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Photochemical Syntheses of 2-Heterobicyclo-[3.2.0]heptane and -[4.2.0]octane Ring Systems

Masazumi Ikeda,* Kazunori Ohno, Ko-ichi Homma, Hiroyuki Ishibashi, and Yasumitsu Tamura

Faculty of Pharmaceutical Sciences, Osaka University, 133-1, Yamada-kami, Suita, Osaka, Japan

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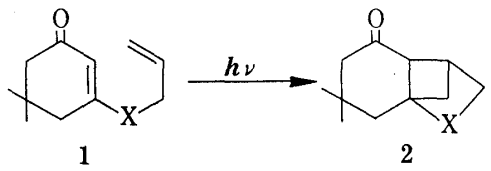
Irradiation of 3-(3-butenyloxy)- and 3-(4-pentenyloxy)-5,5-dimethyl-2-cyclohexen-1-ones resulted in an intramolecular cycloaddition to give the corresponding 2-oxabicyclo-[n.2.0]alkanes rather than the 2-oxabicyclo[n.1.1]alkanes. Similarly 3-(*N*-acetyl-*N*-3-butenylamino)- and 3-(*N*-acetyl-*N*-4-pentenylamino)-5,5-dimethyl-2-cyclohexen-1-ones afforded the 2-azabicyclo[n.2.0]alkanes. Some of the ring opening reactions of these photoadducts are also described.

Keywords——intramolecular photocycloaddition; photo-Fries rearrangement; 2-oxabicyclo[n.2.0]alkane; 2-azabicyclo[n.2.0]alkane; macrolide; enaminoketone; enamide

Recently the intramolecular [2+2] photocycloaddition of enones to olefins has been extensively used in organic synthesis.[1] In connection with our interest in the chemistry of strained heterocyclic compounds, we are investigating the photochemical cycloaddition of some 3-alkenyloxy- and 3-alkenylamino-2-cyclohexen-1-ones.[2,3] Previously we reported on the photochemical conversion of 3-allyloxy and 3-allylamino derivatives (**1**) into 2-oxa- and 2-aza-bicyclo[2.1.1]hexane systems (**2**).[2] We now wish to describe the photochemical behavior of the homologous systems, 3-(3-butenyloxy)- (**4**) and 3-(4-pentenyloxy)-5,5-dimethyl-2-cyclohexen-1-ones (**5**) and their aza analogs (**14**), (**17**), and (**18**).[4] In this paper we also describe some of the ring opening reactions of the photoadducts.



1 2

X=O, NAc, NMe

Chart 1

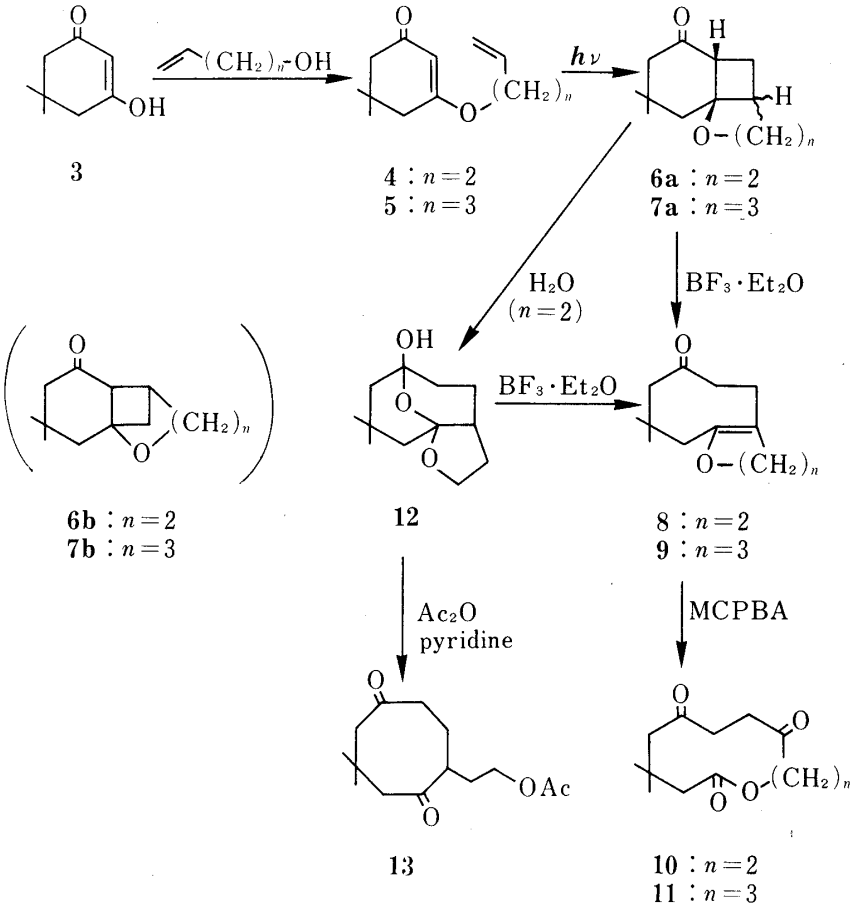
Compounds (**4**) and (**5**) were prepared from dimedone (**3**) and the corresponding alcohols in 79 and 84% yields, respectively.

