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Intramolecular [2+2]Photocycloaddition of 2-[*N*-Acyl-*N*-(2-propenyl)amino]cyclohex-2-enones: Synthesis of 2-Azabicyclo[2.1.1]hexanes

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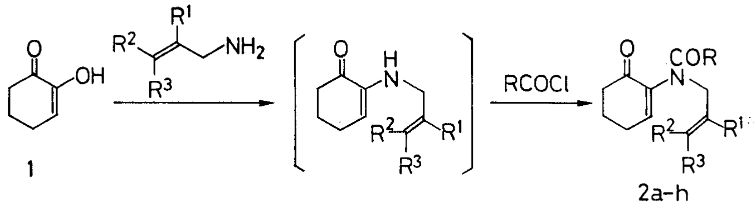
Photoirradiation of 2-[*N*-acyl-*N*-(2-propenyl)amino]cyclohex-2-enones gave the 9-acyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-ones as the major products. In some cases, 1-acetyl-1,4,4a,5,6,7,8,8a-octahydroquinol-8-one, 1-benzoyl-3-vinyl-2,3,3a,4,5,6,7,7a-octahydroindol-7-one, and 1-(2-propenyl)-1-azaspiro[3.5]nonane-2,5-dione were isolated and characterized as minor products.

Keywords——photocycloaddition; hydrogen abstraction; ene reaction; long-range coupling; X-ray analysis; 2-azabicyclo[2.1.1]hexane; beta-lactam; octahydroquinolone; octahydroindolone

2-(*N*-Acyl-*N*-alkylamino)cyclohex-2-enones are known to be photochemically reactive and to take a variety of reaction courses, depending upon the substituents on the nitrogen atom.[1)] In connection with our interest in intramolecular [2+2]photocycloaddition,[2)] we have now examined the photochemical behavior of 2-[*N*-acyl-*N*-(2-propenyl)amino]cyclohex-2-enones (**2**),[3)] and observed the formation of 2-azabicyclo[2.1.1]hexane derivatives as the major photoproducts.[4)] In some cases, 1-acetyl-1,4,4a, 5,6,7,8,8a-octahydroquinol-8-one, 1-benzoyl-3-vinyl-2,3,3a,4,5,6,7,7a-octahydroindol-7-one, and 1-(2-propenyl)-1-azaspiro[3.5]nonane-2,5-dione were isolated and characterized as minor products.

Compounds **2a**—**h** were prepared by refluxing cyclohexane-1,2-dione (**1**) with 2-propenylamines in benzene for 3 h followed by treatment with the corresponding acyl chlorides in the presence of base. In general, a solution of **2** in acetone[5)] was irradiated with a 300 W high-pressure mercury lamp in a Pyrex tube under nitrogen until the starting material disappeared [the reaction was followed by thin layer chromatography (TLC)]. After removal of the solvent, the crude material was subjected to column chromatography.



a: R=Me, $R^1=R^2=R^3=H$
b: R=OMe, $R^1=R^2=R^3=H$
c: R=Ph, $R^1=R^2=R^3=H$
d: R=Ph, R^1=Me, $R^2=R^3=H$
e: R=Ph, R^3=Me, $R^1=R^2=H$
f: R=Ph, R^1=H, $R^2=R^3$=Me
g: R=*tert*-Bu, $R^1=R^2=R^3=H$
h: R=iso-Bu, $R^1=R^2=R^3=H$

Chart 1

In this manner, irradiation of **2a** gave a mixture of at least four products, from which two products were isolated and identified. The major product (52% yield) was isolated as its hydrate **4a**, which was dried at 70 °C *in vacuo* for 20 h to give the ketone **3a**. However, the ketone **3a** readily absorbed water from the air to revert to the hydrate form **4a**. The infrared (IR) spectrum (CCl_4) of **3a** showed two strong carbonyl absorptions at 1720 and 1670 cm^{-1}. The ^1H-nuclear magnetic resonance (^1H-NMR) spectrum of **3a** showed an AB quartet at δ 3.42 and 3.61 ($J=8$ Hz) due to the C-8 protons, and a singlet (3H, $NCOCH_3$) at δ 1.99. Final confirmation of the structure was obtained by an X-ray structure analysis of the hydrate **4a** (Fig. 1). The result indicates that the hydrate form is stabilized by the formation of an intramolecular hydrogen bond between one of the two hydroxyl groups and the acetyl carbonyl oxygen. The minor product (2% yield) was assigned the structure **5** on the basis of spectroscopic evidence. Its IR spectrum ($CHCl_3$) showed two strong carbonyl absorptions at 1720 and 1635 cm^{-1}, and the ultraviolet (UV) spectrum is that of a typical six-membered *N*-acylenamine with λ_{max} 231 nm.[6] The ^1H-NMR spectrum showed a singlet (3H, $COCH_3$) at δ 2.21, a doublet of triplets (1H, 3-H, $J=8$ and 4 Hz) at δ 4.82, a doublet (1H, 8a-H, $J=6$ Hz) at δ 5.21, and a broad doublet (1H, 2-H, $J=8$ Hz) at δ 6.56. The remaining signal is a multiplet between δ 1.4 and 2.8 (9H). Assignment of the *cis*-stereochemistry of the ring fusion in **5** was made on the basis of the coupling constant ($J=6$ Hz) between C-4a and C-8a protons, as well as thermodynamic considerations. If the protons were *trans* oriented, the resulting dihedral

