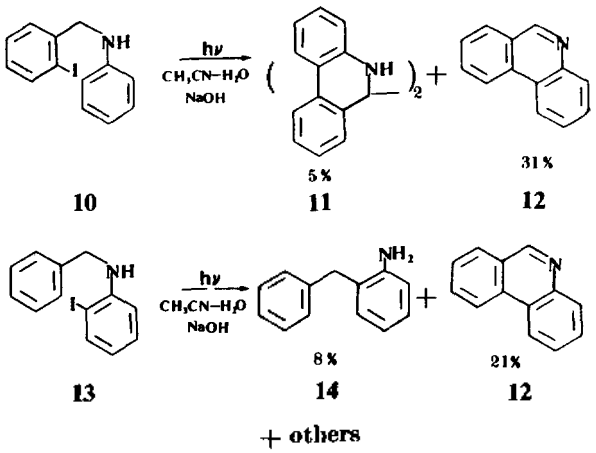

Scheme 3.

a brown solution was obtained. After stripping off the solvent, 100 mL of ethylether was added to dissolve the reaction residue. After being washed with water, the etheral solution was concentrated and developed with benzene/diethyl ether (19/1) solvent on TLC. The products (R_f=0.2), phenanthridine (**12**, 178 mg, 31% yield, mp. 105-106℃, lit mp. 106-107 ℃)[6] and 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl (R_f=0.8, **11**, 30 mg, 5%, mp. 176-183℃, lit. 175-185℃)[7] was obtained. The photochemical reaction of N-benzyl-2-iodoaniline (**13**) gave phenanthridine (**12**) (128 mg, 22%) and 2-benzylaniline (**14**) (96 mg, 16%) under the above photochemical reaction condition of **10**. The latter probably came from secondary Photo-Fries type reaction of photoreduction product *N*-benzylaniline. We are studying the mechanistic pathway of the photocyclization reactions.

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2. The pyridinium salt **4** was prepared by reaction of 2-phenylethyl bromide with 2-bromopyridine, yield 14%, mp. 150 ℃; UV (water): λ_{max} 278 (3.87); IR (potassium bromide): ν Aromatic CH 3040; ν Aliphatic CH 2945; ν Aromatic CC 1610 cm^{-1}; ^{1}H-NMR (D_2O): δ 3.8 (t, J=7 Hz, 2H), 5.5 (t, J=7.0 Hz, 2H), 7.3-7.6 (m, 5H), 8.2 (t, J=6 Hz, 1H), 8.6 (t, J=6 Hz, 1H), 8.9 (m, 2H).
   Anal. Calcd. for $C_{13}H_{13}NBr_2$: C, 45.51; H, 3.82; N, 4.08. Found: C, 45.32; H, 3.61; N, 4.20.
3. We could not obtain the pyridinium bromide salt **6** as a pure product However, we could get clean crystal of the pyridinium perchlorate **9**.
4. The pyridinium salt, **9** was identified with IR, UV and elemental analysis; UV (water): λ_{max} (4.14), IR (potassium bromide) ν Aromatic CH 3060, ν alipatic CH 2900 and aromatic CC 1650 cm^{-1}.
   Anal. Calcd. for $C_{13}H_{12}NClO_4$: C, 55.43; H, 4.29; N, 4.97. Found: C, 55.45; H, 4.32; N, 4.83.
5. N-[(2-Bromophenyl)ethyl]pyridinium bromide (**5**) was prepared by reaction of 2'-(2-bromophenyl)ethyl bromide with pyridne (yield 50%). 2'-(2-bromophenyl)ehtyl bromide was prepared by addition of hydrogen bromide to 2-bromostyrene in the presnece of benzoylperoxide (57% yield). The pyridinium salt **5** was obtained as a white crystal, yield 50%, mp. 187-188℃, UV (H_2O): λ_{max} 259.2 (ε 3.64), IR (potassium bromide): ν aromatic CH 3025, ν alipatic CH 2940, ν aromatic C=C 1670 cm^{-1}: ^{1}H-NMR (D_2O): δ 3.9 (t, J=6 Hz, 2H), 5.3 (t, J=6 Hz, 2H), 7.4-7.9 (m, 4H), 8.3-8.9 (m, 5H).
   Anal. Cald. for $C_{13}H_{13}NBr_2$: C, 45.51; H, 3.82; N, 4.08. Found C. 45.29; H, 3.90; N, 4.06.
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7. K. Mizuno, C. Pac, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **46**, 3316 (1973). The dimer **11** was identified based on mp., IR and NMR data. IR (chloroform): ν N-H stretching 3260 cm^{-1}; ^{1}H-NMR ($CDCl_3$): δ 4.70 (s, 2H, CH), 6.7-9.2 (m, 16H, Aromatic).

