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SYNTHESIS AND CONFORMATIONAL BEHAVIOR OF E-3,4-DIETHYL-2,2,5,5-TETRAMETHYLHEXENE-3$^{1)}$

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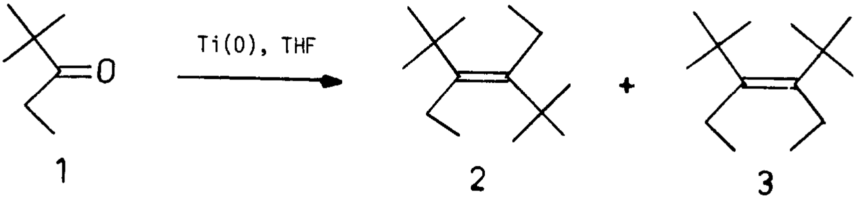
Abstract: Synthesis of 2 is described by reductive coupling of 1; the temperature dependent ^{1}H-NMR-spectrum can be described by the interconversion of the two preferred conformations 2a and 2b ($\Delta G_{300}^{\neq}$= 18.3 kcal/mole), which is qualitatively described by force-field calculations.

According to the increasing interest in the chemistry of strained alkenes$^{2,3)}$ we have prepared some tetraalkyl-substituted alkenes with two vicinal tert-butyl groups at the double bond in order to study their chemical and physical behavior$^{1)}$. The reductive coupling of the tert-butyl ketone 1 by low valent titanium compounds$^{4)}$ results in the formation of the trans-ethylene 2, GC/MS analysis reveals the presence of another compound, most likely the cis-isomer 3.



1   2   3

A mixture of 6.2 g $TiCl_3$ and 0.85 g $LiAlH_4$ in 250 ml abs. THF was refluxed for 1 h. To this slurry 4.2 g ketone 1 was added and heated under reflux for 45 hrs. After usual work-up$^{4)}$ 1.7 g of a crude product was obtained which was chromatographed on 100 g silica gel with n-pentane as eluent. The resulting product consists of a ca. 12:1 mixture of 2 and 3 and was further separated by preparative GC (10% SE-30), resulting in 0.21 g (5.8%) of pure 2 as colourless oil. Ir: 3040, 2955, 2910, 2720, 1470, 1265 cm^{-1}. Raman (CCl_4): 1572 (C = C), 1450, 1378,and 1366 cm^{-1}. MS: m/e = 196 (M^+, 14%) 139 (11), 125 (42), 97 (55), 83 (100), 69 (78), 57 (61).

The NMR spectrum of this compound shows a marked temperature dependence over the range from - 40^{o}C to 100^{o}C (cf. Fig. 1). The well resolved 400 MHz spectrum at - 40^{o}C in toluene-d$_8$ is composed of two different subspectra deriving from two different conformers of $\underline{2}$5). The ratio of these two components is 1.05/1.0, equivalent to ΔG^{o}_{233} = 0.03 kcal/mole energy difference. The large splitting of the two protons of the methylene group, 0.61 and 0.62 ppm respectively, proofs a relatively rigid conformation of the ethyl groups with one methylene proton in very close proximity to the symmetry plane of the double bond resulting in a large

