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Hindered Rotation of the Isopropenyl Group in Substituted Isopropenylcyclohexanes and Identification of Preferred Rotamers by Nuclear Magnetic Resonance. Bent Bonds May Be Better Bonds

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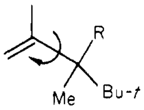
The series of 2,2,6,6-tetramethyl-1-isopropenylcyclohexenes 2–6 shows hindered rotation of the isopropenyl group, the activation barrier $\Delta G^{\ddagger}$ varying from 12.8 to >15.7 kcal/mol. Splitting patterns and chemical shifts of the olefinic protons of the isopropenyl group are analyzed. Whereas H_{cis}, i.e., the olefinic proton cis to the methyl group of the isopropenyl group, appears in the expected ^1H NMR region, the more crowded olefinic proton H_{trans} suffers van der Waals deshielding and is shifted downfield by as much as 0.39 ppm. The α rotamer, in which the tertiary allylic C–H bond eclipses the bond axis of the C=C double bond, is generally preferred over the β rotamer. The isopropenyl group in both rotamers of tetramethylcarvone (6) adopts an axial position.

The barrier to rotation about sp^2–sp^3 carbon–carbon single bonds in olefins and the identification of any preferred rotamers are of fundamental interest and of practical importance for asymmetric syntheses. Hitherto some work has been reported on slow rotation in substituted toluenes[1] but little on slow rotation in acyclic olefins.[2] In olefins of type 1, dynamic NMR gave rotational barriers $\Delta G^{\ddagger}$ of ~9–15 kcal/mol for 1b–d, i.e., when the saturated carbon of the sp^2–sp^3 single bond was quaternary. However, identification and description of individual rotamers by assignment of NMR signals was not possible;[2] on the other hand, compound 1a showed no spectral changes as the temperature was lowered.[2b]



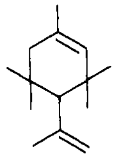
1a, R = H
b, R = Et
c, R = *i*-Pr
d, R = *t*-Bu

We here describe a series of isopropenylcyclohexanes and isopropenylcyclohexenes, in which the central carbon of the isopropenyl group is attached to a *tertiary* sp^3 carbon as in 1a, while steric hindrance to rotation is built up by more remote substituents and also by subtle conformational changes of the six-membered ring. Compounds 2–6 (Chart I) were chosen so as to provide predictable and systematic changes of crowding of the sp^2–sp^3 bond. The syntheses of 2, 3, 4b, and 6 have already been described.[3] Crystalline 4a was obtained cleanly and in high yield by kinetic hydrochlorination of tetramethyllimonene (2) in pentane at −78 °C. Treatment of 4a with zinc formate/sodium formate at low temperature (eq 1)

$$\mathbf{4a} \xrightarrow[\text{2. alkali, reflux}]{\text{1. NaOCHO/Zn(OCHO)}_2\text{, HCO}_2\text{H/ether (1:1), }-39\ ^\circ\text{C}} \mathbf{5} \qquad (1)$$

gave, with inversion of configuration, the formic ester of 5, which was saponified directly to tetramethyl-β-terpineol (5).

Chart I. 1-Isopropenyl-2,2,6,6-tetramethylcyclohexane Derivatives Showing Slow Rotation of the Isopropenyl Group



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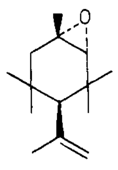

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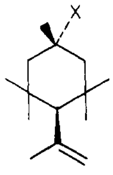
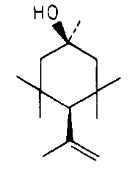
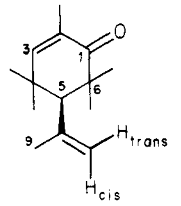


4a, X = Cl
b, X = OH



5



6

Table I. Energy Barriers and Population of Rotamers in 1-Isopropenyl-2,2,6,6-tetramethylcyclohexanes

	T_c,[a] K	$\Delta G^{\ddagger}_{\alpha}$, kcal/mol	proportion of rotamers at low temp,[b] α/β	$\Delta G°$,[c] kcal/mol
2	252	12.8	50:50	
3	272	14.2	64:36	0.27
4a	284	15.6	87:13	0.91
4b	292	15.7	85:15	0.83
5		>15.7[d]	ca. 95:5[d]	
6	278	14.1	63:37	0.25

[a] Coalescence temperature for olefinic methylene protons. [b] Determined by integration of low-temperature NMR spectra. The assignment of NMR signals to α and β rotamers is made in Table III. [c] Calculated value at 240 K. [d] Estimated value.