Catalytic Hydroacylation of Aldehyde with α,ω-dienes by Rh(I) and Isomerization of the Terminal olefin to the Internal olefin

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C-H bond activation by transition metals is one of current interests in organometallic chemistry[1]. Especially aldehydic C-H bond cleavage and its application to organic synthesis of ketones through hydroacylation have been studied[2]. One of the major limitation for this process is decarbonylation[3]. To solve this problem, aldimines were applied for the synthesis of ketimines, the precursor of ketones, through C-H bond cleavage of the aldimines with C=N bond instead of C=O bond, using picoline system which can be used for good cyclometallation tool and can be easily removed by hydrolysis after the reaction[4]. Another good cyclometallation tool is a 8-quinolinyl system which does not show any decarbonylation, since they form the stable 5-membered ring metallacyclic complexes[5]. As a model study for hydrometallation through C-H bond activation, it has been applied to many different reactions such as C-C bond cleavage of the strained ring molecule[6], synthesis of β,γ-unsaturated ketones[7], and to the elucidation of olefin isomerization mechanism[8]. In this paper we report the catalytic hydroacylation of aldehyde and isomerization of olefin by Rh(I) with α,ω-dienes.

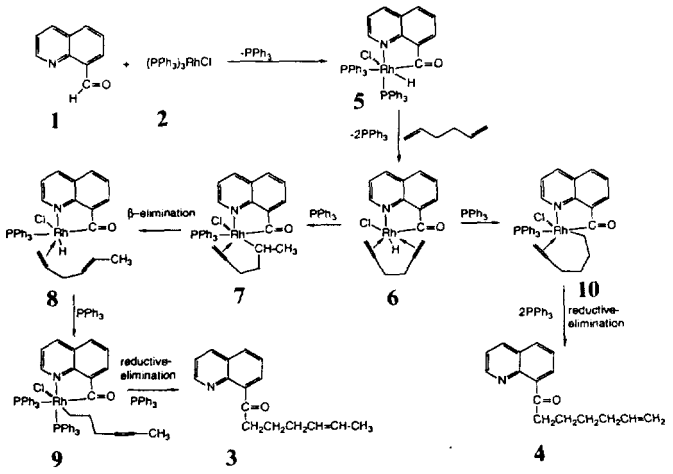
Results and Discussion

Compound **1**, 8-quinolinecarboxaldehyde, reacted with 1,5-hexadiene in toluene under Wilkinson's complex (**2**) as catalyst. After heating for 6 h at 130℃, the reaction mixtures

Table 1. Catalytic Reaction of 8-quinolinecarboxaldehyde 1 and α,ω-diene at 130℃ for 6 h under 10 mol% $(PPh_3)_3RhCl$ as Catalyst

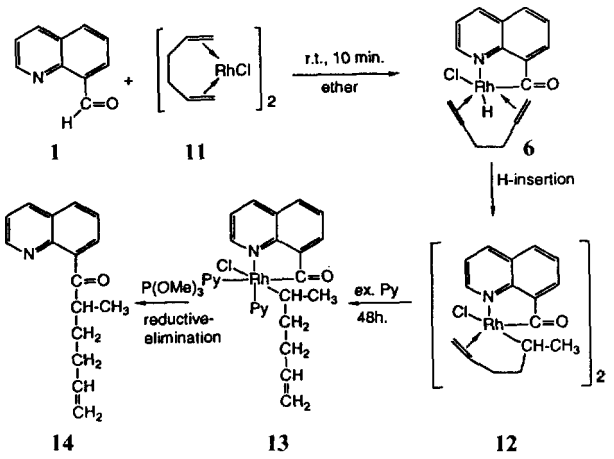
Entry	α,ω-diene	Products (Q-CO-R) -R (components)[a]	ratio[b]	Yield[c]
1	1,4-pentadiene	$CH_2CH_2CH_2CH=CH_2$	67	59%
		$CH_2CH_2CH=CH-CH_3$	33	
2	1,5-hexadiene	$CH_2CH_2CH_2CH_2CH=CH_2$	8	47%
		$CH_2CH_2CH_2CH=CH-CH_3$	92	
3	1,6-heptadiene	$CH_2CH_2CH_2CH_2CH=CH-CH_3$		44%
4	1,7-octadiene	$CH_2CH_2CH_2CH_2CH_2CH=CH-CH_3$		54%

