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STERICALLY HINDERED INTERNAL ROTATION IN ACYCLIC HYDROCARBONS: 2,5-DIMETHYL-3,4-DIISOPROPYL-2,4HEXADIENE

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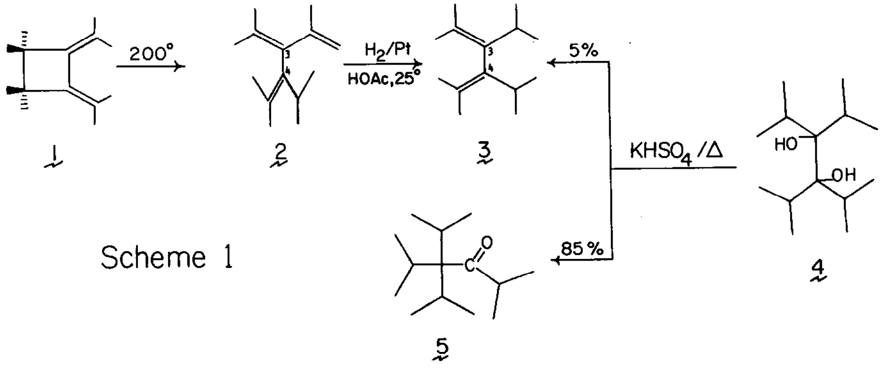
Hindered rotation about single bonds has been observed in a wide variety of molecules. Recent investigations of substituted butadienes have used nmr techniques to characterize this phenomenon, which renders these molecules chiral[1]. We wish to report the preparation of hydrocarbons 2 and 3, substituted dienes that exhibit unusually high barriers to rotation about carbon-carbon single bonds.

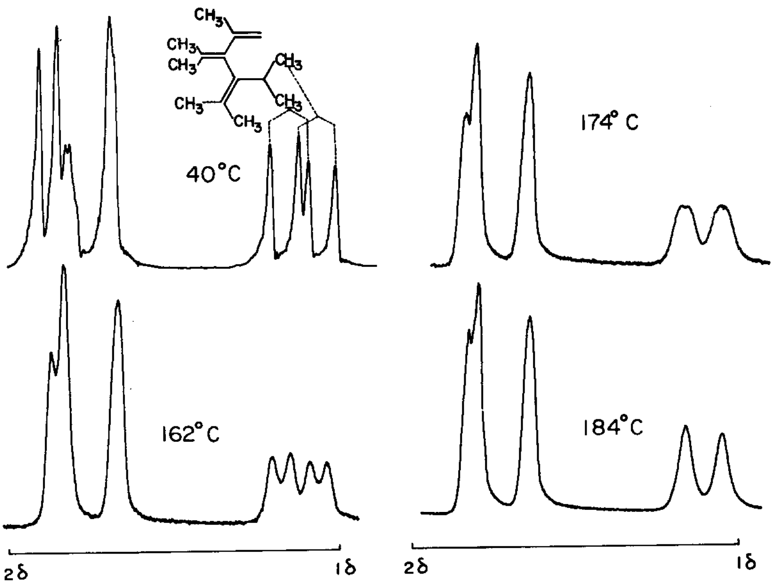


Scheme 1

When the tetramethylallene dimer 1[2] is pyrolyzed in a base-washed quartz tube at 200° C, conversion to 2 is effected. After pyrolysis for 15 hours, the recovered hydrocarbon mixture contains 36% 2 and 56% unreacted starting material, 1 (glpc peak areas). Less than 2% of the mixture consists of tetramethylallene from cycloreversion of 1. Similar thermal conversions have been reported for a number of other substituted vicinal dimethylenecyclobutanes[3]. Compound 2 may be quantitatively prepared by heating a carefully degassed sample of tetramethylallene in a sealed, base-washed Pyrex tube for 80 hours at 220° C: bp 43-44° C (1.2 mm); n_D^{20} 1.4781; ir (CCl_4) 3080, 2965, 2910, 2870, 2860, 1625, 1465(sh), 1455(sh), 1440, 1375, 1365, 1355 cm^{-1}; pmr ($CDCl_3$, 40° C)

