
Scheme I



tandem Wittig reactions and application of the method to a synthesis of unconjugated enones: sex pheromones of the Douglas Fir Tussock moth[4] and Japanese female peach fruit moth.[5] In connection with our continuing interest in these methods, we applied the method to syntheses of (*Z*)-5-undecen-2-one (**4**), a sex pheromone from the pedal gland exudate of the bontebok (*Damaliscus dorcas dorcas*),[6] and 1,4-dicarbonyl compounds[7] that are important precursors of 2-cyclopentenone derivatives.

Results and Discussion

The pheromone of the bontebok is a long-chain enone with *Z* geometry. The most important step in the synthesis of this compound is the construction of a carbon–carbon double bond with *Z* stereoselectivity. Muchowski et al.[2] showed that the Wittig reaction of a five-membered cyclic phosphonium salt with *t*-BuOK as base in THF gave only *Z* olefins.[8] In the preceding paper,[5] we also reported a stereoselective synthesis of (*Z*)-13-eicosen-10-one and (*Z*)-12-nonadecen-9-one via the Wittig reaction of the five-membered cyclic phosphonium salt under Muchowski's reaction conditions. Accordingly, we attempted to construct a *Z* unsaturated bond in enone **4** by the Wittig reaction of phospholanium perchlorate (**1**)[9] with hexanal (Scheme I).

In the ^{13}C NMR of **2** after Kugelrohr distillation, only two peaks for the vinylic carbons (δ 131.6 and 128.0) were observed and assigned to *Z* geometry by comparing the ^{13}C NMR chemical shifts of the allylic carbon atoms with those of the analogous (*Z*)-4-octene and (*E*)-4-octene.[2] The peaks corresponding to the *E* isomer were not observed. By contrast, the Wittig reaction with *n*-butyllithium under the same reaction conditions provided a mixture of *Z* and *E* isomers (6:1). The carbonyl group in enone **4** was introduced via the vinyl sulfide, which could be hydrolyzed to produce the carbonyl functionality. Thus far, a number of methods for the synthesis[10] of vinyl sulfides and their hydrolysis[11] have been reported. Warren et al. developed a synthesis of vinyl sulfides from compounds bearing the diphenylphosphinoyl group.[10f] However, direct sulfenylation of the lithium derivative of the γ-diphenylphosphinoyl ketal in their 1,4-diketone synthesis proceeded in low yield because of the formation of the disulfenylated phosphine oxide.[10i] In the preceding paper, we also reported that the lithiated alkenyldiphenylphosphine oxide was sulfenylated in low yield. Therefore, a one-step synthesis of vinyl sulfides from **2** in the presence of 2 equiv of base was attempted in order to prevent loss of the anion by proton exchange between the initial carbanion and the sulfenylated phosphine oxide. As a result, diene **3** was obtained in 78% yield. It was confirmed by the ^{13}C NMR spectrum that *Z* geometry of the olefin in **3** was retained. Vinyl sulfide **3** was hydrolyzed by means of mercuric chloride in aqueous acetonitrile. The use of 2 equiv of mercuric chloride,[10e] however, resulted in the isomerization of the olefin (*E*:*Z* = 59:41) and low yield (32%). However, hydrolysis with 1 equiv of mercuric chloride suppressed the isomerization to provide an *E*,*Z* mixture (6:94) of enone **4** in 78% yield. The *E*,*Z* ratio was determined by capillary gas chromatography, and the structures were confirmed by ^1H and ^{13}C NMR and mass spectral analyses.