[a]Internal olefinic derivatives are mixtures of *cis*- and *trans*-isomers, detected by GC/MS, which are inseparable by column chromatography. [b]Determined by ^1H-NMR spectra. [c]Isolated by column chromatography.



Scheme 1.

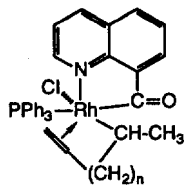
were purified by column-chromatography to give 8-quinolinyl hex-4-enyl ketone (**3**) and 8-quinolinyl hex-5-enyl ketone (**4**) in a 92 : 8 ratio in 47% yield (Table 1). Any other internal olefinic derivative has not been obtained. The mechanism for the formation of the compounds **3** and **4** can be deduced as shown in Scheme 1. The first step of this catalytic reaction must be aldehydic C-H bond cleavage in **1** by Rh(I) of **2** to generate the acylrhodium(III) hydride **5**, already isolated and characterized by the stoichiometric reaction[5]. Subsequent 1,5-hexadiene exchange with the coordinated triphenylphosphine in **5** give **6**. At this stage there are two ways of the hydride insertions into coordinated 1,5-hexadiene in **6**: One is to follow the Markownikoff's rule, and the other the anti-Markownikoff's rule. According to the Markownikoff's rule, the hydride migrates to the C-1 of 1,5-hexadiene in **6** to form the 2° alkenyl rhodium(III) complex **7**, followed by β-elimination of the hex-5-en-2-yl group in **7** to give **8** as a transient intermediate. The hydride insertion into the C-2 of 1,4-hexadiene in **8** generates the acylrhodium(III) hex-4-enyl complex **9**. Reductive-elimination of the resulting complex **9** produces **3** with regeneration of the catalyst **2**. However, according to the anti-Markownikoff's rule, the hydride migrates to the C-2 of the coordinated 1,5-hexadiene in **6** affords the acylrhodium(III) hex-5-enyl complex **10**. Reductive-elimination from **10** produces **4**. Considering the product ratio of 92 : 8 for **3** and **4**, the major olefin-insertion pathway must be **6** to **7** rather than **6** to **10** despite the fact that the 1° alkyl metal complex is must more stable than the 2° alkyl metal complex[9]. The reason must be the formation of the stable metallacyclic complex in **7** compared with that in **10**. Considering that there are many known 5-membered ring metallacyclic complexes which are supposed to be the most stable size, it can be concluded that organometallic complexes have tendencies to form the 5-membered ring metallacycle[10].



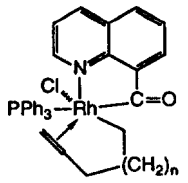
Scheme 2.

To test the formation of the intermediate **7**, stoichiometric reaction was applied as shown in Scheme 2. Compound **1** reacted with (1,5-hexadiene)rhodium(I) chloride dimer (**11**) in ether at r.t. for 10 min to give yellow precipitate which was supposed to be **12** through the formation of the intermediate **6**. To the complex **12** was added pyridine to retard the olefin-isomerization, since the metallacyclic ω-alkenyl complex has tendencies to transform into the π-alkyl complexes without coordinating ligand[8]. After an additional stirring for 15 h, ligand-promoted reductive-elimination from the resulting complex **13** by trimethylphosphite gave 8-quinolinyl hex-5-en-2-yl ketone (**14**) in 97% yield after chromatographic isolation. From the result of obtaining **14** as a final product, the formation of the complex **12** can be easily inferred, explaining that the hydride in **6** migrates to the C-1 of 1,5-hexadiene by the Markownikoff's rule to make the stable 5.5-membered ring metallacyclic complex.

