Recl. Trav. Chim. Pays-Bas 114, 492–497 (1995)
SSDI 0165-0513(95)00099-2
0165-0513/95/11/12492-06$9.50

Photochemical rearrangement of 2-(*N*-allyl-*N*-alkylamino)cyclohex-2-enones

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(Received April 3, 1995)

Abstract. Irradiation at 366 nm of 2-(*N*-allyl-*N*-alkylamino)cyclohex-2-enones led, surprisingly, to very unstable 1-azaspiro[2.5]octan-4-ones rather than to the expected [2 + 2] intramolecular photocycloaddition. The corresponding alcohols could be isolated in good yield by reduction of the crude reaction mixture. When the reaction was carried out in a mixture of acetone/D_2O (9/1), incorporation of one deuterium atom was observed. The proposed mechanism involves an intramolecular γ-H abstraction in the primary step, followed by the molecular rearrangement of a 7-azabicyclo[4.2.0]octan-1-ol intermediate.

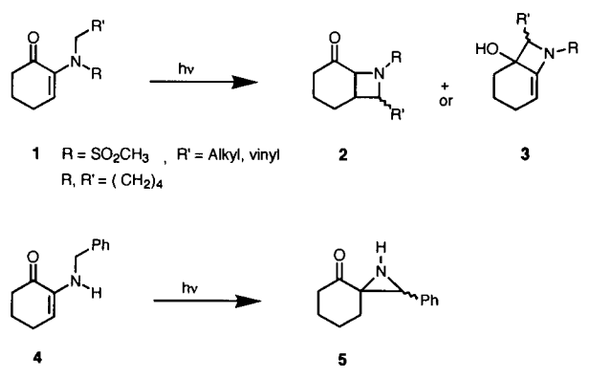
Intramolecular [2 + 2] photocycloadditions have become important processes for the synthesis of polycyclic skeletons[1]. Interestingly, intramolecular photocycloadditions of 2-hetero-substituted cyclohexenones have not retained the attention of the scientific community as much as their 3-substituted analogues and only scarce reports of their successful additions can be found in the literature. For example, cyclobutane derivatives are isolated in good chemical yields from 2-(allyloxy)cyclohex-2-enones, while a complex mixture of photoproducts was obtained from the corresponding 2-(allylmethylamino)-cyclohex-2-enone. However, replacement of the methyl group by an acetyl substituent allowed cyclobutane formation[2]. The difference in the photoreactivity, which seemed to depend both on the nature of the heteroatom and also on the nitrogen substituents, might be due to the ability of the starting molecule to involve intramolecular electron or hydrogen transfer processes, in competition with the [2 + 2] cycloaddition. We have observed previously that 7-azabicyclo [4.2.0]octan-5-ones **2** and 7-azabicyclo[4.2.0]oct-5-en-1-ols **3** could be isolated in preparative yields from 2-(alkylamino)cyclohex-2-enones **1**, according to Scheme 1[3].

As an exception to this general reactivity, a mixture of the two diastereoisomeric 1-azaspiro[2.5]octan-4-ones **5** was observed from 2-(benzylamino)cyclohex-2-enone (**4**)[4]. However our efforts to generalise this reaction were unsuccessful.

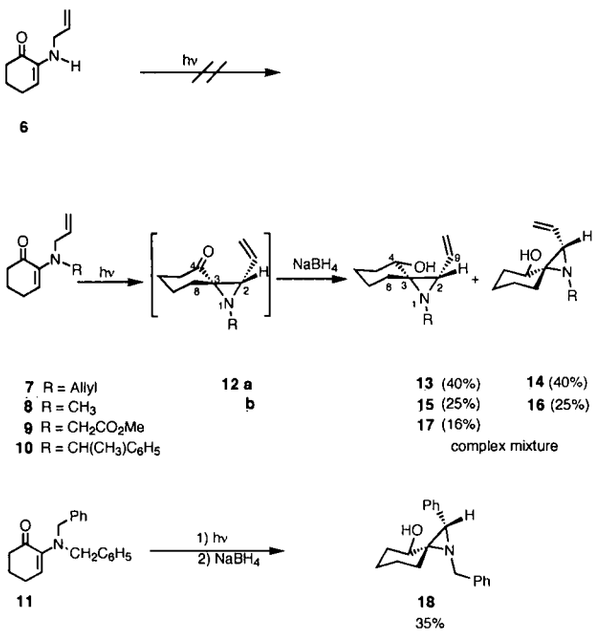
In connection with our interest in intramolecular [2 + 2] photocycloadditions of heterosubstituted cyclohexenones[5], we decided to study the photoreactivity of the 2-(allylamino)cyclohex-2-enones **6–10** and 2-(dibenzylamino)cyclohexenone (**11**). We now report that formation of azaspiranones may be a more favourable process than intramolecular photocycloaddition.

The starting enones **6–11** were conveniently prepared by reaction of allylamines with cyclohexane-1,2-dione, in the presence of a trace of an acidic catalyst. When the enone **6** was irradiated at 366 nm for 100 hours, the starting material was recovered almost quantitatively. The result, which contrast with the photoreactivity of the benzyl analogue **4**, is not completely surprising if we consider the usual inactivity of secondary enaminones[3]. For this reason, we turned next to the *N*-disubstituted aminocyclohexenones **7–10** and the results are summarized in Scheme 2.

Irradiation of **7** in diethyl ether, methylene chloride or better, in acetone, led to complete disappearance of the starting material and clean formation of a very unstable ketonic compound. The ^{1}H- and ^{13}C-NMR spectra of the crude reaction mixture revealed the presence of a single compound. The disappearance of the conjugated double bond and of an allylic hydrogen on the side-chain indicates a cyclization process between the cyclohexanic ring and the side-chain. The presence of a quaternary carbon at 80.92 ppm excluded a 7-azabicyclo[4.2.0]octan-5-one **2** and was only compatible with an azaspiranone structure for the new compound **12a**. When the ^{1}H-NMR spectrum was carried out in dry $CDCl_3$ and in the presence of increasing amounts of $Eu(FOD)_3$, we observed an induced chemical shift which was higher for H-9 than for H-2. This indicates a *syn* relationship between the carbonyl and the vinyl groups.



Scheme 1.



Scheme 2.