Irradiation of a 0.5% cyclohexane solution of **4** with a 300 W high-pressure mercury lamp through a Pyrex filter for 8 h afforded the single photoadduct (**6a**), which was isolated in 60% yield as a colorless oil by passing the reaction mixture through a short alumina column after removal of cyclohexane. The photoadduct (**6a**) was shown to be isomeric with **4** by elemental analysis and mass spectrometry. Its infrared (IR) (absorption at 1705 cm^{-1} typical of a six-membered ketone), ultraviolet (UV), and proton nuclear magnetic resonance (^{1}H-NMR) spectra (see "Experimental") showed no unsaturation, and thus it must be tricyclic. Final confirmation of the structure **6a** was based on the following chemical evidence. Upon treatment with borontrifluoride etherate in benzene at 50—60 °C, **6a** isomerized to the crystalline dihydrofuran (**8**). The IR spectrum of **8** showed strong absorption at 1695 cm^{-1} characteristic of a normal ketone and a five-membered enolether,[5] and the UV spectrum showed absorption at 215 nm. In the ^{1}H-NMR spectrum the signal attributable to the α-methylene group of the dihydrofuran moiety appears at δ 4.13 (2H, t, J=9 Hz). These data are consistent with the values reported for the closely related 4,5-dimethyl-2,3-dihydrofuran.[6] Treatment of **8** with *m*-chloroperoxybenzoic acid (MCPBA)[7] gave the diketolactone (**10**) in 76% yield. Heating **6a** in refluxing water afforded the acetal (**12**), which, upon treatment with acetic anhydride and

pyridine, gave the diketo-acetate (**13**) and, upon treatment with borontrifluoride etherate, gave **8**.

Irradiation of **5** under similar conditions gave the oily single product (**7a**) in 60% yield. The assignment of structure **7a** is based on its composition, spectra (see "Experimental"), and subsequent transformation. Treatment of **7a** with borontrifluoride etherate gave the dihydropyran derivative (**9**), whose structure was assigned on the basis of spectral comparison with 9-oxabicyclo[6.4.0]-1-dodecene.[8] Thus, the IR spectrum of **9** showed absorption bands at 1695 (a six-membered ketone) and 1670 cm^{-1} (an enolether). Oxidation of **9** with MCPBA gave the diketolactone (**11**) in 67% yield.

Attempts to epimerize either **6a** or **7a** with sodium methoxide were unsuccessful, suggesting that the photoadducts (**6a**) and (**7a**) are thermodynamically stable.



3
4 : $n=2$
5 : $n=3$
6a : $n=2$
7a : $n=3$
6b : $n=2$
7b : $n=3$
12
8 : $n=2$
9 : $n=3$
13
10 : $n=2$
11 : $n=3$

Chart 2

We next investigated the photochemical behavior of the amino derivatives (**14**), (**17**), and (**18**). The amines (**14**—**16**) were synthesized from **3** and the corresponding alkenylamines. Acetylation of **15** and **16** with acetic anhydride followed by acid treatment gave the *N*-acetylated products (**17** and **18**, respectively) and the C-acetylated products (**19** and **20**, respectively). The structural assignments of **14**—**20** are consonant with their spectroscopic data (see "Experimental").

The *N*-methyl derivative (**14**) was irradiated in cyclohexane for more than 20 h but most of the starting material was recovered unchanged. This result is in agreement with the observation of Cantrell[9] that 3-dimethylamino-2-cyclohexen-1-one does not add to olefins, but in contrast to the behavior of 3-(*N*-allyl-*N*-methylamino-5,5-dimethyl-2-cyclohexen-1-one (**1**, X=NMe), which undergoes intramolecular cycloaddition to give **2** (X=NMe).[2]

On the other hand, when the *N*-acetyl derivative (**17**) was irradiated in cyclohexane, the starting material disappeared within 1 h, and the single photoadduct (**21a**) was obtained in 96% yield. The structure of **21a** was assigned on the basis of its spectroscopic data and transformation to **23**. The IR spectrum of **21a** showed absorptions at 1700 (a six-membered ketone) and 1635 cm^{-1} (an amide), and the UV and ^1H-NMR spectra indicated no unsaturation. Treatment of **21a** with borontrifluoride etherate in benzene gave the enamide (**23**) in 49% yield. Its IR spectrum showed intense absorptions at 1680, 1665, and 1630 cm^{-1}, and the UV spectrum showed an absorption maximum at 250 nm (log ε 3.64), characteristic of a five-membered enamide.[10] The ^1H-NMR spectrum indicated no olefinic proton signal.

