(6) R. A. Ruden and R. Bonjouklian, *J. Am. Chem. Soc.*, **97,** 6892 (1975); *J. Org. Chem.*, **42,** 4095 (1977).

(7) A benzene solution (25 mL) of $cp_2Ti(CO)_2$ (2.0 g, 8.55 mmol) was reacted with $O{=}C(CO_2Et)_2$ (2.7 mL, 17.68 mmol). The solution heated for 2 h at 40–45 °C loses carbon monoxide and produces on standing and cooling to room temperature red-maroon crystals of III (yield, ~20%). Complex III, which is rather soluble in various solvents, such as benzene, chloroform, and diethyl ether, crystallizes with molecules of solvent. Calcd for $\{cp_2Ti[C_2O_2(CO_2Et)_4]\}\cdot 0.6C_6H_6$ ($C_{24}H_{30}O_{10}Ti\cdot 0.6C_6H_6$): C, 57.82; H, 5.86. Found: C, 57.60; H, 5.95. The presence of C_6H_6 was shown by the ^1H NMR spectrum. The X-ray analysis data collection was performed on these crystals. ^1H NMR ($CDCl_3$ vs. Me_4Si): τ 3.38 (s, cp, 10 H), 5.63 (q, CH_2, 8 H), 8.66 (t, CH_3, 12 H). The IR spectrum (Nujol or CCl_4) shows a strong band of complex envelope centered at 1740 cm^{-1}. The same reaction, when carried out in refluxing diethyl ether produces red-maroon crystals of III containing diethyl ether as crystallization solvent (yield, ~20%). The rather low yield of III does not depend only on its high solubility in the reaction solvents, and investigations are planned to clarify this aspect of reaction 3.

(8) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry", Reinhold, New York, 1961, p 430.

(9) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *J. Org. Chem.*, **43,** 3255 (1978), and references therein.

(10) G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, **100,** 1921 (1978); *Inorg. Chem.*, **17,** 2995 (1978).

(11) $cp_2Ti(CO)_2$ (1.25 g, 3.63 mmol) dissolved in toluene (30 mL) is reacted with *N,N′*-di-*p*-tolylcarbodiimide (1.7 g, 7.66 mmol). The reaction slowly occurs at room temperature. Then the solution, when heated for 2 h at 70 °C, produces deep-red crystals of V along with a green maroon solution. The crystals were washed with hexane and dried (yield, ~60%). Anal. Calcd for $[cp_2Ti(p\text{-TCD})]_2$ ($C_{50}H_{48}N_4Ti_2$): C, 75.0; H, 6.0; N, 7.0. Found: C, 75.28; H, 6.06; N, 6.84.

(12) W. Hoppe, *Acta Crystallogr., Sect. A*, **25,** 67 (1969).

(13) G. Sheldrick, "SHELX-76" system of computer programs, 1976, University of Cambridge.

(14) All hydrogen atoms were located on a difference Fourier map and introduced in refinement as fixed atom contributions with isotropic thermal parameters fixed at 0.08 Å^2.

(15) B. K. Teo, F. Wudl, J. H. Marshall, and A. Kruger, *J. Am. Chem. Soc.*, **99,** 2349 (1977).

(16) R. S. P. Coutts, P. C. Wailes, and R. L. Martin, *J. Organomet. Chem.*, **50,** 145 (1973).

(17) E. J. M. DeBoer and J. H. Teuben, *J. Organomet. Chem.*, **153,** 53 (1978).

(18) B. M. Bycroft and J. D. Cotton, *J. Chem. Soc., Dalton Trans.*, 1867 (1973).

(19) H. Hoberg and J. Korff, *J. Organomet. Chem.*, **150,** C20 (1978).

(20) N. J. Brenner, A. B. Cutcliffe, M. F. Farona, and W. G. Kofron, *J. Chem. Soc. A*, 3264 (1971); J. D. Cotton and S. Zornig, *Inorg. Chim. Acta*, **25,** L133 (1977).

