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PHOTOCHEMICAL SYNTHESIS AND THERMAL CHEMISTRY OF Z-2,2,5,5-TETRAMETHYL-3,4-DIPHENYLHEX-3-ENE, A STERICALLY CONGESTED STILBENE[1]

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Abstract: Stilbene Z-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene isomerized to its Z-isomer with an unusually low rotational barrier, $\Delta H^{\ddagger} = 31.2\pm1.3$ and $\Delta S^{\ddagger} = -4.8\pm3.1$. Theoretical calculations are discussed.

Our continuing interest in the unique properties of geometrically distorted molecules,[1] and the recently reported one-way photoisomerizations in anthryl analogs of stilbenes[2] prompted the synthesis and characterization of Z-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene, **1a**. Such a study a) explored the possibility of steric effects in the stilbene system similar to those seen in the anthryl analogs, b) provided an interesting carbon-carbon double bond model to test theoretical and experimental effects of tert-butyl substitution in stilbenes and c) extended knowledge relating structure to rotational barriers built up over many years.[3-5]

Sterically congested alkenes can frequently be prepared by the low valent Ti promoted coupling of ketones.[6,7] E-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene, **1b**, was obtained in modest, 30%, yield by coupling phenyl tert-butyl ketone in the presence of $TiCl_4/Zn$.[8] Irradiation, 254 nm, of a nitrogen purged solution containing 750 mg of **1b** in 200 ml of hexane rapidly formed **1a**, leading finally to a maximum 26 % conversion of **1b** to **1a**. Separation by flash column chromatography (hexane) gave 160 mg (21%) of pure, crystalline **1a**: mp = 89-90°C; UV max (MeOH) 207 nm (ε 1.1×10^{4}) 240 sh (ε 2.6×10^{3}) 262 sh (ε 3.8×10^{2}); IR (CCl_4) 1597 cm^{-1}m, 1573w (c=c str); ^{1}H NMR ($CDCl_3$) δ 6.9-6.6 (m, 10, Ph), 1.23 (s, 18, t-Bu); ^{13}C NMR ($CDCl_3$)

δ 147.4, 146.9, 130.0,126.2, 123.9 (p-phenyl), 35.9, 33.5 (CH_3); MS, m/z 292 (Base and Molecular Ion).[9] Extended irradiation in the presence of oxygen, gave a trace of another material, possibly 1,2-di-tert-butylphenanthrene, **2**. NMR analysis of **1a** down to -78° in toluene-d_8 showed no evidence of restricted rotation about the tert-butyl or phenyl groups.

Heating cleanly isomerized **1a** (0.1M) to **1b**. The equilibrium isomer ratio at 163.5° in nitrobenzene-d_6 showed 0.4% **1a**. The isomerization was monitored by NMR at 139.5 - 167.5° in nitrobenzene-d_5 solutions containing a little hydroquinone or 3-tert-butyl-4-hydroxy-5-methylphenyl sulfide. First order analysis, Figure 1, gave $E_a = 32.0 \pm 1.3$ kcal/mol and $A = 10^{12}$. Using the usual relationship and substituting back into the Eyring equation gave $\Delta H^{\ddagger} = 31.2 \pm 1.3$ and $\Delta S^{\ddagger} = -4.8 \pm 3.1$.[10] Conversion to **1b** did not exceed 95 % to avoid complications from the reversibility of the reaction.

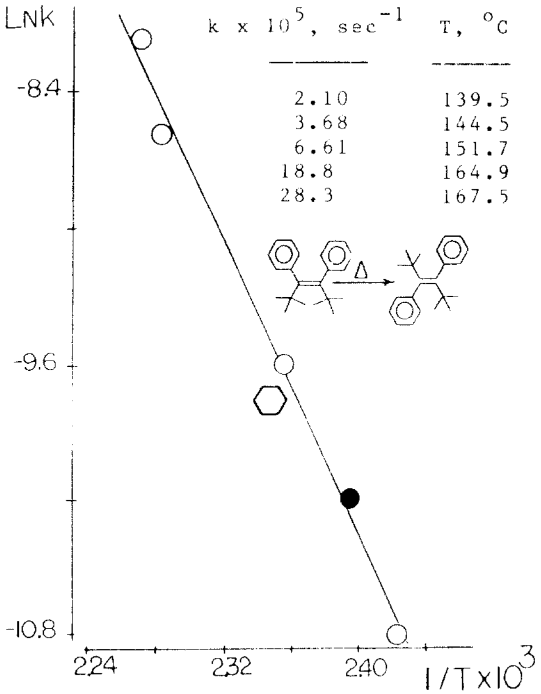

Figure 1. Arrhenius plot and rate constants for the conversion of 1a to 1b; O = runs with hydroquinone present, ● = runs with 2-methyl-4-hydroxy-6-tert-butyl sulfide present, ⬡ = run in decalin-d_{16} with no trapping agent.