Irradiation of an ethereal solution of **18** led to complete disappearance of the starting material after 10 h and the formation of two products. Separation by preparative thin layer chromatography (TLC) gave **22a** (47%) and the photo-Fries[11] rearranged product (**20**) (3%). The structural assignment of **22a** was made on the basis of the spectroscopic and chemical data. The IR spectrum showed absorptions at 1695 (a six-membered ketone) and 1630 cm^{-1} (an amide). The ^1H-NMR spectrum revealed a doublet of doublets at δ 3.21 (1H, J=9 and 5 Hz) attributable to 8-H, suggesting the structure **22a** rather than **22b**. This was further

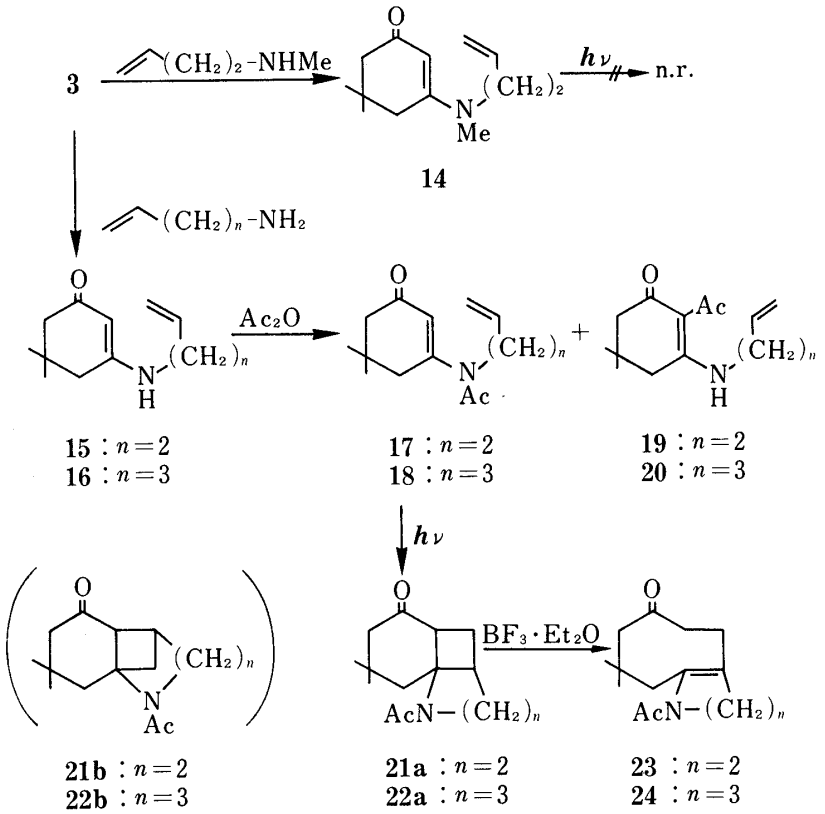


Chart 3

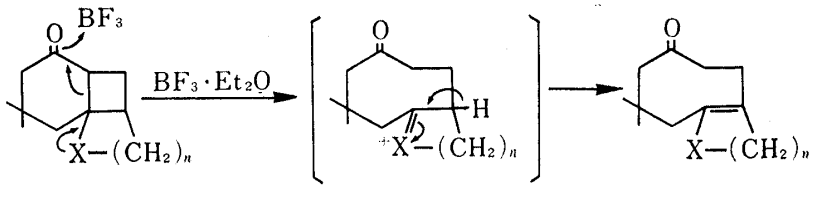
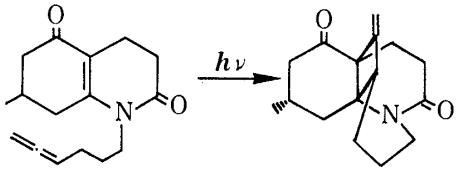


Chart 4

confirmed by transformation to **24**. Thus, treatment of **22a** with borontrifluoride etherate gave the enamide (**24**) in 58% yield. Its IR spectrum showed absorptions at 1685 and 1630 cm^{-1}, and the UV spectrum showed an absorption maximum at 233 nm (log ε 4.00) typical of a six-membered enamide.[12] The ^{1}H-NMR spectrum showed no olefinic proton signal.