(21) S. Cenini and G. LaMonica, *Inorg. Chim. Acta*, **18,** 279 (1976).

(22) T. Herskovitz and L. J. Guggenberger, *J. Am. Chem. Soc.*, **98,** 1615 (1976).

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MNDO Study of Tetra-*tert*-butyltetrahedrane and Tetra-*tert*-butylcyclobutadiene and of Their Thermal Interconversion

Sir:

Tetra-*tert*-butyltetrahedrane (**1**) shows a surprising thermal stability and rearranges to tetra-*tert*-butylcyclobutadiene (**2**) only at temperatures of 130 °C and above.[1] In this communication, we report on a MNDO[2] study of the structure, stability, and thermal interconversion of **1** and **2** and compare the results with those for unsubstituted tetrahedrane (**3**) and cyclobutadiene (**4**).

The optimized geometries of **1** and **2** (see Table I) show some unusual features. **1** is predicted to be a chiral molecule with T symmetry,[3] in analogy to other tetra-*tert*-butyl substituted systems.[4] Relative to the T_d conformation, each *tert*-butyl group is twisted in the same direction by 14.2°, and each methyl group by 4.8°, thereby destroying the planes of symmetry but preserving all of the rotation axes of the T_d point group. It should, however, be difficult to detect the chirality of **1** experimentally since the conformation with T_d symmetry is calculated to be only 2.6 kcal/mol above that with T symmetry which implies free internal rotation of the *tert*-butyl groups. These MNDO results confirm previous empirical force-field calculations[5] which also predict ground-state T symmetry and a low rotational barrier in **1**.

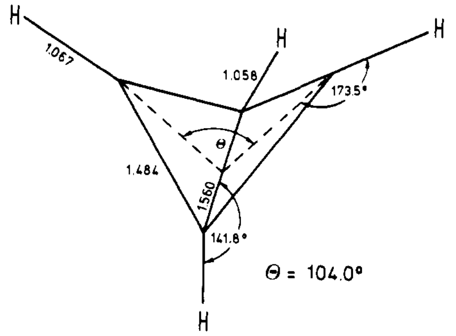

Figure 1. Optimized C_{2v} structure of the MNDO-CI_0 transition state for the reaction **3** → **4**.

Table I. Calculated Heats of Formation and Optimized Geometries[a]

	1[b]	**2**[c]	**3**	**4**[d]
point group	T	D_2	T_d	D_{2h}
ΔH_f, kcal mol^{-1}	81.2	74.5	136.6	90.7
$R(C_r{=}C_r)$, Å		1.381		1.357
$R(C_r{-}C_r)$, Å	1.534	1.557	1.520	1.534
$R(C_r{-}C_t)$, Å	1.501	1.520		
$R(C_t{-}C_m)$, Å	1.559	1.556–1.564		
$R(C{-}H)$, Å	1.108	1.108	1.063	1.071
$\theta(C_rC_tC_m)$, deg	110.4	110.8–112.6		
$\theta(C_tC_mH)$, deg	111.7	111.9		

[a] R, bond lengths; θ, bond angles; ϕ, dihedral angles. Indices for carbon atoms; r, ring atom; t, tertiary atom in butyl group; m, atom in methyl group. [b] For dihedral angles, see text. [c] $\theta(C_r{=}C_r{-}C_t)$, 136.5°; $\phi(C_r{=}C_r{-}C_r{=}C_r)$, 17.9°; $\phi(C_r{-}C_r{=}C_r{-}C_t)$, 157.8°. [d] $\theta(C_r{=}C_r{-}H)$, 138.1°.