This azaspiranone was decomposed in a complex mixture either on silica gel or neutral alumina. The instability of **12a** is probably due to the competitive thermal and acidic rearrangements already described for this type of compound[6,7]. To avoid degradation of the aziridine ring, the crude mixture was transformed by sodium borohydride into a 1 : 1 mixture of two diastereoisomers **13** and **14**. The ratio between these isomers was found to depend on the nature of the reducing agent. With $LiAlH_4$ a 1 : 3 mixture was obtained while a 3 : 2 mixture was observed when using the chelating reducing agent $Zn(BH_4)_2$. In these two isomers, the equatorial hydroxyl group develops intramolecular hydrogen bonding with the aziridine ring, as revealed by IR in very dilute solutions. Although the relative configuration of the hydroxyl group and the aziridine ring cannot be ascertained, the intramolecular hydrogen bonding is stronger in **13** than **14**, in agreement with the proposed stereochemistry[8]. In order to confirm the relative stereochemistry of the aziridine ring and the hydroxyl groups, ^{1}H-NMR spectra of the two stereoisomers were examined in the presence of increasing amounts of $Eu(FOD)_3$. It was observed that the lanthanide-induced chemical shift (LIS) on the signal of H-4 of stereoisomer **14** was higher than for **13**. Furthermore, the higher LIS for H-9 than for H-2 in the two stereoisomers, confirms the *syn* relationship of the vinyl and the hydroxyl group. Unfortunately, the small difference observed for the LIS of the corresponding protons of **13** and **14** did not allow a definitive conclusion on the relative configuration of the C N and C O bonds.

Irradiation of **8** in similar conditions led cleanly to **12b**. Reaction mixtures obtained from the photolysis of enones **10–11** were more complicated; however, analysis of the crude reaction mixture by NMR indicated, in every case, the presence of an azaspiranone. Products **15–18** could be isolated after the reduction of the crude reaction mixture by $NaBH_4$. The stereochemistry of the products was established by comparison of NMR spectra of **12b** and **15–18** with those of **12a** and **13** and **14**.

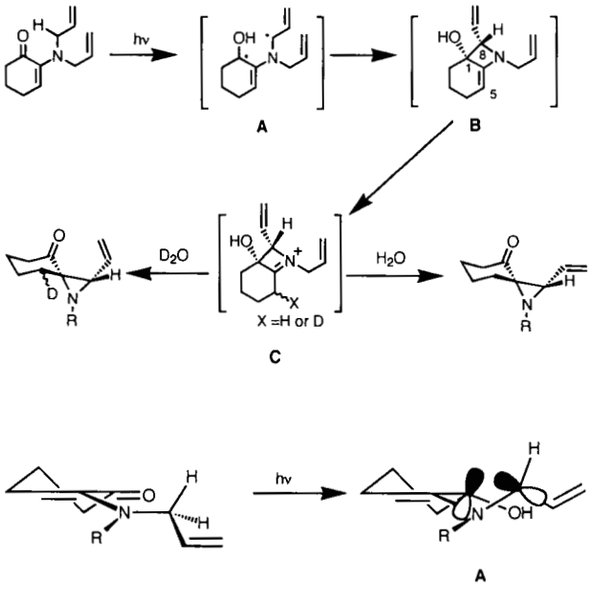
An attempt to provoke an asymmetric induction in the cyclization step of **10**, by means of 2-benzeneethanamine, was not explored very thoroughly, due to the formation of many products in addition to the expected cyclization.

In order to understand the formation of these 1-azaspiro[2.5]octan-4-ones, we carried out the irradiation of **7** in a mixture of D_2O and acetone 1 : 9. The analysis of the mixture of the corresponding alcohols **13** and **14** arising from reduction of the photoproducts by $NaBH_4$, indicated incorporation of one deuterium atom in both **13** and **14**. From ^{13}C-NMR, it appeared that the deuterium was located at C-8 exclusively. Under similar conditions and when the reaction was stopped before complete transformation of the starting material, no deuterium incorporation could be detected in the recovered enone **7**. When the reaction was carried out in dry hexadeuterated acetone and monitored by NMR, no intermediate could be detected between the starting enone **7** and **12**. Furthermore, no deuterium incorporation could be detected in the azaspiranone **12**, under these conditions. The mechanism shown in Scheme 3 is proposed to explain this unusual photoreaction. The primary transformation of the excited enone might involve a γ-hydrogen abstraction, as is usually observed with α-hetero-substituted enones[3,9]. Cyclization of the 1,4-biradical **A** would then produce a very unstable 7-azabicyclo[4.2.0]oct-5-en-1-ol **B**, having a strained enamine functional group. In the absence of an electron-withdrawing group on the nitrogen atom to stabi-

Table I ^{13}*C- and* ^{1}*H-NMR characteristics.*

Compd	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	H-2 [b]	H-4 [b]
12a	62.9	80.9	213.1	38.6	27.9	21.6	37.6	134.6 136.7	116.2 119.1	3.44, d *J* 9.1	–
12D [a]	63.0	81.0	213.4	38.7	28.0	21.7	37.5	134.7 136.8	116.4 119.4	3.44, d *J* 9.1	–
13	69.8	72.6	75.7	33.1	23.8	20.5	30.0	134.3 135.9	116.9 118.4	2.92, d *J* 9.1	3.63, dd *J* 11.2, 4.8
14	62.8	73.8	79.2	35.7	24.1	21.6	32.8	133.6 135.8	117.1 118.2	3.44, d *J* 9.2	3.58, dd *J* 10.9, 4.3
13D	69.6	72.6	75.8	33.0	23.6	20.3	29.4, t *J* 20.7	133.8 135.2	117.2 118.7	2.92, d *J* 9.1	3.63, dd *J* 11.2, 4.8
14D	62.8	73.7	78.9	35.7	23.9	21.6	32.4, t *J* 19.7	133.2 135.1	117.7 118.8	3.44, d *J* 9.2	3.58, dd *J* 10.9, 4.3
15	73.1	72.5	76.0	33.1	23.8	20.4	30.0	133.2	119.4	2.87, d *J* 9.2	3.60–3.66 m
16	66.5	73.5	78.3	35.4	23.9	21.6	30.0	132.3	119.1	3.35, d *J* 9.4	3.59–3.68 m
17	70.4	72.9	75.1	32.9	23.8	20.5	30.1	134.1	118.7	2.93, d, *J* 9.2	3.67, dd *J* 11.1, 4.6
18	70.7	73.8	76.6	33.7	23.7	20.5	29.9	–	–	3.52, s	3.64, dd *J* 11.2, 5.0

[a] **D** means deuterated. [b] *J* in Hz.

