Photo-Aza-Claisen Rearrangements of Cyclic Enaminones

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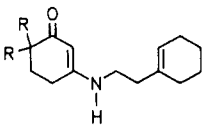
Cyclic enaminones **1–7** were prepared and photolyzed. Compounds **1–4** reacted as expected to provide aza-De Mayo products **10** and **11**, whereas **5** provided enaminone **12** in a novel photo-aza-Claisen rearrangement. Compounds **6** and **7** gave photo-aza-Claisen products **13** and **16**, respectively, along with aza-De Mayo product **15** and 2 + 2 cycloaddition product **17**, respectively.

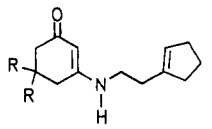
Photochemical reactions of enones with unactivated olefins leading to four-membered ring compounds are well known[1] and have often been used in natural products synthesis.[2] Most of the known photochemistry deals with 2 + 2 photocycloaddition of α,β-unsaturated ketones or derivatives of 1,3-dicarbonyl compounds. Less attention has been paid to β-heteroatom-substituted compounds, especially where the heteroatom is a nitrogen, i.e., vinylogous amides (enaminones) or imides (*N*-acyl enaminones) as the enone component.

Typically, intermolecular photocyclization of simple enones to olefins provides 2 + 2 cycloaddition products often accompanied by compounds formally derived by ene[3] reactions of the components. Despite a variety of intramolecular studies especially from the laboratories of Tamura,[4] Wiesner,[5] Pattenden,[6] Oppolzer,[2] Agosta,[7] and Scheffer,[8] it was not until 1976[9] that a significant yield of an intramolecular ene product was reported. The first example of this reaction was discovered in the course of trying to obtain a simple 2 + 2 addition of a vinylogous amide, and similar intramolecular reactions using vinylogous imides[10] and vinylogous esters[11] have now been reported.

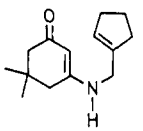
A principal stimulus for the investigation of β-heterosubstituted enones is due to the elegant work of De Mayo,[1b] who showed that initial addition products of vinylogous acids and esters could be transformed to 1,5-dicarbonyls via retro-aldol reaction. Likewise, others have shown that addition products of vinylogous amides can similarly be transformed into 1,5-keto imines[12] via retro-Mannich chemistry. The high yield of this reaction combined with the facile differentiation of the carbonyls produced in the retro-Mannich process made further study appealing. From the broad studies by Agosta[7,13] in the case of enones it is known that the outcome of the photochemical reaction is strongly structure dependent. Even simple structural changes such as introduction of a methyl group produced significant changes in the product ratio of 2 + 2 versus ene or "crossed" versus "straight" addition. In the case of vinylogous amides less systematic studies have been reported; however, simple 2 + 2 cycloaddition, a photo–ene reaction, and an example of the aza-De Mayo sequence have been reported. It was in this latter context that we investigated the photochemistry of compounds **1–7**, only to discover in the case of **5** yet another reaction course for these unpredictable materials.



1 R = H
2 R = CH_3



3 R = H
4 R = CH_3



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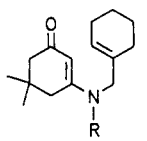
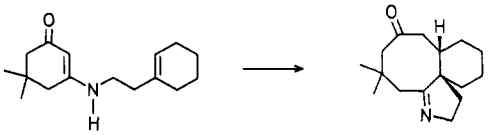


6 R = H
7 R = CH_3

Starting with the known transformation of **8** to **9**, we investigated the influence of structural changes including



8 **9**

substitution pattern, ring size variation, and olefin separation. Irradiation of compounds **1–4** in either methylene chloride or acetonitrile yielded the expected aza-De Mayo products **10a**, **10b**, **11a**, and **11b**, respectively, in even better yields than previously reported.

