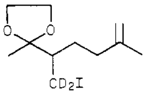
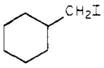
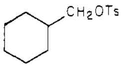
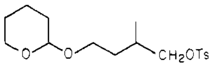
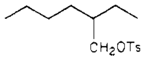
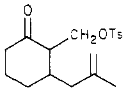
Table I. DBN- and DBU-Promoted Eliminations

no.	alkyl tosylate or iodide	procedure[a]	isolated yield of alkene, %
1		A (DBN in C_6H_6)	91
2		A (DBU in DMF)	~60
3		B	60
4		B	82
5		B	80
6	*n*-$C_8H_{17}OTs$	B	5
7		C	95

[a] A, iodide, 1.5 equiv of amidine, 80–90 °C, 3–4 h; B, tosylate, 2.5 equiv of NaI, DMF, 50 °C, 4–6 h, then 1.5 equiv of DBU, 80 °C, 3–4 h; C, tosylate, DBN, ether, 0 °C, 0.5 h.

sium *tert*-butoxide in dimethyl sulfoxide at 50 °C[5] yielded a 3:2 mixture of the terminal olefin and its rearranged trisubstituted isomer.

The failure of 1-octyl tosylate (**6**) to furnish a serviceable yield of 1-octene in procedure B is in agreement with the original report noted above. Treatment of cyclohexanemethyl tosylate (**3**) directly with DBU (as procedure B, but not sodium iodide) failed to give methylenecyclohexane. With suitable activation, however, the direct elimination of *p*-toluenesulfonic acid is feasible under mild conditions, as is shown by entry **7**. Procedure C consisted in reaction with DBN in ether at 0 °C for 0.5 h.

One additional observation is noteworthy. An equimolar mixture of 1-iodooctane and cyclohexanemethyl iodide (**2**) was treated in procedure B, but using only 0.5 equiv (total) of DBU. The water-insoluble material isolated consisted of four compounds in the indicated approximate yields: cyclohexanemethyl iodide (75%), 1-iodooctane (15%), methylenecyclohexane (10%), and 1-octene (5%). This distribution of products is consistent with selective reaction of DBU with the unbranched 1-iodooctane to form a water-soluble ammonium salt that does not undergo subsequent elimination. Branching at the β-carbon atom appears then to retard the substitution reaction between substrate and amidine leading to an ammonium salt but to accelerate the elimination to alkene. Earlier kinetic studies have demonstrated such an effect of β-alkyl substitution on displacement and elimination reactions at a primary carbon atom.[6]

Experimental Section

Materials and Equipment. General procedures have been described previously.[7] Preparation of **1**, **4**, and **7** is described in forthcoming publications.[8]

General Procedure for Elimination Reactions. A mixture of the tosylate and NaI (2.5 equiv) in DMF (2 mL/mmol) was heated at 50–55 °C for 5 h. This step was omitted for entries **1** and **2**. The mixture was cooled to room temperature, DBN or DBU (1.5 equiv) was added, and the reaction mixture was heated at 80–85 °C for 3 h. The mixture was cooled, poured into ice and water, and extracted with pentane (three times). The combined pentane extracts were washed with water, dilute HCl or oxalic acid, water, saturated $NaHCO_3$ solution, and brine and were dried. After removal of pentane by distillation through a 60-cm Vigreux column, the residue was distilled to afford the desired product. All products had spectra consistent with their assigned structures; NMR spectra indicated 2% or less double-bond isomerization.[9]

Registry No. 1, 82880-47-5; **2**, 5469-33-0; **3**, 3725-11-9; **4**, 82880-48-6; **5**, 78016-72-5; **6**, 3386-35-4; **7**, 82880-49-7; DBN, 3001-72-7; DBU, 6674-22-2; 2-methyl-2-(4-methyl-1-methylene-d_2-4-pentenyl)-1,3-dioxolane, 82890-86-6; methylenecyclohexane, 1192-37-6; 2-(4-methylene-1-oxapentyl)tetrahydropyran, 55975-11-6; 3-methyleneheptane, 1632-16-2; 1-octene, 111-66-0; 2-methylene-3-(2-methyl-2-propenyl)cyclohexanone, 82880-50-0.

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(5) Wood, N. F.; Chang, F. C. *J. Org. Chem.* **1965**, *30*, 2054.

(6) Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. D. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4735 and references cited therein.