δ_H 0.90 (d, J = 7.0 Hz, CHC$\underline{H}_3$), 0.98 (d, J = 7.0 Hz, C$\underline{H}_3$CH), 1.53 (d, J = 0.2 Hz, allylic C$\underline{H}_3$), 1.55 (d, J = 0.4 Hz, allylic C$\underline{H}_3$), 1.70 (m, allylic C$\underline{H}_3$), 1.72 (s, allylic C$\underline{H}_3$), 1.77 (s, allylic C$\underline{H}_3$), 2.63 (septet, J = 7.0 Hz, C$\underline{H}$(CH$_3$)$_2$), 4.76 (m, vinyl proton cis to methyl group), 5.01 (m, vinyl proton trans to methyl group); cmr (CDCl$_3$, 40°C, proton noise-decoupled) δ_C 19.4 (CH$\underline{C}$H$_3$), 19.9 ($\underline{C}$H$_3$CH), 21.0 (allylic $\underline{C}$H$_3$), 22.1 (two allylic $\underline{C}$H$_3$ resonances separated by < 0.03 ppm), 22.5 (allylic $\underline{C}$H$_3$), 22.6 (allylic $\underline{C}$H$_3$), 31.2 ($\underline{C}$H(CH$_3$)$_2$), 114.9 (vinyl $\underline{C}$H$_2$), 126.6 (vinyl carbon), 128.3 (vinyl carbon), 137.2 (vinyl carbon), 138.1 (vinyl carbon), 147.0 (vinyl carbon); mass spectrum (70 V) m/e (relative intensity) 192 (39), 177 (15) 149 (100), 135 (35), 134 (18), 133 (18), 121 (35), 119 (15), 107 (30), 105 (17), 91 (24), 77 (17), 55 (22), 53 (16), 43 (25), 41 (54), 39 (17). The ultraviolet spectrum shows intense end absorption, but no λ_{max} above 200 nm. The nmr spectrum of 2 is temperature dependent; the upfield portion of the pmr spectrum of a neat sample is shown as a function of temperature in Figure 1. The two isopropyl methyl groups, which are nonequivalent in the pmr spectrum at 40°C, become equivalent at elevated temperatures.

FIGURE I: UPFIELD PORTION of 60 MHz PMR SPECTRUM of 2 (Neat)



Examination of molecular models suggests that, in the favored conformation of **2**, none of the double bonds is conjugated. Because the conformation of **2** is skewed about the C_3—C_4 bond, as implied by the drawing in Scheme 1, the stable conformers are chiral. As a result of this molecular asymmetry, the two isopropyl methyl groups are diastereotopic.[1] Coalescence of the two doublets at 174° C implies that the barrier to internal rotation about the C_3—C_4 bond, $\Delta G^{\ddagger} = 105$ KJ/mole (25 Kcal/mole)[4]. The temperature dependence of the pmr spectrum of **2** in DMSO-d_6 is similar to that of a neat sample, and the coalescence temperatures are the same (± 5° C).

The structure assigned to **2** is confirmed by hydrogenation at atmospheric pressure over Adams catalyst to the title compound, **3**, an authentic sample of which may be prepared as a minor product of dehydration of diol **4**. When a 0.8 g sample of **4**[5] is heated vigorously with 1.1 g potassium bisulfate[6] at 22 mm aspirator pressure, 0.6 g of liquid distills at 136° C. Glpc analysis and separation of the distillate shows that the major product (85% of the total peak area) is **5**, the product of a pinacol-pinacolone type rearrangement: n_D^{20} 1.4702; ir (CCl_4) $\nu_{C=O} = 1685\ cm^{-1}$; pmr ($CCl_4$) δ_H 1.02 (d, J = 7.0 Hz, $((C\underline{H}_3)CH)_3C$), 1.05 (d, J = 6.4 Hz, $(C\underline{H}_3)_2CHC{=}O$), 2.54 (septet, J = 7.0 Hz, $C\underline{H}C{=}O$), 3.08 (septet, J = 6.4 Hz, $C\underline{H}CC{=}O$); cmr ($CDCl_3$, proton noise-decoupled) δ_C 20.6 ($((\underline{C}H_3)_2CH)_3C$), 21.0 ($(\underline{C}H_3)_2CHC{=}O$), 31.4 ($((CH_3)_2\underline{C}H)_3C$), 35.7 ($(CH_3)_2\underline{C}HC{=}O$), 64.0 ($\iota$-$Pr_3\underline{C}C{=}O$), 153.4 ($\underline{C}{=}O$); mass spectrum (70 V) *m/e* (relative intensity) 212 (0.15), 170 (1.2), 169 (1.5), 155 (3), 141 (6), 140 (2), 97 (3), 85 (56), 83 (7), 71 (56), 57 (74), 55 (17), 43 (100), 41 (32), 39 (6).

