directionality patterns, including the consequences of reversal of sense of directionality, thus reveals the existence of a stereochemical relationship between sets of molecules with utterly disparate structures[8,9] and suggests the possibility that other unsuspected stereochemical similarities may be uncovered by the same type of analysis.

Experimental Section

NMR spectra were measured on a Bruker WM-250 and mass spectra on a Kratos MS 50 RFA spectrometer.

2,5-Dimethylhex-3-yn-2-ol-d_6 was prepared in 67% yield from (3-methyl-1-butyn-1-yl)magnesium bromide and acetone-d_6 (99 atom % D) according to the procedure described for the unlabeled compound.[10] The compound was found by MS to contain 97+ atom % deuterium at the labeled positions.

Diisopropylacetylene-d_6. 2,5-Dimethylhex-3-yn-2-ol-d_6 (10.5 g, 80 mmol) was reacted with dicobalt octacarbonyl (Strem) followed by treatment with $NaBH_4/CF_3COOH$ according to the procedure previously described for the unlabeled compound.[3] The title compound, obtained in 24% yield, was found by MS to contain 93+ atom % of deuterium at the labeled positions. ^1H NMR ($CDCl_3$) δ 1.10 (d, 6 H, J = 6.7 Hz, $CH(CH_3)_2$), 2.46 (1 H, $CH(CD_3)_2$, br), 2.49 (d of septets, 1 H, ^3J = 6.7 Hz, ^5J = 1.8 Hz, $CH(CH_3)_2$).

Hexaisopropylbenzene-d_{18} was prepared by $Hg[Co(CO)_4]_2$ catalyzed trimerization of diisopropylacetylene-d_6 according to the procedure described for the unlabeled compound.[3] The product was found by MS and the combustion falling-drop method[11] to contain 93+ atom % deuterium at the labeled positions.

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Registry No. 1, 112504-73-1; 2, 112504-74-2; (3-methyl-1-butyn-1-yl)magnesium bromide, 112482-54-9; acetone-d_6, 666-52-4; 2-(methyl-d_3)-5-methylhex-3-yn-2-ol-*1,1,1*-d_3, 112482-52-7; (isopropyl-*1,1,1,3,3,3*-d_6)isopropylacetylene, 112482-53-8.

(7) Brewster, J. H. *J. Org. Chem.* **1986**, *51*, 4751.
(8) The analogy described above is restricted to achiral molecules in which the two external directed cycles are enantiotopic and in which the reversal of the sense of the central cycle (or, equivalently, of the two outer cycles) leads to an achiral isomer.
(9) A similar correspondence exists between the enantiomeric trihydroxyglutaric acids and, for example, the cycloenantiomeric cyclohexaalanyls.[1]
(10) Burawoy, A.; Spinner, E. *J. Chem. Soc.* **1954**, 3752.
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Barrier to Internal Rotation in 1,2-Bis(bromochloromethyl)-3,4,5,6-tetraisopropylbenzene

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The tightly gear meshed arrangement of isopropyl and dichloromethyl groups in hexaisopropyl- and hexakis(dichloromethyl)benzene, respectively, imparts a high barrier to internal rotation. For hexaisopropylbenzene,[1] a lower limit of 22 kcal mol^{-1} was estimated for the topomerization barrier from NMR measurements on a d_{28} isotopomer and a barrier of ca. 35 kcal mol^{-1} was calculated by use of the empirical force field (EFF) method. For hexakis(dichloromethyl)benzene,[2] the calculated (EFF) topomerization barrier was 33.9 kcal mol^{-1}. Consistent with these findings is the lower limit of 24 kcal mol^{-1} estimated (NMR) for the enantiomerization barrier in (1′*RS*,2′*SR*)-1,2-bis(1-bromoethyl)-3,4,5,6-tetraisopropylbenzene.[3]