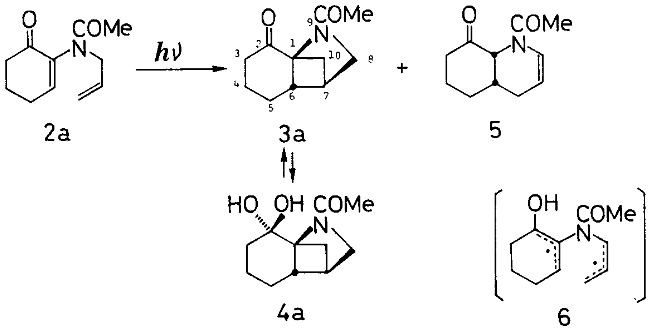


Chart 2

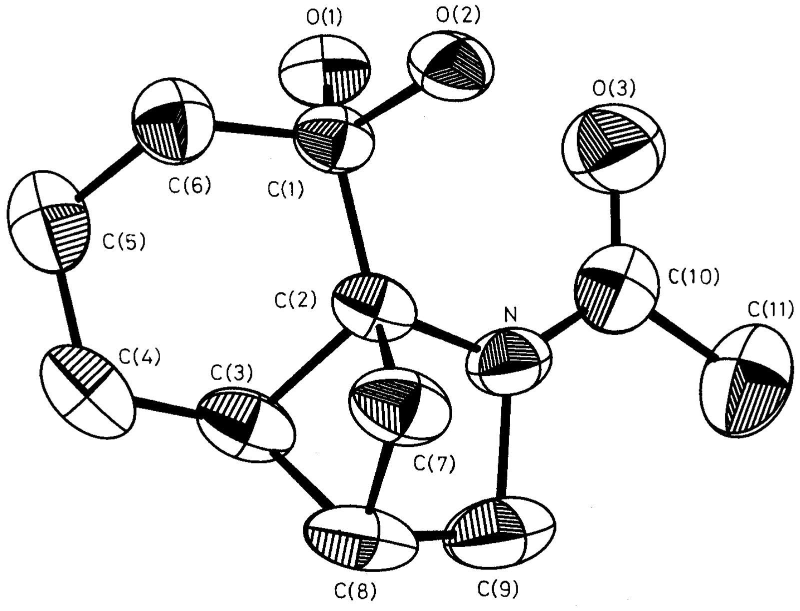
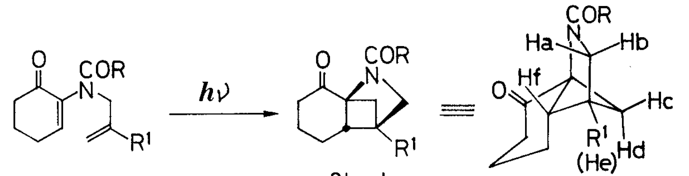


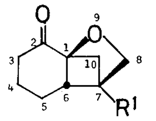
Fig. 1. Perspective ORTEP Drawing of Compound **4a**

angle (~180°) would require spin-coupling of at least 8—14 Hz. When **5** was refluxed in benzene in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), it was recovered unchanged. It is well known that in the 2-substituted *N*-acylpiperidines the axial form of the 2-substituent is more stable than the equatorial form due to the $A^{1,3}$-effect.[7] The formation of **5** may proceed *via* initial hydrogen abstraction by the carbonyl oxygen to give a diradical **6**, which may cyclize.

Irradiation of each of **2b**—**d** afforded one major product along with several unidentified minor products. The major product was the 2-azabicyclo[2.1.1]hexane derivative in each case; the structure was deduced from the spectroscopic evidence. For example, the IR spectrum (CCl_4) of **3c** showed two strong carbonyl absorptions at 1725 (six-membered ketone) and 1660 cm^{-1} (benzamide). Analysis of the ^{1}H-NMR spectrum with the aid of a shift reagent [$Eu(DPM)_3$] revealed a long-range coupling (8 Hz) between Hc and Hf: such coupling would occur only if these protons were in a W configuration in bicyclo[2.1.1]hexane.[8] Confirmation of the structures **3b**—**d** was obtained by comparison of the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra with those of the oxa derivatives **7a** and **7b**[9] (see Table I). Except for the signals of C-1 and C-8 which are adjacent to the hetero atom, the chemical shifts of the rest of the signals of **3b**—**d** are in good agreement with those of **7a** and **7b**. It is of interest to note that the *N*-methoxycarbonyl derivative **3b** was found to exist as a mixture with the hydrate form in a ratio of *ca.* 5 : 1 in $CDCl_3$ solution (by ^{1}H-NMR spectroscopy). In contrast, the *N*-benzoyl derivatives **3c** and **3d** exist essentially in the keto form.