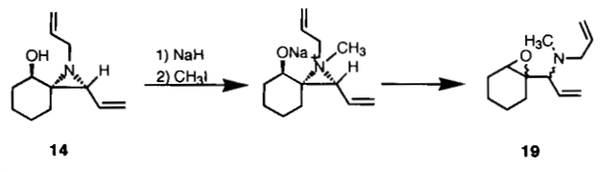


Scheme 3.

lize this very reactive intermediate[3], a spontaneous protonation or deuteriation of the enamine at C-5, followed by a rearrangement of the 1-hydroxyiminium ion **C** would occur. As the configuration of the migrating carbon C-8 should be conserved during the rearrangement, the stereochemistry of the azaspiranone is determined during the cyclization step of the biradical **A**. A cis relative configuration of the tertiary hydroxyl and the vinyl groups should be favoured, since the steric interactions between the two substituents during the cyclization step are weaker than in the competitive transition state leading to the *trans* diastereoisomer[10].

During our studies to establish the stereochemistry of the 2-(1-hydroxyalkyl)aziridines, we tried to transform these alcohols into their methoxy and acetyl derivatives. Interestingly, we observed ring opening of the aziridine, which was faster than substitution on the hydroxyl group even under very mild conditions. For example, when **14** was treated in THF at 0°C, followed successively by NaH and iodomethane, the epoxy derivative **19** could be isolated from the complex reaction mixture. Under similar conditions and as determined by NMR, the stereoisomer **13** led to a mixture of *N*- and *O*-methylated products, which could not be isolated in pure form. The structure of compound **19**, established from its NMR spectra, indicated that a process similar to the *Payne* rearrangement of epoxy alcohols, had occured[11].

In the absence of iodomethane, no reaction of **13** or **14** could be detected, even after long reaction times in the presence of sodium hydride. A similar cooperative effect of an electrophile in the *Payne* rearrangement, has already been reported in the case of epoxy alcohols[12]. The difference in selectivity observed with the two stereoisomers **13** and **14**, might be explained if we consider that the opening of the aziridinium ion can only be concerted when the hydroxyl group and the nitrogen atom have a relative *trans* stereochemistry.



Scheme 4.

In conclusion, we have shown that γ-hydrogen abstraction is the main process of deactivation of cyclic α-enamino ketones, even in the presence of an alkenylamino substituent. The azaspiranones which are produced during the reaction, result from an unusual rearrangement of four-membered ring intermediates.

Experimental

The NMR spectra were recorded in a $CDCl_3$ solution with tetramethylsilane (δ 0 ppm), using a Bruker AC 250 instrument. FT-IR (Fourier transform) spectra were carried out in $CHCl_3$ or in film between NaCl plates on a IR MIDAC spectrometer. Mass spectra were obtained on a D 300-JEOL apparatus at the UFR Pharmacy of the University of Reims. Elementary analyses were determined on a CHN 2400 Perkin Elmer Apparatus. Flash chromatographies were performed on aluminium oxide 90 Merck (70–230 mesh). Preparative-layer chromatography were obtained by using silica gel Merck (60 $PF_{254+366}$). UV spectra were obtained on a UVIKON 941 plus, KONTRON instruments.

Starting materials

2-(Allylamino)cyclohex-2-enone (**6**). A solution of cyclohexane-1,2-dione (2.0 g, 17.8 mmol) and allylamine (JANSSEN) (1.8 ml, 23.2 mmol) in benzene (40 ml) containing *p*-toluenesulfonic acid (90 mg) was refluxed for 5 h with a Dean-Stark separator. The solvent was removed by distillation and the residual oil was chromatographed on alumina (ethyl-acetate/petroleum-ether, 2/98) to give the enaminone **6**; oil, 0.92 g, 34%. ^{1}H-NMR: δ 1.94 (2H, dt, *J* 12.9, 6.3 Hz); 2.36 (2H, dt, *J* 5.7, 5.3 Hz); 2.46 (2H, t, *J* 6.7 Hz); 3.51 (2H, sl); 4.30 (1H, sl); 5.09–5.24 (2H, m); 5.44 (1H, t, *J* 4.7 Hz); 5.86 (1H, ddt, *J* 17.2, 10.3, 5.2 Hz). ^{13}C-NMR: δ 23.43 (CH_2); 24.47 (CH_2); 37.87 (CH_2); 45.70 (CH_2); 111.52 (CH); 115.88 (CH_2); 134.92 (CH); 140.27 (C); 195.69 (C). IR: 3400 (NH); 1675 (C=O); 1630 (C=C) cm^{-1}, UV (Et_2O) λ_{max}/nm (ε/mol·m^{-2}): 204 (ε 6590); 310 (ε 3610). MS *m/e* (%, fragment): 152 (15, $M^+ + 1$); 151 (100, M^+); 150 (23); 122 (57); 95 (38, $M^+ - C_3H_5N$); 94(40); 54 (59).

2-(Diallylamino)cyclohex-2-enone (**7**). **7** was obtained according to that procedure described for enaminone **6** using diallylamine (2.9 ml, 23.2 mmol) and chromatographed on alumina (ethyl-acetate/petroleum-ether, 7/93); oil, 2.4 g, 72%. Anal. calcd for $C_{12}H_{17}NO$: C 75.37, H 8.96, N 7.32; found: C 75.05; H 9.01, N 7.28%. ^{1}H-NMR: δ 1.88 (2H, dt, *J* 13.0, 6.4 Hz); 2.32–2.43 (4H, m); 3.51 (4H, d, *J* 6.5 Hz); 5.02–5.10 (4H, m); 5.73 (1H, ddt, *J* 17.7, 9.7, 6.2 Hz); 5.89 (1H, t, *J* 4.6 Hz). ^{13}C-NMR: δ 22.93 (CH_2); 25.42 (CH_2); 39.66 (CH_2); 53.05 (CH_2); 117.09 (CH_2); 128.55 (CH); 134.66 (CH); 144.36 (C); 196.78 (C). IR: 1680 (C=O); 1605 (C=C) cm^{-1}. UV (CH_2Cl_2) λ_{max}/nm (ε/mol·m^{-2}): 229 (ε 5000); 310 (ε 2500); λ 366 (ε 365). MS *m/e* (%, fragment): 193 (14); 192 (100, $M^+ + 1$); 191 (16, M^+); 150 ($M^+ - C_3H_5N$, 25).