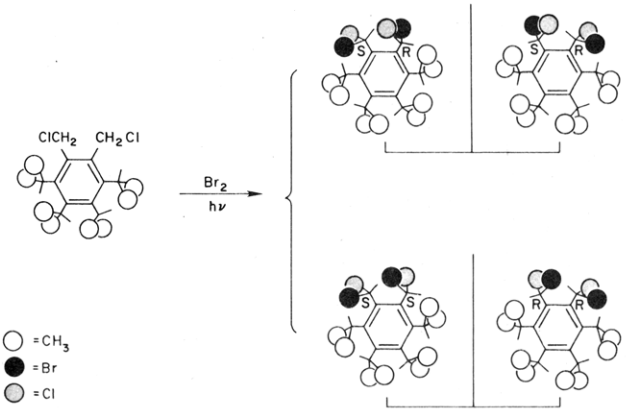

Figure 1. Photobromination of 1,2-bis(chloromethyl)-3,4,5,6-tetraisopropylbenzene to a diastereomeric mixture of 1,2-bis(bromochloromethyl)-3,4,5,6-tetraisopropylbenzene (**1**). Enantiomers are related by vertical mirror lines. Top: 1′*S*,2′*R* and 1′*R*,2′*S* enantiomers. Bottom: 1′*S*,2′*S* and 1′*R*,2′*R* enantiomers.

The title compound **1** was prepared in order to provide an experimental value for this barrier: unlike the diastereomers of 1,2-bis(1-bromoethyl)-3,4,5,6-tetraisopropylbenzene, which suffer dehydrohalogenation at elevated temperature,[3] the diastereomers of **1** are expected to resist decomposition under similar conditions. Cotrimerization of diisopropylacetylene with 1,4-diacetoxy-2-butyne in the presence of $Hg[Co(CO)_4]_2$ gave a mixture of hexaisopropylbenzene, hexakis(acetoxymethyl)benzene, 1,2-bis(acetoxymethyl)-3,4,5,6-tetraisopropylbenzene (**2**), and 1,2-diisopropyl-3,4,5,6-tetrakis(acetoxymethyl)benzene, together with a small quantity of tetraisopropylcyclopentadienone. The mixture was separated, the isolated **2** was hydrolyzed in ethanolic KOH, and the resulting diol was converted to 1,2-bis(chloromethyl)-3,4,5,6-tetraisopropylbenzene (**3**) with thionyl chloride. Photobromination of **3** led to a diastereomeric mixture (Figure 1) that is stereochemically analogous to the mixture depicted in Figure 5 of ref 3.

The two diastereomers are asymmetric on the NMR time scale, and each methyl or methine proton in the mixture should therefore give rise to a distinct NMR signal, barring accidental isochrony. The 250-MHz ^1H NMR spectrum of the mixture in C_6D_6 displays 12 doublets in the methyl region; there is accidental isochrony for four pairs of signals (see Experimental Section). The three doublets at δ 1.58–1.64 appear as an apparent AB quartet, since their coupling (ca. 7.4 Hz) is of the order of their mutual separation. Indeed, when the signal at δ 5.04 was irradiated, the apparent quartet collapsed into three singlets with a 1:2:1 intensity ratio. In the methine region, two overlapping septets were observed at δ 3.65 and 3.70, and the remaining two septets were observed at δ 3.89 and 5.04. The most downfield septet was assigned to the unique isopropyl methine proton in each diastereomer which is tucked into the cleft of a neighboring bromochloromethyl group.[3] In the low-field region, three signals were observed: one at δ 7.61 (integrating for two protons) and the other two (integrating for two protons, and with

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(2) Kahr, B.; Biali, S. E.; Schaefer, W.; Buda, A. B.; Mislow, K. *J. Org. Chem.* **1987**, *52*, 3713.
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a relative intensity ratio of ca. 1:1) at δ 8.86 and 8.87. These signals were assigned to the bromochloromethyl methine protons, with the lower field signal corresponding to the methines tucked into the notch of the neighboring bromochloromethyl group in the two diastereomers; the observation of one signal at δ 7.61 instead of two is evidently the result of an accidental isochrony. It can be safely inferred from the NMR data that the two diastereomers depicted in Figure 1 are present in a nearly 1:1 ratio.