The efficient one-step synthesis of vinyl sulfide **3** and its conversion into the corresponding enone **4** prompted us to synthesize 1,4-diketones that are important intermediates for synthesis of naturally occurring cyclopentenones such as jasmonoids, prostanoids, and methylenomycins. Construction of vinyl sulfides in both steps of the Wittig and the Horner–Wittig reactions from the cyclic phosphonium salt would afford a compound having

Scheme II

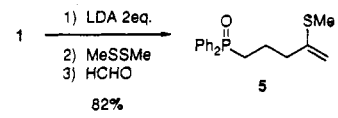
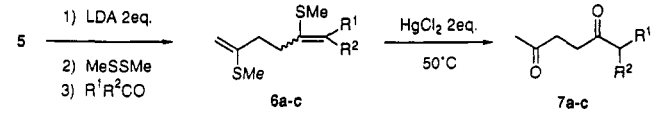


Table I. Synthesis of 1,4-Diketones 7a–c via Vinyl Sulfides from Phosphine Oxide 5



entry	aldehyde or ketone	product	yield,[d] %	diketone	yield,[d] %
1	hexanal	**6a**[a]	87	**7a**[c]	79
2	benzaldehyde	**6b**[b]	58	**7b**[c]	69
3	cyclohexanone	**6c**	16	**7c**	84

[a] *E*/*Z* = 68/32. [b] *E*/*Z* = 75/25. [c] Hydrolyzed without separating *E*,*Z* isomers of diene. [d] Isolated yield.

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two vinyl sulfides, which would lead to 1,4-diketones through hydrolysis promoted by $HgCl_2$ (Scheme II).

The one-pot vinyl sulfenylation of 1 with dimethyl disulfide and formaldehyde gas in the presence of 2 equiv of LDA was attempted and afforded the corresponding phosphine oxide **5** in high yield (82%). Phosphine oxide **5** would be a versatile intermediate for synthesizing 1,4-diketones by the further one-pot vinyl sulfenylation. Some carbonyl compounds were employed in the method (Table I). Although condensation with cyclohexanone gave diene **6c** in low yield (16%), the other reactions proceeded satisfactorily. Hydrolysis of dienes **6a–c** with 2 equiv of mercuric chloride afforded diketones **7a–c** in good yields.

Experimental Section[12]

(*Z*)-1-(Diphenylphosphinoyl)-4-decene (2). Method A. Potassium *tert*-Butoxide as Base. A mixture of phosphonium salt 1[9] (5.00 g, 14.7 mmol) and potassium *tert*-butoxide (1.65 g, 14.7 mmol) in dry THF (30 mL) was stirred at rt under N_2 for 1 h. To the mixture was slowly added a solution of hexanal (1.47 g, 14.7 mmol) in dry THF (15 mL), and the resulting mixture was stirred overnight at rt. After being quenched with saturated aqueous NH_4Cl, the mixture was extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was distilled with Kugelrohr (bp 220–222 °C (0.6 mmHg)) and further purified by column chromatography on silica gel using ethyl acetate to give 3.80 g (76%) of **2** as white crystals (mp 45.5–47.0 °C): IR (neat) 1180 (P=O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.78–7.70 (m, 4 H, P(O)Ph-*o*), 7.54–7.41 (m, 6 H, P(O)Ph-*m*, -*p*), 5.46–5.22 (m, 2 H, C*H*=C*H*), 2.31–1.60 (m, 8 H, CH_2), 1.33–1.26 (m, 6 H, CH_2), 0.86 (t, 3 H, CH_3, J_{HH} = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 133.2 (C_s, J_{PC} = 97.9 Hz), 131.65, 131.60, 131.57 (=CH or Cp), 130.8 (C_o, J_{PC} = 9.2 Hz), 128.6 (C_m, J_{PC} = 11.6 Hz), 128.0 (=CH), 31.5, 29.3 (C_7, C_8), 27.2 (C_6), 29.2 (C_1, J_{PC} = 72.3 Hz), 28.2 (C_3, J_{PC} = 15.1 Hz), 22.5 (C_9), 21.4 (C_2, J_{PC} = 3.7 Hz), 14.0 (C_{10}); MS (75 eV) *m/z* 340 (M^+), 201 (Ph_2PO^+). Anal. Calcd for $C_{22}H_{29}OP$: C, 77.62; H, 8.59. Found: C, 77.50; H, 8.55.