The formation of **8**, **9**, **23**, and **24** from the corresponding photoadducts can be formulated as shown in Chart 4.



25 **26**

Chart 5

The direction of the cycloaddition found in compounds **4**, **5**, **17**, and **18** (the formation of the "parallel" addition products, **6a**, **7a**, **21a** and **22a** rather than the "crossed" addition products, **6b**, **7b**, **21b**, and **22b**) is in good agreement with the known tendency observed in the intramolecular photocycloaddition reaction of non-conjugated 1,6- and 1,7-dienes.[13] The formation of **22a** from **18** is also consistent with the observation of Wiesner and coworkers[14] that *N*-(4,5-hexadienyl)-1,2,3,4,5,6,7,8-octahydroquinoline-2,5-dione (**25**) produces the parallel addition product (**26**).

Experimental[15]

3-(3-Butenyloxy)-5,5-dimethyl-2-cyclohexen-1-one (**4**)——A solution of **3** (8.4 g, 0.06 mol), 3-butenol (10.8 g, 0.15 mol), and *p*-toluenesulfonic acid (400 mg) in benzene (60 ml) was refluxed in a flask equipped with a Dean-Stark water separator for 6 h. The reaction mixture was washed with 10% Na_2CO_3 solution and brine, dried ($MgSO_4$), and concentrated. The residual oil was distilled at 98°C (0.22 mmHg) to give **4** (9.2 g, 79%). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1605. UV ν_{max}^{EtOH} nm (log ε): 251 (4.20). ^{1}H-NMR ($CDCl_3$) δ: 1.08 (6H, s, $2\times CH_3$), 2.21, 2.29 (2H each, both s, 4- and 6-H), 2.3—2.7 (2H, m, $C\underline{H}_2CH=CH_2$), 3.91 (2H, t, $J=7$ Hz, OCH_2), 4.9—5.3 (2H, m, $CH=C\underline{H}_2$), 5.35 (1H, s, 2-H), 5.5—6.2 (1H, m, $C\underline{H}=CH_2$). MS *m/e*: 194 (M^+). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.95; H, 9.67.

3-(4-Pentenyloxy)-5,5-dimethyl-2-cyclohexen-1-one (**5**)——By a procedure similar to that described above, **5** (8.7 g, 84%) was obtained from **3** (7.0 g, 0.05 mol) and 4-pentenol (9.5 g, 0.11 mol), bp 105—107°C (0.16 mmHg). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1605. UV λ_{max}^{EtOH} nm (log ε): 249 (4.22). ^{1}H-NMR ($CDCl_3$) δ: 1.02 (6H, s, $2\times CH_3$), 1.5—2.1 (4H, m), 2.12, 2.18 (2H each, both s, 4- and 6-H), 3.80 (2H, t, $J=6$ Hz, OCH_2), 4.8—5.2 (2H, m, $CH=C\underline{H}_2$), 5.29 (1H, s, 2-H), 5.4—6.2 (1H, m, $C\underline{H}=CH_2$). MS *m/e*: 208 (M^+). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.49; H, 9.58.

10,10-Dimethyl-2-oxatricyclo[5.4.0.0^{1,5}]undecan-8-one (**6a**)——A solution of **4** (3.0 g) in cyclohexane (1 l) was irradiated for 8 h. The solvent was removed and the residual oil was chromatographed on alumina using petroleum ether–ether (9: 1) as an eluent to give **6a** (1.8 g, 60%) as a colorless oil, bp 75—85 °C (bath temperature) (0.06 mmHg). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1705. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.02, 1.06 (3H each, both s, $2\times CH_3$), 1.55—2.4 (4H, m), 2.22, 2.79 (2H each, both s, 9- and 11-H), 2.55—2.9 (2H, m), 3.75—4.3 (2H, m, 3-H). MS *m/e*: 194 (M^+). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.08; H, 9.42.

6,6-Dimethyl-9-oxabicyclo[6.3.0]-1(8)-undecen-4-one (**8**)——A solution of **7a** (400 mg, 1.9 mmol) and $BF_3\cdot Et_2O$ (100 mg, 0.7 mmol) in benzene (3 ml) was heated at 50—60°C for 5 min. Alumina (2 g) was added to the reaction mixture and filtered off. The filtrate was concentrated and the residual oil was distilled at 105—110°C (bath temperature) (0.08 mmHg) to give **8** (205 mg, 51%) which solidified on standing, mp 49.5—50°C (from ether). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695. UV λ_{max}^{EtOH} nm (log ε): 215 (3.74). ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 1.03 (6H, s, $2\times CH_3$), 2.13, 2.33 (2H each, both s, 5- and 7-H), 2.3—2.7 (6H, m), 4.1 (2H, t, $J=$ 9 Hz, 10-H). MS *m/e*: 194 (M^+). *Anal.* Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.38; H, 9.36.

