2,4,6,8-Tetracarbomethoxybarbaralane

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2,4,6,8-Tetracarbomethoxybarbaralane has been synthesized in four steps from malondialdehyde and dimethyl 1,3-acetonedicarboxylate. The P_2I_4-induced Grob fragmentation (Kuhn-Winterstein reaction) of 2,4,6,8-tetracarbomethoxytetracyclo[3.3.1.$0^{2,8}$.$0^{4,6}$]nonane-3,7-*exo,exo*-diol gave in addition to 2,4,6,8-tetracarbomethoxybarbaralane (36%), two side products identified as 2,4,6-tricarbomethoxybarbaralane (3%) and 2,4,6,8-tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene, a dihydrobarbaralane (2%). 2,4,6,8-Tetracarbomethoxybarbaralane was shown to undergo a rapid degenerate Cope rearrangement in solution with an activation energy of $\Delta G^{\ddagger}_{158} = 5.95 \pm 0.2$ kcal/mol, 1.53 kcal/mol lower than that for barbaralane itself. In the solid state the molecule proved to be static on the basis of its CP-MAS ^{13}C NMR spectrum. The X-ray structure of 2,4,6,8-tetracarbomethoxybarbaralane shows a cyclopropane bond of 1.61 Å (C_2-C_8) and an open-end distance of = 2.40 Å (C_4-C_6). The equilibrium for the tricarbomethoxybarbaralane was found to be on the side of the 2,4,6-isomer, on the basis of its spectral data. The X-ray structure confirmed this for the solid state. These findings are in agreement with theoretical expectations.

Introduction

Barbaralane[1] (1) and semibullvalene[2] (2) undergo very fast degenerate Cope rearrangements with $\Delta G^{\ddagger}_{158}$ values of 7.48[1b] and 5.75[2d] kcal/mol. Theoretical calculations[3] predict that π-acceptor substituents in positions 2, 4, 6, and 8 and donor substituents in positions 1 and 5 will lower the activation energy for this process by destabilizing the ground state and stabilizing the transition state. Four cyano groups in positions 2, 4, 6, and 8 of semibullvalene (2) were calculated to decrease $\Delta G^{\ddagger}$ by 9.6 kcal/mol, thus reaching negative values in both systems 1 and 2, assuming that the effect of the four cyano groups is of similar magnitude in the barbaralane system. The transition state for the Cope rearrangement of tetracyanosemibullvalene and the corresponding barbaralane would therefore be lower in energy than the ground state. In other words, within a given system, this would cross the bridge between valence tautomerism, characterized by a positive activation energy, and resonance with a formal "negative activation energy". The experimental verification of this fascinating prediction would thus lead to the first synthesis of a neutral bishomoaromatic system.[4] The known syntheses for barbaralane[5] do not easily allow the introduction of substituents in positions 2, 4, 6, and 8. 3,7-[1b] and 2,6-disubstituted barbaralanes have been reported, and their dynamic behavior in solution has been investigated. Substituents in positions 3 and 7 show only a slight or no effect on the activation energy,[1b] while cyano and phenyl substituents in positions 2 and 6 lower the activation energy for the Cope rearrangement by 1.82[6b] and 2.44[6c] kcal/mol, respectively. Very recently, Quast and his group reported the synthesis of 2,4,6,8-tetraphenyl-[7] and of 2,6-dicyano-4,8-diphenylbarbaralane through oxidative cyclization of the respective substituted bicyclo[3.3.1]nona-2,6-dienyldipotassium. A 3,7-diethoxy-2,4,6,8-tetraazabarbaralane[8] as well as 9-phospha-,[9] 9-thia-,[10] 9-sila-,[11] and 9-azabarbaralanes[12] has been reported and shown to undergo rapid degenerate Cope rearrangements. The room-temperature X-ray structure of a 9-phospheniumbarbaralane[13] exhibits bond distances suggesting a structure corresponding to the symmetrical intermediate for the

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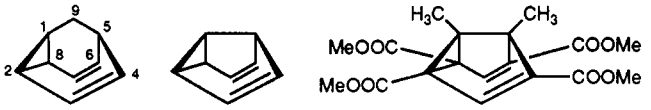
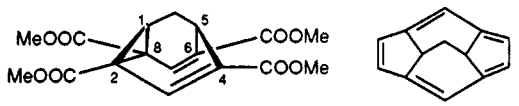
Cope rearrangement, but a qualitative evaluation of the dynamic solution NMR behavior indicates an activation energy quite similar to that of other known barbaralanes.