To correlate the stability of the metallacycles, formed from α,ω-dienes, with the product distribution, various α,ω-dienes were applied to the catalytic reactions under the identical reaction conditions. The final results are also shown in Table 1. With 1,4-pentadiene, the product ratio of 8-quinolinyl pent-4-enyl ketone and 8-quinolinyl pent-3-enyl ketone is 67 : 33, in which the major pathway follows the anti-Markownikoff's rule (entry No. 1). It explains that the 5.5-membered metallacyclic omplex like **16a** is more stable than the smaller ring-sized 4.5-membered ring metallacyclic complex like **15a** as an intermediate. However in the case of long chain α,ω-diene



15a n=1
15b n=3
15c n=4



16a n=1
16b n=3
16c n=4

such as 1,6-heptadiene and 1,7-octadiene, each reaction resulted in 8-quinolinyl hept-5-enyl ketone and 8-quinolinyl oct-6-enyl ketone exclusively (entries 3 and 4). On the contrary to the reaction of 1,4-pentadiene, those of 1,6-heptadiene and 1,7-octadiene follows the Markownikoff's rule to make the small ring as possible as it can, since they should form **15b** and **15c** rather than **16b** and **16c** to stabilize the intermediates.

Conclusion

From the above results, it is possible to synthesize different alkenyl ketones from aldehyds with α,ω-dienes by hydroacylation. Depending on the ring-size of the intermediate, internal olefinic ketone or terminal olefinic ketone has been obtained. In the case of 1,4-pentadiene, major product is pent-4-enyl ketone while in α,ω-diene, longer than 1,4-pentadiene such as 1,6-heptadiene and 1,7-octadiene, the major product consists of alkenyl ketones having an internal olefin group. Further hydroacylation of aldehyde and the olefin isomerization mechanism is under study.

Experimental

Compound **1** was prepared by the published procedure[11]. Wilkinson's complex, (1,5-hexdiene) rhodium(I) chloride diemer, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene and 1,7-octadiene were purchased from Aldrich Chemical Co., and used without further purification. Solvents were distilled and stored over molecular sieves (4 Å). NMR spectra were recorded with a Brucker AC-200 (200 MHz) spectrometer. The chemical shifts (δ) are in ppm relative to internal Me_4Si. Infrared spectra were recorded with a Perkin-Elmer 683 spectrometer. Mass spectra were obtained on Hewlett-Packard HP 5971A mass spectrometer equipped with a HP 5890 series II Gas Chromatograph. Column-Chromatography was performed on Merck Silica Gel 60.

General Procedure

Catalytic Reaction of 1 and α,ω-Diene. A scew-capped pressure vial was charged with Wilkinson's complex (**2**) (6.2×10^{-2} mmol) dissolved in toluene (1 m*l*) and the solution flushed with nitogen, and 8-quinolinecarboxaldehyde (**1**) (6.3×10^{-1} mmol) added. After stirring for 5 min at room temperature, α,ω-diene (6.1 mmol) was added. After the reaction vial was kept at 130℃ for 6 h, with stirring, the products were separated and purified by column-chromatography with hexane and ethylacetate (5 : 2) as an eluent. The product ratio was determined by ^{1}H-NMR spectra, comparing the integrations of the terminal olefinic (=CH_2) peaks at 4.8-5.1 ppm and the internal olefinic (-CH=CH-) peaks at 5.4 ppm in the product mixture.

Stoichiometric Reaction of 1 and (1,5-Hexadiene) Rhodium(I) Chloride Dimer(11). A dry Schlenk vessel was charged with **1** (1.9×10^{-1} mmol) dissolved in THF (0.05 m*l*), flushed with nitrogen, and **11** (0.9×10^{-2} mmol) added. After 5 min stirring at room temperature, pyridine (1 m*l*) was added. The mixture was kept at room temperature for 15 h, and trimethylphosphite (0.5 m*l*) was added and stirred for additional 1 h. The resulting mixture was reduced in volume and the product separated by column-chromatography with hexane and ethylacetate (5 : 2) to give pure **14** in 97% yield. **14**: ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.92 (dd, J=4.2 & 1.9 Hz, H of. C-2 in quinoline), 8.2-7.3 (m, 5H, of quinoline), 5.8 (m, 1H, -CH=), 5.01-4.86 (ABX system, 2H, =CH_2), 3.85 (hexet, J=6 Hz, 1H, α-CH to CO), 2.13 (m, 2H, -CH_2-C=), 1.96 (m, 1H, one of diastereotopic H in β-CH_2 to CO), 1.52 (m, 1H, another diastereotopic H in β-CH_2 to CO), 1.24 (d, J=6.9 Hz, 3H, CH_3); IR (neat) 1685 cm^{-1} for CO; mass spectrum; m/e (relative intensity), 239 (M^+, 24), 238 (M^+-1, 23), 211 (M^+-CO, 11), 198 (M^+-C_3H_5, 100), 185 (53), 156 (quinolinylCO$^+$, 95), 128 (quinolinyl$^+$, 100).

