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Cyclobutyl Cation Rearrangements of 6-Protoilluden-8 α -ol, 7-Protoilluden-6-ol and Related Compounds

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6-Protoilluden-8 α -ol (**15**) was formolyzed and then reduced with LiAlH₄ to give 7-protoilluden-6-ol (**16**) and its stereoisomer (**17**). 3-*epi*-6-Protoilluden-8 α -ol (**19**) also gave the same products under the same conditions. These and other related reactions imply that the 7-protoilludene C-6 cation (**10**) is an important intermediate in the biosynthesis of illudane (**11**), marasmane (**12**) and illudalane (**13**) type sesquiterpenes.

Keywords—sesquiterpene; 6-protoilluden-8 α -ol; 7-protoilluden-6-ol; biomimetic reaction; formolysis; cyclobutyl cation rearrangement; Basidiomycete; 7-protoilludene C-6 cation

Introduction

A group of sesquiterpenes with unique carbon skeletons, such as protoilludanes (*e.g.*, illudol (**1**)¹⁾), illudanes (*e.g.*, illudin-M (**2**)^{1a,2)} and -S (**3**)^{1a,2,3)}), marasmanes (*e.g.*, marasmic acid (**4**)⁴⁾) and illudalanes (*e.g.*, fomajorin D (**5**)⁵⁾), are produced by Basidiomycetes. These compounds⁶⁾ were postulated to be biosynthesized through 6-protoilludene (**7**)^{7,8)} as illustrated in Chart 1. In our previous work, the hydrocarbon **7** was shown to be a real biosynthetic precursor of illudin-M (**2**) and -S (**3**) by feeding *dl*-[13,13,13-²H₃]-6-protoilludene to the illudin-producing fungus *Omphalotus olearius* (ATCC 11719).⁹⁾ The biosynthetic route from the hydrocarbon **7** to illudanes such as **2** and **3** as well as marasmanes and illudalanes may be as follows. The allylic carbonium ion **9** is generated from the hydrocarbon **7** by the introduction of a functional group such as a hydroxy group at C-8 (**8**) followed by solvolytic removal of the group. The cation **9** would easily isomerize to the 7-protoilludene C-6 cation **10**, and then this would undergo the cyclobutyl cation rearrangement to form illudane (**11**), marasmane (**12**) and illudalane (**13**) carbon skeletons. The aim of this study was to clarify the intermediary role of the 7-protoilludene C-6 cation **10** in the biosynthesis of **11**, **12** and **13**.

Fig. 1

This cation (**10**) was chemically generated from 6-protoilluden-8 α -ol (**15**),¹⁰ an equivalent of **8** (Chart 2). It was shown that cations **11** and **20** were formed by the cyclobutyl cation rearrangement of **10** and that the cations **10**, **11** and **20** were in equilibrium. The same equilibrium was attained by the solvolysis of 3-*epi*-6-protoilluden-8 α -ol (**19**). The formation of the cation **13** from the cation **10** was also demonstrated (Chart 6). In connection with the results described above, the cyclobutyl cation rearrangement of related cations, such as **29**, **32**, **35**, **39** and **40** (Chart 5) and **47** (Chart 7), is discussed.^{11,12}

Results

The allyl alcohol (**15**),¹⁰ which was obtained by LiAlH₄(LAH) reduction of 6-protoilluden-8-one (**14**),¹⁰ was treated with HCOOH(30%)-tetrahydrofuran (THF) (70%) overnight at room temperature, and the resulting formates were reduced with LAH. Two allyl alcohols **16** and **17** were obtained in a ratio of 4:5 (Chart 2). Their chromatographic properties (gas chromatography (GC) and thin-layer chromatography (TLC)) and proton nuclear magnetic resonance (¹H-NMR) spectra were similar. The ¹H-NMR spectrum of **16** showed four methyl signals at δ 0.96, 1.00, 1.21 and 1.74 and an olefinic proton signal at δ 5.27, and that of **17** showed four methyl signals at δ 0.97, 1.04, 1.15 and 1.80 and an olefinic proton signal at δ 5.66. The mass spectra (MS) of **16** and **17** were also very similar and showed the molecular ion peak (M^+) at m/z 220 and fragment ions at 205 ($M^+ - CH_3$), 192 ($M^+ - CH_2 = CH_2$) and 177 ($M^+ - CH_3 - CH_2 = CH_2$). Intense MS peaks at m/z 192 and 177 indicated the presence of a cyclobutanol moiety. The spectral and chromatographic data of **16**