1 2 3

Results and Discussion

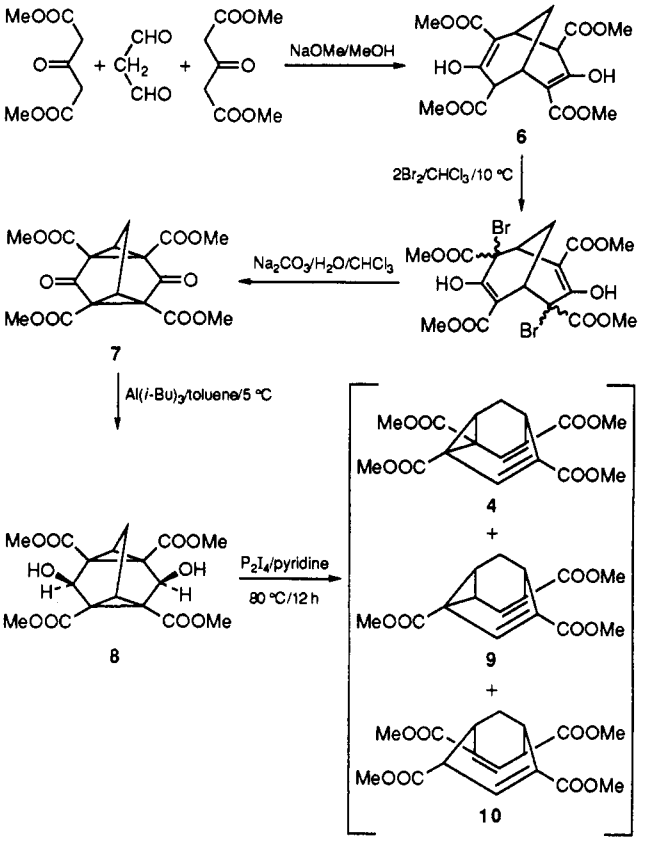
The successful synthesis of 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene (3)[14] and its characterization as a molecule "approaching the bishomoaromatic transition state" prompted us to investigate the related barbaralane system. In this paper, we wish to report the synthesis and structure of 2,4,6,8-tetracarbomethoxybarbaralane (4).[15] The synthesis is based upon the Grob fragmentation of a substituted tetracyclo[3.3.1.$0^{2,8}$.$0^{4,6}$]nonane-3,7-diol. The synthetic accessibility makes 4 a key compound in the preparation of other substituted barbaralanes. The four carbomethoxy groups are good π-acceptors and therefore are predicted to lower the activation energy, as demonstrated in the corresponding semibullvalene 3.[16] Conversion of the ester functionality into nitrile groups is well documented. Furthermore, the ester groups are suitable handles toward the synthesis of symmetrically 2,8- and 4,6-doubly-bridged barbaralanes like 5, which have been predicted[17] to exist as neutral bishomoaromatic, highly strained 10π-systems. In addition, the barbaralane system is also thermodynamically more stable relative to the semibullvalene system, which is known to rearrange readily to cyclooctatetraenes.[14,18]



4 5

Our synthesis of 2,4,6,8-tetracarbomethoxybarbaralane (4)[15] is designed after the general synthesis of substituted semibullvalenes developed in our laboratory.[14,19] Bromination of 2,4,6,8-tetracarbomethoxybicyclo[3.3.1]nonane-3,7-dione (6) (in its enol form, readily available from malondialdehyde and dimethyl acetonedicarboxylate according to Bertz[20]) with 2 mol of bromine in chloroform gave an uncharacterized dibromide, which upon shaking with a 10% aqueous solution of Na_2CO_3 smoothly eliminated 2 mol of HBr to form the highly symmetrical tetracyclic diketo tetraester (7) in excellent yield (Scheme

Scheme 1. Synthesis of 2,4,6,8-Tetracarbomethoxybarbaralane (4)



1). Reduction of 7 with triisobutylaluminum in toluene yielded predominantly the *exo,exo*-diol 8, the structure of which was conclusively proven by X-ray crystallography. Reduction of 7 with $NaBH_4$ in methanol gave a mixture of diols. Attempts to convert the *exo,exo*-diol 8 into a bismesylate to be followed by NaI in acetone to induce Grob fragmentation[14,15,19] did not succeed. Only one compound corresponding to a monomesylate was obtained.[21] However, the reaction of the *exo,exo*-diol 8 with freshly prepared P_2I_4[22] in anhydrous pyridine at 85 °C for 12 h gave 2,4,6,8-tetracarbomethoxybarbaralane (4) directly in 30–35% yield after column chromatography. This Kuhn–Winterstein reaction[23] had been applied by Kessler[24] and Hanafusa[25] for the synthesis of related 1,4-dienes. 2,4,6,8-Tetracarbomethoxybarbaralane (4) forms colorless crystals, mp 99–100 °C. The proton and carbon NMR spectra of 4 at room temperature show the symmetric structure expected for a system undergoing a rapid degenerate Cope rearrangement.