Method B. *n*-Butyllithium as Base. A solution of 1 (0.83 g, 2.49 mmol) in dry THF (20 mL) was stirred with *n*-BuLi (1.51 mL, 1.64 N in hexane, 2.49 mmol) for 1 h. The mixture was reacted with hexanal (0.25 g, 2.49 mmol) for 2 h at rt to give a mixture of *E*/*Z* isomers (1:6) of **2** (0.42 g, 51%): ^{13}C NMR ($CDCl_3$) δ 128.4 and 132.1 (*E*-CH=CH), 131.69, 131.65, 131.58 (*Z*-=CH or Cp), 128.0 (*Z*-=CH), 32.5 (*E*-C_6), 27.2 (*Z*-C_6). The ratio of *E*/*Z* isomers was determined from peak intensities of allylic carbons in the inverse gated heteronuclear decoupling ^{13}C NMR spectrum.

(*Z*)-2-(Methylthio)-1,5-undecadiene (3). A solution of *n*-BuLi (9.0 mL, 1.64 N in hexane, 14.7 mmol) was added dropwise to diisopropylamine (1.48 g, 14.7 mmol) in dry THF (50 mL) at −78 °C under N_2. The mixture was stirred at 0 °C for 30 min. A solution of **2** (2.50 g, 7.35 mmol) in dry THF (10 mL) was added dropwise to the mixture at −78 °C. After 30 min, a solution of dimethyl disulfide (0.69 g, 7.35 mmol) in dry THF (5 mL) was then added and the resulting mixture was stirred for 20 min. Dry formaldehyde gas was bubbled into the mixture until the solution became turbid. After being stirred for 6 h, the mixture was quenched with saturated aqueous NH_4Cl and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using CCl_4 to give 1.14 g (78%) of **3** as colorless liquid: IR (neat) 1605 cm^{-1} (C=C); ^1H NMR (250 MHz, $CDCl_3$) δ 5.45–5.33 (m, 2 H, C*H*=C*H*), 5.02 (s, 1 H, C=CH_2), 4.60 (s, 1 H, C=CH_2), 2.29–2.23 (m, 7 H, CH_2 and SCH_3), 2.07–1.99 (m, 2 H, CH_2), 1.37–1.25 (m, 6 H, CH_2), 0.89 (t, 3 H, CH_3, J_{HH} = 6.75 Hz); ^{13}C NMR ($CDCl_3$) δ 146.7 (C_2), 130.9, 128.2 (C_5, C_6), 104.0 (C_1), 37.5, 31.6, 29.4, 27.3, 26.8, 22.6, 14.6, 14.1; MS (75 eV) *m/z* 198 (M^+).

(*E*)- and (*Z*)-5-Undecen-2-one (4).[6d] A mixture of **3** (1.00 g, 5.04 mmol), dry CH_3CN (30 mL), distilled water (10 mL), and $HgCl_2$ (1.37 g, 5.04 mmol) was stirred at 50 °C for 20 h. After being cooled to rt, the suspension was neutralized with saturated aqueous $NaHCO_3$. The supernatant was filtered off through hyflo-supercel, and the filtrate was extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using $CHCl_3$ to give 0.66 g (78%) of **4** (*E*/*Z* = 6/94) as a pale yellow liquid: IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.42–5.29 (m, 2 H, C*H*=C*H*), 2.50–1.99 (m, 6 H, CH_2), 2.14 (s, 3 H, CH_3), 1.29 (m, 6 H, CH_2), 0.89 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 208.5 (C=O), 128.1 and 131.6 (*E*-CH=CH), 127.6 and 131.3 (*Z*-CH=CH), 43.6, 32.5, 31.5, 29.9, 29.3, 29.1, 27.1, 26.7, 22.6, 21.7, 14.0; MS (75 eV) *m/z* 168 (M^+). The ratio of *E* and *Z* isomers was determined by capillary GC (a DB-1 megabore column 30 m × 0.53 mm). Capillary GC (initial temperature, 80 °C; rate, 1.0 °C/min; final temperature, 150 °C; He flow rate, 83.7 mL/min) of **4** indicated a 6:94 mixture of *E* and *Z* isomers (*E* = 43.88 min, *Z* = 43.47 min). In a similar manner, **3** (0.10 g, 0.50 mmol) was treated with 2 equiv of $HgCl_2$ (0.28 g, 1.0 mmol) to give 27 mg of **4** as a mixture of pale yellow syrup and solid. The ratio of *E* and *Z* isomers was shown to be 59:41 by capillary GC.