2-(N-Allyl-N-methylamino)cyclohex-2-enone (**8**). A solution of cyclohexane-1,2-dione (2.0 g, 17.8 mmol) and *N*-methylallylamine (2.0 ml, 21.4 mmol) in ether (40 ml) containing $MgSO_4$ was refluxed for 10 h. After filtration, the solvent was removed by distillation and the residual oil was chromatographed on alumina (ethyl-acetate/petroleum-ether, 2/98) to give the enaminone **8**; oil, 0.32 g, 11%. ^{1}H-NMR: δ 1.94 (2H, dt, *J* 13.1, 6.2 Hz); 2.38–2.50 (4H, m); 2.52 (3H, s); 3.52 (2H, d *J* 6.5 Hz); 5.08–5.16 (2H, m); 5.82 (1H, ddt, *J* 17.8, 9.7, 6.5 Hz); 5.91 (1H, t, *J* 4.8 Hz). ^{13}C-NMR: δ 23.02 (CH_2); 25.38 (CH_2); 38.42 (CH_3); 39.65 (CH_2); 56.28 (CH_2); 117.07 (CH_2); 126.03 (CH); 134.63 (CH); 146.11 (C); 196.52 (C). UV (CH_2Cl_2) λ_{max}/nm (ε/mol·m^{-2}): 234 (ε 2680); 307 (ε 2620); λ 366 (ε 370).

N-Allyl-N-(6-oxocyclohex-1-enyl)glycine methyl ester (**9**). *N*-Allylglycine methyl ester was prepared from glycine methyl ester (2.0 g, 15.9 mmol) and allyl bromide (1.5 ml, 17.5 mmol) in refluxing CH_3CN (120 ml) for 12 h in the presence of K_2CO_3 (4.8 g, 35.0 mmol). After filtration, the solvent was removed by distillation. On ^{1}H-NMR spectroscopy, the secondary amine (55%) was identified, and the presence of the tertiary amine was noted. The tertiary amine did not react with cyclohexane-1,2-dione; the crude secondary amine was used without any purification. ^{1}H-NMR of *N*-allylglycine methyl ester: δ 3.24 (2H, dt, *J* 6.49, 1.24 Hz); 3.70 (3H, s); 5.12–5.24 (2H, m); 5.86 (1H, ddt, *J* 17.16, 10.30, 6.68 Hz). ^{13}C-NMR: δ 51.27 (CH_3);

53.64 (CH_2); 57.12 (CH_2); 118.04 (CH_2); 135.08 (CH); 171.64 (C).
A solution of cyclohexane-1,2-dione (2.0 g, 17.8 mmol) and the amine in toluene (40 ml) containing *p*-toluenesulfonic acid (90 mg) was refluxed for 5 h with a Dean-Stark separator. The solvent was removed by distillation and the residual oil was chromatographed on alumina (ethyl-acetate/petroleum-ether, 2/98) to give the enaminone **9**; oil, 0.42 g, 12%. Anal. calcd for $C_{12}H_{17}NO_3$: C 64.55, H 7.67, N 6.27; found: C 64.20, H 7.54, N 5.99%. ^{1}H-NMR: δ 1.93 (2H, dt, *J* 13.1, 6.4 Hz); 2.38–2.49 (4H, m); 3.67 (2H, d, *J* 4.3 Hz); 3.68 (3H, s); 3.89 (s, 2H); 5.14–5.22 (2H, m); 5.84 (1H, ddt, *J* 16.8, 10.6, 6.2 Hz); 6.00 (1H, t, *J* 4.6 Hz). ^{13}C-NMR: δ 22.97 (CH_2); 25.50 (CH_2); 39.75 (CH_2); 51.11 (CH_2); 51.36 (CH_3); 54.54 (CH_2); 117.88 (CH_2); 126.92 (CH); 134.60 (CH); 143.82 (C); 171.81 (C); 196.83 (C). IR: 1745 (C=O ester); 1680 (C=O); 1610 (C=C) cm^{-1}. UV (CH_2Cl_2) λ_{max}/nm (ε/mol·m^{-2}): 228 (ε 2500); 306 (ε 1600); λ 366 (ε 166). MS *m/e* (%, fragment): 223 (12, M^+); 164 (100, $M^+ - CO_2Me$); 151 (41); 150 (37, $M^+ - CH_2CO_2Me$); 136 (24); 101 (30).

(S)-*2-[Allyl-1-phenylethyl)amino]cyclohex-2-enone* (**10**). (*S*)-*N*-Allyl-*N*-(1-phenylethyl)amine was obtained from the (−)(*S*) α-methylbenzylamine (3.0 ml, 23.3 mmol) and allylbromide (2.2 ml, 25.6 mmol) in refluxing CH_3CN (130 ml) for 12 h in the presence of K_2CO_3 (3.9 g, 27.9 mmol). ^{1}H-NMR: δ 1.35 (3H, d, *J* 6.61 Hz); 3.10 (2H, dt, *J* 6.10, 1.40 Hz); 3.80 (1H, q, *J* 6.61 Hz); 5.03–5.17 (2H, m); 5.89 (1H, ddt, *J* 17.17, 10.30, 6.29 Hz); 7.22–7.33 (5H, m). ^{13}C-NMR: δ 24.10 (CH_3); 57.52 (CH); 115.67 (CH_2); 126.62 (CH); 126.90 (CH); 128.41 (CH); 136.90 (CH); 145.43 (C).
A solution of cyclohexane-1,2-dione (2.9 g, 25.6 mmol) and the amine in toluene (50 ml) containing *p*-toluenesulfonic acid (90 mg) was refluxed for 5 h with a Dean-Stark separator. The solvent was removed by distillation and the residual oil was chromatographed on alumina (ethyl-acetate/petroleum-ether, 2/98) to give the enaminone **10**; oil, 2.03 g, 34%. Anal. calcd for $C_{17}H_{21}NO$: C 79.96, H 8.29, N 5.48; found: C 79.47, H 8.17, N 5.98%. ^{1}H-NMR: 2 rotamers in proportion 75 (maj)/25 (min) at room temperature. Maj: δ 1.33 (3H, d, *J* 6.9 Hz); 1.90 (2H, dt, *J* 13.0, 6.9 Hz); 2.40–2.47 (4H, m); 3.25 and 3.41 (AB, J_{AB} 15.2 Hz, 2H, dt, *J* 5.8, 1.4 Hz); 4.56 (1H, q, *J* 6.9 Hz); 4.93–5.08 (2H, m); 5.59 (1H, ddt, *J* 17.4, 10.1, 6.2 Hz); 6.05 (1H, t, *J* 4.6 Hz); 7.00–7.50 (5H, m). Min: 1.43 (3H, d, *J* 6.9 Hz); 2.15–2.24 (2H, m); 2.33–2.40 (4H, m); 3.75–3.95 (2H, m); 4.13 (1H, q, *J* 6.9 Hz); 5.08–5.13 (2H, m); 5.16 (1H, t, *J* 4.8 Hz); 5.75–5.92 (1H, m); 7.00–7.50 (5H, m). ^{13}C-NMR: Maj: δ 17.78 (CH_3); 22.99 (CH_2); 25.69 (CH_2); 39.88 (CH_2); 49.06 (CH_2); 58.12 (CH_2); 115.93 (CH_2); 125.68 (CH); 126.60 (CH); 126.70 (CH); 127.50 (CH); 128.46 (CH); 135.67 (CH); 143.75 (C); 197.95 (C). Min: δ 17.78 (CH_3); 23.38 (CH_2); 24.88 (CH_2); 37.83 (CH_2); 49.06 (CH_2); 58.12 (CH_2); 116.64 (CH_2); 125.68 (CH); 126.60 (CH); 126.70 (CH); 127.50 (CH); 128.46 (CH); 136.10 (CH); 143.28 (C); 195.92 (C). IR: 1675 (C=O); 1630 (C=C) cm^{-1}. UV (CH_2Cl_2) λ_{max}/nm (ε/mol·m^{-2}): 240 (ε 2600); 311 (ε 2300); λ 366 (ε 250). MS *m/e* (%, fragment): 256 (4, $M^+ + 1$); 255 (15, M^+); 214 (52, $M^+ - C_3H_5N$); 200 (38); 151 (23); 150 (84, $M^+ - CH(CH_3)Ph$); 105 (100); 77 (41).