Following Data Were Used for Identification of Products.

8-Quinolinyl hex-4-enyl Ketone (3). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.9 (dd, J=4.2 & 1.8 Hz, 1H, H of C-2 on quinoline), 8.2-7.3 (m, 5H, Hs of quinoline), 5.42 (m, 2H, -CH=CH-), 3.31 (t, J=7.3 Hz, 2H, CH_2-CO), 2.08 (m, 2H, CH_2-C=), 1.82 (quintet, J=7.2 Hz, 2H, CH_2 of C-2 in hex-4-enyl group), 1.62 (d, J=5.4 Hz, 3H, CH_3); IR (neat) 1680 cm^{-1} for CO; mass spectrum; m/e (relative intensity), 238 (M^+-1, 9), 211 (M^+-CO, 4), 184 (M^+-C_4H_7, 94), 171 (70), 156 (quinolinylCO$^+$, 100), 128 (quinolinyl$^+$, 66).

8-Quinolinyl hex-5-enyl Ketone (4). ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.95 (dd, J=4.3 & 1.8 Hz, 1H, H of C-2 in quinoline), 8.2-7.4 (m, 5H, Hs of quinoline), 5.8 (m, 1H, -CH=), 5.03-4.90 (ABX system, 2H, =CH_2), 3.33 (t, J=7.5 Hz, CH_2-CO), 2.10 (q, 2H, CH_2-C=), 1.80 (m, 2H, CH_2 of C-2 in hex-5-enyl group), 1.50 (m, 2H, CH_2 of C-3 in hex-5-enyl group); IR (neat) 1689 cm^{-1} for CO; mass spectrum; m/e (relative intensity) 239 (M^+, 17), 238 (M^+-1), 211 (M^+-CO, 4), 198 (M^+-C_3H_5, 8), 184 (46), 171 (13), 156 (quinolinylCO$^+$, 100), 128 (quinolinyl$^+$, 45).

8-Quinolinyl pent-3-enyl Ketone. ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.93 (dd, J=4.2 & 1.8 Hz, 1H, H of C-2 in quinoline), 8.2-7.3 (m, 5H, Hs of quinoline), 5.48 (m, 2H, -CH=CH-), 3.40 (t, J=7.3 Hz, 2H, CH_2CO), 2.46 (m, 2H, CH_2-C=), 1.62 (d, J=4.7 Hz, 3H, CH_3); mass spectrum: m/e (relative intensity) 225 (M^+, 7), 224 (M^+-1, 9), 196 (M^+-CO, 17), 182 (M^+-C_4H_7, 43), 156 (quinolinylCO$^+$, 72), 129 (quinoline, 100).

8-Quinolinyl pent-4-enyl Ketone. ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.93 (dd, J=4.2 & 1.8 Hz, 1H, H of C-2 in quinoline), 8.2-7.3 (m, 5H, Hs of quinoline), 5.8 (m, 1H, -CH=), 5.1-4.8 (ABX system, 2H, =CH_2), 3.34 (t, J=7.4 Hz, 2H, CH_2-CO), 2.17 (m, 2H, CH_2-C=), 1.88 (m, 2H, CH_2 of C-2 in pent-4-enyl group); IR (neat) 1680 cm^{-1} for CO; mass spectrum: m/e (relative intensity), 224 (M^+-1, 19), 184 (M^+-C^3H^5, 91), 156 (quinolinyCO$^+$, 100), 128 (quinolinyl$^+$, 50).