The cyclobutadiene ring in **2** is calculated to be nonplanar, with a dihedral angle of 17.9° for the two double bonds. This puckering increases the nonbonding distances between the *tert*-butyl groups and thus stabilizes the system. When planarity is enforced during the optimization, the resulting structure is 11.1 kcal/mol higher in energy than the nonplanar one. The MNDO structure of **2** thus differs from the X-ray structure of the related, but sterically less hindered, methyl tri-*tert*-butyl[4]annulenecarboxylate which contains a planar cyclobutadiene ring.[6]

At the optimized geometries, the energy difference between the tetrahedrane and cyclobutadiene system (see Table I) is predicted to decrease from 45.9 to 6.7 kcal/mol when replacing the four hydrogen atoms by four *tert*-butyl groups. This shift of 39.2 kcal/mol[7] is undoubtedly due to steric effects since the *tert*-butyl groups occupy much more favorable positions in the tetrahedrane system. Based on previous experience,[8] the MNDO heat of formation of **4** is expected to be too low; the magnitude of the steric effect is believed to be somewhat overestimated, but of a reasonable order of magnitude.

The thermal rearrangement **3** → **4**, and the C_4H_4 potential surface in general, has recently been investigated both by semiempirical[9,10] and ab initio[11-13] methods. Since the rearrangement is "forbidden" thermally and involves a HOMO/LUMO crossing, a minimal 2 × 2 configuration interaction treatment (CI_0) is required for a correct description. The MNDO-CI_0 activation energy for this reaction is 15.2 kcal/mol. The transition state corresponds to a bicyclobutanediyl

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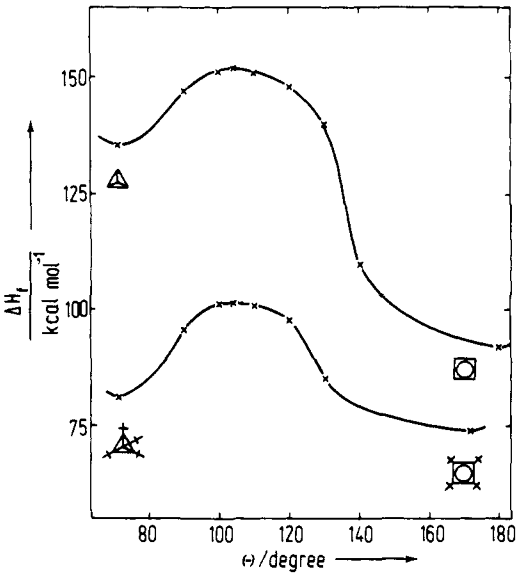

Figure 2. Reaction profiles for the rearrangements **1** → **2** and **3** → **4**. The MNDO-ClO heat of formation is plotted as function of the angle θ (see text and Figure 1).

biradicaloid with C_{2v} symmetry (see Figure 1); its structure has been completely optimized by minimizing the gradient norm, and its force constant matrix has a single negative eigenvalue.[14] Figure 2 shows the MNDO-ClO reaction profile for the rearrangement **3** → **4** assuming C_{2v} symmetry. It should be pointed out that no local C_{2v} minimum corresponding to a bicyclobutanediyl biradical is found, contrary to a previous study.[10,15]

For the tetra-*tert*-butyl substituted systems, it is computationally too expensive to carry out complete MNDO-ClO optimizations and compute a rigorous activation energy for the reaction **1** → **2**. To obtain an estimate of the activation energy, a reaction profile for the rearrangement **1** → **2** was constructed by optimizing the geometries at the MNDO SCF level[16] and then carrying out a single MNDO-ClO calculation at these geometries. From the resulting curve (see Figure 2), the activation energy is estimated to be 20 kcal/mol,[17] which seems to be compatible with the observed[1] thermal stability of **1**.

Our calculations thus indicate that the activation energy for the thermal decay of the tetrahedrane to the cyclobutadiene system is increased only by ~5 kcal/mol when replacing the four hydrogen atoms by four *tert*-butyl groups. This is probably related to the fact that the transition state comes early on the reaction coordinate (see Figure 2); the *tert*-butyl groups still occupy favorable positions so that the steric effect on the activation energy is fairly small. On the other hand, given the observed thermal stability of tetra-*tert*-butyltetrahedrane, our results strongly suggest that unsubstituted tetrahedrane should be long lived enough to be easily detected if it can be prepared by some mechanism.