When the linking unit was shortened, a change in the direction of addition was expected, as reported earlier by Tamura.[4] Irradiation of **5** in acetonitrile produced a single characterizable compound along with starting material and

(1) (a) Eaton, P. E. *Acc. Chem. Res.* **1968**, *1*, 50. (b) De Mayo, P. *Ibid.* **1971**, *4*, 41. (c) Baldwin, S. W. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123.
(2) Oppolzer, W. *Acc. Chem. Res.* **1982**, *15*, 135.
(3) Recently an example was reported where the ene product is the main product. Berry, N. M.; Darey, M. C. P.; Harwood, L. M. *Tetrahedron Lett.* **1986**, *27*, 2319.
(4) Tamura, Y.; Ishibashi, H.; Hirai, M.; Kita, Y.; Ikeda, M. *J. Org. Chem.* **1975**, *40*, 2702.
(5) Wiesner, K.; Poon, L.; Jirkovsky, I.; Fishman, M. *Can. J. Chem.* **1969**, *47*, 433.
(6) Birch, A. M.; Pattenden, G. *J. Chem. Soc., Perkin Trans. I* **1983**, 1913 and references cited therein.
(7) Matlin, A. R.; Wolff, S.; Agosta, W. C. *Tetrahedron Lett.* **1983**, *24*, 2961. Matlin, A. R.; George, C. F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 3385 and references cited therein.
(8) Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317.
(9) Tamura, Y.; Ishibashi, H.; Ikeda, M. *J. Org. Chem.* **1976**, *41*, 1277.
(10) (a) Schell, F. M.; Cook, P. M. *J. Org. Chem.* **1978**, *43*, 4420. (b) Schell, F. M.; Cook, P. M.; Hawkinson, S. W.; Cassady, R. E.; Thiessen, W. E. *Ibid.* **1979**, *44*, 1380.
(11) Oppolzer, W.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, *62*, 1199.
(12) (a) Schell, F. M.; Cook, P. M. *J. Org. Chem.* **1984**, *49*, 4067. (b) For another example of intramolecular cycloaddition of a vinylogous amide, see: Winkler, J. D.; Hershberger, P. M.; Springer, J. P. *Tetrahedron Lett.* **1986**, *27*, 5177.
(13) Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1292, 1299.

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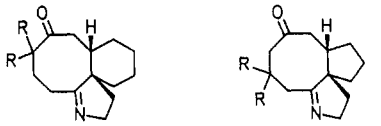
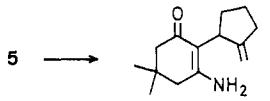
some polymeric material. The yield of the new product was 57% on the basis of consumed **5**. Inspection of the ^{13}C NMR spectrum surprisingly revealed the product to be an olefinic enone. Furthermore, the enone and one olefinic carbon were nonprotonated and the remaining olefinic carbon was a methylene. The proton NMR corroborated these observations with olefinic absorptions at 4.93 (1 H) and 4.67 (1 H) and also a broad resonance at 4.97 (2 H) which proved to have a very concentration-dependent chemical shift. These data and the presence of a single aliphatic methine suggested structure **12** for the product formed via a photo-aza-Claisen rearrangement. This is fully supported by detailed analysis of homo- and heteronuclear 2-D COSY spectra and 2-D COLOC spectra, which clearly define the connection between the methine carbon and both olefinic systems.



10 a R=H
10 b R=CH_3

11 a R=H
11 b R=CH_3



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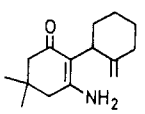
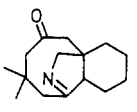
In order to find out whether this transformation is a singular example or a synthetically useful reaction, we have also examined structurally related systems. Changing the ring size in the olefin part from a five-membered to a six-membered ring led to compound **6**[10b] whose irradiation provided two products. One of them can be rationalized by its NMR spectra as the expected photo-aza-Claisen rearrangement product **13**. The second is a compound



13



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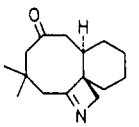
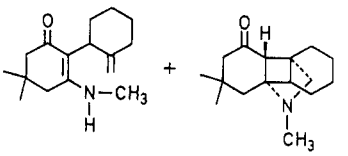