This compound was also obtained from **12** by a similar treatment.

3,3-Dimethyl-5,8-dioxodecanolide (**10**)——A solution of **8** (150 mg, 0.77 mmol) in dry CH_2Cl_2 (4.5 ml) was added dropwise to a solution of MCPBA (495 mg, 2.32 mmol) in dry CH_2Cl_2 (6 ml) and the mixture was stirred at room temperature for 15 min. The reaction mixture was washed with 10% Na_2CO_3 solution and brine, dried ($MgSO_4$), and concentrated. The residual oil was distilled at 135—140°C (bath temperature) (0.1 mmHg) to give **10** (132 mg, 76%) as an oil. IR ν_{max}^{Nujol} cm^{-1}: 1730, 1705. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (6H, s, $2\times CH_3$), 2.37 (4H, s, 2- and 4-H), 2.4—2.9 (6H, m, 6-, 7-, and 9-H), 4.24 (2H, t, $J=6$ Hz, 10-H). MS *m/e*: 226 (M^+, Calcd for $C_{12}H_{18}O_4$: 226.1206. Found: 226.1209).

10,10-Dimethyl-2,12-dioxatricyclo[6.3.1.0^{1,5}]undecan-8-ol (**12**)——A mixture of **6a** (168 mg) and water (10 ml) was refluxed for 5 h. Water was removed and the residual solid was recrystallized from petroleum ether to give **12** (105 mg, 57%), mp 71—72°C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580. No carbonyl absorption was observed

in the carbonyl region. MS *m/e*: 212 (M^+). *Anal.* Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.69; H, 9.39.

2-(2-Acetoxyethyl)-7,7-dimethylcyclooctane-1,5-dione (13)——A mixture of **12** (50 mg), acetic anhydride (0.5 ml), and pyridine (0.5 ml) was allowed to stand at room temperature overnight. The solvent was remaved and the residual oil was subjected to preparative TLC on alumina using benzene–AcOEt (4: 1) to give **13** (28 mg, 47%), mp 35—36°C (from ether–petroleum ether). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1735, 1700. ^{1}H-NMR ($CDCl_3$) δ: 1.08, 1.10 (3H each, both s, $2\times CH_3$), 1.5—2.6 (7H, m), 1.96 (3H, s, $COCH_3$), 2.34 (4H, s, 6- and 8-H), 4.01 (2H, t, $J=6$ Hz, OCH_2). MS *m/e*: 254 (M^+). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.01; H, 8.77.

11,11-Dimethyl-2-oxatricyclo[6.4.0.0^{1,6}]dodecan-9-one (7a)——A solution of **5** (4.0 g) in cyclohexane (1 l) was irradiated for 7 h. The solvent was removed and the residual oil was chromatographed on alumina using petroleum ether–ether (7: 3) to give **7a** (2.4 g, 60%), bp 82—85°C (bath temperature) (0.06 mmHg). IR $\nu_{max}^{CCl_4}$ 1705. ^{1}H-NMR (100 MHz, $CDCl_3$) δ: 0.96, 1.02 (3H each, both s, $2\times CH_3$), 1.4—2.15 (7H, m), 1.83 (2H, s, 10- or 12-H), 2.10, 2.33 (1H each, ABq, $J=15$ Hz, 12- or 10-H), 3.26 (1H, bt, 8-H), 3.6—3.7 (2H, m, 3-H). MS *m/e*: 208 (M^+). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.76; H, 9.64.

6,6-Dimethyl-9-oxabicyclo[6.4.0]-1(8)-dodecen-4-one (9)——By a procedure similar to that described for **8**, **9** (361 mg, 80%) was obtained from **7a** (450 mg), mp 40.5°C (from petroleum ether). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1695, 1670. UV λ_{max}^{EtOH} nm (log ε): 207 (3.82). ^{1}H-NMR ($CDCl_3$) δ: 0.90 (6H, s, $2\times CH_3$), 1.5—1.9 (4H, m), 2.02 (2H, bs, 5- or 7-H), 2.20 (2H, s, 7- or 5-H), 2.1—2.5 (4H, m), 3.70 (2H, bt, 10-H). MS *m/e*: 208 (M^+). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.83; H, 9.61.