In addition to the tetracarbomethoxybarbaralane 4, two minor products were isolated from the P_2I_4 reaction: The first compound, isolated in 3% yield, was identified as 2,4,6-tricarbomethoxybarbaralane (9) (mp = 106–107 °C) on the basis of its spectral data and the X-ray structure.

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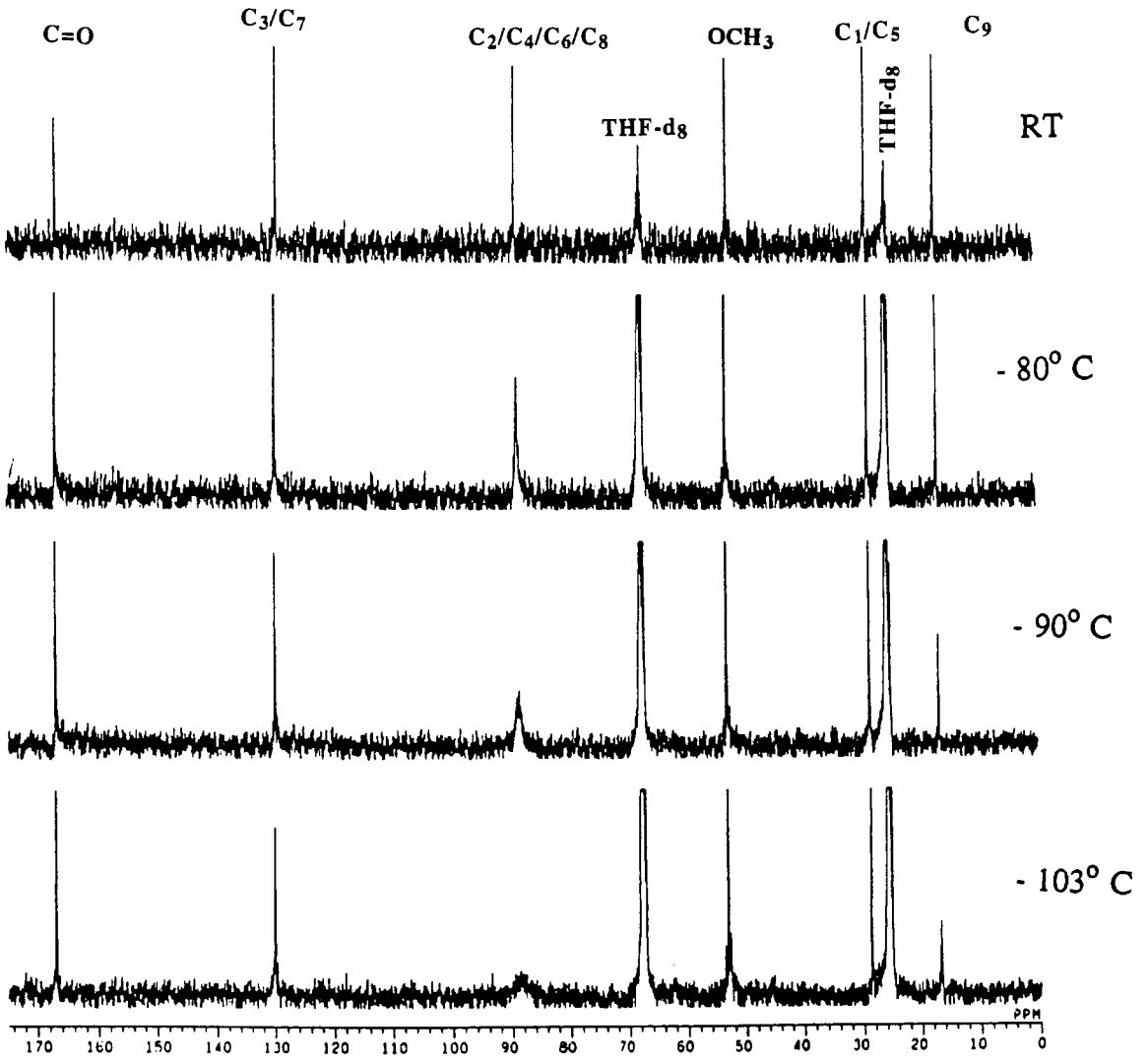
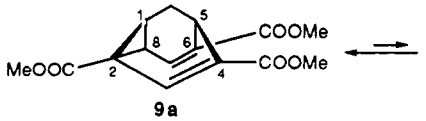
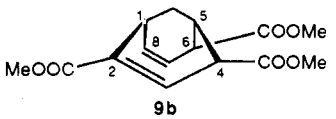


Figure 1. Variable-Temperature carbon ^{13}C FT NMR spectra of 2,4,6,8-tetracarbomethoxybarbaralane (4).