A minor product from dehydration of **4** (5% of the total glpc peak area), when purified by preparative glpc, shows the same ir, pmr, mass spectrum, and glpc retention times as **3** from the hydrogenation of **2**: n_D^{20} 1.4712; ir(CCl_4) 2960, 2915, 2900, 2865, 2850(sh), 1460(Broad), 1365, 1355, 1330, 1315 cm^{-1}; pmr ($CDCl_3$, 40°C) δ_H 0.96 (d, J = 7.2 Hz, $CHC\underline{H}_3$), 1.08 (d, J = 7.2 Hz, $C\underline{H}_3CH$), 1.49 (s, allylic $C\underline{H}_3$), 1.72 (s, allylic $C\underline{H}_3$), 2.72 (septet, J = 7.2 Hz, $(CH_3)_2C\underline{H}$); cmr ($CDCl_3$, 40° C, proton noise-decoupled) δ_C 19.7 ($CH\underline{C}H_3$), 21.0 ($\underline{C}H_3CH$), 22.7 (allylic $\underline{C}H_3$), 23.3 (allylic $\underline{C}H_3$), 31.4 ($(CH_3)_2\underline{C}H$), 125.9 (vinyl carbon), 139.6 (vinyl carbon); mass spectrum (70 V) *m/e* (relative intensity) 194 (64), 151 (54), 137 (36), 123 (19), 109 (100), 96 (86), 95 (55), 91 (22), 84 (42), 81 (67), 79 (20), 77 (21), 69 (19), 67 (39), 57 (57), 55 (46), 53 (22), 43 (52), 41 (86), 39 (23).

The pmr spectrum of **3** is also temperature dependent. At 40° C, the vicinal coupling constants for the two nonequivalent isopropyl methyl doublets are the same and, at 60 MHz, equal to the chemical shift difference of 0.12 ppm. At temperatures above 75° C, the apparent triplet presented by these overlapping resonances is transformed into a pair of doublets with the same coupling constant and a chemical shift difference of 0.09 ppm.

The simplicity of the cmr spectrum of **3**, which contains but seven resonances, indicates that **3** has a twofold symmetry element, while the nonequivalence of the isopropyl methyl resonances implies that the molecule does not possess a mirror plane of symmetry. The inference is that **3** is dissymmetric on the nmr time scale, and this dissymmetry is presumed to arise from restricted rotation about the C_3—C_4 single bond. The diastereotopic isopropyl methyl groups remain nonequivalent at 195° C, the highest probe temperature accessible. Therefore, the barrier to rotation about the C_3—C_4 bond, $\Delta G^{\ddagger} > 110$ KJ/mole.[4]

Unfortunately, the lack of pronounced line broadening in the temperature-dependent nmr spectra does not permit a precise computation of kinetic parameters. Current efforts are being directed toward the use of other nmr techniques for the examination of hindered rotors in these highly congested molecules.

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REFERENCES

1. A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *Tetrahedron Letters*, 2153 (1974), and references contained therein.

2. J.R. McClenon, Ph.D. Thesis, University of California at Los Angeles, 1964.

3. E.F. Kiefer and C.H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969); J.J. Gajewski and C.N. Shih, *J. Amer. Chem. Soc.*, **94**, 1675 (1972).

4. J.A. Pople, W.G. Schneider, and H.J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, pp. 218-224.

5. I.N. Nasarov, *Doklady Akad. Nauk SSSR*, **4**, 291 (1934); *C.A.*, 2914 (1935).

6. C.L. Leese and R.A. Raphael, *J. Chem. Soc.*, 2725 (1950).