(7) Ayral-Kaloustian, S.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1977**, *99*, 5984.

(8) Wolff, S.; Agosta, W. C., submitted for publication.

(9) For grants in support of this research we are grateful to the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

Crystal and Molecular Structure of 1,1,1,3,3,3-Hexaphenylpropane

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In connection with our studies of correlated rotation in systems containing two 9-triptycyl (Tp) groups attached to a common center,[1] we recently determined the X-ray structures of bis(9-triptycyl)carbinol (Tp_2CHOH),[1b] bis(9-triptycyl)methane (Tp_2CH_2),[1f] and bis(9-triptycyl) ketone (Tp_2CO).[1f] The most striking feature of these structures was found to be the greatly expanded central C–C–C bond angle which assumes the extraordinary value of 129° in all three compounds. Obviously, repulsive nonbonded interaction between the bulky Tp groups is to be held accountable for this phenomenon.

The observation of greatly expanded central bond angles in bis(triphenylmethyl) ether (127.9°)[2] and sulfide (119.8°)[3] suggests that the space-demanding properties of trityl (Tt) and Tp groups might be comparable in magnitude, and led to the prediction[1f] that the central bond angle in bis-

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(1) (a) Hounshell, W. D.; Johnson, C. A.; Guenzi, A.; Cozzi, F.; Mislow, K. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6961. (b) Cozzi, F.; Guenzi, A.; Johnson, C. A.; Mislow, K.; Hounshell, W. D.; Blount, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 957. (c) Johnson, C. A.; Guenzi, A.; Mislow, K. *Ibid.* **1981**, *103*, 6240. (d) Bürgi, H.-B.; Hounshell, W. D.; Nachbar, R. B., Jr.; Mislow, K., *J. Am. Chem. Soc.*, in press. (e) Guenzi, A.; Johnson, C. A.; Cozzi, F.; Mislow, K., *J. Am. Chem. Soc.*, in press. (f) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K., *J. Am. Chem. Soc.*, in press.

(2) Glidewell, C.; Liles, D. C. *Acta Crystallogr., Sect. B* **1978** *34*, 696.

(3) Jeffrey, G. A.; Robbins, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 1820.

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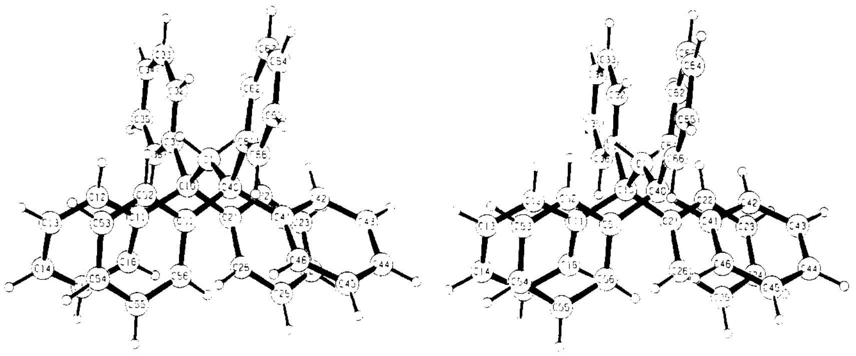

Figure 1. Stereoview of the X-ray structure of 1,1,1,3,3,3-hexaphenylpropane (Tt_2CH_2).

(triphenylmethyl)methane (1,1,1,3,3,3-hexaphenylpropane, Tt_2CH_2)[4] might assume a value close to that found for Tp_2CH_2. The present work was undertaken to test this prediction.

Results and Discussion

Crystals of Tt_2CH_2 are triclinic, space group $P\bar{1}$. There are two enantiomeric molecules in the unit cell, related by the center of symmetry. Positional coordinates of the carbon atoms are listed in Table I, and a stereoview of the molecule is shown in Figure 1. The value of the central bond angle C(10)–C(1)–C(40) is 128.0 (2)°, comparable in magnitude to the value of 129.3° observed[1f] for Tp_2CH_2 and thus in accord with our prediction.[5] In its molecular conformation, however, the structure of Tt_2CH_2 differs dramatically from that of Tp_2CH_2. This contrast, elaborated below, is easily appreciated by a visual inspection of the X-ray structures of Tt_2CH_2 (Figure 1) and Tp_2CH_2 (Figure 2 in ref 1f) and by comparison of the appropriate torsion angles listed in Table II.