2b-d 3b-d



7a: $R^1=H$
7b: $R^1=Me$

b: $R=OMe$, $R^1=H$ **c**: $R=Ph$, $R^1=H$ **d**: $R=Ph$, $R^1=Me$

Chart 3

TABLE I. ^{13}C-NMR Spectral Data for Compounds **7a, b** and **3b**—**d**[a]

Carbon	**7a**	**7b**	**3b**	**3c**	**3d**
1	88.3 (s)	87.0 (s)	72.0 (s)	71.5 (s)	69.8 (s)
2	202.9 (s)	203.8 (s)	201.4 (s)	201.8 (s)	202.1 (s)
3[b]	41.4 (t)	45.2 (t)	42.1 (t)	40.5 (t)	44.0 (t)
4[c]	25.1 (t)	23.4 (t)	23.8 (t)	23.6 (t)	21.9 (t)
5[c]	27.1 (t)	27.0 (t)	24.4 (t)	24.1 (t)	23.9 (t)
6	55.2 (d)	57.2 (d)	52.7 (d)	52.5 (d)	54.6 (d)
7	41.8 (d)	48.9 (s)	39.1 (d)	39.6 (d)	46.7 (s)
8	70.4 (t)	75.2 (t)	55.0 (t)	57.4 (t)	62.4 (t)
10[b]	39.9 (t)	39.9 (t)	39.0 (t)	38.8 (t)	38.8 (t)
Others		12.5 (q)	53.0 (q) 159.7 (s)	128.2 (d) 128.9 (d) 131.6 (d) 134.3 (s) 175.0 (s)	13.6 (q) 128.2 (d) 129.0 (d) 131.6 (d) 134.3 (s) 174.7 (s)

a) Measured in $CDCl_3$; chemical shifts are given in parts per million from internal tetramethylsilane. *b, c*) Assignments may be interchanged in each column.

Irradiation of **2e** gave a mixture of at least four products, among which two products were identified. The major product (25% yield) was a 2-azabicyclo[2.1.1]hexane (**3e**), whose stereochemistry was tentatively assigned on the basis of the fact that long-range coupling between the C-10 and C-6 protons is not observed. The minor product (16% yield) was assigned as *trans*-1-benzoyl-3-vinyl-2,3,3a,4,5,6,7,7a-octahydroindol-7-one (**8**) on the basis of the following spectroscopic evidence. The IR spectrum ($CHCl_3$) showed two strong carbonyl absorptions at 1730 and 1635 cm^{-1}. The ^1H-NMR spectrum revealed the presence of a vinyl group [δ 4.75—5.25 (2H, m) and 5.25—6.0 (1H, m)] and *N*-CH_2 protons [δ 3.45 and 3.75 (1H each, ABq with further splitting)]. The *trans*-stereochemistry of the ring-junction was assigned on the basis of the coupling constant (12 Hz) of the C-7a proton, which appeared as a doublet at δ 4.30. Compound **8** is a product of an intramolecular "ene" reaction.[10)]

Unfortunately, irradiation of **2f** and **2g** gave complex mixtures, and we were unable to isolate any products in pure form.

Irradiation of the *N*-isobutyryl derivative **2h** gave two products. The major product (26% yield) was assigned the structure **3h** (which exists as a mixture with the hydrate form in $CDCl_3$ solution) on the basis of the spectral comparison with **3a**. The minor product (20% yield) was deduced to be the β-lactam **9**. The IR spectrum (CCl_4) showed two carbonyl absorption at 1765 (β-lactam) and 1715 cm^{-1} (six-membered ketone). The ^1H-NMR spectrum showed the presence of the allyl group [δ 5.0—5.3 (2H), 5.6—6.1 (1H), 3.62 (1H), and 4.10 (1H)] and two methyl singlets at δ 1.13 and 1.38. The remaining signals formed a multiplet (8H) between δ 0.8 and 2.8. A mechanistic rationalization for the formation of the β-lactam **9** involves the assumption that **2h** is first converted to the 1,4-diradical intermediate **10** *via* the abstraction of a hydrogen on the *N*-acyl group by the β-carbon atom of the α,β-enone system. Cyclization of the diradical intermediate may lead to the observed product **9**. The details will be discussed in a separate paper.