Interpretation of NMR Spectra and Identification of Rotamers. Thanks to the availability of a series of compounds, three of which have a plane of symmetry (cf. 4a,b and 5), we not only are able to determine rotational barriers but, for the first time, we can also deduce the structure of individual rotamers of compounds of this type by using temperature-dependent ^1H NMR in combination with low-temperature ^{13}C NMR spectroscopy. NMR spectra (90 MHz) of 2–6 are especially informative in the range of the olefinic protons. At 300 K two broadened signals appear, which on cooling of the sample to 240 K appear as two pairs of signals of generally unequal intensity

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(1) (a) Förster, H.; Vögtle, F. *Angew. Chem.* **1977**, *89*, 443; *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 429 and leading references. (b) Lomas, J. S.; Luong, P. K.; Dubois, J. E. *J. Org. Chem.* **1977**, *42*, 3394. Tidwell, T. *Tetrahedron* **1978**, *34*, 1855.

(2) (a) Bartlett, P. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1968**, *90*, 4421. (b) Anderson, J. E.; Doecke, C. W.; Rawson, D. I. *Tetrahedron Lett.* **1975**, 3531.

(3) Giguere, R. J.; von Ilsemann, G.; Hoffmann, H. M. R. *J. Org. Chem.* **1982**, *47*, 4948. See also: Giguere, R. J.; Hoffmann, H. M. R. *Tetrahedron Lett.* **1981**, *22*, 5039.

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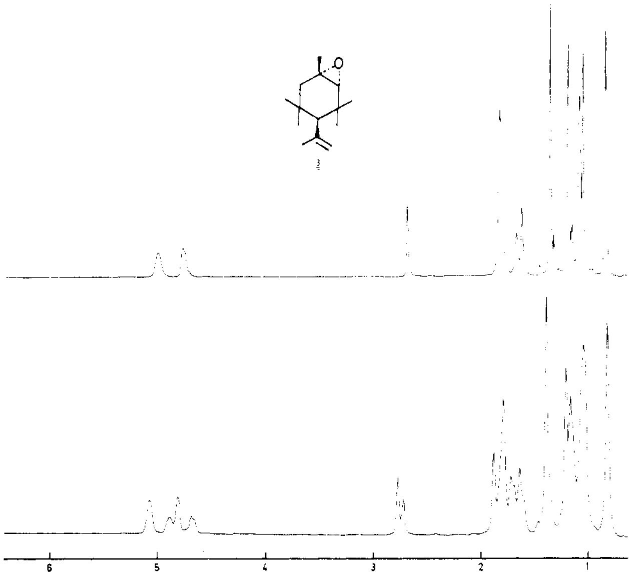


Figure 1. ^{1}H NMR spectrum (parts per million, relative to $SiMe_4$) of 4-isopropenyl-1,3,3,5,5-pentamethylcyclohexene oxide (**3**) at 300 (above) and at 240 K (below).

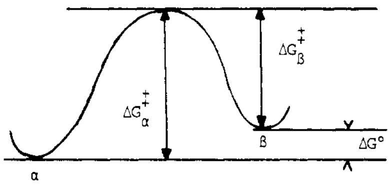


Figure 2. Definition of barriers and rotamer populations.

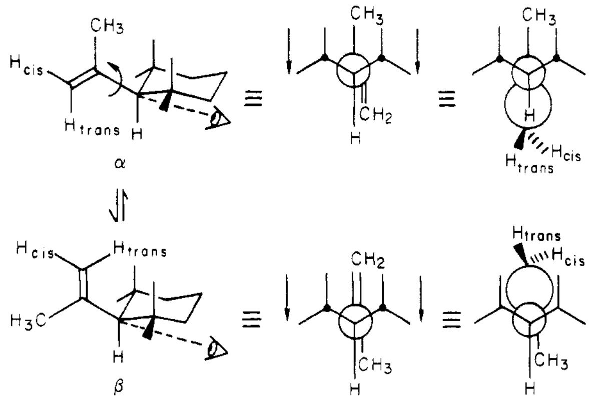
Table II. Slow Rotation of Isopropenyl Group in Tetramethylcarvone (6) Determined by Five Different ^{1}H NMR Signals[a]