Chart 2

coincided with those of 7-protoilluden-6-ol isolated from *Fomitopsis insularis*⁷⁾ and, therefore, **16** was determined to be *dl*-7-protoilluden-6-ol. From the almost identical MS and the similarity of ¹H-NMR signals between **16** and **17**, compound **17** was assumed to be a stereoisomer of **16**. The ring junction at C-3 and C-6 of **17** was supposed to be *cis* because the *cis* junction would be less strained than the *trans* junction. Moreover, the *cis* junction would be expected when formate ion attacks the cation **20** from the less hindered side. This was supported by the reported observation¹³⁾ that both *cis*- and *trans*-bicyclo[4.2.0]octan-1-ol esters gave only *cis*-bicyclo[4.2.0]octan-1-ol under solvolytic conditions. Thus, the *cis-syn-cis* structure would be the most plausible one for the major product **17**.

The structure assignment of **17** was supported by the following experiments. The *cis-syn* allyl alcohol **19**, which was obtained by LAH reduction of 3-*epi*-6-protoilluden-8-one (**18**),¹⁴⁾ was treated with HCOOH(30%)-THF(70%) and then reduced with LAH. The product was again a mixture of **16** and **17** in the same ratio (4:5) as that obtained from the *cis-anti* allyl alcohol **15**. The transformation of both **15** and **19** to the mixture of **16** and **17** can be well explained by the formation of cations **10** and **20** from **15** and **19**, respectively. The cations **10** and **20** could attain equilibrium through the illudane cation **11**. Attack of formate ion on the cations **10** and **20** at C-6 and LAH reduction of the formates would lead to **16** and **17** in a ratio of 4:5. Thus, compound **17** was assigned as the *cis-syn-cis* stereoisomer of **16**.¹⁵⁾ A similar epimerization between protoilludane type compounds **14** and **18** through an illudane C-3 cation **22** has also been observed under acidic conditions (CF₃COOH-CHCl₃ or BF₃·Et₂O-benzene) (Chart 3).¹⁴⁾

Chart 3

R=3,5-dinitrobenzoyl

Chart 4

In the simpler model of bicyclo[4.2.0]octyl 1-derivatives, Wiberg *et al.* showed that solvolysis of *cis*- and *trans*-bicyclo[4.2.0]octyl 1-(3,5-dinitrobenzoates) (24 and 25) gave spiro[2.5]octan-4-ol (26) and *cis*-bicyclo[4.2.0]octan-1-ol (27) in a ratio of 2.5—2.6:1 (Chart 4).¹³⁾ However, in the case of the 7-protoilludene system, all the products were derived from cyclobutyl cations 10, 20, 21 and 23, and no products from cyclopropylcarbinyl cations 11 and 22, which correspond to 26, could be identified.¹⁶⁾ A possible reason may be that the C-7(8) double bond of 10, 20, 21 and 23 stabilizes the carbonium cation at C-6. In addition, in the

Chart 5

case of formolysis of **15** and **19**, formate ion might not be able to attack C-3 of **11** because of the steric hindrance around this center. In the course of our chemical studies on protoilludanes, we obtained several illudane type compounds (**30**,¹⁰ **33**,^{8,17,18} **36**,⁸ **41** and **42**^{10,19}) from protoilludane C-6 cations (**29**, **32**, **35**, **39** and **40**), and all of them possessed a double bond at C-2(3) (Chart 5).