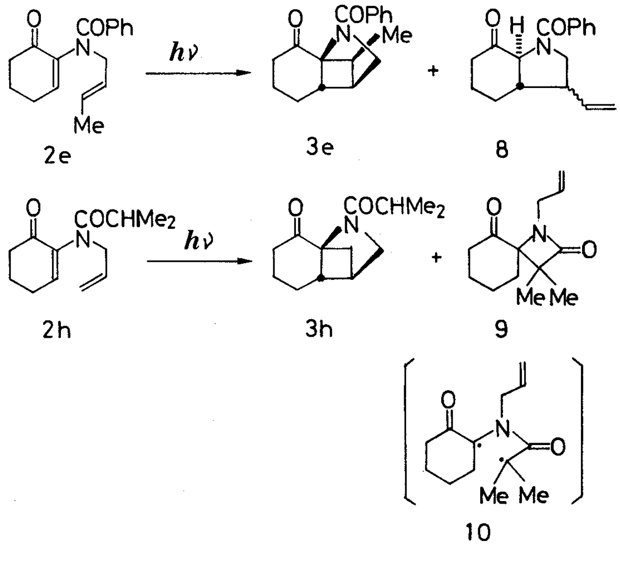
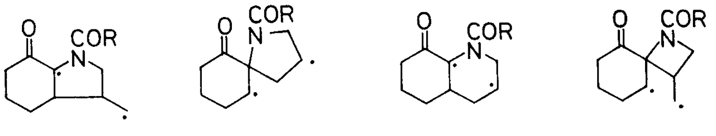


Chart 4

In conclusion, our observations seem to point to a preference for the cycloaddition reaction rather than other competing processes such as hydrogen abstraction by the carbonyl oxygen[1)] or β-carbon atom of the α,β-enone system, photo-Fries rearrangement,[1)] or ene reaction.

The intramolecular [2+2]photocycloaddition may occur either in a head-to-head (parallel addition) or in a head-to-tail (cross addition) manner. It is well recognized that the preferred orientation of 1,5-diene systems is head-to-tail rather than head-to-head, and this has been explained in terms of the so-called "rule of five":[11] the intial formation of the five-membered ring diradical (A) or (B) is preferred to other possible six-membered (C) or four-membered (D) ring diradicals. In this sense, the formation of the 2-azabicyclo[2.1.1]hexanes **3** is unexceptional. However, it would be interesting to know which intermediate, (A) or (B), is actually formed. Considering the fact that the ene product **8** was formed from **2e**, it is reasonable to assume that the bond C(2′)-C(3) is formed first. In the resulting intermediate (A) one of the radical centers is stabilized by the "capto-dative substituent effect."[12]



(A) (B) (C) (D)

Chart 5

Experimental[13]

2-[*N*-Acetyl-*N*-(2-propenyl)amino]cyclohex-2-enone (2a)——A solution of **1** (2.6 g, 24 mmol) and allylamine (1.9 g, 33 mmol) in benzene (55 ml) was refluxed for 3 h using a Dean–Stark water separator. Triethylamine (4.6 ml) and then acetyl chloride (2.4 ml) were added to the cooled mixture. The whole was refluxed for 1 h and then diluted with water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined extract was washed with brine, dried ($MgSO_4$), and concentrated. The residual oil was distilled [bp 150—169 °C (3 mmHg)] to give **2a** (2.1 g, 46%) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1690, 1665, 1630. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 227 sh (3.69), 262 sh (3.23). ^{1}H-NMR ($CDCl_3$) δ: 1.83 (3H, s, $COCH_3$), 1.9—2.3, 2.4—2.7 (2H and 4H, respectively, m), 3.4—4.6 (2H, br, NCH_2), 4.9—5.25 (2H, m, $CH{=}C\underline{H}_2$), 5.72 (1H, m, $C\underline{H}{=}CH_2$), 6.87 (1H, t, $J=4$ Hz, 3-H). MS *m/z*: 193 (M^+). *Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.40; H, 7.84; N, 7.42.

2-[*N*-Methoxycarbonyl-*N*-(2-propenyl)amino]cyclohex-2-enone (2b)——Pyridine (2.4 g) and *N*,*N*-dimethylaminopyridine (DMAP) (370 mg) were added to a reaction mixture obtained from **1** (1.1 g, 10 mmol) and allylamine (685 mg, 12 mmol) in benzene (15 ml). Methyl chloroformate (1.4 g, 15 mmol) was then added dropwise at −20 °C. The reaction mixture was stirred at room temperature overnight. Work-up gave an oily residue, which was purified by column chromatography [silica gel: ethyl acetate–*n*-hexane (3 : 2)] to give **2b** (260 mg, 13%) as an oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725, 1695, 1640. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 219 (3.89), 255 (3.35). ^{1}H-NMR ($CDCl_3$) δ: 1.8—2.2 (2H, m), 2.4—2.7 (4H, m), 3.63 (3H, s, OCH_3), 3.9—4.1 (2H, br d, NCH_2), 4.95—5.2 (2H, m, $CH{=}C\underline{H}_2$), 5.5—6.0 (1H, m, $C\underline{H}{=}CH_2$), 6.76 (1H, t, $J=4$ Hz, 3-H). MS *m/z*: 209 (M^+). *Anal.* Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.96; H, 7.26; N, 6.61.