2-(Dibenzylamino)cyclohex-2-enone (**11**). A solution of cyclohexane-1,2-dione (2.0 g, 17.8 mmol) and dibenzylamine (4.5 ml, 23.2 mmol) in benzene (40 ml) containing *p*-toluenesulfonic acid (90 mg) was refluxed for 5 h with a Dean-Stark separator. The solvent was removed by distillation and the residual oil was chromatographed on alumina (ethyl-acetate/petroleum-ether, 7/93) to give the enaminone **11**; solid, 2.86 g, 55%. Anal. calcd for $C_{20}H_{21}NO$: C 82.44, H 7.26, N 4.81; found: C 82.48, H 7.31, N 4.66%. ^{1}H-NMR: δ 1.79 (2H, dt, *J* 13.4, 6.4 Hz); 2.13–2.20 (2H, m); 2.40 (2H, dt, *J* 6.7 Hz); 4.10 (4H, s); 5.82 (1H, t, *J* 4.6 Hz); 7.00–7.35 (10H, m). ^{13}C-NMR: δ 22.94 (CH_2); 25.52 (CH_2); 39.97 (CH_2); 54.58 (CH_2); 126.79 (CH); 128.08 (CH); 128.38 (CH); 130.19 (CH); 138.33 (C_{Ar}); 144.09 (C); 197.09 (C). IR: 1680 (C=O); 1605 (C=C) cm^{-1}. UV (CH_2Cl_2) λ_{max}/nm (ε/mol·m^{-2}): 228 (ε 7000); 310 (ε 2500); λ 366 (ε 345). MS *m/e* (%, fragment): 292 (2, $M^+ + 1$); 291 (6, M^+); 200 (100, $M^+ - CH_2Ph$); 105 (42); 91 (100).

Irradiation products

1-Allyl-2-vinyl-1-azaspiro[2.5]octan-4-one (**12a**). A solution of **7** (250 mg, 1.31 mmol) in dry acetone (75 ml, *c* 0.01 mol/l), CH_2Cl_2 (75 ml, *c* 0.01 mol/l), ether (75 ml, *c* 0.01 mol/l) or acetone (15 mol, *c* 0.05 mol/l) was poured in pyrex tubes and deoxygenated by bubbling with argon. The tubes were placed around a HPW 125 Philips lamp which was placed in a cooling-well. The irradiation was carried out until complete disappearance of the starting material (TLC control), for 6 h. The solvent was removed under reduced pressure at room temperature and the residual oil was characterized by ^{1}H- and ^{13}C-NMR spectroscopy and directly submitted to the reduction step. Azaspiranone **12a** was unstable, even at low temperature and on neutral alumina or on silica gel. In contrast to the reaction carried out in CH_2Cl_2 or diethyl ether which led to a mixture of products, the photolysis in acetone led clearly to **12a** as the new compound, in the reaction mixture. ^{1}H-NMR: δ 1.12–2.53 (8H, m); 2.95 and 3.19 (AB, J_{AB} 13.9 Hz, 1H, m and 1H, dt, *J* 5.1, 1.6 Hz); 3.44 (1H, d; *J* 9.1 Hz); 4.98–5.15 (3H, m); 5.29 (1H, dd, *J* 10.2, 2.0 Hz); 5.52–5.75 (2H, m). ^{13}C-NMR: δ 21.59 (CH_2); 27.88 (CH_2); 37.62 (CH_2); 38.56 (CH_2); 48.43 (CH_2); 62.90 (CH); 80.92 (C); 116.16 (CH_2); 119.12 (CH_2); 134.64 (CH); 136.72 (CH); 213.08 (C). IR: 2945; 1710 cm^{-1}. UV(Ether) λ_{max}/nm (ε/mol·m^{-2}): 215 (ε 5400), 254 (ε 4500).
Europium induced shift experiment[13]. To a solution of **12a** (5 mg, 0.026 mmol) in dry $CDCl_3$ (0.3 ml), a solution of dry Eu(FOD)$_3$ (Europium(III)-tris-(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate) (27 mg, 0.026 mmol) in dry $CDCl_3$ (0.2 ml) was added in 16 portions (in 10^{-2} mol·eq^{-1}). In each addition, the ^{1}H-NMR spectra was registered. We determined the slope of the straight line $(\delta_i - \delta_i^0) = f(\delta_r - \delta_r^0)$, where δ_i^0 and δ_i are the chemical shift (in ppm) of the aziridinic proton (H-2) or vinylic proton (H-9) in the absence or presence of Eu(FOD)$_3$, respectively and δ_r^0 and δ_r are the chemical shift of the proton H-12 in the absence or presence of Eu(FOD)$_3$, respectively.