Since the formation of the cation **10** from the allyl alcohol **16** in acidic media was also expected, **16** was treated with formic acid. The allyl alcohol **16** was recovered unchanged after treatment with HCOOH(30%)–THF(70%) for 14 h at room temperature. Under more drastic conditions (99% HCOOH, 1 h at room temperature), the illudalane type compound **45** was obtained from **16** as a sole product after LAH reduction (Chart 6). Likewise the allyl alcohols **15**, **17** and **19** were also converted to **45** under the same conditions. These reactions could be explained by the formation of the illudalane cation **13** from intermediary cations **10**, **11** or **20**, followed by dehydrogenation to give cation **43**. The alcohol **45** has, indeed, been isolated from mycelium of *F. insularis* along with the alcohol **16**.⁷⁾

Another illudalane type compound **48** was obtained from the epoxyketone **46**²⁰) by treatment with CF₃COOH in benzene. The structure of **48** was determined by ¹H-NMR and MS. A possible pathway leading to **48** is shown in Chart 7. The methyl ether **49** was obtained by Anchel and Morris.^{2b)}

Discussion

Although no illudane type compound could be isolated, the results of solvolysis of the allyl alcohols **15** and **19** indicated the intervention of the illudane cation **11** (Chart 2). In the reaction of the allyl alcohols **15** and **16** to the illudalane **44**, rearrangement of the cation **10** into the illudalane cation **13** was also found (Chart 6). These facts suggest that, in enzymatic reactions also, 6-protoilludene (**7**) would undergo the cyclobutyl cation rearrangement to give illudane (**11**) and illudalane (**13**) cations through the cation **10**.

Under our solvolytic conditions [HCOOH(30%)–THF(70%) overnight at room temperature], when a double bond is present at C-7(8) (e.g., in **10**), the protoilludane C-6 cation would be stabilized, and indeed the isolated products were *cis-anti-cis* protoilludane (**16**) and stereoisomeric *cis-syn-cis* protoilludane (**17**) type compounds. On the other hand, protoilludane C-6 cations without a double bond at C-7(8) gave illudane type compounds (**30**, **33**, **36**, **41** and **42**).

The rearrangements of cyclobutanones through cyclopropylcarbinyl cations under acidic conditions were studied by Katz and Dessan,²¹⁾ Erman *et al.*²²⁾ and Ceccherelli *et al.*²³⁾ They showed that two carbons on the cyclobutane ring were interchangeable during the rearrangement. The allyl alcohols **15** and **19**, and the enones **14** and **18** are vinyls of cyclobutanol and cyclobutanone systems. Therefore, C-4 and C-5 of **14**, **15**, **18** and **19** might be transposed during the rearrangement (Chart 8 for **10** from **15** and a similar process for **14**, **18** and **19**). However, this could not be clarified in this work. Concerning this point, Hanson *et al.*²⁴⁾ concluded on the basis of their biosynthetic study that if protoilludane were the precursor of illudin-M (**2**) and -S (**3**), the C3–C4 bond of the protoilludane would migrate from the α -side to produce **2** and **3**.

Although conversion of the cation **10** to the marasmane cation **12** was expected, we could not obtain marasmanes as stable compounds. In order to stabilize the marasmane C-5 primary cation, some modification of the protoilludane C-6 cation, *e.g.*, **50** (R = electron-donating group), may be necessary (Chart 9). Expecting the formation of an illudane type compound, Matsumoto *et al.* formylized protoilludane C-7 cation (**6**) equivalents, but illudane type compounds were not obtained.²⁵⁾

Thus, our results indicate that the 7-protoilludene C-6 cation (**10**), formed from 6-protoilluden-8 α -ol (**15**),²⁶⁾ is the true intermediate in the rearrangement to illudanes (**11**) and illudalanes (**13**). The appropriately modified cation **10** may give marasmanes (**12**). In biological reactions, prior to the rearrangement of the cation **10**, some modification (*e.g.*, oxidation) might also occur and the introduced functionality could influence the course of the rearrangement.

Chart 8

Chart 9

Experimental

¹H-NMR spectra were measured on a JEOL GX-400 FT-NMR spectrometer (400 MHz for ¹H) and chemical shifts were recorded in δ units relative to internal tetramethylsilane (TMS) ($\delta=0$) in CDCl₃. Infrared (IR) spectra were measured on a JASCO DS-301 and MS on a Shimadzu-LKB 9000 at 70 eV.