The second side product, isolated in 2% yield, proved to be 2,4,6,8-tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene (10), a dihydrobarbaralane, on the basis of its spectral data and an X-ray structure (mp 158–159 °C). The formation of 2,4,6-tricarbomethoxybarbaralane (9) can be best explained as the result of an iodide-induced ester cleavage followed by decarboxylation. This was confirmed by heating tetracarbomethoxybarbaralane 4 with NaI in pyridine for 12 h. Triester 9 was obtained in 51% yield. The proton and carbon NMR spectra of 9 are noteworthy. On the basis of these data, the equilibrium for the Cope rearrangement in tricarbomethoxybarbaralane 9 clearly favors tautomer **9a,** thus identifying it as a 2,4,6-tricarbomethoxybarbaralane.



9a



9b

The presence of a quaternary cyclopropyl carbon signal at 34.9 ppm for C_2 and of two quaternary olefinic carbon signals at 129.4 and at 131.8 ppm for C_4 and C_6 (as well as the proton NMR spectrum) and the observation that the NMR spectra of 9 do not change at −101 °C indicate that tautomer **9a** is the major component in the equilibrium **9a/9b**. The X-ray structure confirms this result for the solid state. The position of the equilibrium agrees with the theoretical expectations.[3a]

^{13}C-DNMR Studies of 2,4,6,8-Tetracarbomethoxybarbaralane (4). In order to assess the effect of four carbomethoxy groups on the activation energy of the Cope rearrangement in the barbaralane system, we measured the ^{13}C-NMR spectrum of 4 between rt and −103 °C (solvent: THF-d_8). The rather dramatic changes in its spectrum, especially for the signal at 87.9 ppm ($C_2/C_4/C_6/C_8$), are shown in Figure 1.

It is quite clear from Figure 1 that decoalescence[26] of the signals for carbons 2, 4, 6, and 8 ($\delta_{average}$ = 87.9 ppm) is not reached at the lowest available temperature. Therefore, we can only determine an upper limit for the free energy of activation $\Delta G^{\ddagger}_{T_c}$ of the Cope rearrangement in 4 by using an extrapolated coalscence temperature T_c

(26) Coalescence is defined as the merging of two or more individual NMR signals approaching a half-line width of $w_{1/2} = \infty$. The term decoalscence is frequently used to describe the opposite process starting with the averaged (fast exchange) signal. See, e.g.: Oki, M. *Applications of Dynamic NMR Sprectroscopy to Organic Chemistry*; Verlag Chemie: 1985; pp 3–4.