15

whose IR and ^{13}C NMR spectra quickly reveal its imino ketone nature and thus its De Mayo origins. The nature of the imino carbon with a very high chemical shift (198.2 ppm) was only recognized with certainty due to the IR stretch at 1640 cm^{-1}. The latter value is also abnormal for imines in these systems where we and others have reported[12,14,15] values in the range 1610–1625 cm^{-1}. The abnormalities in these values forced us to consider the "straight adduct" **15**, whereas production of "crossed adduct" **14** would have seemed more likely. In fact, close inspection of the ^{13}C NMR data demonstrated that **15** is, indeed, the "straight" addition product. Thus, the quaternary center in the six-membered ring has a low-field shift as in **9** while the quaternary in the "crossed adduct" **14** would be expected to appear at much higher field.[16] Likewise, the methine center in **15** appears at 36.3 ppm (37.6 ppm in **9**), which is higher than would be expected if next to an imino carbonyl center. The difficult part of the structure assignment is the stereochemical relationship of the methine hydrogen and the amino methylene.

Comparison of the cyclohexane methylene chemical shifts in compounds **9** and **15** shows them to be quite dissimilar. In the former case the six-membered ring has been assumed to be in the chair conformation, having diaxial substitution to account for the high methylene values, but this cannot be the situation for **15**. Furthermore, if the amino methylene–hydrogen relationship in **14** is cis, then there would have to be a serious axial interaction of the amino methylene with a chair cyclohexane ring. Thus, either the cyclohexane ring cannot be in the chair conformation or the relationship of the hydrogen and amino methylene must be trans. Irradiation of one of the amino methylene hydrogens does produce an enhancement in the proton absorption at the nearby keto methylene which is in accord with the trans relationship and a rigid cyclohexane ring.

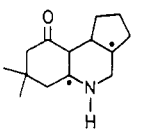
Introducing a methyl group at the nitrogen atom in **6** produced **7**, which upon irradiation provided two products that could be isolated and characterized, although in low yield. One of them is the photo-aza-Claisen rearrangement product **16**, which was easily recognized by comparison of



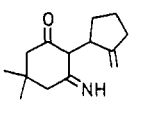
16 **17**

spectral details with those from compound **13** above. The other product was the expected "crossed" cycloaddition product whose structure was partially defined as **17** by NMR analysis.[17] Thus, the keto methine appears as a broad singlet, which was shown to be W-coupled to one of the amino methylene protons by using a COSY analysis. There are four possible stereo structures for this adduct. Only those two in which the keto methine and the amino methylene bridge are anti could display the observed W-coupling.

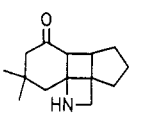
The photo-aza-Claisen products reported herein can be rationalized by assuming the intermediacy of a diradical such as **18**, which can unravel directly to the keto imine tautomer **19**. However, we have no evidence to rule out



18



19



20

direct formation of, or collapse of the diradical **18** to, [2.2.0]bicycle **20** followed by cycloreversion to the same tautomer. This possible "straight" addition of 1,5-hexadienes has now been observed with vinylogous amides, for example, as reported above in the conversion of **6** to **15**.

The net reaction, **5** to **12**, is a **photo-aza-Claisen rearrangement**,[18,19] which to our knowledge is the first example of such a photochemically induced process involving

(14) Swindell, C. S.; Patel, B. P.; deSolms, S. J.; Springer, J. P. *J. Org. Chem.* **1987**, *52*, 2346.
(15) See Experimental Section.
(16) See, for example, the quaternary center of the crossed adduct in Swindell et al., ref 14.
(17) The cyclohexane–cyclobutane ring fusion in **17** is most likely cis on the basis of comparison of chemical shift data with that reported[14] for a similar photoproduct with an *N*-acetyl rather than *N*-methyl substituent. Except for those carbons directly affected by the change in nitrogen substitution, chemical shifts agree well. Unfortunately, this congruence is blemished by a disagreement in multiplicity assignments, in particular, at least one of the signals reported for the neopentyl methyls in the reference compound is at too high a field for such substitution.
(18) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205. For certainty the starting material was also heated to reflux in benzene, whereas the photochemistry was performed at 16 °C. No thermal rearrangement was detectable.
(19) An analogous photo-Claisen rearrangement is reported by Smith, A. B., III; Agosta, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 1961.

a nitrogen chromophore. The presence of a β-nitrogen substituent clearly provides enones with a tendency for the unusual and it will be of interest to see if they undergo other unexpected reactions.