3,3-Dimethyl-5,8-dioxoundecanolide (11)——A solution of **9** (150 mg, 0.72 mmol) in dry CH_2Cl_2 (5 ml) was added dropwise to a solution of MCPBA (460 mg, 2.7 mmol) in dry CH_2Cl_2 (6 ml) and the mixture was stirred at room temperature for 4.5 h. The reaction mixture was washed with saturated $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated. The residual oil was chromatographed on alumina using *n*-hexane–AcOEt (1: 1) to give **11** (116 mg, 67%), mp 54.5—55°C (from *n*-hexane). IR ν_{max}^{KCl} cm^{-1}: 1725, 1695. ^{1}H-NMR ($CDCl_3$) δ: 1.10 (6H, s, $2\times CH_3$), 1.8—2.1 (2H, m), 2.41, 2.46 (2H each, both s, 2- and 4-H), 2.4—2.8 (6H, m), 4.01 (2H, t, $J=5.5$ Hz, 11-H). *Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.00; H, 8.52.

3-(*N*-3-Butenyl-*N*-methylamino)-5,5-dimethyl-2-cyclohexen-1-one (14)——A solution of **3** (280 mg, 2.0 mmol) and *N*-3-butenyl-*N*-methylamine (196 mg, 2.3 mmol) in anhydrous benzene (6 ml) was heated in a sealed tube at 140°C for 4 h. The reaction mixture was washed with saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed on silica gel using AcOEt to give **14** (276 mg, 95%). IR ν_{max}^{film} cm^{-1}: 1605, 1545. UV λ_{max}^{EtOH} nm (log ε): 301 (4.30). ^{1}H-NMR ($CDCl_3$) δ: 1.07 (6H, s, $2\times CH_3$), 2.12, 2.24 (2H each, both s, 4- and 6-H), 2.0—2.4 (2H, m), 2.90 (3H, s, N–CH_3), 3.1—3.4 (2H, m, N–CH_2), 5.10 (1H, s, 2-H), 4.9—5.2 (2H, m, CH=C$\underline{H}_2$), 5.5—5.9 (1H, m, C$\underline{H}$=CH_2). MS *m/e*: 207 (M^+, Calcd for $C_{13}H_{21}NO$: 207.1624. Found: 207.1624).

3-(*N*-3-Butenylamino)-5,5-dimethyl-2-cyclohexen-1-one (15)——A solution of **3** (3.0 g, 21.4 mmol) and 3-butenylamine (1.5 g, 21.1 mmol) in benzene (50 ml) was heated in a sealed tube at 100°C for 8 h. The reaction mixture was washed with 10% Na_2CO_3 solution and brine, dried ($MgSO_4$), and concentrated. The residual solid was recrystallized from AcOEt–*n*-hexane to give **15** (3.4 g, 82%), mp 96—98°C. IR ν_{max}^{Kcl} cm^{-1}: 1585, 1560, 1540. UV λ_{max}^{EtOH} nm (log ε): 289 (4.44). ^{1}H-NMR ($CDCl_3$) δ: 1.04 (6H, s, $2\times CH_3$), 2.13, 2.14 (2H each, both s, 4- and 6-H), 2.32 (2H, q, $J=6$ Hz, –C$\underline{H}_2$C$\underline{H}$=CH_2), 3.0—3.25 (2H, m, NCH_2), 4.32 (1H, b, NH), 5.07 (1H, s, 2-H), 4.9—5.2 (2H, m, CH=C$\underline{H}_2$), 5.4—6.0 (1H, m, C$\underline{H}$=CH_2). *Anal.* Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.48; H, 9.96; N, 7.11.