signal	$\Delta\nu$, Hz	T_c, K	$\Delta G^\ddagger_\alpha$,[b] kcal/mol	$\Delta G^\ddagger_\beta$,[b] kcal/mol	$\Delta G°$, kcal/mol
H_{trans}	36	278	14.07	13.87	0.2
9-CH_3	27.5	274	14.01	13.81	0.2
H_{cis}	15	268	14.01	13.82	0.19
3-H	12	266	14.02	13.83	0.19
5-H	7.5	260	13.94	13.75	0.19

[a] For the computational method see: Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961. [b] Values for $\Delta G^\ddagger$ are significant for the first three figures.

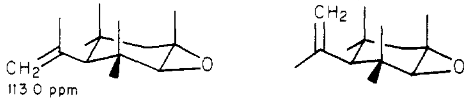
(Figure 1). The rotational barrier $\Delta G^\ddagger$ was determined from the coalescence temperature (Table I), and several signals were used to determine $\Delta G^\ddagger$ independently. For tetramethylcarvone (**6**) five different signals were used to determine $\Delta G^\ddagger$ values (cf. Figure 2) which were in excellent agreement (Table II). As usual, integration of the signals in the frozen out spectra gave the population of rotameric pairs, here designated as α and β rotamers. As it turned out, in the more stable α rotamer the tertiary allylic C—H bond eclipses the axis of the C=CH_2 double bond, and in the β rotamer the same C—H bond eclipses the C—CH_3 σ bond (Scheme I). Alternatively, the β rotamer is the average of two equally populated skew rotamers. Note that only the α and β conformations need to be considered when freezing of rotation sets in. The assignment of ^{1}H NMR signals to individual α and β rotamers was not trivial and required low-temperature ^{13}C NMR for corroboration (see below).

Scheme I. α and β Rotamers of Substituted Isopropenylcyclohexanes: Newman Projections (Center) and Bent Bond Model (Right)[a]



[a] Straight Arrows Denote Flattening of Six-Membered Ring caused, e.g., by sp^2 Centers in the Ring.

Chart II. ^{13}C NMR Shifts of Methylene Carbon in 3α and 3β



3α (major) 3β (minor)

Table III. Assignment of Chemical Shifts of H_{trans} and H_{cis} in α and β Rotamers

	chemical shift, δ			
compd	trans,α	trans,β	cis,α	cis,β
2	5.04	4.86	4.78	4.67
3	5.07	4.88	4.80	4.66
4a	5.06	4.84	4.67	4.67 or 4.69
4b	5.04	4.76	4.66	4.66
5	5.07	*a*	4.79	*a*
6	4.76	5.16	4.70	4.87

[a] 5β is not clearly discernible by NMR (cf. Table I).

The line shape of the olefinic protons of the isopropenyl group furnished first clues. As an example, consider tetramethyllimonene oxide (**3**, Figure 1). The major rotamer shows a broad signal with weak coupling at δ 5.07 and a sharper signal without discernible coupling at δ 4.80. The minor rotamer shows a broad, weakly split signal at δ 4.88 and a sharper signal upfield at δ 4.66, which is clearly split into a doublet (J = 2.1 Hz).[4]

This pattern of the olefinic protons for the two rotamers is also observed for tetramethyllimonene (**2**) and **4a**,**b**; the chemical shifts are also practically identical (maximum deviation Δδ = 0.12 ppm). Now the key question remains— is the major rotamer the α conformer and the minor rotamer the β conformer or vice versa? The low-temperature ^{13}C NMR spectrum of tetramethyllimonene oxide (**3**) provides a clear answer (Chart II). At 230 K the methylene carbon of the isopropenyl group of the minor rotamer is shifted downfield by 5.8 ppm vis-à-vis the major rotamer! Deshielding of this magnitude can be rationalized by the δ effect[5] of the two synaxial methyl groups which is possible in the β rotamer but not the α rotamer. Thus, the major rotamer of **3** is **3α**. Previously, Neuenschwander