5-(Diphenylphosphinoyl)-2-(methylthio)-1-pentene (5). A solution of *n*-BuLi (38.7 mL, 1.6 N in hexane, 61.9 mmol) was added dropwise to a diisopropylamine (6.27 g, 61.9 mmol) in dry THF (130 mL) at −78 °C under N_2. After being warmed to 0 °C, the mixture was stirred for 30 min. To the mixture was added phosphonium salt 1 (10.0 g, 29.0 mmol). After 1 h, a solution of dimethyl disulfide (2.92 g, 31.0 mmol) in dry THF (110 mL) was added, and the resulting mixture was stirred for 30 min. Dry formaldehyde gas was then bubbled into the mixture at rt. The mixture was quenched with water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using CH_2Cl_2–ethyl acetate (gradient elution, 1:0 to 0:1) to give 7.61 g (82%) of **5** as pale yellow crystals (mp 86.8–89.9 °C): IR (neat) 1180 (P=O) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 7.85–7.22 (m, 10 H, P(O)Ph), 4.90 (s, 1 H, C=CH_2), 4.50 (s, 1 H, C=CH_2), 2.17 (s, 3 H, SCH_3), 2.50–1.50 (m, 6 H, CH_2); MS (75 eV) *m/z* 316 (M^+), 201 (Ph_2PO^+). Anal. Calcd for $C_{18}H_{21}OPS$: C, 68.33; H, 6.69. Found: C, 68.04; H, 6.92.

(5*E*)- and (5*Z*)-2,5-Bis(methylthio)-1,5-undecadiene (6a). A solution of *n*-BuLi (11.6 mL, 1.64 N in hexane, 19.0 mmol) was added dropwise to a solution of diisopropylamine (3.65 g, 19.0 mmol) in dry THF (20 mL) at −78 °C under N_2. After being warmed to 0 °C, the mixture was stirred for 30 min. A solution of **5** (3.00 g, 9.50 mmol) in dry THF (45 mL) was added to the mixture at −78 °C. After 30 min, to the mixture was added dropwise a solution of dimethyl disulfide (0.89 g, 9.50 mmol) in dry THF (5 mL) and the resulting mixture was stirred for 20 min. A solution of hexanal (0.95 g, 9.5 mmol) in dry THF (5 mL) was then added dropwise to the mixture. After 1 h, the mixture was warmed to rt and further stirred for 1 h. The solution was quenched with saturated aqueous NH_4Cl and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on silica gel using CCl_4 to give 2.02 g (87%) of **6a** as a colorless syrup. The product was a mixture of *E* and *Z* isomers (68:32) from the peak areas of vinylic protons in the ^1H NMR spectrum: IR (neat) 1600 (C=C) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.57 (t, C*H*=C, J_{HH} = 7.0 Hz), 5.19 (t, C*H*=C, J_{HH} = 7.3 Hz) (total 1 H), 5.05, 5.04 (each s, 1 H, C=CH_2), 4.61 (s, 1 H, C=CH_2), 2.49–2.41 (m, 4 H, CH_2), 2.30–2.06 (m, 8 H, SCH_3 and CH_2), 1.43–1.23 (m, 6 H, CH_2), 0.91–0.86 (m, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 146.3, 134.4, 133.8, 131.5, 124.3, 104.5, 104.4 (*E*,*Z*-CH=CH), 36.7, 35.9, 31.6, 31.5, 29.7, 29.3, 29.1, 28.6, 22.6, 22.5, 14.9, 14.8, 14.6, 14.1; MS (75 eV) *m/z* 244 (M^+).