First, in Tt_2CH_2 the bonds attached to C(1)–C(40) are staggered, as are those attached to C(1)–C(10). Accordingly, the central frame (i.e., the C(10)–C(1)–C(40) fragment plus the eight atoms attached thereunto) has very nearly $C_{2v}(2/2)$ symmetry, and thus resembles the ground state of propane,[1c] with the benzene ipso carbons (i.e., C(11), C(21), etc.) in Tt_2CH_2 taking the place of the methyl hydrogens in propane. On the other hand, while the bonds attached to C(1)–C(40) in Tp_2CH_2 are also staggered, those attached to C(1)–C(10) are now nearly eclipsed. Accordingly, the central frame—and the molecule in the crystal—acquires approximate C_s symmetry; a C_{2v} (2/2) central frame would raise the energy of the molecule ca. 61 kcal mol^{-1} above the ground state.[1c] In this connection it is instructive to consider also the conformations of Tt_2O and Tt_2S (Table II): remarkably, the conformation of the central frame in Tt_2O closely resembles that in Tp_2CH_2 (i.e., near C_s symmetry) rather than that in the superficially more analogous Tt_2CH_2. It thus appears that the presence of the methylene hydrogens on C(1) in Tt_2CH_2 enforces the observed all-staggered conformation.[6]

Second, the Tt groups in Tt_2CH_2 assume the shape of two irregular homochiral propellers, thus imparting approximate C_2 symmetry to the molecule.[7] Such propeller shapes are ruled out in Tp_2CH_2 by the bonding constraints of the Tp groups. In particular, two of the benzene rings in Tt_2CH_2 (C(31)⋯C(36) and C(61)⋯C(66)) are virtually coplanar with each other and the C(10)–C(1)–C(40) plane, whereas the remaining four rings are tilted away from, and subtend large angles with, this plane. This arrangement is obviously impossible in Tp_2CH_2 and related molecules, all of which resemble tightly meshed gear systems.[1]

Table I. Final Atomic Parameters for Tt_2CH_2 with Standard Deviations in Parentheses

atom	x	y	z
C(1)	0.5673 (2)	0.6019 (2)	0.28507 (11)
C(10)	0.4864 (2)	0.7473 (2)	0.33525 (11)
C(11)	0.3931 (2)	0.8634 (2)	0.28515 (11)
C(12)	0.2921 (2)	0.8435 (2)	0.24095 (13)
C(13)	0.1992 (3)	0.9478 (3)	0.20040 (14)
C(14)	0.2019 (3)	1.0762 (3)	0.20399 (16)
C(15)	0.2969 (3)	1.0985 (2)	0.24931 (16)
C(16)	0.3904 (3)	0.9943 (2)	0.29024 (14)
C(21)	0.6166 (2)	0.7755 (2)	0.36530 (12)
C(22)	0.6416 (3)	0.7426 (2)	0.44649 (13)
C(23)	0.7689 (3)	0.7573 (2)	0.47007 (16)
C(24)	0.8723 (3)	0.8059 (2)	0.41312 (19)
C(25)	0.8481 (3)	0.8401 (2)	0.33331 (17)
C(26)	0.7224 (2)	0.8256 (2)	0.30941 (13)
C(31)	0.3521 (2)	0.7423 (2)	0.41713 (11)
C(32)	0.3137 (2)	0.6299 (2)	0.43734 (12)
C(33)	0.1938 (3)	0.6322 (2)	0.51227 (13)
C(34)	0.1109 (3)	0.7471 (2)	0.56867 (12)
C(35)	0.1455 (3)	0.8606 (2)	0.54905 (13)
C(36)	0.2635 (3)	0.8583 (2)	0.47449 (13)
C(40)	0.7085 (2)	0.5512 (2)	0.19846 (11)
C(41)	0.8761 (2)	0.5392 (2)	0.20654 (11)
C(42)	0.9190 (2)	0.5036 (2)	0.28308 (12)
C(43)	1.0717 (3)	0.4822 (2)	0.29083 (14)
C(44)	1.1884 (3)	0.4935 (2)	0.22019 (16)
C(45)	1.1500 (3)	0.5252 (3)	0.14284 (16)
C(46)	0.9971 (3)	0.5468 (2)	0.13541 (13)
C(51)	0.6524 (2)	0.6369 (2)	0.12475 (11)
C(52)	0.5467 (2)	0.6098 (2)	0.08769 (12)
C(53)	0.4864 (3)	0.6864 (2)	0.02433 (14)
C(54)	0.5325 (3)	0.7922 (2)	−0.00524 (14)
C(55)	0.6342 (3)	0.8222 (2)	0.03102 (15)
C(56)	0.6931 (3)	0.7466 (2)	0.09584 (13)
C(61)	0.7394 (2)	0.3998 (2)	0.17580 (12)
C(62)	0.6812 (3)	0.3191 (2)	0.23328 (14)
C(63)	0.7161 (3)	0.1838 (2)	0.20917 (18)
C(64)	0.8100 (3)	0.1264 (2)	0.12797 (19)
C(65)	0.8716 (3)	0.2037 (2)	0.07036 (16)
C(66)	0.8369 (3)	0.3375 (2)	0.09452 (13)