3-(*N*-Acetyl-*N*-3-butenylamino-5,5-dimethyl-2-cyclohexen-1-one (17) and 2-Acetyl-3-(*N*-3-butenylamino)-5,5-dimethyl-2-cyclohexen-1-one (19)——A solution of **15** (1.3 g, 7.8 mmol) in acetic anhydride (7.5 ml) was refluxed for 2.5 h. Excess acetic anhydride was removed *in vacuo*, the residue was dissolved in $CHCl_3$, and the solution was washed with 10% Na_2CO_3 solution and brine, dried ($MgSO_4$), and concentrated. The residue was dissolved in methanol (5 ml) and 10% HCl (1 ml) and the mixture was allowed to stand at room temperature for 48 h, neutralized with saturated $NaHCO_3$ solution, and extracted with $CHCl_3$. The extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was chromatographed on silica gel. Elution with ether gave **19** (173 mg, 10%) as an oil. IR ν_{max}^{film} cm^{-1}: 3460, 1635, 1580. UV λ_{max}^{EtOH} nm (log ε): 260 (4.08), 290 (4.11). ^{1}H-NMR ($CDCl_3$) δ: 1.06 (6H, s, $2\times CH_3$), 2.24, 2.43 (2H each, both s, 4- and 6-H), 2.1—2.6 (6H, m), 2.50 (3H, s, $COCH_3$), 3.3—3.55 (2H, m, NCH_2), 5.0—5.3 (2H, m, CH=C$\underline{H}_2$), 5.5—6.0 (1H, m, C$\underline{H}$=CH_2), 12.6 (1H, b, NH). MS *m/e*: 235 (M^+, Calcd for $C_{14}H_{21}NO_2$, 235.1573. Found: 235.1575). Further elution with the same solvent gave **17** (311 mg, 17%) as an oil. IR ν_{max}^{film} cm^{-1}: 1655, 1620. UV λ_{max}^{EtOH} nm (log ε): 275 (3.85). ^{1}H-NMR ($CDCl_3$) δ: 1.12 (6H, s, $2\times CH_3$), 2.1—2.5 (2H, m), 2.10 (3H, s, $COCH_3$), 2.28, 2.40 (2H each, both s, 4- and 6-H), 3.60 (2H, bt, $J=7$ Hz, N–CH_2), 4.9—5.2 (2H, m, CH=C$\underline{H}_2$), 5.81 (1H, bs, 2-H), 5.5—5.9 (1H, m, C$\underline{H}$=CH_2). MS *m/e*: 235 (M^+, Calcd for $C_{14}H_{21}NO_2$: 235.1573. Found: 235.1579.

2-Acetyl-10,10-dimethyl-2-azatricyclo[5.4.0.0^{1,5}]undecan-8-one (21a)——A solution of **17** (200 mg, 8.5 mmol) in cyclohexane (40 ml) was irradiated for 1 h and the solvent was removed. The residue was passed through a short alumina column using ether–AcOEt (2: 1) to give **21a** (191 mg, 96%) as a colorless oil. IR ν_{max}^{film} cm^{-1}: 1700, 1635. ^{1}H-NMR ($CDCl_3$) δ: 0.98, 1.08 (3H each, both s, $2\times CH_3$), 2.08 (3H, s, $COCH_3$),

1.6—3.0 (10H, m), 3.6—3.85 (2H, m, 3-H). MS *m/e*: 235 (M^+, Calcd for $C_{14}H_{21}NO_2$, 235.1570. Found: 235.1569.

9-Acetyl-6,6-dimethyl-9-azabicyclo[6.3.0]-1(8)-undecen-4-one (23)——$BF_3 \cdot Et_2O$ (103 mg, 0.72 mmol) was added to a solution of **21** (170 mg, 0.72 mmol) in benzene (2 ml), and the mixture was heated at 50—60°C for 2.5 h. Alumina (0.5 g) was added to the reaction mixture and filtered off. After removal of the solvent from the filtrate, the residue was chromatographed on alumina using *n*-hexane–AcOEt (2: 3) to give **23** (84 mg, 49%) as colorless crystals, mp 108.5—110°C (from ether–*n*-hexane). IR ν_{max}^{KCl} cm^{-1}: 1680, 1665, 1630. UV λ_{max}^{EtOH} nm (log ε): 250 (3.64). ^{1}H-NMR ($CDCl_3$) δ: 1.03 (6H, s, $2\times CH_3$), 2.02 (3H, s, $COCH_3$), 2.09, 2.31 (2H each, both s, 5- and 7-H), 1.7—3.1 (6H, m), 3.6—3.9 (2H, m, 10-H). *Anal.* Calcd for $C_{14}H_{21}NO_3$: C, 71.46; H, 8.99; N, 5.95. Found: C, 71.27; H, 9.18; N, 5.91.

3-(*N*-4-Pentenylamino)-5,5-dimethyl-2-cyclohexen-1-one (16)——A mixture of 3 (2.8 g, 20 mmol) and 4-pentenylamine (1.85 g, 21.7 mmol) in benzene (60 ml) was refluxed in a flask equipped with a Dean-Stark water separator for 2 h. The solution was washed with saturated $NaHCO_3$ solution and brine, dried (Na_2SO_4), and concentrated. The residual solid was recrystallized from AcOEt–*n*-hexane to give **16** (3.14 g, 76%), mp 103—104°C. IR ν_{max}^{KCl} cm^{-1}: 1560, 1535. UV λ_{max}^{EtOH} nm (log ε): 289 (4.37). ^{1}H-NMR ($CDCl_3$) δ: 1.06 (6H, s, $2\times CH_3$), 1.66 (2H, quint, $J=7$ Hz, $NCH_2\underline{CH_2}$), 2.14 (4H, s, 4- and 6-H), 1.9—2.25 (2H, m, $\underline{CH_2}CH=CH_2$), 2.95—3.25 (2H, m, NCH_2), 4.5 (1H, b, NH), 5.07 (1H, s, 2-H), 4.8—5.15 (2H, m, $CH=\underline{CH_2}$), 5.5—6.0 (1H, m, $\underline{CH}=CH_2$). *Anal.* Calcd for $C_{13}H_{21}NO$; C, 75.32; H, 10.21; N, 6.76. Found: C, 75.45; H, 10.16; N, 6.88.