8-Quinolinyl hept-5-enyl Ketone. ^{1}H-NMR (200 MHz,

$CDCl_3$) δ (ppm) 8.92 (dd, J=4.2 & 1.8 Hz, 1H, H of C-2 in quinoline), 8.17-7.3 (m, 5H, Hs of quinoline), 5.41 (m, 2H, -CH=CH-), 3.32 (t, J=7.2 Hz, 2H, CH_2CO), 2.02 (m, 2H, CH_2-C=), 1.77 (m, 2H, CH_2 of C-2 in hept-5-enyl group), 1.61 (d, J=4.3 Hz, 3H, CH_3), 1.47 (m, 2H, CH_2 of C-3 in hept-5-enyl group); IR (neat) 1680 cm^{-1} for CO; mass spectrum: m/e (relative intensity), 253 (M^+, 15), 252 (M^+-1, 13), 225 (M^+-CO, 7), 198 (M^+-C_4H_7, 8), 184 (76), 171 (12), 156 (quinolinylCO$^+$, 100), 128 (quinolinyl$^+$, 54).

8-Quinolinyl oct-6-enyl ketone. ^{1}H-NMR (200 MHz, $CDCl_3$) δ (ppm) 8.93 (dd, J=4.1 & 1.7 Hz, 1H, H of C-2 in quinoline), 8.2-7.3 (m, 5H, Hs of quinoline), 5.38 (m, 2H, -CH=CH-), 3.32 (t, J=7.4 Hz, CH_2-CO), 1.99 (m, 2H, CH_2-C=), 1.76 (m, 2H, CH_2 of C-2 in oct-6-enyl group), 1.62 (d, J=4.8 Hz, 3H, CH_3), 1.38 (m, 4H, CH_2 of C-3 and C-4 in oct-6-enyl group); IR (neat) 1680 cm^{-1} for CO; mass spectrum: m/e (relative intensity), 267 (M^+, 5), 266 (M^+-1, 9), 239 (M^+-CO, 5), 212 (M^+-C_4H_7, 2), 198 (10), 184 (63), 171 (26), 156 (quinolinylCO$^+$, 100), 128 (quinolinyl$^+$, 55).

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Carbon-13 Two Dimensional INADEQUATE Experiment of Cholestane

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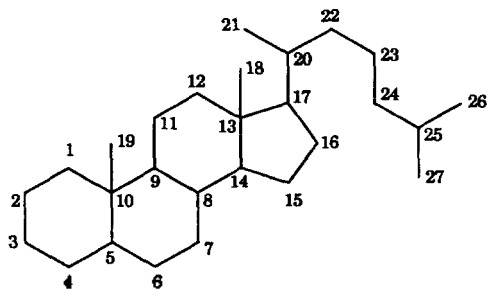
Cholestane (**1**) is one of the most important parent compound in the family of steroids which are of great biological interests, and still new steroids are continuously being isolated from plants. Because many of their proton resonances fall in a fairly narrow shift range, the carbon chemical shifts are in general far more informative than proton resonances for structural analysis of steroids. Therefore, the early study of steroids was concentrated on the carbon-13 NMR and also was greatly facilitated by using many substitution products which permitted a reasonable assignment of the carbon resonances in terms of the known substitution effects on conformationally fixed cyclohexane rings.[1-4] The analysis of the carbon-13 spectra of a series of steroids by Roberts and his co-workers is a particularly elegant example of this application and many of their data provide a good basis for the carbon-13 spectra of related materials.[1,2] However, the contradictory assignments in the parent hydrocarbon, cholestane (**1**), exist in the literature; such as carbons 12 and 16.[1,3,4] In addition, the chemical shifts of carbons 4 and 6, of carbons 18 and 19, and of carbons 10 and 22 are reported to be overlapped in the 100 MHz NMR (25 MHz at carbon).[3,4] Although unambiguous assignment of the parent compound, **1**, is absolutely prerequisite before attempting the exact evaluation of substitution effects, no high field NMR of cholestane (**1**) has ever been studied.

In order to elucidate the carbon skeleton of organic molecules, there are numerous indirect ways nowadays.[5] For example, in the case of protonated carbons the combination of COSY and HETCOR or long range HETCOR experiment provides the necessary information required to establish the carbon connectivity.[5] Although the application of long range HETCOR for the assignment of quaternary carbons is very useful, the result may be ambiguous because of the uncertainties regarding the bond length of the polarization pathway. In addition, this indirect approach fails and some ambiguities remain further in the assignment of carbon resonances when the proton spectra do not exhibit well resolved



Cholestane (1)