Thus, while the present work has confirmed the prediction that the Tp groups in Tp_2X and the Tt groups in

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[4] (a) Schlenck, W.; Bornhardt, C. *Justus Liebigs Ann. Chem.* **1912**, *394*, 183. (b) Müller, E.; Moosmayer, A.; Rieker, A. *Z. Naturforsch. B* **1963**, *18*, 982.

[5] The value of 126.9 Hz found for $^1J(^{13}C(1)-^1H)$ is somewhat higher than the 122.7 Hz calculated from the empirical relationship between $^{13}C-^1H$ coupling constants and internuclear C–C–C bond angles in hydrocarbons of the type R_2CH_2 [Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *23*, 31].

[6] The short C–O bond lengths (1.454 and 1.465 Å)[2] in Tt_2O may play an ancillary role.

[7] The near-equality of the central bond lengths in Tt_2CH_2, C(1)–C(10) = 1.571 (2) Å and C(1)–C(40) = 1.567 (2) Å, is in accord with this view. In contradistinction, these bond lengths differ significantly in Tp_2CH_2 (1.578 and 1.532 Å, respectively).[1f]

Table II. Selected Torsion Angles[a] in 1,1,1,3,3,3-Hexaphenylpropane and Related Compounds

torsion angle	Tt_2CH_2,[b] X = C(1)	Tp_2CH_2,[c] X = C(1)	Tt_2O,[d] X = O	Tt_2S,[e] X = S
C(40)-X-C(10)-C(11)	65.0	10.8	−2.8	−46.4
C(40)-X-C(10)-C(21)	−62.7	−114.3	121.4	83.9
C(40)-X-C(10)-C(31)	179.9	133.1	−127.0	−164.1
C(10)-X-C(40)-C(41)	68.5	54.3	78.0	78.2
C(10)-X-C(40)-C(51)	−61.6	−75.3	−53.8	−48.5
C(10)-X-C(40)-C(61)	−178.6	171.7	−171.8	−165.8
X-C(10)-C(11)-C(12)	43.6	−2.5	−76.9	128.6
X-C(10)-C(11)-C(16)	−144.1	−178.9	102.2	−50.1
X-C(10)-C(21)-C(22)	−91.5	2.4	1.2	168.5
X-C(10)-C(21)-C(26)	83.6	−170.2	177.6	−6.7
X-C(10)-C(31)-C(32)	−1.6	−2.0	−33.1	127.2
X-C(10)-C(31)-C(36)	178.5	172.5	151.5	−55.5
X-C(40)-C(41)-C(42)	32.8	−1.8	16.6	−141.8
X-C(40)-C(41)-C(46)	−155.3	176.7	−171.2	42.6
X-C(40)-C(51)-C(52)	−76.8	4.7	−61.0	−123.6
X-C(40)-C(51)-C(56)	99.2	−172.5	121.2	62.5
X-C(40)-C(61)-C(62)	−14.7	−3.8	147.2	−124.2
X-C(40)-C(61)-C(66)	168.2	177.5	−39.6	58.2

[a] In degrees. [b] Present work. [c] Calculated from atomic parameters in ref 1f (Table II, unprimed molecule). [d] Reference 2, with atoms renumbered. Torsion angles calculated by the Cambridge crystallographic database program GEOM78. [e] Torsion angles calculated from the atomic coordinates in ref 3 (Table 2; atoms renumbered).