A sample of the mixture in *cis*-decahydronaphthalene-d_{18} did not show any appreciable line broadening of the ^{1}H NMR signals at 250 MHz up to 420 K. We therefore resorted to the saturation spin transfer method. The advantage of this method over the normal (coalescence) DNMR method is that the measured rates are comparable to $1/T_1$ and the measurements are therefore conveniently carried out at relatively low temperatures. The experiment was carried out in *cis*-decahydronaphthalene-d_{18} at 429 K by delivering a selective 180° pulse on the higher field bromochloromethyl methine signal, followed by a nonselective 90° pulse after increasingly longer delay times.[4] Both low-field bromochloromethyl methine signals showed a clear diminution of intensities. Treatment of the change of intensities of the irradiated and perturbed signals according to the literature procedure[5] afforded an exchange rate constant of 0.19 s^{-1}. From the Eyring equation and assuming a transmission coefficient equal to unity, a barrier ($\Delta G^{\ddagger}_{429}$) of 26.8 kcal mol^{-1} was calculated.[6,7]

The experimentally determined barrier to internal rotation of the side chains in **1** is substantially smaller (by 7–8 kcal mol^{-1}) than that calculated for hexaisopropyl- and hexakis(dichloromethyl)benzene. It seems unlikely that structural differences between **1** and these closely related compounds can be held to account for a discrepancy of this magnitude.[8] Neglecting possible entropy effects, the present results therefore suggest that the calculated barriers for hexaisopropyl- and hexakis(dichloromethyl)-benzene may have been significantly overestimated.[9]

Experimental Section

NMR spectra were recorded on a Bruker WM-250 spectrometer. Temperature measurements were based on the chemical shift separation of an ethylene glycol sample and utilization of the Van Geet relationship.[10] Mass spectra were measured on a Kratos MS 50 RFA spectrometer. Melting points were recorded on a Thomas-Hoover melting point apparatus and are corrected. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY.

1,2-Bis(acetoxymethyl)-3,4,5,6-tetraisopropylbenzene (2). A mixture of diisopropylacetylene[1] (6 g, 54.5 mmol), 1,4-diacetoxy-2-butyne[11] (2 g, 11.8 mmol), and $Hg[Co(CO)_4]_2$[12] (2 g, 3.66 mmol) was refluxed under an atmosphere of argon for 72 h (bath temperature 110–120 °C). After extraction with 125 mL of boiling chloroform, the filtered solvent was evaporated and the residue was chromatographed on silica gel (60–200 mesh, eluent 9:1 hexane/chloroform). First to be eluted were hexaisopropylbenzene (60 mg, mp 281–282 °C (lit.[13] mp 285–287 °C)) and tetraisopropylcyclopentadienone (72 mg of red crystals, mp 119–120 °C (lit.[13] mp 119–120 °C)). The third fraction consisted of the desired compound (**2**): 300 mg (7% based on 1,4-diacetoxy-2-butyne); mp 134 °C after recrystallization from ethanol; ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 24 H, J = 7.3 Hz, $CH(CH_3)_2$, br), 2.07 (s, 6 H, $COCH_3$), 3.39 (m, 1 H, $CH(CH_3)_2$, br), 3.71 (m, 3 H, $CH(CH_3)_2$, br), 5.11 (s, 2 H, CH_2, br), 5.28 (s, 2 H, CH_2, br); mass spectrum (high resolution), m/z 390.2760 (390.2770 calcd for $C_{24}H_{38}O_4$). Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.81; H, 9.81. Found: C, 74.07; H, 10.16.