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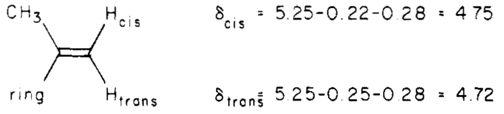
(4) Rummens et al. (Rummens, F. H. A.; Lomas, J. S.; Tiffon, B.; Coupry, C.; Lumbroso-Bader, N. *Org. Magn. Reson.* **1982**, *19*, 35) have reported NOE measurements on **1a** and related compounds showing hindered rotation around crowded sp^2–sp^3 bonds. An important difference between their compounds and ours is that their sp^3 center is quaternary and ours is tertiary. On cooling our compound **3** to 230 K there was practically no NOE. We thank Dr. G. Schrumpf of the University of Göttingen for the NOE measurement.

(5) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1976; p 40.

Chart III. Chemical Shifts of Olefinic Protons of 2-Substituted Propenes Predicted by Increment Data[7]



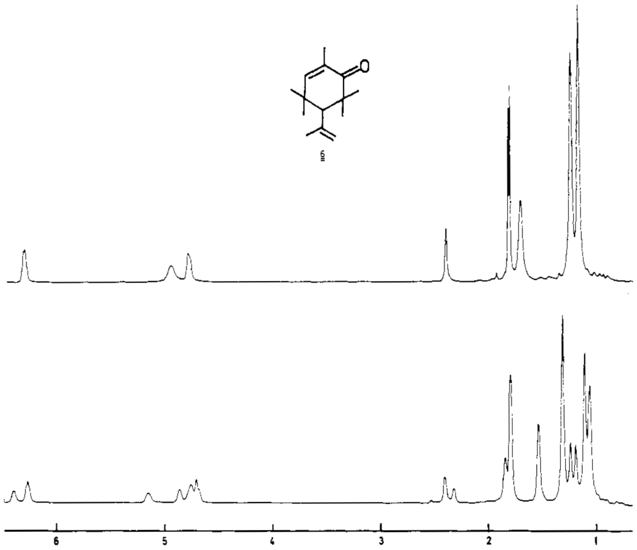


Figure 3. ^1H NMR spectrum (parts per million, relative to $SiMe_4$) of 5-isopropenyl-2,4,4,6,6-pentamethyl-2-cyclohexenone (**6**) at 300 (above) and at 240 K (below).

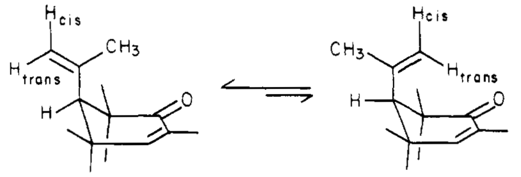
et al.[6] have concluded from the low-temperature ^{13}C NMR spectrum of tetramethyllimonene (**2**) that rotation of the isopropenyl group is hindered. However, because of the equal population of rotamers in this case, an assignment of signals to rotamers was not possible, and $\Delta G^{\ddagger}$ was not determined either.

The detailed assignment of ^1H NMR signals to H_{cis} and H_{trans} in the α and β rotamers is summarized in Table III. It should be noted that increment data[7] predict chemical shifts of H_{cis} and H_{trans} which hardly differ (δ 4.75 vs. 4.72; cf. Chart III). However, in our compounds only one of the olefinic protons appears close to the predicted value. The downfield shift of one proton (Table III) can be explained by van der Waals deshielding of the crowded H_{trans} proton. Since $H_{trans,\alpha}$ appears further downfield than $H_{trans,\beta}$, we conclude that $H_{trans,\alpha}$, which is eclipsed by the rigid 1,5-interaction with the tertiary CH proton, suffers stronger van der Waals repulsion than $H_{trans,\beta}$ which is mainly crowded by synaxial methyl groups (cf. Scheme I).

Tetramethylcarvone (6). Because of its additional carbonyl group tetramethylcarvone (**6**) shows very simple well-resolved 90-MHz ^1H NMR spectra (Figure 3). At 240 K the splitting pattern for olefinic proton C(3)–H is different for **6**α and **6**β (Figure 3). Low-temperature double-resonance experiments establish long-range coupling (^4J = 1.2 Hz) between the olefinic proton C(3)–H and tertiary allylic proton C(5)–H in **6**α, whereas no corresponding coupling appears in **6**β ($^4J \approx 0$).