1-Allyl-2-vinyl-1-azasprio[2.5]octan-4-ol (**13**) *and* (**14**). Reduction by $NaBH_4$. The oil (1.31 mmol) was dissolved in methanol and the solution was cooled to 0°C. Then, $NaBH_4$ (98 mg, 2.61 mmol) was added in portions. Stirring was continued for 30 min. Then water (0.5 ml) and methylene chloride (3 ml) were added. The mixture was filtered, and the solvent was removed under reduced pressure to give a viscous oil. This residue was extracted with ether, filtered through anhydrous magnesium sulfate and the solvent evaporated. The products were purified by TLC (thin-layer chromatography) on alumina (ethyl-acetate/petroleum-ether, 20/80), **13** and **14** (118 mg, 40% and 118 mg, 40%).
Reduction by $LiAlH_4$. The oil (1.31 mmol) was added to a suspension of $LiAlH_4$ (60 mg, 1.57 mmol) in ether at 0°C. Stirring was continued for 1 h. After hydrolysis, the mixture was filtered and the solvent was removed under reduced pressure to give a crude product. The products were purified by TLC on alumina (ethyl-acetate/petroleum-ether, 20/80), **13** and **14** (58 mg, 23% and 157 mg, 63%).
Reduction by $Zn(BH_4)_2$[14]. To a solution of the oil (1.31 mmol) in anhydrous ether (2 ml) was added zinc borohydride in ether (10.5 ml, 1.57 mmol) under argon. After stirring for 1 h at 0°C, 1 ml of water was added and stirring was continued for an additional 30 min. The solvent was dried over $MgSO_4$ before being removed on a rotary evaporator and the products were purified as above, **13** and **14** (130 mg, 52% and 82 mg, 33%).
13; oil. HRMS (High-resolution mass spectroscopy): calcd for $C_{12}H_{19}NO$: 193.1462; found 193.1467. ^{1}H-NMR: δ 0.85–1.80 (8H, m); 2.92 (1H, d, *J* 9.1 Hz); 3.06 and 3.32 (AB, J_{AB} 13.8 Hz, 1H, dt, *J* 6.5, 1.3 Hz and 1H, dt, *J* 5.6, 1.5 Hz); 3.63 (1H, dd, *J* 11.2, 4.8 Hz); 5.02 (1H, dd, *J* 17.2, 1.9 Hz); 5.09–5.21 (2H, m); 5.25 (1H, dd, *J* 10.2, 1.9 Hz); 5.63 (1H, ddd, *J* 17.2, 10.2, 9.1); 5.85 (1H, m);. ^{13}C-NMR: δ 20.50 (CH_2); 23.75 (CH_2); 29.96 (CH_2); 33.11 (CH_2); 48.76 (CH_2); 69.83 (CH); 72.59 (C); 75.71 (CH); 116.88 (CH_2); 118.35 (CH_2); 134.29 (CH); 135.87 (CH). IR: 3400 (OH); dilution: 3546 (fine); 3322; 3257 cm^{-1}. MS *m/e* (%, fragment): 194 (11, $M^+ + 1$); 193 (14, M^+); 154 (56).
14; oil. HRMS: calcd for $C_{12}H_{19}NO$: 193.1462; found 193.1467. ^{1}H-NMR: δ 1.10–2.10 (8H, m); 3.05 and 3.30 (AB, J_{AB} 13.7 Hz; 1H, dt, *J* 6.8, 1.2 Hz and 1H, dt, *J* 5.5, 1.5 Hz); 3.44 (1H, d, *J* 9.2 Hz); 3.58 (1H, dd, *J* 10.9, 4.3 Hz); 5.07 (1H, dd, *J* 17.2, 1.8 Hz); 5.12–5.29 (3H, m); 5.69 (1H, ddd, *J* 17.2, 10.2, 9.2 Hz); 5.85 (1H, m);. ^{13}C-NMR: δ 21.62 (CH_2); 24.12 (CH_2); 32.84 (CH_2); 35.72 (CH_2); 48.52 (CH_2); 62.79 (CH); 73.80 (C); 79.22 (CH); 117.10 (CH_2); 118.17 (CH_2); 133.65 (CH); 135.81 (CH). IR: 3400 (OH); dilution: 3559 (fine but

	Eu(FOD)$_3$ concentration (10^{-2}·mol·eq^{-1})							
	0	12.5	25	37.5	50	62.5	75	$(\delta_i - \delta_i^0)/(\delta_r - \delta_r^0)$
$\delta_r - \delta_r^0$ (H-12)	0	–	–	0.08	0.09	0.13	0.15	1
$\delta_i - \delta_i^0$ (H-2)	0	0.01	0.04	0.09	0.15	0.21	0.27	1.6
$\delta_i - \delta_i^0$ (H-9)	0	0.01	0.07	0.13	0.36	0.49	0.65	4.0

less than **13**); 3333; 3257 cm^{-1}. MS *m/e* (%, fragment): 194 (M^+ + 1,34); 193 (M^+, 16); 154 (56).

Europium induced shift experiment. To a solution of **13** or **14** (5 mg, 0.026 mmol) in dry $CDCl_3$ (0.3 ml), a solution of dry $Eu(FOD)_3$ (27 mg, 0.026 mmol) in dry $CDCl_3$ (0.2 ml) was added in 16 portions as described for **12a**.

1-Allyl-2-vinyl-1-[8-^{2}H]azaspiro[2.5]octan-4-one (**12D**) (D means deuterated). A solution of **7** (300 mg, 1.57 mmol) in a mixture of dry acetone (141 ml) and D_2O (16 ml), was irradiated for 12 h under a nitrogen atmosphere at 366 nm. The solvent was removed under reduced pressure and the residual oil was directly submitted to the reduction step by $NaBH_4$; oil. ^{1}H-NMR: δ 1.12–2.53 (7H + D, m); 2.95 and 3.19 (AB, J_{AB} 13.9 Hz; 1H, m, and 1H, dt, *J* 5.1, 1.6 Hz); 3.44 (1H, d, *J* 9.1 Hz); 4.98–5.15 (3H, m); 5.29 (1H, dd, *J* 10.2, 2.0 Hz); 5.52–5.75 (2H, m). ^{13}C-NMR: δ 21.72 (CH_2); 27.97 (CH_2); 37.49 (CHD, t, *J* 20.7 Hz); 38.73 (CH_2); 48.51 (CH_2); 62.97 (CH); 81.00 (C); 116.45 (CH_2); 119.43 (CH_2); 134.68 (CH); 136.79 (CH); 213.42 (C).

