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STERICALLY HINDERED INTERNAL ROTATION IN ACYCLIC HYDROCARBONS: TETRAISOPROPYLETHYLENE

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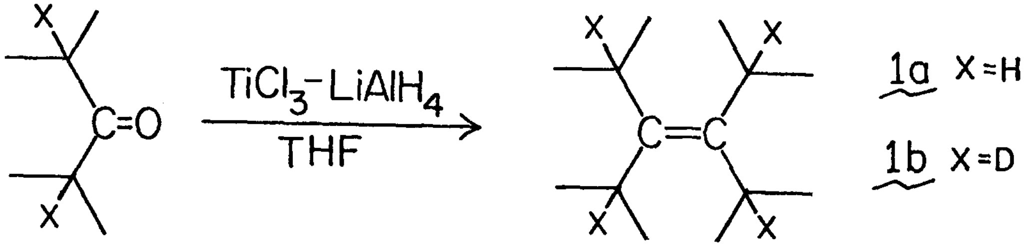
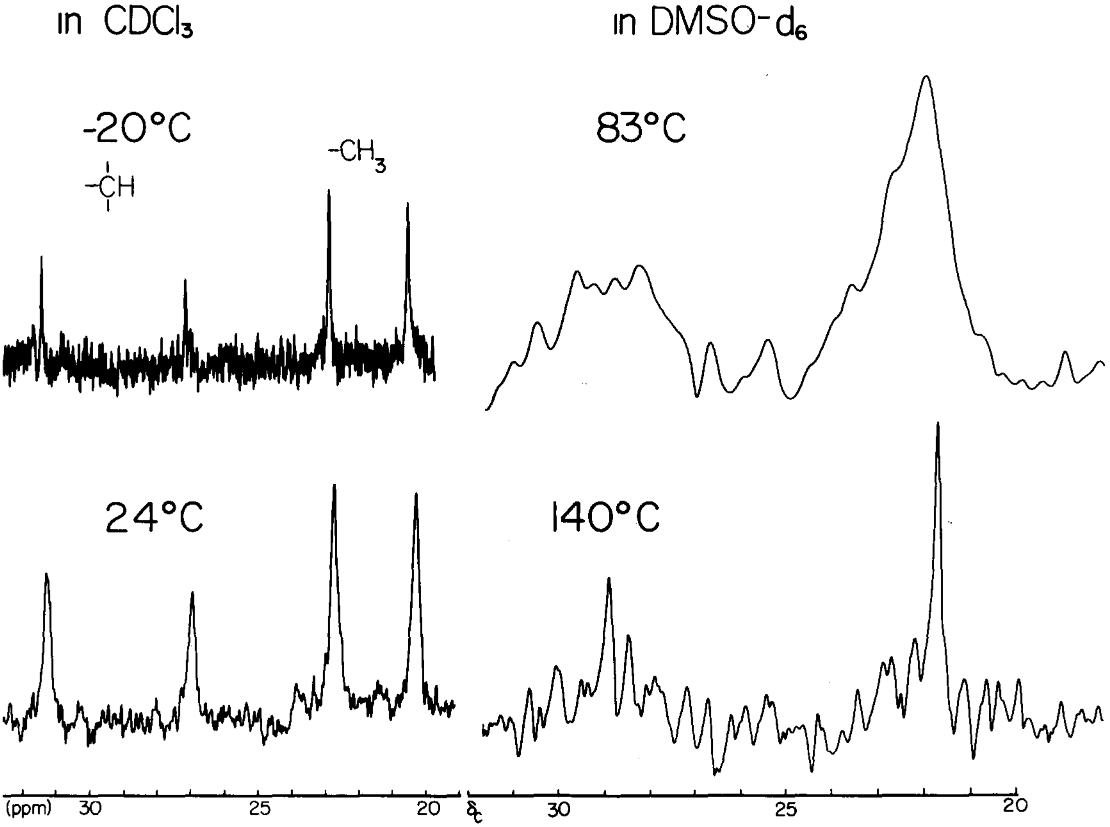
In continuation of our studies of sterically crowded, acyclic hydrocarbons with hindered rotation about carbon-carbon single bonds[1], we have prepared tetraisopropylethylene, **1a**, and its tetradeuterio analogue, **1b**, by the reductive coupling reaction of McMurry and Fleming, reaction 1.[2] Compound **1a**, which is sublimed out of the reaction mixture at 130°C under a steady stream of nitrogen, is obtained from 2,4-dimethyl-3-pentanone in 12% yield: colorless needles, mp 125-125.5°C, ir (KBr pellet) 3050, 2960, 2930, 2870, 1460, 1365, 1185, 1165, 1090, 970, 920 cm^{-1}; pmr ($CDCl_3$, -30°C) δ 0.94 (d, J = 7 Hz, C$\underline{H}_3$), 1.13 (d, J = 7 Hz, C$\underline{H}_3$), 2.30 (septet, J = 7 Hz, C$\underline{H}$), 2.97 (septet, J = 7 Hz, C$\underline{H}$); cmr ($CDCl_3$, 24°C, proton noise-decoupled): δ_C 20.2 ($\underline{C}H_3$), 22.7 ($\underline{C}H_3$), 26.9 ($\underline{C}$H), 31.2 ($\underline{C}$H), 143.6 (vinyl carbon); mass spectrum (70V) m/e (relative intensity) 196 (2.9), 98 (8.7), 97 (8.2), 83 (100), 69 (22), 67 (7.9), 55 (11), 43 (14), 41 (18); elemental analysis satisfactory for $C_{14}H_{28}$[3].