Furthermore, compared with spectra for the series **2–5**, the spectra of **6** are unusual in several respects. (i) While the pattern of the olefinic methylene protons in **6** is similar to that of **2–5**, the signals of the major rotamer are now at highest field. (ii) In **6** the chemical shift difference of H_{trans} and H_{cis}, i.e., $\Delta\delta = \delta_{trans}$ (major rotamer) − δ_{cis} (major rotamer) = 0.06 ppm, is small compared with $\Delta\delta \approx 0.3$–0.4 ppm for **2–5**. On the other hand, $\Delta\delta = \delta_{trans}$ (minor rotamer) − δ_{cis} (minor rotamer) = 0.29 ppm. (iii) In **6** the methyl protons of the isopropenyl group of the major rotamer appear upfield by $\Delta\delta$ = 0.31 ppm compared with those of the minor rotamer. For **2–5** this difference is practically zero. (iv) The tertiary allylic methine proton in **6** appears at δ = 2.37 ppm, whereas the corresponding signal for **2–5** is below δ 1.80! The unusual spectroscopic properties of **6** are caused by the special geometry of the cyclohexenone system. According to low-frequency Raman spectra, the parent 2-cyclohexenone in the gaseous state adopts a conformation with five carbon atoms and an oxygen in one plane; only C-5 lies outside this plane. Ring inversion at C-5, i.e., the barrier to planarity, amounts to 2.67 kcal/mol.[8] In principle then, **6** could exist as two easily interconvertible conformers, having an equatorial and axial isopropenyl group, respectively. However, in particular, point iv suggests that the tertiary allylic methine proton is axial in **2–5** and equatorial in **6**. Furthermore, coupling of ^4J = 1.2 Hz between C(5)–H and C(3)–H as in **6**α is known to appear when C(5)–H is equatorial.[9] Absence of corresponding ^4J coupling in **6**β does not indicate an axial C(5)–H proton, i.e., equatorial isopropenyl group, for a number of reasons. If C(5)–H were to change its position on going from **6**α to **6**β, a large difference in chemical shifts should be observed. In fact, $\delta_{6\alpha} - \delta_{6\beta}$ for 5-H amounts to 7 Hz only, which is the smallest chemical shift difference among the five signals measured (Table II). Furthermore, the olefinic methylene protons H_{cis} and H_{trans} in **6**β should be in a similar steric environment as the olefinic methylene protons in **2**β–**5**β: similar chemical shifts for these protons would be expected. Table III shows that this is not the case.

Scheme II. Proposed Conformation of Major and Minor Rotamer of 6



6α (63%) **6**β (37%)

There are indications that ^4J depends on the distortion of the (substituted) 2-cyclohexenone.[9] A sterically demanding substituent at C-5 is more likely to adopt the axial position in 2-cyclohexenones than in cyclohexane, because there is no 1,3-diaxial repulsion. In summary, the isopropenyl group in *both* rotamers of tetramethylcarvone (**6**) is axial.

In the major rotamer **6**α the methyl group moves into the anisotropic shielding region of the cyclohexene double bond, appearing upfield (cf. iii above). The small difference of chemical shifts for H_{trans} and H_{cis} in **6**α (cf. ii) suggests, as is supported by models, that the minima due to the α and also the β conformer are now much flatter; i.e., the isopropenyl group is more free to rotate back and forth and to populate metastable conformations close to **6**α and **6**β. This opinion is supported by the nearly normal shifts of $\delta_{trans,\alpha}$ = 4.76 and $\delta_{cis,\alpha}$ = 4.70 (Table III and Scheme II).

Ground-State and Transition-State Effects. In discussing our data we have to distinguish the effects of functionalization of the six-membered ring and steric

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(6) Escher, A.; Übersax, B.; Neuenschwander, M. *Chimia* **1981**, *35*, 251.

(7) Matter, U. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 691, 2023.

(8) Carreira, L. A.; Towns, T. G.; Malloy, T. B., Jr. *J. Chem. Phys.* **1979**, *70*, 2273.