When a solution of **7** (200 mg, 1.05 mmol) in dry CD_3COCD_3 (30 ml) was irradiated for 12 h under a nitrogen atmosphere at 366 nm, we observed no incorporation of deuterium according to the singlet observed at 37.62 ppm in the ^{13}C-NMR spectrum with proton decoupled. Furthermore when the reaction was monitored in a ^{1}H-NMR tube at room temperature, we observed only the appearance of the signals of the azaspiranone **12a** and the disappearance of the protons of the starting material.

1-Allyl-2-vinyl-1-[8-^{2}H]azaspirol[2.5]octan-4-ol (**13D**) *and* (**14D**). **13D**; oil, 75 mg, 26%. HRMS: calcd for $C_{12}H_{18}DNO$: 193.1540; found 193.1529. ^{1}H-NMR: δ 0.85–1.80 (7H + D, m); 2.92 (1H, d, *J* 9.1 Hz); 3.06 and 3.32 (AB, J_{AB} 13.8 Hz, 1H, dt, *J* 6.5, 1.3 Hz, and 1H, dt, *J* 5.6, 1.5 Hz); 3.63 (1H, dd, *J* 11.2, 4.8 Hz); 5.02 (1H, dd, *J* 17.2, 1.9 Hz); 5.09–5.21 (2H, m); 5.25 (1H, dd, *J* 10.2, 1.9 Hz); 5.63 (1H, ddd, *J* 17.2, 10.2, 9.1); 5.85 (1H, m);. ^{13}C-NMR: δ 20,34 (CH_2); 23.62 (CH_2); 29.44 (CHD, t, *J* 18.7 Hz); 33.01 (CH_2); 48.56 (CH_2); 69.63 (CH); 72.56 (C); 75.75 (CH); 117.23 (CH_2); 118.74 (CH_2); 133.81 (CH); 135.22 (CH). IR: 3400 (OH); 2165 (C–D) cm^{-1}. MS *m/e* (%, fragment): 195 (22, M^+ + 1); 194 (15, M^+); 155 (31).

14D; oil, 75 mg, 26%. ^{1}H-NMR: δ 1.10–2.10 (7H + D, m); 3.05 and 3.30 (AB, J_{AB} 13.7 Hz, 1H, dt, *J* 6.8, 1.2 Hz, and 1H, dt, *J* 5.5, 1.5 Hz); 3.44 (1H, d, *J* 9.2 Hz); 3.58 (1H, dd, *J* 10.9, 4.3 Hz); 5.07 (1H, dd, *J* 17.2, 1.8 Hz); 5.12–5.29 (3H, m); 5.69 (1H, ddd, *J* 17.2, 10.2, 9.2); 5.85 (1H, m). ^{13}C-NMR: δ 21.56 (CH_2); 23.91 (CH_2); 32.35 (CHD, t, *J* 19.7 Hz); 35.69 (CH_2); 48.32 (CH_2); 62.78 (CH); 73.71 (C); 78.91 (CH); 117.72 (CH_2); 118.79 (CH_2); 133.15 (CH); 135.10 (CH). IR: 3400 (OH); 2170 (C–D) cm^{-1}. MS *m/e* (%, fragment): 195 (22, M^+ + 1); 194 (11, M^+); 155 (54).

1-Methyl-2-vinyl-1-azaspiro[2.5]octan-4-one (**12b**). **12b** was obtained according to a similar procedure as described for **12a**, using **8**. ^{1}H-NMR: δ 1.25–2.65 (8H, m); 2.15 (3H, s); 3.36 (1H, d, *J* 9.0 Hz); 5.21 (1H, dd, *J* 17.2, 2.1 Hz); 5.38 (1H, dd, *J* 10.2, 2.0 Hz); 5.67 (1H, ddd, *J* 17.2, 10.1, 9.1 Hz). ^{13}C-NMR: δ 21.52 (CH_3), 27.85 (CH_2), 33.36 (CH_2); 37.63 (CH_2); 38.44 (CH_2); 66.45 (CH); 80.72 (C); 119.12 (CH_2); 134.44 (CH); 213.10 (C).

1-Methyl-2-vinyl-1-azaspiro[2.5]octan-4-ol (**15**) *and* (**16**). **15** and **16** were obtained using $NaBH_4$ in the reduction step. The two products could be separated by preparative TLC on silica gel (ethyl-acetate) using five successive migrations. The isomer **15** could be isolated in pure form, while **16** could not.

15; oil, 57 mg, 26%. ^{1}H-NMR: δ 1.15–2.55 (8H, m); 2.39 (3H, s); 2.87 (1H, d, *J* 9.2 Hz); 3.60–3.66 (1H, m); 5.11 (1H, dd, *J* 17.4, 1.7 Hz); 5.32 (1H, dd, *J* 10.3, 1.5 Hz); 5.69 (1H, ddd, *J* 17.2, 10.3, 9.2 Hz). ^{13}C-NMR: δ 20.44 (CH_2); 23.84 (CH_2); 29.99 (CH_2); 32.90 (CH_3); 33.08 (CH_2); 72.53 (C); 73.06 (CH); 76.03 (CH); 119.40 (CH_2); 133.24 (CH).

16; oil, 57 mg, 26%. ^{1}H-NMR: δ 1.05–2.50 (8H, m); 2.36 (3H, s); 3.35 (1H, d, *J* 9.4 Hz); 3.59–3.68 (1H, m); 5.00–5.40 (2H, m); 5.55–5.90 (1H, m). ^{13}C-NMR: δ 21.59 (CH_2); 23.87 (CH_2); 30.04 (CH_2); 32.58 (CH_3); 35.38 (CH_2); 66.48 (CH); 73.51 (C); 78.31 (CH); 119.08 (CH_2); 132.29 (CH).