Experimental Section

NMR spectroscopy employed a Bruker WM 250 spectrometer. Proton spectra were obtained at 250 MHz with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Carbon-13 spectra were obtained operating at 62.89 MHz with $CDCl_3$ as solvent and standard ($CDCl_3$ = 77.00 ppm). Multiplicities of carbons were determined by use of DEPT experiments. Infrared spectroscopy employed a Zeiss IMR-25 spectrometer, using $CHCl_3$ or CCl_4 solutions, films on NaCl plates, or KBr pellets. Mass spectroscopy employed a Varian MAT 311 A (high resolution) 44 S (capillary GC-MS) instrument at 70 eV. Photochemical reactions were run with use of a low pressure mercury lamp, HANAU 500–750 W, in a Pyrex glass apparatus.

Preparation of Amines. A suspension of LAH in dry diethyl ether was placed in a three-necked flask equipped with a reflux condenser, a drying tube, and an ice bath. The nitrile dissolved in dry ether was dropped slowly into the reaction flask by means of a dropping funnel. The color of the reaction mixture turned to yellow green. After the addition was finished, the cooling bath was removed and the resulting solution stirred for another 14 h at room temperature and 1 h at reflux. Hydrolysis was accomplished by addition of the stoichiometric amount of water under external cooling with ice. The solids were filtered and washed well with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the solvent was removed on a rotatory evaporator. The crude amine then was purified by short path distillation to prevent loss of the fairly volatile material.

(Cyclopentenylmethyl)amine: 5.09 g of 1-cyano-1-cyclopentene, 4.68 g of $LiAlH_4$, 10.17 g of water, 400 mL of diethyl ether; yield 2.6 g (49%); bp (15 Torr) = 62 °C.

(Cyclohexenylmethyl)amine: 16.4 g of 1-cyano-1-cyclohexene, 12.73 g of $LiAlH_4$, 24.12 g of water, 350 mL of diethyl ether; yield 12.1 g (73%); bp (15 Torr) = 55 °C.

General Procedure for the Preparation of Vinylogous Amides. The amine and the appropriate dione were dissolved in benzene and heated to reflux with continuous removal of water by a Dean–Stark trap. After water removal ceased, benzene was distilled from the reaction mixture. The residual orange oil was dissolved in methylene chloride and washed twice with 5% NaOH solution (50 mL) and once with water. After drying over magnesium sulfate, methylene chloride was removed by distillation and the remaining oil was chromatographed first on alumina (Woelm) with chloroform and then on silica using methylene chloride/ethanol. The individual products were recrystallized from the solvents indicated below.

3-[(2-Cyclohexenylethyl)amino]-2-cyclohexen-1-one (1): 5.0 g of 1,3-cyclohexanedione, 6.1 g of (2-cyclohexenylethyl)-amine;[10a] reaction time 12 h; yield 7.3 g (75%) of 1; mp 106–107 °C (diethyl ether). ^1H NMR: 5.50 (m, 1 H), 5.43 (bs, 1 H), 5.10 (s, 1 H), 3.15 (q, 2 H), 2.35 (t, 2 H), 2.3 (t, 2 H), 2.23 (t, 2 H), 1.85–2.05 (m, 6 H), 1.5–1.7 (m, 4 H). ^{13}C NMR: CH_2 (40.52, 36.43, 36.43, 29.56, 27.84, 25.12, 22.67, 22.18, 21.95), CH (123.69, 96.23), C (196.98, 164.81, 134.14). MS: calcd for $C_{14}H_{21}NO$ 219.1623, found 219.1623; fragments (intensity) 219 (48), 125 (100), 124 (96), 112 (26), 96 (34), 67 (32). IR (CCl_4) cm^{-1}: 3420 (NH), 3260 (NH), 2940 (CH), 1630 (vin. amide), 1590 (vin. amide), 1500 (vin. amide).