(9) Barieux, J. J.; Gore, J.; Richer, J. C. *Bull. Soc. Chim. Fr.* **1974**, 1020.

crowding on $\Delta G^{\ddagger}$, i.e., the transition-state effect, from the effect of crowding on the relative population of the rotamers, i.e., the ground-state effect (cf. Figure 2). Structural changes for compounds **2**–**5** are slight and are remote from the slowly rotating sp^2–sp^3 bond. In contrast, the presence of at least one *tert*-butyl group attached directly to the sp^3 carbon of the sp^2–sp^3 bond in the series **1a**–**d** leads to more severe changes in ground-state geometries of the rotamers, which are more difficult to estimate.

Along the series of compounds **2**–**5** the six-membered ring becomes increasingly more puckered, first of all because of the disappearance of unsaturation. Furthermore, the ring should be more puckered in **5** than in **4a**,**b**, because the size[1a] of the axial OH group in **5** is less than the size[1a] of the methyl group which takes the corresponding axial position in **4a**,**b**. As a consequence, synaxial repulsion[10] is less in **5** than in **4a**,**b**, and puckering of the six-membered ring is more effective in **5** than in **4a**,**b**. Restated in another way, the environment of the slowly rotating sp^2–sp^3 bond is assumed to be increasingly more crowded along the series **2**–**5**. It is then reasonable to conclude that such crowding raises the free energy gap between the more stable rotamer and the transition state, i.e., the barrier $\Delta G^{\ddagger}$. Tetramethylcarvone (**6**) changes its conformation drastically, and the activation barrier $\Delta G^{\ddagger} = 14.0$ kcal/mol cannot be directly compared to the value for the other members of this series, although the α rotamer is again preferred (see above).

A further challenging problem concerns the factors determining the relative populations of α and β rotamer, i.e., the difference in free energy between the minima in the energy profile (Figure 2). Along the series **2**–**5**, increases in $\Delta G^{\ddagger}$ parallel increases in the relative stability of the α rotamer (Table I). In **5** we have destabilized the β rotamer relative to the α rotamer to the extent that it is barely discernible as a shoulder on peaks of the α rotamer. Apparently, the α rotamer is favored by increasing steric congestion near the critical sp^2–sp^3 bond in this series. In tetramethylcarvone (**6**) the six-membered ring changes its conformation, and the isopropenyl group is now axial. Nonetheless, in the major rotamer the methyl group points into the cavity of the six-membered ring with adoption of the α conformation.

Although challenged occasionally, the bent-bond model of double bonds[11] seems useful for rationalizing the preferred existence of the α rotamer. In this model, electron repulsion is minimized in the α rotamer in which all bonds are staggered, whereas bonds are eclipsed in the β rotamer (Scheme I). Thus, although the Hückel σ,π model of double bonds has been useful in dealing with conjugated systems, *bent bonds may be better bonds* for discussing stereochemical problems such as the preferred conformation of olefins,[11a] enol ethers, and enamines[12] as well as carbonyl compounds[11a] and similar compounds containing sp^2–sp^3 σ bonds.

The isopropenylcyclohexane moiety is an important building block of terpenes, and knowledge of its preferred conformation should help in planning asymmetric syntheses. Hydroboration on the isopropenyl double bond of limonene itself has been only moderately stereoselective, leading to a 3:2 preference of one stereoisomer.[13] For high acyclic stereoselection to occur it seems necessary that the attacking reagent is also chelated with the substrate.[14]

In conclusion, isopropenylcyclohexane derivatives **2**–**6** are useful models for studying hindered rotation of isopropenyl groups. While a single rotamer is not populated exclusively, the preferred population of the α rotamer can be reconciled with the van't Hoff–Pauling model of double bonds. In future studies, the scope and limitation of this model will have to be examined more closely. Finally, the NMR data now assigned and accumulated will help our understanding of related systems.