2-[*N*-Benzoyl-*N*-(2-propenyl)amino]cyclohex-2-enone (2c)——Pyridine (1.2 g), DMAP (92 mg) and then benzoyl chloride (1.05 g, 7.5 mmol) were added to a reaction mixture obtained from **1** (560 mg, 5.0 mmol) and allylamine (371 mg, 6.5 mmol) in benzene (20 ml) at 0 °C. The whole was stirred at room temperature overnight and diluted with water. The organic layer was separated and the aqueous layer was extracted with benzene. The combined extract was washed with 10% HCl, saturated $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated. The oily residue was purified by column chromatography [silica gel: ethyl acetate–*n*-hexane (1 : 2)] to give **2c** (638 mg, 50%). mp 89—90 °C (from ethyl acetate). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1690, 1660, 1630. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 221 sh (4.07), 260 sh (3.65). ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.0, 2.15—2.45 (2H and 4H, respectively, m), 3.9—4.4 (2H, br, NCH_2), 5.0—5.25 (2H, m, $CH{=}C\underline{H}_2$), 5.4—6.1 (1H, m, $C\underline{H}{=}CH_2$), 6.62 (1H, t, $J=4$ Hz, 3-H), 7.1—7.4 (5H, m, aromatic protons). MS *m/z*: 255 (M^+). *Anal.* Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.10; H, 6.59; N, 5.48.

2-[*N*-Benzoyl-*N*-(2-methyl-2-propenyl)amino]cyclohex-2-enone (2d)——By means of a procedure similar to that described above for **2c**, **2d** (1.2 g, 44%) was obtained from **1** (1.1 g, 10 mmol) and 2-methyl-2-propenylamine (850 mg, 12 mmol) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1695, 1660, 1630. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 220 sh (4.12), 260 (3.66). ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.1 (2H, m), 1.77 (3H, s, CH_3), 2.15—2.4 (4H, m), 3.7—4.6 (2H, br, NCH_2), 4.7—4.9 (2H, m, $C{=}CH_2$), 6.59 (1H, t, $J=4$ Hz, 3-H), 7.1—7.4 (5H, m, aromatic protons). MS *m/z*: 269 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.89; H, 6.95; N, 5.11.

2-[*N*-Benzoyl-*N*-(3-methyl-2-propenyl)amino]cyclohex-2-enone (2e)——By means of a procedure similar to that described for **2c**, **2e** (779 mg, 58%) was obtained from **1** (560 mg, 5 mmol) and 3-methyl-2-propenylamine (462 mg, 6.5 mmol) as a colorless oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1690, 1655, 1630 sh. ^{1}H-NMR ($CDCl_3$) δ: 1.5—2.6 (6H, m), 1.65 (3H, br d, $J=4$ Hz, $C{=}CHC\underline{H}_3$), 3.6—4.6 (2H, m, NCH_2), 5.2—5.8 (2H, m, $CH{=}CH$), 6.56 (1H, t, $J=4$ Hz, 3-H), 7.0—7.5 (5H, m, aromatic protons). MS *m/z*: 269 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.74; H, 6.96; N, 5.14.

2-[*N*-Benzoyl-*N*-(3-methyl-2-butenyl)amino]cyclohex-2-enone (2f)——By means of a procedure similar to that described for **2c**, **2f** (600 mg, 42%) was obtained from **1** (560 mg, 5 mmol) and 3-methyl-2-butenylamine (553 mg, 6.5 mmol) as an oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1695, 1650, 1630. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.1, 2.2—2.5 (2H and 4H, respectively, m), 1.61, 1.73 (3H each, s, 2×CH_3), 3.9—4.4 (2H, br, NCH_2), 5.19 (1H, br t, J=7 Hz, C=CH), 6.15 (1H, t, J=4 Hz, 3-H), 7.0—7.4 (5H, m, aromatic protons). MS m/z: 283 (M^+): *Anal.* Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47; N, 4.94. Found: C, 76.00; H, 7.69; N, 4.97.

2-[*N*-Pivaloyl-*N*-(2-propenyl)amino]cyclohex-2-enone (2g)——By means of a procedure similar to that described for **2c**, **2g** (759 mg, 32%) was obtained from **1** (1.12 g, 10 mmol), allylamine (685 mg, 12 mmol), and pivaloyl chloride (1.80 g, 15 mmol) as an oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1695, 1645, 1630. ^{1}H-NMR ($CDCl_3$) δ: 1.18 [9H, s, $C(CH_3)_3$], 2.0—2.3, 2.45—2.7 (2H and 4H, respectively, m), 3.8—4.2 (2H, br, NCH_2), 4.9—5.2 (2H, m, CH=C$\underline{H}_2$), 5.6—6.1 (1H, m, C$\underline{H}$=CH_2), 6.82 (1H, t, J=4 Hz, 3-H). MS m/z: 235 (M^+). *Anal.* Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.24; H, 9.27; N, 5.93.

2-[*N*-Isobutyryl-*N*-(2-propenyl)amino]cyclohex-2-enone (2h)——By means of a procedure similar to that described for **2c**, **2h** (742 mg, 34%) was obtained from **1** (1.1 g, 10 mmol), allylamine (685 mg, 12 mmol), and isobutyryl chloride (1.6 g, 15 mmol) as an oil. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1695, 1670, 1630. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 223 (3.84), 259 (3.36). ^{1}H-NMR ($CDCl_3$) δ: 1.05 [6H, d, J=7 Hz, CH(C$\underline{H}_3$)$_2$], 1.95—2.2 (2H, m), 2.4—2.6 (5H, m), 3.4—4.6 (2H, br, NCH_2), 4.9—5.2 (2H, m, CH=C$\underline{H}_2$), 5.5—6.0 (1H, m, C$\underline{H}$=CH_2), 6.82 (1H, t, J=4 Hz, 3-H). MS m/z: 221 (M^+). *Anal.* Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.23; H, 8.81; N, 6.24.