7-Protoilluden-6-ol (16) and *cis-syn-cis* 7-Protoilluden-6-ol (17) from 6-Protoilluden-8 α -ol (15)—The allyl alcohol **15**¹⁰⁾ (10 mg) was dissolved in 0.1 ml of HCOOH(30%)–THF(70%) and the solution was allowed to stand overnight at room temperature. After removal of the reagent and solvent with an N₂ stream and then with a rotary pump, the residue was dissolved in Et₂O and reduced with LAH. The products were analyzed by GC. Total yield was more than 95% and the ratio of **16** and **17** was 4 : 5. When the allyl alcohol **15** was treated with HCOOH(10%)–THF(90%), the reaction rate was very slow and **15** was recovered after 18 h at room temperature. Treatment of **15** with 99% HCOOH at room temperature gave only illudalane **44**, as described below. Compounds **16** and **17** were separated by TLC. The *R_f* values of **15**, **16** and **17** (precoated silica gel plate, benzene : acetone = 9 : 1) and relative

retention times (R_{tR}) of **15** and **17** with respect to **16** (1.5% OV-17, 1.5 m, 150 °C, **16**, 3.0 min) were as follows.

	15	16	17	19
R_f	0.32	0.37	0.30	0.33
R_{tR}	1.50	1.00	1.33	1.39

16: $^1\text{H-NMR}$ (CDCl_3) δ : 0.96 (3H, s, CH_3), 1.00 (3H, s, CH_3), 1.21 (3H, s, CH_3), 1.74 (3H, s, $\text{CH}_3\text{-C}=\text{C}$), 2.64 (1H, br s, H-9), 5.27 (1H, br s, H-8). MS m/z (110—220): 220 (M^+ , 2.5%), 205 ($\text{M}^+ - 15$, 2.5%), 192 ($\text{M}^+ - 28$, 65%), 177 ($\text{M}^+ - 28 - 15$, 15%), 136 (55%), 135 (100%), 124 (88%), 121 (25%). **17**: $^1\text{H-NMR}$ (CDCl_3) δ : 0.97 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.15 (3H, s, CH_3), 1.8 (3H, s, $\text{CH}_3\text{-C}=\text{C}$), 2.66 (1H, br s, H-9), 5.66 (1H, s, H-8). MS m/z (110—220): 220 (M^+ , 2%), 205 ($\text{M}^+ - 15$, 2%), 192 ($\text{M}^+ - 28$, 50%), 177 ($\text{M}^+ - 28 - 15$, 13%), 136 (48%), 135 (100%), 124 (88%), 121 (23%).

Reduction of 3-*epi*-6-Protoilluden-8-one (18**) to 3-*epi*-6-Protoilluden-8 α -ol (**19**)**—The enone **18**¹⁴⁾ (74 mg) was reduced with LAH (13 mg)/ Et_2O (1 ml). The allyl alcohol (**19**) was purified by silica gel column chromatography (56 mg, 75% yield). The R_f and R_{tR} values of the allyl alcohol **19** were shown above. $^1\text{H-NMR}$ (CDCl_3) δ : 0.93 (3H, s, CH_3), 1.04 (3H, s, CH_3), 1.16 (3H, s, CH_3), 1.62 (3H, br s, $\text{CH}_3\text{-C}=\text{C}$), 2.42 (1H, br s, H-5), 2.65 (1H, br s, H-5), 4.43 (1H, br s, H-8). The stereochemistry of the hydroxy group of **19** was assigned as α from the negligibly small coupling constant between the protons on C-8 and C-9, which would not be expected for the β -isomer.

Conversion of **19 to the Allyl Alcohols **16** and **17****—The allyl alcohol **19** (10 mg) was treated with 0.1 ml of HCOOH (30%)– THF (70%) and then with LAH as described for **15**. The product was again a mixture of **16** and **17** in the same yield and ratio as those from **15**.

Conversion of the Allyl Alcohols **15, **16**, **17** and **19** to 5-(2-Hydroxyethyl)-2,2,4,6-tetramethylindan (**45**)**—Each allyl alcohol (5 mg) was treated with 99% HCOOH (0.05 ml) for 1 h at room temperature. After HCOOH was removed with an N_2 stream, the product was reduced with LAH in Et_2O to give the alcohol **45**, quantitatively. The $^1\text{H-NMR}$ data, R_f on TLC and R_{tR} on GC were in agreement with those reported for natural **45**.⁷⁾