Experimental Section

1,3,3,5,5-Pentamethyl-4-(1-methylethenyl)chlorocyclohexane (4a). Dried (P_4O_{10}) HCl gas is passed for 3 h into a solution of tetramethyllimonene (**2**)[3] (3.85 g, 20 mmol) in pentane at −78 °C. After being allowed to reach room temperature, the mixture is diluted with pentane (40 mL) and washed with a saturated solution of aqueous $NaHCO_3$ until the aqueous phase stays alkaline. The organic phase is dried (Na_2SO_4), and the pentane is evaporated at room temperature to leave crystals, which are redissolved in pentane at 22 °C. The resulting solution is cooled to −40 °C, and pentane is decanted from the precipitated crystals. After another recrystallization and removal of residual pentane at room temperature, colorless crystals of **4a** (4.34 g, 95%; mp 69–71 °C) are obtained, which may be stored at −20 °C. Our procedure can also be scaled up (0.2 mol of **2**): 90-MHz ^1H NMR ($CDCl_3$) δ 0.96 (s, 6 H, equatorial CH_3's), 1.15 (s, 6 H, axial CH_3's), 1.87 (s, 7 H; CH_3, olefinic CH_3, tertiary CH), 2.04 (s, 4 H, 2 CH_2's), 4.71 (m, 1 H, H_{cis}), 5.03 (m, 1 H, H_{trans}); mass spectrum, *m/e* 230/228 (M^+, 1/4), 177 (10), 149 (10), 137 (16), 121 (17), 117 (11), 97 (42), 96 (100), 90 (11), 83 (20), 81 (43), 79 (10), 69 (10), 67 (10), 55 (33), 41 (19).

Formic Ester of 5. Sodium formate (1.36 g, 10 mmol) and zinc formate (2.81 g, 10 mmol; obtained by adding zinc chloride to an excess of formic acid and evaporating to dryness) are suspended in a mixture of 15 mL of absolute ether and 15 mL of formic acid at room temperature. The suspension is cooled to −39 °C, and **4a** (1.14 g, 5 mmol) in 10 mL of absolute ether is vigorously stirred in. After 20 h at −39 °C (cryostat) the mixture is poured into an excess of a saturated solution of $NaHCO_3$, and the ether phase is separated. The aqueous layer is extracted with pentane (2 × 30 mL) and the combined organic phase is dried (Na_2SO_4). After evaporation of the solvent a pale yellow oil remains which consists of the desired formic acid ester of **5** dissolved in tetramethyllimonene (**2**).

***cis*-1,3,3,5,5-Pentamethyl-4-(1-methylethenyl)cyclohexan-1-ol (5).** The crude formic ester is added to a solution of 2 g of NaOH in 8 mL of methanol and 0.8 mL of water. After being refluxed for 1 h the solution is diluted with 40 mL of water and extracted with pentane (3 × 50 mL). The combined pentane phase is washed with water until neutral and dried (Na_2SO_4). After removal of the pentane a pale yellow oil remains which is chromatographed on neutral aluminum oxide (Merck, activity II–III, ratio product:aluminum oxide 1:50; solvent pentane; elution with dichloromethane). GC shows 95% of cis alcohol **5** and 5% of trans alcohol **4b**. Slow chromatography on aluminum oxide (ratio 1:200) allows separation of **5** and **4b**, giving 262.5 mg (40%) of **5**: 90-MHz ^1H NMR ($CDCl_3$) δ 0.84 (s, 6 H, 2 CH_3), 0.92 (s, 1 H, OH), 1.18 (s, 3 H, $C(OH)CH_3$), 1.28 (s, 6 H, 2 CH_3), 1.44 (δ_A 1.32, δ_B 1.57, $J = 13$ Hz, AB system, 4 H), 1.61 (m, 1 H, tertiary CH), 1.82 [m, 3 H, $=C(CH_3)$], 4.79 (s, 1 H), 5.03 (s, 1 H); mass

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[10] For further recent examples of flattening of six-membered rings induced by synaxial methyl–methyl repulsion see: Hoffmann, H. M. R.; Vathke, H. *Chem. Ber.* **1980**, *113*, 3416 and literature cited therein.

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spectrum, *m/e* 210 (3, M$^+$), 177 (12), 121 (16), 99 (45), 97 (40), 96 (100), 81 (34), 55 (13), 43 (27), 41 (12). Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.87; H, 12.48.

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Registry No. **2**, 68930-33-6; **3**, 78310-15-3; **4a**, 84602-70-0; **4b**, 83379-15-1; **5**, 83379-14-0; **6**, 81517-77-3; *cis*-1,3,3,5,5-pentamethyl-4-(1-methylethenyl)cyclohexan-1-ol formate, 84602-71-1; sodium formate, 141-53-7; zinc formate, 557-41-5; zinc chloride, 7646-85-7; formic acid, 64-18-6.