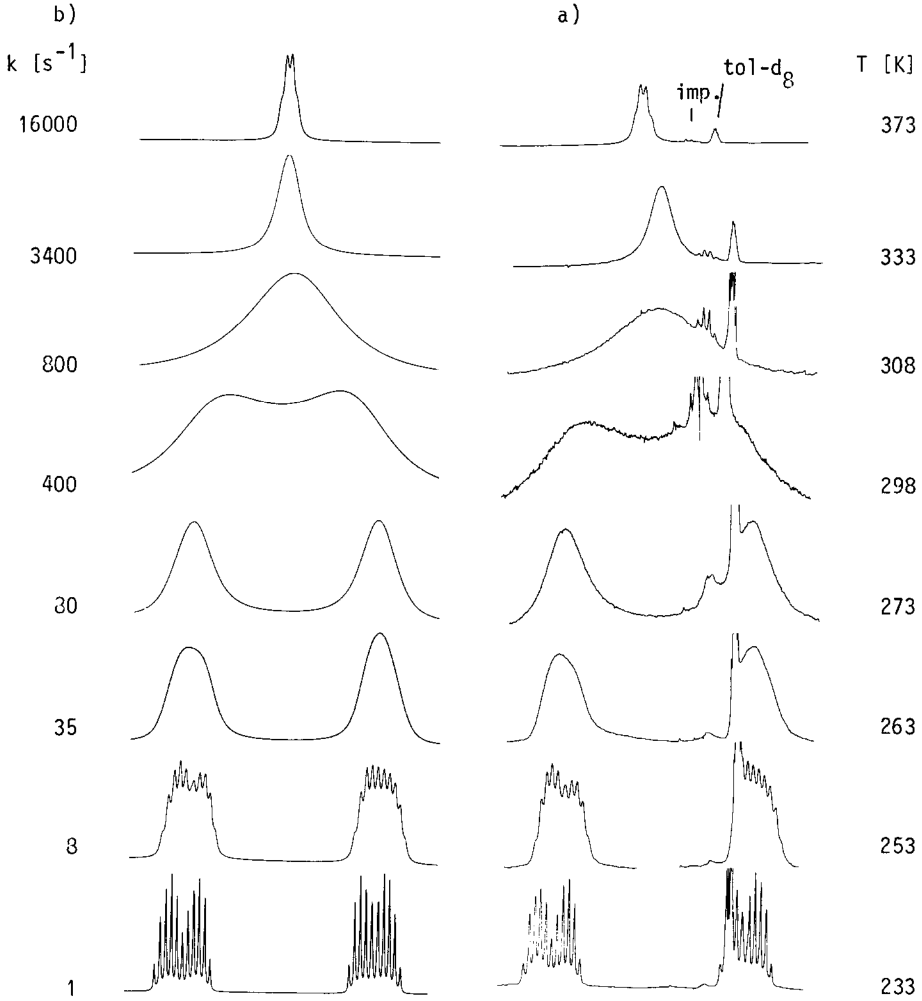


Fig. 1: Methylene proton region from ^{1}H NMR spectrum a) experimental temperature dependent 400 MHz spectra b) calculated spectra with optimized rate constants.

downfield shift. The other proton is almost unaffected by the double bond anisotropy.

The two species are assigned as the cisoid 2a and transoid 2b conformers of 2 (Fig. 2). The temperature dependent NMR spectra fitted with a modified DNMR5-program[6] are shown in Fig. 1 This gives rise to the conclusion, that not the rotation of the tert-butyl groups but rather that of the ethyl groups is responsible for the temperature dependence. The main process of the interconversion is the rotation of only one ethyl group at the same time. This result is in marked contrast with the proposed concerted mechanism ("gear" or cogwheel"-effect) for related compounds[7]. But still part of the mobility (ca. 30%) can be attributed to a concerted process of isomer 2b, i.e. $2b(R) \rightleftharpoons 2b(S)$[9].
The activation parameters obtained from a regressional analysis of $\ln\left(\frac{k}{T}\right) = f\left(\frac{1}{T}\right)$ are $\Delta H^{\ddagger}=$ 11.3 kcal/mole, $\Delta S^{\ddagger}=-23.4$ cal/grd and $\Delta G_{300}^{\ddagger}=18.3$ kcal/mole. For tetra-isopropyl ethylene the barrier of the rotation was found $\Delta G^{\ddagger}=17$ kcal/mole[7].
Force-field calculations using Allinger's MM2[8] have been performed on the structure of 2. Starting from a large number of different geometries many local minima have been found (Tab. 1). They have been combined to five groups of closely related conformers according to the dihedral angles formed by the ethyl groups ($C = C - CH_2 - CH_3$; cf. Fig. 2).

Three of the conformations are cisoid (2b) and two are transoid (2a). The energy difference between the most stable cisoid and transoid conformers is calculated to 1.8 kcal/mole and is only in qualitative agreement with the ^1H NMR experiment.

Table I. Results of Force-field Calculations of 2

Conformation	ΔH_f[kcal/mole][a]	Dihedral angles[a][b]	Local minima[c]
transoid	- 43.3	- 98.0/+ 98.0	93-105/87-98
cisoid	- 41.5	+ 99.4/+ 99.4	96-99/97-102
cisoid	- 40.8	+ 98.0/+109.7	94-99/105-110
cisoid	- 40.8	+ 93.4/+ 99.4	80-93/99-105
transoid	- 39.3	+ 83.5/- 83.5	84/84

[a] Preferred conformation within the related group; [b] of the $C = C - CH_2 - CH_3$ fragments; [c] variation of dihedral angles around specified minimum.

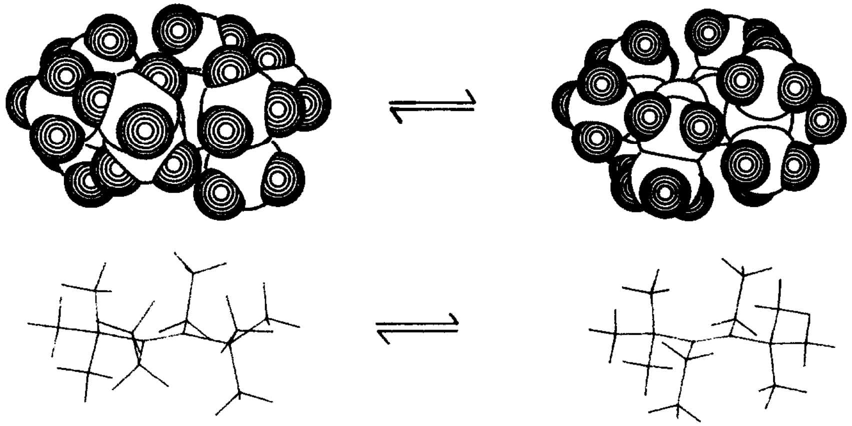


Fig. 2: Equilibrium of the two conformers of 2 in stick and space filling representation.

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5. Conformer 2a δ 1.408s, t-Bu; δ 1.239t, Me; δ 2.856dq, C-H_a; δ 2.245dq, C-H_b; J(H,CH_3) = 7.0, J(H_a,H_b) = 14.4 Hz, Conformer 2b δ 1.414s, t-Bu; δ 1.177t, Me; δ 2.767dq, C-H_a; δ 2.151dq, C-H_b; J(H,CH_3) = 7.0, J(H_a,H_b) = -14.4 Hz.

6. DNMR5-program: (QCPE 465), D. Binsch and A. Stephenson, J. Magn. Reson. 32, 131, 145 (1978); modified for larger exchange matrices.

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