The fourth fraction was found to consist of **1,2-diisopropyl-3,4,5,6-tetrakis(acetoxymethyl)benzene** (730 mg, 32% based on 1,4-diacetoxy-2-butyne): mp 146 °C after recrystallization from ethanol; ^{1}H NMR ($CDCl_3$) δ 1.37 (d, 12 H, J = 7.3 Hz, $CH(CH_3)_2$), 2.05 (s, 6 H, $COCH_3$), 2.06 (s, 6 H, $COCH_3$), 3.52 (m, 1 H, $CH(CH_3)_2$, br), 3.72 (m, 1 H, $CH(CH_3)_2$, br), 5.23 (s, 4 H, CH_2, br), 5.33 (s, 4 H, CH_2, br); mass spectrum (high resolution), m/z 450.2238 (450.2253 calcd for $C_{24}H_{38}O_8$). Anal. Calcd for $C_{24}H_{38}O_8$: C, 63.98; H, 7.61. Found: C, 63.84; H, 7.65. The fifth fraction consisted of hexakis(acetoxymethyl)benzene (370 mg, mp 166 °C after recrystallization from ethanol (lit.[14] mp 167–168 °C)); ^{1}H NMR ($CDCl_3$) δ 2.05 (s, 18 H, $COCH_3$), 5.38 (s, 12 H, CH_2).

1,2-Bis(chloromethyl)-3,4,5,6-tetraisopropylbenzene (3). A solution of 1,2-bis(acetoxymethyl)-3,4,5,6-tetraisopropylbenzene (290 mg, 0.74 mmol) and KOH (300 mg) in 10 mL of absolute ethanol was heated under reflux for 3 h. The mixture was cooled, and 15 mL of ethanol was added. Filtration of the precipitated solid gave 150 mg of 1,2-bis(hydroxymethyl)-3,4,5,6-tetraisopropylbenzene (77%): mp 150–152 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (d, 12 H, J = 7.3 Hz, $CH(CH_3)_2$), 1.39 (d, 12 H, J = 7.4 Hz, $CH(CH_3)_2$), 1.59 (s, 2 H, OH, br), 3.71 (m, 4 H, $CH(CH_3)_2$, br), 4.75 (s, 2 H, CH_2, br), 5.00 (s, 2 H, CH_2, br). A solution of 1,2-bis(hydroxymethyl)-3,4,5,6-tetraisopropylbenzene (69 mg, 0.22 mmol) in 12 mL of benzene was heated to 65 °C, and 2 mL of $SOCl_2$ was added. The solution was kept at 65 °C for 5 min, and the solvent was evaporated. The ^{1}H NMR spectrum of the residue showed that the conversion was essentially complete. The compound was recrystallized from $CHCl_3$ to yield 40 mg (53%) of **3**: mp 188 °C; ^{1}H NMR ($CDCl_3$) δ 1.35 (d, 12 H, J = 7.3 Hz, $CH(CH_3)_2$), 1.41 (d, 12 H, J = 7.3 Hz, $CH(CH_3)_2$), 3.69 (m, 4 H, $CH(CH_3)_2$), 4.94 (s, 4 H, CH_2, br); mass spectrum (high resolution), m/z 342.1857 (342.1881 calcd for $C_{20}H_{32}Cl_2$).

1,2-Bis(bromochloromethyl)-3,4,5,6-tetraisopropylbenzene (1). Bromine (120 mg, 0.75 mmol) was added to a solution of 1,2-bis(chloromethyl)-3,4,5,6-tetraisopropylbenzene (90 mg, 0.26 mmol) in 10 mL of dry and degassed CCl_4, and the well-stirred mixture was irradiated with a 150-W lamp at room temperature. After 1 h of irradiation, the solvent was evaporated and the residue was treated with 10 mL of ethanol. The white residue that remained undissolved was separated and washed with 5 mL of ethanol to afford 26 mg (20%) of pure product: mp >300 °C; ^{1}H NMR (C_6D_6) δ 1.19 (d, 3 H, J = 7.55 Hz), 1.20 (d, 9 H, J = 7.33), 1.21 (d, 3 H, J = 7.24), 1.22 (d, 3 H, J = 7.42), 1.27 (d, 6 H, J = 7.22), 1.28 (d, 3 H, J = 7.45), 1.30 (d, 3 H, J = 6.78), 1.31 (d, 3 H, J = 7.59), 1.33 (d, 3 H, J = 7.04), 1.58 (d, 3 H, J = 7.44), 1.61 (d, 6 H, J = 7.41 Hz), 1.64 (d, 3 H, J = 7.41 Hz), 3.65 (septet, 2 H, $CH(CH_3)_2$), 3.70 (septet, 2 H, $CH(CH_3)_2$), 3.89 (septet, 2 H, $CH(CH_3)_2$), 5.04 (septet, 2 H, $CH(CH_3)_2$), 7.61 (s, 2 H, BrClCH), 8.86, 8.87 (s, 2 H, BrClCH); mass spectrum (high resolution), m/z 498.0080 (498.0090 calcd for $C_{20}H_{30}{}^{35}Cl_2{}^{79}Br_2$), m/z 500.0074