4-Hydroxy-2-vinyl-1-azaspiro[2.5]octane-2-acetic acid methyl ester (**17**). **17** was obtained by a similar procedure as that described for the formation of **15** and **16** from **9**, using $NaBH_4$ in the reduction step. Nevertheless, the reaction was not as clean as for **7** or **8**. Only one product could be isolated from the reduction by $NaBH_4$. **17** was separated by preparative TLC on silica gel (ethyl-acetate); oil, 54 mg, 16%. ^{1}H-NMR: δ 0.90–1.90 (8H, m); 2.93 (1H, d, *J* 9.2 Hz); 3.34 and 3.42 (AB, J_{AB} 17.4 Hz, 2H); 3.67 (1H, dd, *J* 11.1, 4.6 Hz); 3.73 (3H, s); 5.06 (1H, dd, *J* 17.2, 1.1 Hz); 5.25 (1H, dd, *J* 10.3, 1.9); 5.64 (1H, ddd, *J* 17.2, 10.2, 9.1 Hz). ^{13}C-NMR: δ 20.49 (CH_2); 23.82 (CH_2); 30.08 (CH_2); 32.86 (CH_2); 47.51 (CH_2); 51.93 (CH_3), 70.43 (CH); 72.87 (C); 75.10 (CH); 118.74 (CH_2); 134.08 (CH); 172.27 (C). IR: 3425 (OH); 1745 (C=O ester) cm^{-1}. MS *m/e* (%, fragment): 226 (9, M^+ + 1); 225 (8, M^+); 207 (14); 128 (45); 83 (100).

Irradiation of (S)-*2-[Allyl-1-phenylethyl)amino]cyclohex-2-enone* (**10**). Irradiation of **10** according to a similar procedure as that described for **7** gave a mixture of four products. According to ^{1}H-NMR spectroscopy, we observed hydrogen abstraction from the allylic position (2 methyl doublet in ^{1}H-NMR) and from the benzilic center (2 methyl singlet in ^{1}H-NMR). After reduction by $NaBH_4$, we observed more than eight new products by TLC control which could not be isolated in pure form.

N-Benzyl-2-phenyl-1-azaspiro[2.5]-octan-4-ol (**18**). **18** was obtained by a similar procedure as that described for the irradiation of 2-diallylaminocyclohex-2-enone with $NaBH_4$ in the reduction step, although the azaspiranone was not obtained as clearly as **12**. Only one product could be isolated form the reduction and the presence of the benzyl group made **18** less polar than the other azaspiranols. **18** was isolated in pure form by preparative TLC on silica gel (ethyl-acetate/petroleum-ether, 40/60); oil, 155 mg, 35%. ^{1}H-NMR: δ 0.75–1.0 (8H, m); 3.24 and 3.44 (AB, J_{AB} 12.6 Hz, 2H); 3.64 (1H, dd, *J* 11.2, 5.0 Hz); 3.52 (1H, s); 7.17–7.40 (10 H). ^{13}C-NMR: δ 20.50 (CH_2); 23.72 (CH_2); 29.94 (CH_2); 33.67 (CH_2); 50.85 (CH_2); 70.71 (CH); 73.84 (C); 76.59 (CH); 127.34 (CH); 127.55 (CH); 127.86 (CH); 128.12 (CH); 128.34 (CH); 128.44 (CH); 138.89 (C); 139.01 (C). IR: 3385 (OH) cm^{-1}. MS *m/e* (%, fragment): 292 (40, M^+ + 1); 291 (1, M^+); 196 (100); 91 (88).

Allylmethyl[1-(7-oxabicyclo[4.1.0]hept-1-yl)allyl]amine (**19**).

14 (50 mg, 0.26 mmol) was added to a suspension of NaH (13 mg, 0.31 mmol, 60% in oil) in THF (3 ml) which was cooled to 0°C. Stirring was continued for 12 h. After the usual workup, **14** could be recovered almost quantitatively.

14 (91 mg, 0.47 mmol) was added to a suspension of NaH (23 mg, 0.56 mmol, 60% in oil) in THF (5 ml) which was cooled to 0°C. Then, CH_3I (35 μl, 0.56 mmol) was added and stirring was continued for 12 h. Excess NaH was destroyed with 0.5 ml of water and the

	$Eu(FOD)_3$ concentration (10^{-2}·mol·eq^{-1}) $(\delta_i - \delta_i^0)/(\delta_r - \delta_r^0)$										
13	0	6.2	12.5	18.8	25	31.2	37.5	50	62.5	75	
$\delta_r - \delta_r^0$ (H-12)	0	0.03	0.06	0.10	0.14	0.18	0.22	0.33	0.44	0.60	1
$\delta_i - \delta_i^0$ (H-2)	0	0.02	0.05	0.08	0.12	0.14	0.17	0.23	0.32	0.37	0.7
$\delta_i - \delta_i^0$ (H-9)	0	0.06	0.16	0.34	0.41	–	–	0.77	1.01	1.35	2.4
14											
$\delta_r - \delta_r^0$ (H-12)	0	0.06	0.12	0.21	0.30	0.36	0.45	0.68	0.91	1.18	1
$\delta_i - \delta_i^0$ (H-2)	0	0.10	0.21	0.36	0.49	0.57	0.72	0.95	1.18	–	1.5
$\delta_i - \delta_i^0$ (H-9)	0	0.11	0.22	0.45	0.60	0.72	0.88	1.40	1.91	2.48	2.0

products were extracted with methylene chloride, evaporated and filtered through anhydrous magnesium sulfate. **19**, which was purified by preparative TLC on silica gel (ethyl-acetate), was the only product which could be isolated in pure form from a mixture of at least five products, as revealed by TLC; oil, 14 mg, 14%. ^{1}H-NMR: δ 1.05–1.85 (7H, m); 1.92–2.05 (1H, m); 2.37 (3H, s); 2.91 (1H, dd, *J* 7.9, 13.2 Hz); 3.47 (1H, d, *J* 9.6 Hz); 5.10–5.22 (3H, m); 5.38–5.43 (1H, m); 5.79–5.95 (1H, m); 5.99 (1H, dd, *J* 17.2, 10.1 Hz). ^{13}C-NMR: δ 21.84 (CH_2); 23.97 (CH_2); 32.43 (CH_2); 36.06 (CH_2); 39.67 (CH_3); 58.65 (CH_2), 67.71 (CH); 74.73 (C); 78.79 (CH); 118.70 (CH_2); 120.92 (CH_2); 129.57 (CH); 135.01 (CH). MS *m/e* (%, fragment): 208 (6, $M^+ + 1$); 207 (4, M^+); 166 (16); 111 (100); 96 (36).

The same reaction carried out with **13** (1.2 eq NaH, then 1.2 eq CH_3I) gave a mixture of more than six products which was not further characterized.

Acknowledgements

One of us (*C.M.*) is grateful to *M.E.R.S.* for a grant. We thank *Pr. J. Bouquant* for helpful discussions and *Dr. T.G.C. Bird* (Zeneca, Reims) for his help during translation of this manuscript.

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