6-Trifluoroacetoxyethyl-2,2,5,7-tetramethylindan-4-ol (48**) from 9-*epi*-6,7-Epoxyprotoilluden-8-one (**46**)**—A solution of **46** (10 mg) in benzene (0.3 ml) was combined with a solution of CF_3COOH (80 mg) in benzene (0.3 ml) and the mixture was allowed to stand overnight at room temperature. The reagent and the solvent were removed with an N_2 stream. Compound **48** was purified by silica gel column chromatography (5 mg, 35% yield). IR (CHCl_3): 1782 cm^{-1} (CF_3COO). MS m/z : 330 (M^+), 315 ($\text{M}^+ - 15$), 216 ($\text{M}^+ - \text{CF}_3\text{COOH}$), 203 ($\text{M}^+ - \text{CF}_3\text{COOCH}_2$). $^1\text{H-NMR}$ (CDCl_3) δ : 1.18 (6H, s), 2.16 (3H, s), 2.23 (3H, s), 2.64 (2H, s), 2.69 (2H, s), 3.31 (2H, t, $J = 8\text{ Hz}$), 4.38 (2H, t, $J = 8\text{ Hz}$).

References and Notes

- 1) a) M. Anchel, A. Hervey and W. J. Robbins, *Proc. Natl. Acad. Sci. U.S.A.*, **36**, 300 (1950); Y. C. McMorris, M. S. R. Nair and M. Anchel, *J. Am. Chem. Soc.*, **89**, 4562 (1967).
- 2) a) T. C. Morris and M. Anchel, *J. Am. Chem. Soc.*, **85**, 831 (1963); b) *Idem, ibid.*, **87**, 1594 (1965).
- 3) a) H. Shirahama, Y. Fukuoka and T. Matsumoto, *Bull. Chem. Soc. Jpn.*, **35**, 1047 (1962); b) T. Matsumoto, H. Shirahama, A. Ichihara, Y. Fukuoka, Y. Takahashi, Y. Mori and M. Watanabe, *Tetrahedron*, **21**, 2671 (1965); c) K. Nakanishi, M. Tada, Y. Yamada, M. Ohashi, K. Komatsu and H. Terakawa, *Nature* (London), **197**, 292 (1963); d) K. Nakanishi, M. Ohashi, M. Tada and Y. Yamada, *Tetrahedron*, **21**, 1231 (1965).
- 4) a) F. Kavanagh, A. Hervey and W. J. Robbins, *Proc. Natl. Acad. Sci. U.S.A.*, **35**, 343 (1949); b) J. J. Dugan, P. de Mayo, M. Nisbet and M. Anchel, *J. Am. Chem. Soc.*, **87**, 2768 (1965); c) J. J. Dugan, P. de Mayo, M. Nisbet, J. R. Robinson and M. Anchel, *ibid.*, **88**, 2838 (1966).
- 5) D. M. X. Donnelly, J. O'Reilly, J. Polonsky and G. W. van Eijk, *Tetrahedron Lett.*, **23**, 5451 (1982).
- 6) Review: W. A. Ayer and L. M. Browne, *Tetrahedron*, **37**, 2199 (1981).
- 7) S. Nozoe, H. Kobayashi, S. Urano and J. Furukawa, *Tetrahedron Lett.*, **1977**, 1381.
- 8) J. Furukawa, N. Morisaki, H. Kobayashi, S. Iwasaki, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 440 (1985).
- 9) N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, S. Nozoe and S. Okuda, *Tetrahedron Lett.*, **26**, 4755 (1985).
- 10) N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, A. Itai, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 2783 (1985).
- 11) a) Y. Ohfuné, S. Misumi, A. Furusaki, H. Shirahama and T. Matsumoto, *Tetrahedron Lett.*, **1977**, 279; b) Review of biomimetic syntheses of illudoid sesquiterpenes: H. Shirahama, Y. Ohfuné, S. Misumi and T. Matsumoto, *Yuki Gosei Kagaku Kyokai Shi*, **36**, 569 (1978).