(4) This method could not be employed with the d_{28} isotopomer of hexaisopropylbenzene[1] because the chemical shift differences of the diastereotopic isopropyl protons are too small. Although the same experiment could in principle have been carried out on 1,2-bis(dichloromethyl)-3,4,5,6-tetraisopropylbenzene, we were unsuccessful in various attempts to prepare this compound; for example, photochlorination of **3** gave an intractable mixture of polychlorinated compounds.

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(7) The magnitude of this barrier suggests that resolution of (1′*RS*,2′*SR*)-**1** should in principle be feasible at room temperature. However, attempts to separate the isomers by chromatography on cellulose tris(3,5-dimethylphenylcarbamate), cellulose tris(3,5-dichlorophenylcarbamate), amylose tris(3,5-dichlorophenylcarbamate), microcrystalline cellulose triacetate, and (+)-poly(triphenylmethyl methacrylate) were unsuccessful (Okamoto, Y., private communication).

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(9) However, the observed topomerization barrier in chloropentakis(dichloromethyl)benzene, 20 kcal mol^{-1}, is well reproduced by the calculated (EFF) barrier of 22 kcal mol^{-1}. See: Biali, S. E.; Buda, A. B. *J. Org. Chem.* **1988**, *53*, 135.

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(500.0070 calcd for $C_{20}H_{30}{}^{35}Cl_2{}^{79}Br^{81}Br$), m/z 502.0057 (502.0050 calcd for $C_{20}H_{30}{}^{35}Cl_2{}^{81}Br_2$). Anal. Calcd for $C_{20}H_{30}Cl_2Br_2$: C, 47.93; H, 6.03. Found: C, 47.80; H, 6.03.

Acknowledgment. We thank the National Science Foundation (CHE-8510067) for support of this work.

Registry No. (R^*,R^*)-(±)-**1**, 112506-35-1; (R^*,S^*)-**1**, 112506-36-2; **2**, 112506-31-7; **3**, 112506-34-0; diisopropylacetylene, 927-99-1; 1,4-diacetoxy-2-butyne, 1573-17-7; hexaisopropylbenzene, 800-12-4; tetraisopropylcyclopentadienone, 99458-90-9; hexakis(acetoxymethyl)benzene, 41267-57-6; 1,2-diisopropyl-3,4,5,6-tetrakis(acetoxymethyl)benzene, 112506-32-8; 1,2-bis(hydroxymethyl)-3,4,5,6-tetraisopropylbenzene, 112506-33-9.

Studies on the Keto–Enol Equilibria of the Methyl 2-Oxocycloalkanoates $MeOOCCH(CH_2)_nCO$ (n = 3–6) by IR, ^{13}C NMR, and Mass Spectrometry

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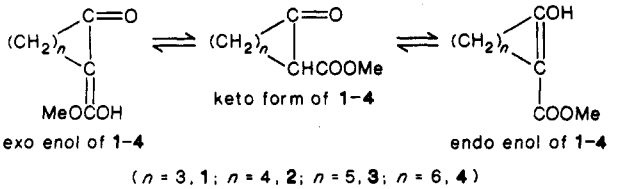
The alkyl esters of 2-oxocycloalkanecarboxylic acids are receiving considerable attention, not only from the viewpoints of synthesis[1–4] and reactivity[5–7] but also because of their spectroscopic behavior.[8] Several groups have examined the keto–enol equilibria of this class of β-keto esters. The extent of enolization has been found to depend upon solvent and temperature.