Scope and Limitations of Aliphatic Friedel–Crafts Alkylations. Lewis Acid Catalyzed Addition Reactions of Alkyl Chlorides to Carbon–Carbon Double Bonds

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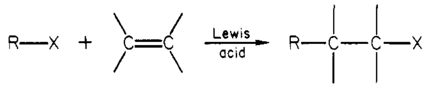
Lewis acid catalyzed addition reactions of alkyl halides **1** with unsaturated hydrocarbons **2** have been studied. 1:1 addition products **3** are formed if the addends **1** dissociate faster than the corresponding products **3**; otherwise, polymerization of **2** takes place. For reaction conditions under which **1** and **3** exist mainly undissociated, solvolysis constants of model compounds can be used to predict the outcome of any such addition reactions if systems with considerable steric hindrance are excluded.

Friedel–Crafts-type reactions are of great importance in the chemistry of aromatic compounds.[1] Their synthetic value in aliphatic chemistry appears to be rather limited,[1,2] since alkyl halides with Lewis acids are well-known initiating systems in carbocationic polymerizations of alkenes.[3] Examples have been reported, however, where reactions of type 1 gave 1:1 addition products in high yields.[2]



(1)

1 2 3

Prins[4] found that polychloroalkanes alkylate chlorinated alkenes readily in the presence of aluminum chloride (eq 2). Schmerling showed that monohaloalkanes, particularly

$$CHCl_3 + CH_2{=}CHCl \xrightarrow[AlCl_3]{} Cl_2CHCH_2CHCl_2 \quad (2)$$

$$(CH_3)_3CCl + CH_2{=}CH_2 \xrightarrow[AlCl_3]{} (CH_3)_3CCH_2CH_2Cl \quad (3)$$

tert-alkyl halides, also undergo Lewis acid catalyzed addition reactions with halogenated as well as nonhalogenated alkenes (eq 3).[5] However, "only relatively few Friedel–Crafts alkylations of alkenes by means of alkyl halides are as free from complications as the examples cited above".[6] The problem arises of how to predict those cases for which Friedel–Crafts alkylations of type 1 work properly.

Table I. Solvolysis Rates of Alkyl Chlorides **1a–m** in 80% Aqueous Ethanol at 25 °C

RX	k_1, s^{-1}	ref
$(CH_3)_2CHCl$ (**1a**)	2×10^{-9}	8a
$CH_2{=}CHCH(CH_3)Cl$ (**1b**)	5×10^{-7}	8b
$CH_3CH{=}CHCH_2Cl$ (**1c**)	$\sim 1 \times 10^{-6}$	*a*
$(CH_3)_3CCl$ (**1d**)	9×10^{-6}	8b,d
$PhCH(CH_3)Cl$ (**1e**)	1×10^{-5}	8e
$(CH_3)_2C{=}CHCH_2Cl$ (**1f**)	$\sim 4 \times 10^{-4}$	*a*
$PhC{\equiv}CC(CH_3)_2Cl$ (**1g**)	2×10^{-3}	8f
$PhC(CH_3)_2Cl$ (**1h**)	$\sim 2 \times 10^{-3}$	*b*
Ph_2CHCl (**1i**)	2×10^{-3}	8b
CH_3OCH_2Cl (**1j**)	15	8h
Ph_3CCl (**1k**)	$\sim 2 \times 10^{2}$	8i
$CH_3OCH(CH_3)Cl$ (**1l**)	>15	
$CH_3OCH(Ph)Cl$ (**1m**)	$\gg 15$	

[a] Calculated from relative rates of **1b,c,f** in 80% ethanol at 44.6 °C.[8c] [b] Solvolysis rates of **1h** and **1i** are similar in ethanol.[8g]

Predominant formation of 1:1 products **3** can be expected if **1** reacts faster with **2** than **3**. If the 1:1 product **3** is more reactive than **1**, higher addition products will be formed. Recently, one of us suggested that solvolysis rates of model compounds of **1** and **3** (Table I) may be used to differentiate between these two cases.[7] It was stated that "Lewis acid catalyzed additions of alkyl halides to carbon–carbon multiple bonds can only lead to 1:1 products if the educts dissociate more rapidly than the products". This conclusion is based on the assumption that the relative addition rates of any alkyl halides AX and BX to a common alkene $(\Delta G^{\ddagger}{}_2)_R$ are reflected by the relative dis-

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