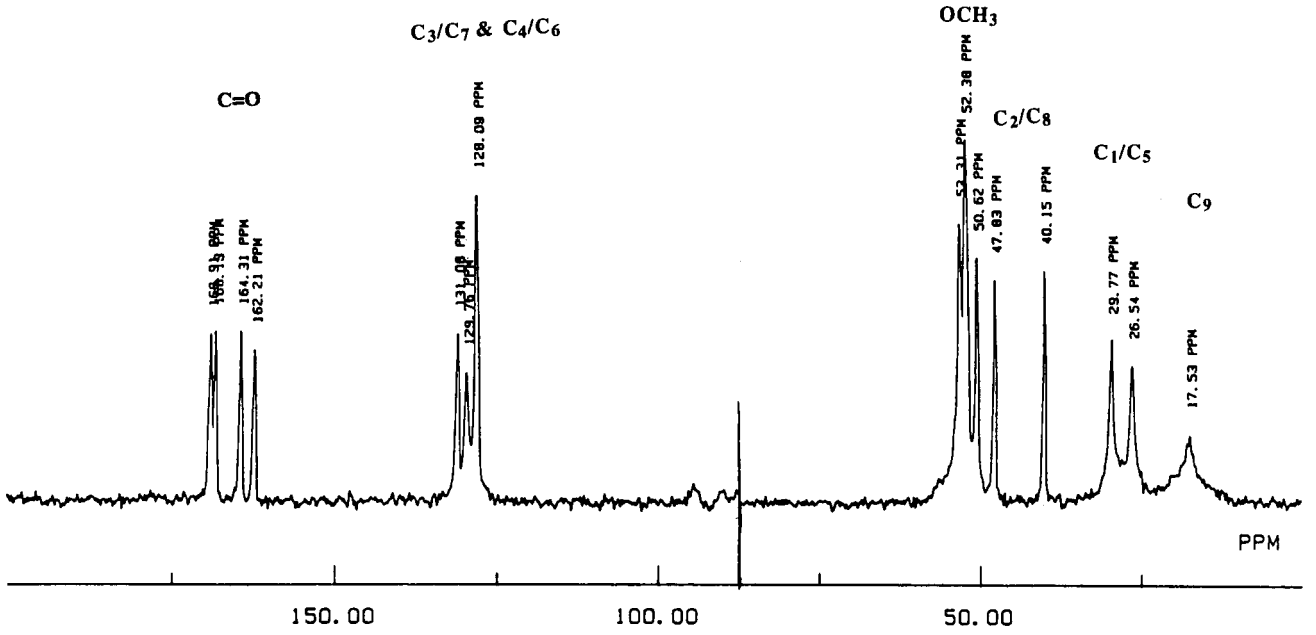


Figure 2. Solid-State CP-MAS ^{13}C NMR spectrum of 2,4,6,8-tetracarbomethoxybarbaralane (4) at −20 °C.

of −115 ± 5 °C. An approximate determination of $\Delta G^{\ddagger}$ at the coalescence temperature can be carried out using the standard expression[27] $\Delta G^{\ddagger} = 4.57T_c(9.97 + \log T_c/\Delta\delta)$ in kcal/mol provided of course that the chemical shift difference $\Delta\delta$ between C_2/C_8 and C_4/C_6 is known.

Solid-State NMR Measurements. As stated above, the equation for the determination of $\Delta G^{\ddagger}$ at the coalescence temperature T_c required the individual chemical shifts for C_2/C_8 (cyclopropyl carbons) and for C_4/C_6 (olefinic carbons). These values were obtained using two independent methods. First, the solid-state CP-MAS ^{13}C-NMR spectrum of 4 was measured at 22 and at −22 °C[28] (Figure 2).

The solid-state carbon spectrum confirms the results of the X-ray structure analysis that 2,4,6,8-tetracarbomethoxybarbaralane (4) in the solid state is a static molecule with no detectable Cope rearrangement. Separate carbon signals for the cyclopropyl carbons (C_2/C_8, δ = 47.8 and 40.2 ppm) and for the olefinic carbons (C_4/C_6 and C_4/C_6, δ = 128.1, 128.2, 129.8, and 131.1 ppm) were observed. As the X-ray structure confirms, the four carbomethoxy groups are all different, thus giving rise to four signals for the carbonyl carbons (δ = 162.2, 164.3, 166.2, and 168.9 ppm). The same applies to the methoxy carbon signals (δ = 50.6, 52.4, 52.6, and 53.3 ppm). The two cyclopropyl carbons C_2 and C_8 have very different chemical shifts due to the relative orientations of the two ester carbonyl groups, with one of them bisecting the cyclopropane ring while the other does not.[32] The signals between δ = 128.1 and 131.1 ppm correspond to the olefinic carbons C_3/C_7 and C_4/C_6. An accurate assignment proves to be difficult.[29] These values allowed us to calculate $\Delta G^{\ddagger}_{158}$ for the Cope rearrangement of 4 at the extrapolated coalescence temperature (T_c = −115 ± 5 °C = 158 ± 5 K).[30] The resulting value of 5.95 ± 0.2 kcal/mol is ca. 1.53 kcal/mol lower than the value for barbaralane itself ($\Delta G^{\ddagger}_{158}$ = 7.48 kcal/mol[1b]).

The second source for the chemical shift values of the cyclopropyl carbons (C_2/C_8) and of the olefinic carbons (C_4/C_6) uses the rigid 2,4,6-tricarbomethoxybarbaralane **9a** as a model,[31] resulting in a $\Delta G^{\ddagger}_{158}$ of 5.92 ± 0.2 kcal/mol. Both methods yield nearly identical values for $\Delta G^{\ddagger}_{158}$ which are qualitatively in accord with the theoretical predictions. However, they are nevertheless smaller than expected. An effect of similar magnitude has been observed for 1,5-dimethyl-2,4,6,8-tetracarbomethoxysemibullvalene (3) relative to semibullvalene (2).[16] More accurate measurements are in progress. A possible cause for the relatively small effect of the four ester groups on the activation energy for the Cope rearrangement in the barbaralane and semibullvalene system could be the dipole/oxygen lone-pair repulsion present when both ester carbonyl groups at C_2 and C_8 bisect the cyclopropane ring as required for effective conjugation.[32]