On the basis of bromine titrations and UV and ^1H NMR studies, Rhoads[9] concluded that amongst the ethyl esters of the C_5–C_{10} 2-oxocycloalkanecarboxylic acids, the even-membered systems exhibit 60–80% enol content while the odd-membered series exist as enols to a much lower extent, the lowest value of ~11% being observed for the cyclopentane derivative. On the other hand, Sterk[10] found that the C_5 keto ester (the terminology C_5, C_6, C_7, and C_8 in the current discussion and tables refer to the ring size of the cycloalkane derivatives) mentioned above exists exclusively in the keto form in DMSO or nitrobenzene in the temperature range of 20–120 °C, while the corresponding C_6 analogue showed an enol content of 80–50% in the same temperature range. However, Strohmeier and Hohne[11] concluded that the enol content of ethyl 2-oxocyclopentanecarboxylate varies from 27.6% to 13.5% over the 0–200 °C range. In addition to the apparent confusion concerning the C_5 cyclic β-keto ester, no gas-phase studies have been performed on the C_6–C_8 analogues and the methyl esters have not been examined at all. Furthermore, no ^{13}C NMR or mass spectral studies have been performed on either the methyl or the ethyl esters. Accordingly, we undertook an examination of the tautomeric equilibria of the methyl esters **1–4** by FTIR, ^{13}C NMR, and mass spectrometry to ascertain whether any differences exist in the keto:enol ratio for the pure liquid, solution, and gas phases (see Scheme I for the structures of the keto and enol forms).

Scheme I. Keto and Enol Forms of the Compounds Investigated



(n = 3, **1**; n = 4, **2**; n = 5, **3**; n = 6, **4**)

Results and Discussion

The ^{13}C NMR spectra of **1–4** in chloroform solution are given in Table I. In the solution phase, the keto:enol ratios were computed from peak integration corresponding to the alkoxy and carbonyl carbons of the carbomethoxy function representing enol and keto modifications. For the pure liquid form, the ester carbonyl peak absorbances in the IR at ~1750 (keto form) and ~1650 cm^{-1} (enol form) were used to calculate the keto:enol ratios. The low-resolution mass spectra of **1–4** did not yield any conclusive evidence concerning the extent of enolization, the major fragments observed being the $[M - CO]^+$, $[M - MeO^\bullet]^+$, and $[M - MeOH]^+$ ions. However, injection of the keto esters **1–4** into the inlet system saturated with D_2O would only exchange the enolic hydrogen with deuterium. Since the enolic form is expected to lose methanol through the participation of COOMe and the enolic hydrogen exclusively (in analogy with methyl salicylate[12]), the extent of MeOD loss must be proportional to this tautomeric form in the vapor phase. On the other hand, the extent of MeOH elimination from M^+ must be proportional to the keto form of the parent ions, since it is known[13] that methyl cyclohexane carboxylate loses MeOH by the involvement of the C_3 axial hydrogen. Thus, the $[M - MeOH]^+$:$[M - MeOD]^+$ ratio must represent the keto:enol ratio at equilibrium in the vapor phase. In addition to this approach, the metastable ion spectra of the molecular ions from **1–4** were examined to check whether any information could be obtained on the two tautomeric forms. In the MIKES spectra, if the loss of CO is attributed to the keto form exclusively, and elimination of H_2O from M^+ solely to the enol form, then the ratio of the intensities of these two ions must at least semiquantitatively represent the keto:enol ratio in the gas phase for the esters **1–4**. This argument seems to be valid, since the ratios obtained by this method were found to be close to those resulting from the deuterium-exchange experiments. The keto:enol ratios obtained by the three spectroscopic techniques described above are given in Table II.

The data in Table II indicates that methyl 2-oxocyclopentanecarboxylate exists solely in the keto form in all

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