(1)



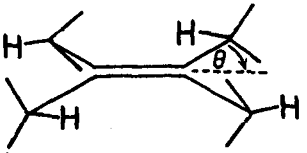
Of particular interest are the nmr spectra of compound **1a**, which exhibit marked temperature dependence. At 35°C, the two methyl doublets in the pmr of **1a** coalesce, and, at 75°C, the pmr shows a single doublet at δ 1.04 (J = 7 Hz) and a single septet at δ 2.64. The upfield portion of the natural abundance ^{13}C nmr spectrum of 1a is shown as a function of temperature in Figure 1. From the observed line broadening at 24°C, we calculate the barrier to interconversion of the magnetically nonequivalent isopropyl groups at this temperature to be $\Delta G^{\ddagger}$ = 17 Kcal/mole (70 KJ/mole)[4].

FIGURE 1: 22.6 MHz CMR SPECTRA OF 1a



We attribute the nonequivalence of the isopropyl groups to a steric barrier to internal rotation from the favored conformation of 1a shown in Figure 2.[5] The observed barrier for 1a is significantly higher than barriers reported for the "gear effect" in other sterically crowded compounds containing isopropyl groups.[6]

FIGURE 2: THE STABLE CONFORMATION OF **1a**



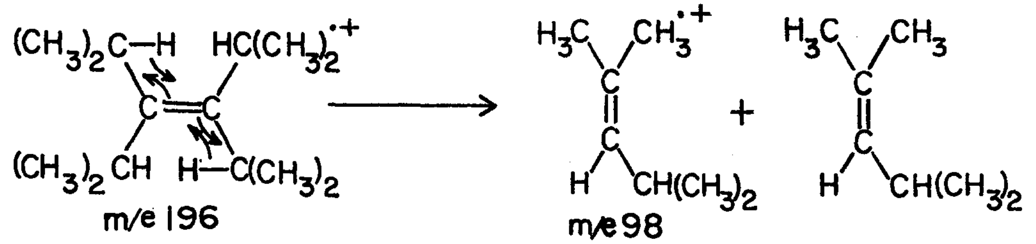
The laser Raman spectrum of **1a** (488.0 nm exciting line, crystalline sample) shows a band at 1638 cm^{-1} (C=C stretch) with a shoulder at 1625 cm^{-1}, as well as bands at 1470 (sh), 1455, 1445, 1385, 1365, 1320, 1300, 1230, 1150, 1115, 1080, 1010, 950, 920, 890, 820, 725, 620, 585, 465, 410, 295, 235, and 220 cm^{-1}. The observed C=C stretching frequency of **1a** is lower than that we observe from its dehydro analogue, 2,5-dimethyl-3,4-diisopropyl-2,4-hexadiene[1] (488.0 nm exciting line, neat liquid) at 1645 cm^{-1}, and is consistent with Raman stretching frequencies reported for other sterically crowded olefins[8].

We assign the shoulder at 1625 cm^{-1} as a combination of one of the bending vibrations (in the range 1300 - 1385 cm^{-1}) and a rocking mode (in the range 220 - 295 cm^{-1}). This assignment is confirmed by the laser Raman spectrum of compound **1b** (97 atom % D, prepared by reductive coupling of 2,4-dimethyl-3-pentanone-2,4-d_2, 97 atom % D from four repetitive exchanges of 2,4-dimethyl-3-pentanone with 0.3 M NaOD in D_2O), which shows an intense band at 1625 cm^{-1} (C=C stretch) with no shoulders, and bands at 1475 (sh), 1460, 1450, 1385, 1240, 1165, 1150, 1135, 1040, 935, 930, 860, 825, 725, 605, 565, 465, 405, 290, 235, and 220 cm^{-1}.

The isotope effect upon the C=C stretching frequency may be predicted by the method of Risen and Watters[9] as $\sqrt{\frac{\mu'_{1a}}{\mu'_{1b}}}$, where the values of μ' represent reduced masses corrected for the projection of the substituents onto the axis of the C=C stretch. For the symmetrical compounds **1**, μ' is equal to $\frac{C + 2S\cos\theta}{2}$, where C is the mass of the vinyl carbon atom (12 amu), S the mass of the substituent (43 amu for isopropyl, 44 amu for isopropyl - d_1), and θ the angle between the substituent bond and the axis of the C=C stretch (in Figure 2, $\theta \cong 60^{\circ}$). By this method, the C=C stretch of **1b** is predicted to occur at a frequency 15 cm^{-1} lower than the C=C stretch of **1a**, which is in good agreement with the observed shift of 13 cm^{-1}.

The mass spectrum of tetraisopropylethylene also manifests some unusual characteristics. The ion which constitutes the base peak (m/e 83, 57% of the total ionization at nominal 12 V) cannot be formed by any fragmentation involving simply fissions of single bonds, but must result from a sequence of hydrogen shifts within the molecular ion. Moreover, this ion is observed to arise via loss of a methyl group from the abundant odd-electron species m/e 98 (9% of the total ionization at nominal 12 V), for a metastable peak is observed at m/e 70.2 (calculated for 98→83, 70.29). The 70 V mass spectrum of **1b**, $C_{14}H_{24}D_4$ (corrected for ^{13}C natural abundance and a 10% d_3 impurity) is consistent with our speculation that the double hydrogen shift depicted in reaction 2 gives rise to the odd-electron ion at half the mass of the molecular ion: *m/e* (relative intensity) 200 (1.8), 100 (5.2), 98 (3.5), 85 (79), 57 (12), 56 (9.8), 45 (6.6), 44 (100), 43 (13), 42 (88), 41 (66), 40 (29), 39 (30).

(2)



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