X-ray Measurements. X-ray measurements have played and continue to play a very important role in the analysis of potentially neutral homoaromatic structures. In a symmetric intermediate, equal distances are expected for C_2–C_8 and for C_4–C_6 as well as for C_2–C_3, C_3–C_4, C_6–C_7, and for C_7–C_8. Unusually long bond distances have been observed for the cyclopropane ring, together with average bond lengths for the double and single bonds in the semibullvalene and barbaralane system. However, considerable caution has to be exercised in attributing these bond lengths to the presence of a symmetrical structure.[13,14,33]

(27) See Günther, H. *NMR-Spektroskopie*; Georg Thieme Verlag: Stuttgart, Germany, 1973; p 248. Oki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*; Verlag Chemie: 1985; p 5.

(28) We express our thanks to Prof. L. Jackman and A. Benesi at Penn State University for measuring the solid-state carbon spectra.

(29) The solid-state spectrum of 4 shows four different olefinic carbons with δ = 128.1, 128.2, 129,8 and 131.1 ppm. These signals correspond to C_3/C_7 and C_4/C_6. At this time we cannot accurately assign the chemical shifts for C_4 and C_6. However the average δ value of 129.3 ± 1.2 ppm results in a $\Delta\delta$ of 85.3 ± 1.2 ppm. With this one obtains at the extrapolated coalescence temperature of 158 K $\Delta G^{\ddagger}$ of 5.95 ± 0.01 kcal/mol.

(30) With an extrapolated range of the coalescence temperature of T_c = −115 ± 5 °C = 158 ± 5 K, one obtains $\Delta G^{\ddagger}_{158}$ = 5.95 ± 0.2 kcal/mol.

(31) The carbon NMR spectrum of **9a** yields a $\Delta\delta$ of 95.2 ppm = 9520 Hz. This results in a $\Delta G^{\ddagger}_{158}$ of 5.92 ■ 0.2 kcal/mol (with T_c = −115 ± 5 °C = 158 ± 5 K).

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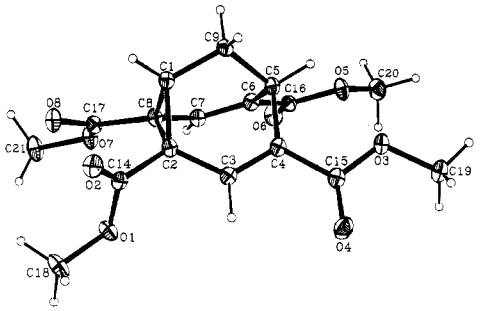

Figure 3. X-ray structure of tetracarbomethoxybarbaralane (4) at −160 °C.

Table 1. Selected Structural Parameters for 4

distances (Å)	295 K	110 K	distances (Å)	295 K	110 K
C_1–C_2	1.490	1.494	C_4–C_5	1.515	1.519
C_2–C_3	1.473	1.473	C_2–C_8	1.611	1.608
C_3–C_4	1.337	1.342	C_4–C_6	2.400	2.400

The crystal structure of 2,4,6,8-tetracarbomethoxybarbaralane (4) was determined at room temperature and at 110 K (−163 °C). The results clearly establish a static solid-state structure, with no Cope rearrangement occurring within the temperature range of the measurements. Only minor changes of the bond distances and bond angles were observed upon lowering the temperature to 110 K (−163 °C). The X-ray structure of 4 is shown in Figure 3, and selected structural parameters are listed in Table 1.

The orientation of the four carbomethoxy groups in the crystal is noteworthy. Only one carbonyl group (at C_8) bisects the cyclopropane ring, while the other one (at C_2) is more or less parallel. The ester carbonyl groups attached to the olefinic carbons C_4 and C_6 point downward, in opposite direction to those of the ester carbonyl groups at C_2 and C_8.

The infrared spectrum of 4 in CCl_4 shows one carbonyl band at 1720 cm^{-1} and one double-bond band at 1630 cm^{-1}. But an FT-IR spectrum in the solid state (KBr pellet) exhibited four overlapping carbonyl bands, indicating the presence of four different carbonyl groups in the solid state. This observation is in complete agreement with the X-ray and the solid-state NMR measurements. Further studies on the IR spectra are in progress.