(1*E*)- and (1*Z*)-2,5-Bis(methylthio)-1-phenyl-1,5-hexadiene (6b). In a similar manner, **5** (1.00 g, 3.16 mmol) was treated with dimethyl disulfide (0.30 g, 3.16 mmol) and benzaldehyde (0.34 g, 3.16 mmol) to give 0.46 g (58%) of **6b** (*E*/*Z* = 75/25) as a colorless syrup. The ratio of *E*,*Z* isomers was calculated from the peaks of vinylic protons in ^1H NMR: IR (neat) 1600 (C=C) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 7.1 (s, 5 H, Ph), 6.4, 6.0 (s and s, 1 H, PhC*H*=C), 5.0, 4.9 (s and s, 1 H, C=CH_2), 4.5, 4.47 (s and s, 1 H, C=CH_2), 2.82–1.77 (m, 10 H, CH_2 and SCH_3); MS (75 eV) *m/z* 250 (M^+).

(12) Analytical instruments employed in this study are the same as in ref 5.

1-Cyclohexylidene-1,4-bis(methylthio)-4-pentene (6c). In a similar manner, **5** (1.00 g, 3.16 mmol) was treated with dimethyl disulfide (0.30 g, 3.16 mmol) and cyclohexanone (0.31 g, 3.16 mmol) to give 0.12 g (16%) of **6c** as a pale yellow syrup: IR (neat) 1600 (C=C) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 4.90 (s, 1 H, C=CH_2), 4.43 (s, 1 H, C=CH_2), 2.53-1.77 (m, 14 H), 1.77-1.23 (m, 6 H); MS (75 eV) m/z 242 (M^+).

2,5-Undecanedione (7a).[7h] A mixture of **6a** (1.86 g, 7.60 mmol) in dry CH_3CN (45 mL), distilled water (15 mL), and $HgCl_2$ (4.13 g, 15.2 mmol) was stirred at 50 °C for 20 h. After being cooled to rt, the suspension was neutralized with saturated aqueous Na_2CO_3. The supernatant was filtered off through hyflo-supercel and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by Kugelrohr distillation (102 °C (1 mmHg)) to yield **7a** (1.11 g, 79%) as crystals (mp 32.1-33.0 °C): IR (neat) 1720 (C=O) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 2.54 (s, 4 H), 2.37 (t, 2 H, J_{HH} = 6 Hz), 2.10 (s, 3 H, CH_3), 1.87-0.63 (m, 11 H); MS (75 eV) m/z 184 (M^+).

1-Phenyl-2,5-hexanedione (7b).[7h] In a similar manner, **6b** (0.42 g, 1.68 mmol) was treated with $HgCl_2$ (0.91 g, 3.36 mmol). The residue was purified by Kugelrohr distillation (125-130 °C (3.0 mmHg)) followed by chromatography on silica gel using $CHCl_3$ to give 0.22 g (69%) of **7b** as a pale yellow syrup: IR (neat) 1710 (C=O) cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 7.10 (s, 5 H, Ph), 3.57 (s, 2 H, PhCH_2), 2.50 (s, 4 H, CH_2), 2.03 (s, 3 H, COCH_3); MS (75 eV) m/z 190 (M^+).

1-Cyclohexyl-1,4-pentanedione (7c).[7i] In a similar manner, **6c** (0.09 g, 0.37 mmol) was treated with $HgCl_2$ (0.20 g, 0.74 mmol). The residue was purified by Kugelrohr distillation (125-130 °C (10 mmHg)) followed by chromatography on silica gel using $CHCl_3$ to give 0.057 g (84%) of **7b** as a pale yellow syrup: IR (neat) 1710 (C=O) cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 2.57 (s, 4 H, CH_2), 2.07 (s, 3 H, COCH_3), 1.90-1.0 (m, 10 H, cyclic CH_2); MS (75 eV) m/z 182 (M^+).