(1*RS*,6*RS*,7*SR*)-9-Acetyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3a) and *cis*-1-Acetyl-1,4,4a,5,6,7,8,8a-octahydroquinol-8-one (5)——A solution of **3a** (200 mg, 1.0 mmol) in acetone (20 ml) was irradiated for 13 h under nitrogen. After removal of the solvent, the residue was subjected to column chromatography [silica gel: *n*-hexane–ethyl acetate (1 : 8)] to give **4a** (113 mg, 52%), **5** (3 mg, 2%), and small amounts of two unidentified products. The hydrate **4a** was dried at 70 °C *in vacuo* for more than 20 h to give the ketone **3a**. mp 111—114 °C (from ether). IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1710, 1650. ^{1}H-NMR ($CDCl_3$) δ: 1.4—2.8 (10H, m), 1.99 (3H, s, $COCH_3$), 3.42, 3.61 (1H each, ABq with further splitting of the upper doublet, J=8 Hz, NCH_2). *Anal.* Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 67.91; H, 7.98; N, 7.13. The hydrate **4a**: IR $\nu_{\max}^{\mathrm{KCl}}$ cm^{-1}: 3280, 1605. ^{1}H-NMR ($CDCl_3$) δ: 1.4—2.8 (10H, m), 2.12 (3H, s, $COCH_3$), 3.52 (2H, s, NCH_2), 4.88, 5.05 (1H, each, br s, OH). In $CDCl_3$ solution, **4a** exists as a mixture with **3a** in a ratio of 7 : 3.

Compound **5** was an oil: IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 1720, 1635. UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε): 231 (3.67). ^{1}H-NMR ($CDCl_3$) δ: 1.65—2.8 (9H, m), 2.21 (3H, s, $COCH_3$), 4.82 (1H, dt, J=8, 4 Hz, 3-H), 5.21 (1H, d, J=6 Hz, 8a-H), 6.56 (1H, br d, J=8 Hz, 2-H). Analysis was carried out by high-resolution mass spectrometry: Calcd for $C_{11}H_{15}NO_2$, 193.1101; found, 193.1089.

(1*RS*,6*RS*,7*SR*)-9-Methoxycarbonyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3b)——A solution of **2b** (71 mg, 0.35 mmol) in acetone (7 ml) was irradiated for 3 h. After removal of the solvent, the residue was chromatographed [silica gel: *n*-hexane–ethyl acetate (3 : 2)] to give **3b** (40 mg, 56%). mp 74—75 °C [from ether–petroleum ether (bp 30—60 °C)]. In $CDCl_3$ solution, **3b** exists as a mixture with the hydrate form in a ratio of *ca.* 5 : 1. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3500, 1730, 1680. ^{1}H-NMR ($CDCl_3$) δ: 1.1—2.8 (10H, m), 3.46, 3.61 (1H × 5/6 each, ABq with further splitting of the upper doublet, J=8 Hz, NCH_2), 3.44 (2H × 1/6, s, NCH_2), 3.71, 3.76 (3H × 5/6 and 3H × 1/6, respectively, s, OCH_3), 4.3, 5.05 (1H × 1/6 each, br s, OH). In the presence of Eu(DPM)$_3$, the absorption of Hc was shown to be a triplet (J=8 Hz). MS m/z: 209 (M^+). *Anal.* Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 62.74; H, 7.25; N, 6.61.

(1*RS*,6*RS*,7*SR*)-9-Benzoyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3c)——A solution of **2c** (400 mg, 1.6 mmol) in acetone (40 ml) was irradiated for 46 h. After removal of the solvent, the residue was chromatographed [silica gel: *n*-hexane–ethyl acetate (1 : 1)] to give **3c** (245 mg, 61%) and small amounts of two unidentified products.

Compound **3c** showed mp 129.5—131 °C (from ether–*n*-hexane). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.9 (10H, m), 3.31, 3.89 (1H each, ABq with broadening of the upper doublet, J=8 Hz, NCH_2), 7.2—7.6, 7.7—7.9 (3H and 2H, respectively, m, aromatic protons). In the presence of Eu(DPM)$_3$, the absorption of Hc was shown to be a triplet (J=8 Hz). MS m/z: 255 (M^+). *Anal.* Calcd for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.10; H, 6.72; N, 5.42.

(1*RS*,6*RS*,7*SR*)-9-Benzoyl-7-methyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3d)——A solution of **2d** (800 mg, 30 mmol) in acetone (80 ml) was irradiated for 22 h. Wrok-up gave **3d** (432 mg, 54%) and small amounts of two unidentified products.