Clearly, the E/Z-photoisomerization of **1b** to **1a** does not encounter the unusual, one-way effect noted in the sterically congested anthryl system. In contrast to previous reports of the photochemistry of sterically congested stilbenes such as **4** and **5**, the tert-butyl substituents have significantly perturbed the photochemical yields.[11,12]

In the current study, isomerization of **1a** to **1b** by direct rotation about the carbon-carbon double bond along the ground state energy surface was supported by a) a preexponential factor within the 10^{12} - 10^{13} range,[13] b) the reaction was insensitive to the type and concentration of trapping agent, c) sterically congested alkenes generally show low reactivity,[14] and, d) the reaction rate was similar in decalin with no trapping agent, Figure

Strain energies were calculated by MMPII for **1a**, **1b**, Z-stilbene, and E-stilbene. The results, along with thermolysis parameters from this study are given in Figure **2**. Calculated and experimental changes in enthalpy for Z/E isomerization agree reasonably well for **1** (ΔH^{Calc} = -4.2, ΔH^{Obs} = ~-4.8) and stilbene (ΔH^{Calc} = -3.9; ΔH^{Obs} = -2.3).[3] Substitution of tert-butyl for the vinylic hydrogens in stilbene lead to a pronounced increase in strain energy, Figure 2, for both **1a**, 23.2 kcal/mol, and **1b**, 22.9 kcal/mol. If there were no steric strain in the transition state, this increase in ground state energy would have reduced the rotation barrier, **1a** -> **1b**, to 19.6 kcal/mol. The measured rotation barrier of 31.2 kcal/mol revealed 11.6 kcal/mol of residual strain energy in the transition strain. Even when the molecule is twisted 90°, the tert-butyl are not far enough removed from other groups to eliminate all strain. Nonetheless, the tert-butyl groups have made the rotational barrier in **1a** lower than in any other known symmetrically substituted stilbene. Since the rotation barrier in 2-butene, 62.4 kcal/mol,[4] is only slightly less than the rotation barrier in ethylene, 65 kcal/mol,[5] this reduction is due primarily to the steric effect rather than electronic effects. The absence of significant rotation of the tert-butyl group in **1a** at low temperatures further supports the view that the tert-butyl group is best viewed as a slightly bumpy ball.[15]

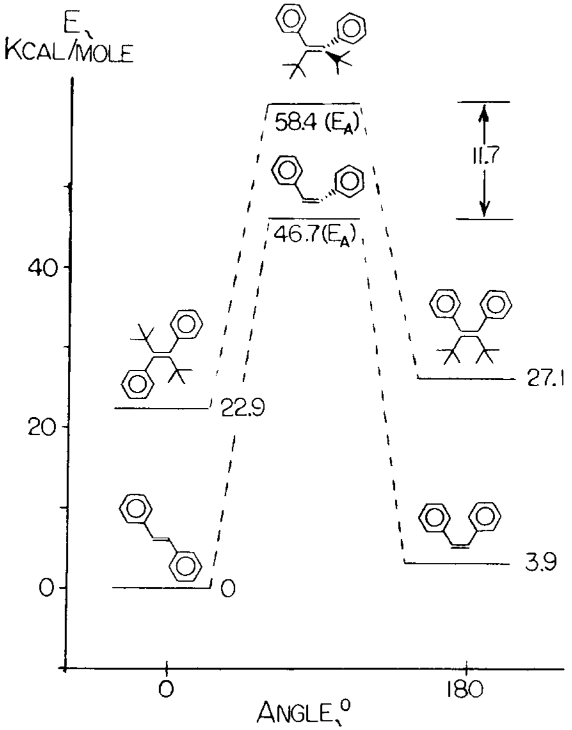

Figure 2. Energy diagram constructed from MMP2 and measured activation energies.

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References and Notes

1) For current related papers see: a) Lenoir, D.; Malwitz, D.; Meyer, B. Tetrahedron Lett. **1984**, 2965; b) Gano, J.E.; Wettach, R.H.; Platz, M.S.; Senthilnathan, V.P. J. Am. Chem. Soc. **1982**, 104, 2326.

2) Arai, T.; Karatsu, T.; Sakuragi, H.; Tokumaru, K. Tetrahedron Lett. **1983**, 24, 2873

3) For a general review of alkene photoisomerizations, see: Saltiel, J.; Charlton, J.L. "Rearrangements in the Ground and Excited States", In DeMayo, P., Ed.; Academic: New York, 1980; p 25.

4) Cundall, R.B.; Palmer, J.F. Trans. Faraday Soc. **1958**, 80, 2384.

5) Douglas, J.E.; Rabinovich, B.S.; Looney, F.S. J. Chem. Soc. **1955**, 23, 315.

6) (a) Lenoir, D. Synthesis **1977**, 554; (b) Lenoir, D.; Burghard, H. J. Chem. Res. (S) **1980**, 396; (c) Unfortunately, mesityl tert-butyl ketone does not yield coupling products.

7) Usually an enthalpy difference of $\geq$ 5 kcal/mol is suggested to give only one isomer.[6]

8) Synthesis of **1b** has been reported; Lenoir, D. J. Chem. Res. **1980**, (S) 396, (M) 4715.

9) An X-Ray structure determination of **1a** is currently in progress.

10) Alberty, F.; Daniels, R.A. "Physical Chemistry" Wiley: New York, 1962; pp 726.

11) Since the uv spectrum of **1b** is red shifted from **1a**, as is typical of stilbene isomers (See e.g. Calvert, J.; Pitts, J.N.Jr. "Photochemistry" Wiley: New York, **1966**, p 506), the yield could be increased by irradiation at longer wavelengths. Further details relating to the photochemistry will appear elsewhere.

12) Gegiou, D.; Muszkat, K.A.; Fischer, E. J. Am. Chem. Soc. **1968**, 90, 3907.

13) Kalinowski, H.-O.; Kessler, H. Top. Stereochem., Allinger, N.L.; Eliel, E.L., Eds. Wiley: New York, **1973**, 7, 295.

14) For example, **1b** fails to react with bromine in CCl_4

15) Berg, U.; Liljefors, T.; Roussel, C.; Sandström , J. Acc. Chem. Res. **1985**, 18, 80.

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