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References and Notes

(1) Maier, G.; Pfriem, S.; Schäfer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552.
(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.
(3) Herzberg, G. "Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules"; Van Nostrand: Princeton, N.J., 1945; p 9.
(4) Iroff, L. D.; Mislow, K. *J. Am. Chem. Soc.* **1978**, *100*, 2121.
(5) Hounshell, W. D.; Mislow, K. *Tetrahedron Lett.* **1979**, 1205.
(6) Delbaere, L. T. J.; James, M. N. G.; Nakamura, N.; Masamune, S. *J. Am. Chem. Soc.* **1975**, *97*, 1973.
(7) Using empirical force-field calculations, a stabilization of ~43 kcal/mol due to steric effects of *tert*-butyl substitution has been found: K. Mislow, private communication.
(8) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
(9) Dewar, M. J. S. *Pure Appl. Chem.* **1975**, *44*, 767, and private communication.
(10) Böhm, M. C.; Gleiter, R. *Tetrahedron Lett.* **1978**, 1179.
(11) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739.
(12) Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6941.
(13) Kollmar, H., private communication.
(14) McIver, J. W., Jr., Komornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.
(15) The existence of such minima in ref 10 might be due to incomplete geometry optimization.
(16) To reduce the computational effort in the reaction path calculation, all methyl groups were assumed to have equal bond lengths, equal bond angles, and threefold symmetry.
(17) According to test calculations on simple systems, this value is believed to deviate from the rigorous MNDO-ClO value by <3 kcal/mol.

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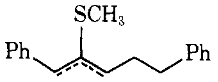
Enol Thioethers in Synthesis. Regiocontrolled Arylation via Organopalladium Chemistry

Sir:

The unusual versatility of sulfur has led to many important developments in organic synthesis. Surprisingly, this versatility remains unrealized for enol thioethers which normally are considered less useful enol derivatives compared with enol ethers, enol esters, enamines, etc. We report here an unusual ambidence in the regioselectivity of arylation of enol thioethers catalyzed by palladium that can provide new avenues for applications of these intermediates for structural elaboration.

The arylation of olefins catalyzed by palladium has been outstandingly developed by Heck and his co-workers who state "double bonds substituted with electron donating substituents tend to produce significant amounts of 2-aryl adducts in addition to the major 1-aryl isomers".[2,3] We find that intermolecular arylations of enol thioethers lead regioselectively to the 2-aryl adducts, whereas intramolecular arylations lead regioselectively to the 1-aryl system. Table I summarizes the intermolecular reactions. The arylations were performed in two ways. In the first, 1 equiv of phenylmercuric chloride was reacted with ~6 mol % of $\mathrm{Li_2PdCl_4}$ and 1 equiv of cupric chloride in THF at room temperature in the presence of 1 equiv of vinyl sulfide. After 24 h, the reaction was filtered, evaporated, and chromatographed. Enol thioethers from aldehydes (entries 1-4) and ketones (entries 5 and 6) both react. In the last case, the sensitivity of the enol thioether **7** to hydrolysis led to its conversion into the ketone **6** during silica gel chromatography. In each case, only one regioisomer which resulted



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from β-phenylation was detected. Entry 6 illustrates that the thermodynamically less stable enol thioether reacts without prior equilibration.[6] Thus, the arylation is fully regiocontrolled. When the enol thioethers are a mixture of stereoisomers, the products are also a mixture of stereoisomers although in different ratios. NMR allowed determination of the isomeric ratios by examination of the vinyl proton geminal to the sulfur substituent (**1**, δ 6.84 (*E*), 6.52 (*Z*); **2**, δ 6.6 (*E*), 6.3 (*Z*); **3**, δ 6.48 (*E*), 6.2 (*Z*); **4**, δ 6.04 (*E*), 5.52 (*Z*)). In the second ap-

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