Tt_2X have a similar effect in the widening of the central C–X–C bond angle,[8] it has also brought to light a striking difference in the effect of these groups on molecular conformation.[9]

Experimental Section

A solution of triphenylmethyl chloride (1.0 g) in 20 mL of anhydrous benzene was stirred with activated zinc powder (1.5 g) for 5 days at room temperature under an inert atmosphere. The suspension was filtered and a solution of diazomethane in alcohol–ether was slowly added until the color characteristic of the trityl radical had disappeared. The reaction mixture was stirred for an additional 8 h and quenched with acetic acid. The solvent was evaporated and the residual white solid recrystallized from acetic acid and then from heptane. The product (0.41 g, 46%) had the following properties: mp 214–216 °C (lit.[4a] mp 216 °C); ^1H NMR (89.5 MHz, $C^2H_2Cl_2$) δ 4.25 (s, 2 H), 7.00 (m, 30 H); $^{13}C\{^1H\}$ NMR (22.5 MHz, $C^2H_2Cl_2$) δ 48.92, 125.63, 127.58, 129.86, 147.57; $^1J_{CH}$ (central CH_2) = 126.9 Hz.

The crystals were triclinic, space group $P\bar{1}$, with $a = 9.267$ (3), $b = 10.654$ (4), $c = 15.976$ (5) Å, $\alpha = 88.13(2)$, $\beta = 74.53$ (2), $\gamma = 67.31$ (2)°, and $d_{calcd} = 1.189$ g cm^{-3} for $Z = 2$ ($C_{39}H_{32}$, $M_r = 500.68$). The intensity data were measured on a Hilger–Watts diffractometer (Ni-filtered Cu Kα radiation, θ–2θ scans, pulse-height discrimination). The size of the crystal used for data collection was approximately 0.15 × 0.25 × 0.25 mm. A total of 3758 independent reflections were measured for $\theta < 57°$, of which 3125 were considered to be observed [$I > 2.5\sigma(I)$]. The structure was solved by a multiple-solution procedure[10] and was refined by full-matrix least squares. Eight reflections that were strongly affected by extinction were excluded from the final refinement and difference map. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.040$ and $wR = 0.044$ for the remaining 3117 observed reflections. The final difference map has no peaks greater than ±0.2 e A^{-3}.

Acknowledgment. We thank the National Science Foundation (CHE-8009670) for support of this work, and Professor A. Rieker for helpful correspondence.

Registry No. Tt_2CH_2, 82891-67-6; triphenylmethyl chloride, 76-83-5; diazomethane, 334-88-3; trityl radical, 2216-49-1.

Supplementary Material Available: Final atomic parameters for hydrogen atoms, final anisotropic thermal parameters, bond lengths, bond angles, with standard deviations (Tables III–VI) (4 pages). Ordering information is given on any current masthead page.

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[8] It therefore becomes safe to predict that the C–O–C angle in Tp_2O [Kawada, Y.; Iwamura, H. *J. Org. Chem.* **1980**, *45*, 2547] assumes a value close to that found[2] for Tt_2O.

[9] A somewhat related conformational difference is exhibited by 9,9′-bitriptycyl(Tp–Tp) [Ardebili, M. H. P.; Dougherty, D. A.; Mislow, K.; Schwartz, L. H.; White, J. G. *J. Am. Chem. Soc.* **1978**, *100*, 7994] and hexaphenylethane (Tt–Tt) [Hounshell, W. D.; Dougherty, D. A.; Hummel, J. P.; Mislow, K. *J. Am. Chem. Soc.* **1977**, *99*, 1916. Ōsawa, E.; Onuki, Y.; Mislow, K. *Ibid.* **1981**, *103*, 7475].

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Attempted Spin Trapping of *tert*-Butylperoxyl Radical by Trifluoronitrosomethane[1]

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Although there appears to be rather general agreement that peroxyl radicals, ROO·, can be spin trapped by certain nitrones,[3-9] there is no such agreement regarding their trapping by nitroso compounds. The most popular nitroso spin trap, 2-methyl-2-nitrosopropane (MNP), has been reported to give peroxyl radical spin adducts, $Me_3CN(\dot{O})OOR$.[8] It has also been reported to give only the spin adducts of the corresponding alkoxyl radical, $Me_3CN(\dot{O})OR$.[10] It occurred to us that trifluoronitrosomethane

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[2] NRCC Research Associate, 1979–1982.

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