- 12) In this paper, the carbons of the cations **11**, **12** and **13** are numbered as illustrated in Chart 1.
- 13) K. B. Wiberg, J. E. Hiatt and K. Hsieh, *J. Am. Chem. Soc.*, **92**, 544 (1970).
- 14) N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, A. Itai, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 2792 (1985).
- 15) The allyl alcohols (**53**), obtained by LAH reduction of 9-*epi*-6-protoilluden-8-one (**52**), gave another alcohol (**54**) on treatment with HCOOH (30%)–THF (70%) followed by LAH reduction. Though the stereochemistry has not been determined, compound **54** was a different isomer from **16** and **17**: N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, A. Itai, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 2783 (1985)

- 16) A small amount of a ketone derived from **22** was obtained in the course of the epimerization of **14** to **18**: after 40 d, the yield was about 10% from **14**: N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, A. Itai, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 2792 (1985).
- 17) Under the usual LAH reduction conditions, the tosylate of **31** was converted to the hydrocarbon **33** as a major product: J. Furukawa, N. Morisaki, H. Kobayashi, S. Iwasaki, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 440 (1985).
- 18) Y. Ohfuné, S. Misumi, A. Furusaki, H. Shirahama and T. Matsumoto, *Tetrahedron Lett.*, **1977**, 279.
- 19) In order to obtain 8-acetoxy-6-protoilludenes (acetates of **15** and its 8-epimer), the acetates **37** and **38** were treated with MsCl/dimethylaminopyridine/triethylamine. However, they rearranged to the illudane type compounds **41** and **42**, respectively. **41**: MS m/z : 262 (M^+). $^1\text{H-NMR}$ (CDCl_3) δ : 0.68 (3H, d, $J=7$ Hz), 1.02 (3H, s), 1.06 (3H, s), 1.30 (3H, s), 2.07 (3H, br s), 5.2 (1H, br s), 0.5–0.8 (*ca.* 3H). **42**: MS m/z : 202 ($M^+ - 60$). $^1\text{H-NMR}$ (CDCl_3) δ : 0.61 (3H, d, $J=7$ Hz), 1.00 (3H, s), 1.05 (3H, s), 1.24 (3H, s), 2.09 (3H, s), 4.7 (1H, dd, $J=10, 10$ Hz), 0.3–0.8 (4H).
- 20) When the crystalline *trans-anti* enone **52** was left to stand in air, it slowly changed to an oil, which contained **46** (after 2 weeks, **52**:**46** = 1:1). MS showed that compound **46** had one more oxygen atom than **52**. The structure of **46** was determined from the spectral data and its formation from **52** with $\text{H}_2\text{O}_2/\text{NaOH-MeOH}$. Though **46** was obtained as a single isomer, the configuration has not been established. The air oxidation of **52** to **46** was accelerated by heat. **46**: MS m/z : 234 (M^+), 219 ($M^+ - 15$), 201, 191 ($M^+ - 15 - 28$). $^1\text{H-NMR}$ (CDCl_3) δ : 0.98 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.25 (3H, s, CH_3), 1.35 (3H, s, CH_3), 2.6 (1H, H-2), 2.8 (1H, H-9). IR (CHCl_3): 1712 cm^{-1} (C=O): N. Morisaki, J. Furukawa, H. Kobayashi, S. Iwasaki, A. Itai, S. Nozoe and S. Okuda, *Chem. Pharm. Bull.*, **33**, 2783 (1985).
- 21) T. J. Katz and R. Dessan, *J. Am. Chem. Soc.*, **85**, 2172 (1963).
- 22) W. F. Erman, R. S. Treptow, P. Bakuzis and E. Wenkert, *J. Am. Chem. Soc.*, **93**, 657 (1971).
- 23) C. Ceccherelli, M. Curini, R. Pellicciari and E. Wenkert, *J. Org. Chem.*, **47**, 3173 (1982).
- 24) A. Peter, W. Badshaw, J. R. Hanson and I. H. Sadler, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2445.
- 25) Y. Ohfuné, H. Shirahama and T. Matsumoto, *Tetrahedron Lett.*, **1970**, 2869.
- 26) In this work, the 8 α -OH isomer (**15** or **19**), which was the sole product of LAH reduction of the enone **14** or **18**, was used. Both 6-protoilluden-8 α -ol and 6-protoilluden-8 β -ol derivatives were isolated from Basidiomycetes: D. Donnelly, S. Sanada, J. O'Reilly, J. Polonsky, T. Prange and C. Pascard, *J. Chem. Soc., Chem. Commun.*, **1982**, 1267.