Summary. A new four-step general synthesis of 2,4,6,8-tetrasubstituted barbaralenes, starting from the readily available 2,4,6,8-tetracarbomethoxybicyclol3.3.1]nonane-3,7-dione and utilizing the P_2I_4-induced Grob fragmentation, has been developed. Two side products of this reaction were identified as 2,4,6-tricarbomethoxybarbaralane and 2,4,6,8-tetracarbomethoxybicyclo[3.3.1]-nona-2,6-diene, a dihydroarbaralane. A detailed investigation of the substituent effects on the activation energy of the Cope rearrangement, with the goal of synthesizing the first neutral bishomoaromatic molecule, is in progress. Tetracarbomethoxybarbaralane 4 was found to undergo a rapid degenerate Cope rearrangement in solution, while being static in the solid state. The four carbomethoxy groups were found to lower the activation energy by 1.53 kcal/mol with respect to the unsubstituted molecule.

Experimental Section

General. All air- and moisture-sensitive reactions were performed under a positive pressure of purified Ar or N_2. All solvents and reagents were distilled, dried, and/or recrystallized prior to use according to standard laboratory procedures. Melting points are uncorrected. Proton and carbon NMR spectra were measured in $CDCl_3$ on a GE/Bruker QE 300 MHz spectrometer. VT-^{13}C NMR experiments were carried out on a JEOL GX 400-MHz instrument. CP-MAS solid-state ^{13}C NMR measurements were obtained on a ChemMagnetic System at 75 MHz. Analytical thin layer chromatography (TLC) was conducted on Polygram Sil G/UV254 plates (0.25 mm) from Macherey & Nagel. Flash column chromatography was performed using 230–400 mesh silica gel. Mass spectra were obtained on a Hewlet-Packard 5989A GC mass spectrometer (EI). X-ray structures were determined on an Enraf-Nonius CAD4 diffractometer (graphite-monochromated Cu Kα radiation). Structures were solved by a multiple solution procedure and refined by full matrix least squares. In the final refinement, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure factor calculations but their parameters were not refined. The final discrepancy indices are $R = 0.05$ and $R_w = 0.05$.

2,4,6,8-Tetracarbomethoxytetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonane-3,7-dione (7). Compound 7 was prepared from compound 6 by a two-step reaction. Compound 6 (12.85 g, 33.0 mmol) in 100 mL of dry $CHCl_3$ was brominated at rt by adding a solution of Br_2 (4 mL, 12.4 g, 77.6 mmol) in dry $CHCl_3$ (50 mL), over a period of 4 h. It was stirred at rt overnight. The reaction mixture was poured into 200 mL of ice/water containing 50 mL of a 20% aqueous solution of $NaHSO_3$. A saturated aqueous Na_2CO_3 solution (50 mL) was cautiously added and the two-phase system was carefully shaken in a separatory funnel. The off-white precipitate formed was filtered off, washed with water, and dried. The organic layer in the filtrate was dried over $MgSO_4$ and concentrated in vacuo. The white solid was combined with the filtered material and recrystallized from methanol to give 9.0 g (74%) of the title compound 7, mp 245–246 °C. ^{1}H NMR: δ = 2.59 ppm (t, 2H, J = 2.5 Hz, H_9), 3.41 (t 2H, J = 2.5 Hz, H_1/H_8), 3.79 (s, 12H, OCH_3). ^{13}C-NMR: δ = 16.0, 39.2, 49.1, 53.8, 164.0, 186.8 ppm. IR($CHCl_3$): 1745, 1700, 1170 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_{10}$: C, 53.67; H, 4.24. Found: C, 53.44; H, 4.28.

2,4,6,8-Tetracarbomethoxytetracyclo[3.3.1.0^{2,8}.0^{4,6}]nonane-3.,7(exo,exo)-diol (8). To an ice-cooled stirred suspension of 7.6 g (20 mmol) of 7 in 300 mL of dry toluene under argon was added a solution of Al(i-Bu)$_3$ in toluene (25% by wt) (1.0 M, 50 mL) slowly. The slightly cloudy solution was stirred overnight. After the clear light yellow solution was cooled in an ice bath, 100 mL of cold 4 N H_2SO_4 was cautiously added with stirring. A thick white suspension was obtained. After 2.5 h of stirring at 5 °C, the precipitate was filtered off and washed with some toluene. The organic layer was washed with saturated aqueous $NaHCO_3$ (2 × 75 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Recrystallization of the residue and the filtered precipitate from ethyl acetate afforded 6.0 g (79%) of *exo,exo*-diol 8: mp 185–186 °C. ^{1}H NMR: δ = 2.46 ppm (t, 2H, J = 2.3 Hz), 2.50 (m, 2H), 3.19 (bs, 2H), 3.71 (s, 12 H), 5.23 (s, 2 H). IR ($CHCl_3$): 3580, 1720, 1175, 1065 cm^{-1}. X-ray structure, see ref 34.