Compound **3d** showed mp 135—136 °C (from ethyl acetate). IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 1725, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.8 (9H, m), 1.17 (3H, s, 7-CH_3), 3.26, 3.63 (1H each, ABq with further splitting of the upper doublet, J=8 Hz, NCH_2), 7.2—7.5, 7.7—7.9 (3H and 2H, respectively, m, aromatic protons). In the presence of Eu(DPM)$_3$, the absorption of Hc was shown to be a triplet (J=8 Hz). MS m/z: 269 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.83; H, 7.15; N, 5.23.

9-Benzoyl-10-methyl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3e) and 1-Benzoyl-3-vinyl-2,3,3a,4,5,6,7,7a-octahydroindol-7-one (8)——A solution of **2e** (400 mg, 1.4 mmol) in acetone (40 ml) was irradiated for 20 h. After removal of the solvent, the residue was chromatographed [silica gel: *n*-hexane–ethyl acetate (2 : 1)] to give **3e** (101 mg, 25%), **8** (66 mg, 16%) and two unidentified products (55 and 76 mg).

TABLE II. Bond Lengths (Å) and Bond Angles (°) for Compound **4a** with E.S.D.'s in Parentheses

O(1)–C(1)	1.424 (4)	O(2)–C(1)	1.422 (4)
O(3)–C(10)	1.236 (5)	N–C(2)	1.501 (4)
N–C(9)	1.504 (5)	N–C(10)	1.324 (4)
C(1)–C(2)	1.516 (5)	C(1)–C(6)	1.533 (5)
C(2)–C(3)	1.563 (5)	C(2)–C(7)	1.568 (4)
C(3)–C(4)	1.523 (5)	C(3)–C(8)	1.548 (5)
C(4)–C(5)	1.524 (6)	C(5)–C(6)	1.531 (6)
C(7)–C(8)	1.573 (6)	C(8)–C(9)	1.503 (6)
C(10)–C(11)	1.511 (6)		
C(2)–N–C(9)	101.8 (3)	C(2)–N–C(10)	132.8 (3)
C(9)–N–C(10)	125.4 (3)	O(1)–C(1)–O(2)	111.1 (3)
O(1)–C(1)–C(2)	110.8 (3)	O(1)–C(1)–C(6)	107.1 (3)
O(2)–C(1)–C(2)	107.6 (3)	O(2)–C(1)–C(6)	111.0 (3)
C(2)–C(1)–C(6)	109.3 (3)	N–C(2)–C(1)	121.2 (3)
N–C(2)–C(3)	100.8 (3)	N–C(2)–C(7)	99.9 (3)
C(1)–C(2)–C(3)	119.4 (3)	C(1)–C(2)–C(7)	121.4 (3)
C(3)–C(2)–C(7)	87.6 (3)	C(2)–C(3)–C(4)	113.0 (3)
C(2)–C(3)–C(8)	81.4 (3)	C(4)–C(3)–C(8)	120.5 (3)
C(3)–C(4)–C(5)	110.6 (3)	C(4)–C(5)–C(6)	111.3 (3)
C(1)–C(6)–C(5)	112.9 (3)	C(2)–C(7)–C(8)	80.5 (3)
C(3)–C(8)–C(7)	87.9 (3)	C(3)–C(8)–C(9)	102.7 (3)
C(7)–C(8)–C(9)	101.6 (3)	N–C(9)–C(8)	98.4 (3)
O(3)–C(10)–N	122.9 (3)	O(3)–C(10)–C(11)	118.5 (3)
N–C(10)–C(11)	118.5 (3)		

TABLE III. Atomic Coordinates ($\times 10^4$) and Thermal Parameters for Non-hydrogen Atoms of Compound **4a** with E.S.D.'s in Parentheses

Atom	x	y	z	B_{eq}[a]	Atom	x	y	z	B_{eq}[a]
O(1)	1801 (2)	45 (2)	4789 (2)	4.1	O(2)	1309 (2)	420 (2)	6572 (2)	4.2
O(3)	2525 (3)	2480 (3)	5345 (3)	6.8	N	4477 (3)	1366 (3)	6638 (2)	4.0
C(1)	2207 (3)	−275 (3)	6053 (3)	3.3	C(2)	3850 (4)	59 (3)	6789 (3)	3.5
C(3)	5124 (4)	−839 (4)	6706 (3)	4.3	C(4)	4746 (4)	−2271 (4)	6694 (4)	5.3
C(5)	3133 (5)	−2530 (3)	5794 (4)	5.3	C(6)	1983 (4)	−1737 (3)	6120 (3)	4.2
C(7)	4570 (4)	−129 (4)	8219 (3)	4.8	C(8)	6049 (4)	−149 (4)	7931 (3)	5.4
C(9)	6111 (4)	1222 (4)	7529 (3)	5.8	C(10)	3849 (4)	2435 (3)	6092 (3)	4.4
C(11)	4809 (5)	3640 (4)	6299 (4)	6.3					

a) Equivalent isotropic thermal parameters were calculated from the refined anisotropic thermal parameters.