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Registry No. 1, 55759-75-6; (*Z*)-2, 133967-68-7; (*E*)-2, 133967-69-8; 3, 133967-70-1; (*E*)-4, 58761-29-8; (*Z*)-4, 21944-96-7; 5, 133983-56-9; (*E*)-6a, 133967-71-2; (*Z*)-6a, 133967-72-3; (*E*)-6b, 133967-73-4; (*Z*)-6b, 133967-74-5; 6c, 133967-75-6; 7a, 7018-92-0; 7b, 32776-14-0; 7c, 61771-79-7; hexanal, 66-25-1; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; dimethyl disulfide, 624-92-0.

Supplementary Material Available: ^1H NMR spectra for compounds 2-5, 6a-c, and 7a-c (14 pages). Ordering information is given on any current masthead page.

Reexamination of the Conformational Preference of the Benzyl Group in Cyclohexane. Enthalpic and Entropic Contributions to $\Delta G°(CH_2Ph)$†

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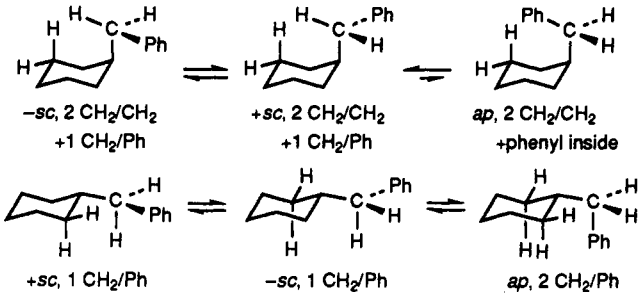
Introduction

The energy differences between the equatorial and axial conformations of monosubstituted cyclohexanes (*A* values) are of great interest to organic chemists since they serve as models for more complicated molecules.[1] Alkyl groups prefer equatorial over axial positions in order to avoid the repulsive steric interactions with the axial hydrogens of the 3- and 5-positions, and it is usually observed that bulkier the alkyl group the larger the preference for the equatorial form.[2]

Scheme I

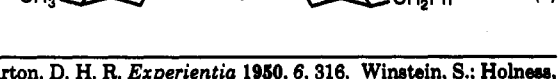


In this regard, the accepted *A* values for methyl, ethyl, and isopropyl are 1.74, 1.8, and 2.15, respectively,[2] in line with their increasing size. However, early force-field calculations indicated that the *enthalpic* contributions to the equatorial preference actually *decrease* along this series.[3] By contrast, more recent force-field results suggest that the axial-equatorial enthalpy differences do not decrease, but vary slightly along the methyl, ethyl, and isopropyl series.[4] Nevertheless, experimental NMR data agreed with the early theoretical results, affording, in kcal/mol, $-\Delta H°$(Me) = 1.75, $-\Delta H°$(Et) = 1.6, and $\Delta H°$(*i*-Pr) = 1.52.[5]

The conformational study of benzylcyclohexane was deemed important in this context because the analysis of the gauche interactions present in the axial and equatorial conformers (Scheme I) suggests that the overall enthalpy difference must be *less* than the two gauche butane interactions present in axial methylcyclohexane. On the other hand, three populated rotamers in equatorial benzylcyclohexane versus two in the axial form[6] imply that the entropy of mixing should make a substantial contribution to the free energy difference.

Results and Discussion

cis- and *trans*-1-benzyl-4-methylcyclohexanes (*cis*- and *trans*-1) were prepared and separated according to the procedure of Anderson.[7] The ambient-temperature 270-MHz NMR spectrum of *cis*-1 (solvent CD_2Cl_2) presents a doublet (J = 7.9 Hz) at δ 2.57 due to the benzyl methylene hydrogens. At 202 K the signal appears as two doublets at δ 2.65 and 2.46, in a 56.4:43.6 ratio. Because the methylene signal in conformationally fixed *trans*-1 has δ 2.47, a reasonable conclusion is that the downfield signal corresponds to the axial benzyl. Therefore, at low temperature the conformational equilibrium of *cis*-1 (eq 1) appears to be displaced to the left, with $\Delta G°_{202K}$ = +0.10 kcal/mol.



(1)

† Dedicated to Professor Fernando Walls, Instituto de Química, UNAM, on the occasion of his 60th birthday.

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