2,4,6,8-Tetracarbomethoxybarbaralane (4), 2,4,6-Tricarbomethoxybarbaralane (9a), and 2,4,6,8-Tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene (10). The P_2I_4-Induced Grob Fragmentation. Pure *exo,exo*-diol 8 (10.56 g, 27.5 mmol) was added to a solution of P_2I_4 (31.33 g, 55 mmol) in dry pyridine (500 mL) under argon. The reaction was stirred at 80 °C overnight. Most of the pyridine (350 mL) was distilled off. The dark residue was poured onto ice/water (500 mL) containing concentrated HCl (100 mL). The pyridine odor had disappeared and the

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(34) The authors have deposited atomic coordinates for 4 and 7–10 with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crsytallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

solution was slightly acidic. An aqueous $NaHSO_3$ solution (50 mL, 20%) was added. The reaction mixture was extracted with ether (4 × 300 mL). The extracts were washed with saturated aqueous $NaHCO_3$ solution (2 × 100 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography on silica gel (20% EtOAc/hexane) afforded 3.4 g (36%) of 2,4,6,8-tetracarbomethoxybarbaralane (**4**), mp 99–100 °C, followed by 2,4,6-tricarbomethoxybarbaralane (**9**) (3%, mp 106–107 °C) and 0.22 g of 2,4,6,8-tetracarbomethoxybicyclo[3.3.1]nona-2,6-diene (**10**) (2%, mp 158–159 °C). Compounds **4**, **9**, and **10** could be further purified and separated by careful fractionate recrystallization from ether/hexane mixtures.

Spectral Characteristics of 2,4,6,8-Tetracarbomethoxybarbaralane (4). IR (CCl_4): 3000, 2950, 1720, 1630, 1450, 770 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.86 ppm (2H, t, J = 2.6 Hz, H_9), 3.79,(12 H, s, OCH_3), 3.82 (2 H, t, J = 2.4 Hz, H_1/H_8), 7.07 (2 H, s, H_3/H_7). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.2 ppm (t, C_9), 27.9 (d, C_1/C_8), 57.6 (q, OCH_3), 87.9 (s, $C_2/C_4/C_6/C_8$), 129.2 (d, C_3/C_7), 166.7 (s, C=O). UV (EtOH): λ_{max} = 238 nm, plus a characteristic shoulder at 250 nm. MS (70 eV): m/z 350 (M^+). X-ray structure see supplementary material and text.

Spectral Characteristics of 2,4,6-Tricarbomethoxybarbaralane (9a). IR (CCl_4): 3000, 2950, 1720, 1630, 1440, 1250, 1220, 1060, cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.3 2 ppm (2 H, AB, CH_2) 3.05 (1 H, dt, J = 6.6 Hz, H_1), 3.12 (1 H, t, J = 6.6 Hz, H_8), 3.76 , 3.78, 3.82 (3 H each, s, OCH_3), 4.08 (1 H, m, H_5), 6.82 (1 H, d, J = 6.6 Hz, H_7), 7.4 (1 H, s, H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 ppm (t, C_9), 27.3, (d), 28.3 (d), 34.7 (d), 34.9 (s, C_2), 51.7 (q, 2 OCH_3), 52.5 (q, OCH_3), 129.4, (s, C_4 or C_6), 130.3 (d, C_7), 130.7 (d, C_3), 131.8 (s, C_4 or C_6), 164.8, 164.8, and 170.4 (s, C=O's). X-ray structure, see ref 34.

Spectral Data for 2,4,6,8-Tetracarbomethoxybicyclo-[3.3.1]nona-2,6-diene (10). IR (CCl_4) : 3000, 2950, 1720, 1645, 1170 cm^{-1}. ^1H NMR: δ = 1.84 ppm (t, 2H, J =2.9 Hz), 3.28 (d, 2H, J = 5.1 Hz), 3.41 (bs, 2H), 3.76 (s, 6H), 3.77 (s, 6H), 7.03 (d, 2H, J = 5 Hz). ^{13}C NMR : δ = 23.3 (t), 28.7 (d), 45.6 (d), 52.0(q), 52.5(q), 133.9(d), 135.8(s), 166.3,(s), 171.1(s). UV (EtOH): λ_{max} = 213 nm (ϵ = 8374). X-ray structure, see ref 34.

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