3-(*N*-Acetyl-*N*-4-pentenylamino)-5,5-dimethyl-2-cyclohexen-1-one (18) **and 2-Acetyl-3-(*N*-4-pentenylamino)-5,5-dimethyl-2-cyclohexen-1-one** (20)——By a procedure similar to that described for the preparation of **17** and **19**, **18** (311 mg, 17%) and **20** (173 mg, 10%) were obtained from **16** (1.5 g). Compound **18** was an oil. IR ν_{max}^{film} cm^{-1}: 1655, 1620. UV λ_{max}^{EtOH} nm (log ε): 275 (4.07). ^{1}H-NMR ($CDCl_3$) δ: 1.11 (6H, s, $2\times CH_3$), 1.62 (2H, quint, $J=7$ Hz, $NCH_2\underline{CH_2}$), 1.9—2.2 (2H, m, $\underline{CH_2}CH=CH_2$), 2.10 (3H, s, $COCH_3$), 2.27, 2.39 (2H each, both s, 4- and 6-H), 3.4—3.7 (2H, m, $N-CH_2$), 4.9—5.2 (2H, m, $CH=\underline{CH_2}$), 5.78 (1H, s, 2-H), 5.5—6.6 (1H, m, $\underline{CH}=CH_2$). MS *m/e*: 249 (M^+, Calcd for $C_{15}H_{23}NO_2$: 249.1726. Found: 249.1723). Compound **20** was an oil. IR ν_{max}^{film} cm^{-1}: 3280, 1715, 1580. UV λ_{max}^{EtOH} nm (log ε): 260 (4.07), 291 (4.09). ^{1}H-NMR ($CDCl_3$) δ: 1.08 (6H, s, $2\times CH_3$), 1.73 (2H, quint, $J=7$ Hz, $NCH_2\underline{CH_2}$), 2.0—2.3 (2H, m, $\underline{CH_2}CH=CH_2$), 2.25, 2.41 (2H each, both s, 4- and 6-H), 2.52 (3H, s, $COCH_3$), 3.2—3.45 (2H, m, $N-CH_2$), 4.9—5.2 (2H, m, $CH=\underline{CH_2}$), 5.5—6.0 (1H, m, $\underline{CH}=CH_2$), 12.7 (1H, b, NH). MS *m/e*: 249 (M^+, Calcd for $C_{15}H_{23}NO_2$: 249.1726. Found: 249.1724).

2-Acetyl-11,11-dimethyl-2-azatricyclo[6.4.0.0^{1,6}]dodecan-9-one (22a)——A solution of **18** (182 mg, 0.73 mmol) in ether (40 ml) was irradiated for 10 h and concentrated. The residue was subjected to preparative TLC on silica gel using ether as an eluent to give **22** (86 mg, 47%) and **20** (6 mg, 3%). Compound **22a** was an oil. IR ν_{max}^{film} cm^{-1}: 1695, 1630. ^{1}H-NMR ($CDCl_3$) δ: 1.02, 1.06 (3H each, both s, $2\times CH_3$), 2.08 (3H, s, $COCH_3$), 1.4—2.7 (11H, m), 2.87 (1H, m, 3-H), 3.21 (1H, dd, $J=9$ and 5 Hz, 8-H), 3.69 (1H, dt, $J=13$ and 4 Hz, 3-H). MS *m/e*: 249 (M^+, Calcd for $C_{15}H_{23}NO_2$: 249.1728. Found: 249.1733.

9-Acetyl-6,6-dimethyl-9-azabicyclo[6.4.0]-1(8)-dodecen-4-one (24)——By a procedure similar to that described for the preparation of **23**, **24** (46 mg, 58%) was obtained from **22a** (80 mg). mp 136—137°C (from *n*-hexane–AcOEt). IR ν_{max}^{KCl} cm^{-1}: 1685, 1630. UV λ_{max}^{EtOH} nm (log ε): 233 (4.00). ^{1}H-NMR ($CDCl_3$) δ: 0.98 (6H, s, $2\times CH_3$), 1.6—2.7 (12H, m), 2.06 (3H, s, $COCH_3$), 3.1—3.6 (2H, b, 10-H). *Anal.* Calcd for $C_{15}H_{23}NO_2$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.07; H, 9.44; N, 5.56.

References and Notes

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