Compound **3e** showed mp 170.5—171.5 °C (from isopropanol). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1720, 1660. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (3H, d, J=7 Hz, CH_3: it became a singlet on irradiation of the signal at δ 2.98), 1.5—2.8 (8H, m), 2.98 (1H, dq, J=7 and 4 Hz, 10-H), 3.21, 3.73 (1H, each, ABq with broadening of the upper doublet, J=8 Hz, NCH_2), 7.2—7.9 (5H, m, aromatic protons). MS m/z: 269 (M^+). *Anal.* Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.78; H, 7.33; N, 4.96.

Compound **8** was an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1635. ^{1}H-NMR ($CDCl_3$) δ: 1.0—3.0 (8H, m), 3.45 (1H, A part of ABq with broadening, J=12 Hz, one of NCH_2), 3.75 (1H, B part of ABq with further splitting, J=12, 6 Hz, one of NCH_2), 4.30 (1H, d, J=12 Hz, 7a-H), 4.75—5.25 (2H, m, $CH=C\underline{H}_2$), 5.25—6.0 (1H, m, $C\underline{H}=CH_2$), 7.1—7.8 (5H, m, aromatic protons). Analysis was carried out by high-resolution mass spectrometry: Calcd for $C_{17}H_{19}NO_2$, 269.1415; found, 269.1433.

(1*RS*,6*RS*,7*SR*)-9-Isobutyryl-9-azatricyclo[5.2.1.0^{1,6}]decan-2-one (3h) and 3,3-Dimethyl-1-(2-propenyl)-1-azaspiro[3.5]nonane-2,5-dione (9)——A solution of **2h** (200 mg, 0.9 mmol) in acetone (20 ml) was irradiated for 24 h. After removal of the solvent, the residue was chromatographed [silica gel: n-hexane–ethyl acetate (1 : 1)] to give **3h** (51 mg, 26%) and **9** (40 mg, 20%).

Compound **3h** was an oil. In a solution it exists as a mixture with the hydrate in a ratio of *ca.* 2:3. IR $\nu_{\max}^{\mathrm{CCl_4}}\,\mathrm{cm}^{-1}$: 3435, 1720, 1665, 1620. ^{1}H-NMR ($CDCl_3$) δ: 0.75—2.9 (11H, m), 1.17 [6H × 3/5, d, J=7 Hz, $CH(C\underline{H}_3)_2$], 1.14 [6H × 2/5, d, J=7 Hz, $CH(C\underline{H}_3)_2$], 3.56 (s, 2H × 3/5, NCH_2), 3.46, 3.69 (1H × 2/5 each, ABq with broadening of the upper doublet, J=8 Hz, NCH_2), 4.9, 5.15 (1H × 3/5 each, br, OH). Analysis was carried out by high-resolution mass spectrometry: Calcd for $C_{13}H_{19}NO_2$, 221.1415; found, 221.1429.

Compound **9** was an oil. IR $\nu_{\max}^{\mathrm{CCl_4}}\,\mathrm{cm}^{-1}$: 1765, 1715, 1640. ^{1}H-NMR ($CDCl_3$) δ: 0.8—2.8 (8H, m), 1.13, 1.38 (3H each, s, 2 × CH_3), 3.62 (1H, br dd, J=16, 7 Hz, one of NCH_2), 4.10 (1H, dd with further splitting, J=16, 5 Hz, one of NCH_2), 5.0—5.3 (2H, m, $CH=C\underline{H}_2$), 5.6—6.1 (1H, m, $C\underline{H}=CH_2$). Analysis was carried out by high-resolution mass spectrometry: Calcd for $C_{13}H_{19}NO_2$, 221.1415; found, 221.1385.

X-Ray Analysis of Compound 4a——Crystal Data: Compound **4a**, $C_{11}H_{17}NO_3$, mol. wt. 193. Monoclinic, a= 9.550 (4), b=10.340 (3), c=11.755 (4) Å, β=112.3 (3)°, Z=4, Dx=1.31 g/cm^3. Space group $P2_1/n$. Mo-$K\alpha$ radiation, μ(Mo-$K\alpha$)=1.0 cm^{-1}.

Data Collection: The crystal data and intensity data were derived from measurements on a Syntex R_3 four-circle diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Intensity data were collected on the diffractometer with the same radiation using an $\omega-2\theta$ scanning technique within 2θ less than 50°. Three reference reflections monitored periodically showed no significant intensity fluctuations during the course of data collection. A total of 1422 reflections were used for the structure analysis. Intensity data were corrected for Lorentz and polarization factors, but not for absorption.

Structure Determination and Refinement: The structure was solved by the direct method (MULTAN method).[14] The atomic coordinates were refined by block-diagonal least-squares method, using anisotropic temperature factors for all the non-hydrogen-atoms and isotropic ones for hydrogen atoms. The final R-value was 0.056. The atomic scattering factors were taken from "International Tables for X-ray Crystallography."[15] Bond lengths and bond angles are listed in Table II. Atomic coordinates for non-hydrogen atoms are given in Table III.

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