3-[(2-Cyclohexenylethyl)amino]-6,6-dimethyl-2-cyclohexen-1-one (2): 12.5 g of 6,6-dimethyl-1,3-cyclohexanedione, 12.3 g of (2-cyclohexenylethyl)amine;[10a] reaction time 14 h; yield 17.4 g (79%) of 2; mp 83–85 °C (diethyl ether). ^1H NMR: 5.50 (m, 1 H), 4.96 (s, 1 H), 4.58 (bs, 1 H), 3.10 (ddd, 2 H), 2.40 (t, 2 H), 2.23 (dd, 2 H), 1.9–2.1 (m, 4 H), 1.83 (t, 2 H), 1.5–1.7 (m, 4 H), 1.1 (s, 6 H). ^{13}C NMR: CH_3 (24.87), CH_2 (40.33, 40.33, 36.34, 35.57, 27.60, 26.21, 22.45, 21.97), CH (123.64, 94.81), C (202.23, 162.92, 134.19, 39.21). MS: calcd for $C_{16}H_{25}NO$ 247.1936, found 247.1937; fragments (intensity) 247 (50), 153 (100), 152 (40), 140 (30), 108 (40), 96 (60). IR ($CHCl_3$) cm^{-1}: 3400 (NH), 3280 (NH), 2860 (CH), 1580 (vin. amide), 1540 (vin. amide).

3-[(2-Cyclopentenylethyl)amino]-2-cyclohexen-1-one (3): 11.2 g of 1,3-cyclohexanedione, 12.4 g of (2-cyclopentenylethyl)amine;[20] reaction time 18 h; yield 13.7 g (67%) of 3; mp 114–116 °C (acetone/diethyl ether). ^1H NMR: 5.44 (m, 1 H), 5.13 (s, 1 H), 4.77 (bs, 1 H), 3.18 (q, 2 H), 2.1–2.45 (m, 10 H), 1.8–2.0 (m, 4 H). ^{13}C NMR: CH_2 (40.60, 36.13, 34.50, 32.11, 29.45, 29.14, 22.89, 21.64), CH (125.57, 114.54), C (197.01, 165.2, 140.7). MS: calcd for $C_{13}H_{19}NO$ 205.1467, found 205.1467; fragments (intensity) 205 (38), 125 (84), 124 (100), 112 (40), 96 (34). IR ($CHCl_3$) cm^{-1}: 3400 (N–H), 3260 (NH), 2840 (CH), 1580 (vin. amide), 1540 (vin. amide).

3-[(2-Cyclopentenylethyl)amino]-5,5-dimethyl-2-cyclohexen-1-one (4): 14.0 g of 5,5-dimethyl-1,3-cyclohexanedione, 12.4 g of (2-cyclopentenylethyl)amine; reaction time 17 h; yield 15.6 g (67%) of 4; mp 110–113 °C (diethyl ether). ^1H NMR: 5.44 (m, 1 H), 5.11 (s, 1 H), 4.78 (bs, 1 H), 3.19 (ddd, 2 H), 2.4–2.2 (m, 6 H), 2.18 (s, 4 H), 1.87 (m, 2 H), 1.06 (s, 6 H). ^{13}C NMR: CH_3 (27.87), CH_2 (50.03, 40.71, 34.51, 32.35, 32.11, 29,47, 22.90), CH (125.56, 94.37), C (196.42, 163.89, 140.69, 32.17). MS: calcd for $C_{15}H_{23}NO$ 233.1779, found 233.1779; fragments (intensity) 233 (20), 153 (54), 152 (48), 140 (36), 138 (40), 94 (20), 83 (100). IR (KBr) cm^{-1}: 3220 (NH), 3010 (C=CH), 2940 (CH), 2860 (CH), 1580 (vin. amide), 1560 (vin. amide), 1530 (vin. amide).

3-[(Cyclopentenylmethyl)amino]-5,5-dimethyl-2-cyclohexen-1-one (5): 1.2 g of (cyclopentenylmethyl)amine, 1.9 g of 5,5-dimethyl-1,3-cyclohexanedione; reaction time 16 h; yield 1.5 g (57.0%) of 5, mp 139 °C (petroleum ether/acetone). ^1H NMR: 5.55 (m, 1 H), 5.22 (bs, 1 H), 5.1 (s, 1 H), 3.75 (m, 2 H), 2.26–2.37 (m, 4 H), 2.22 (s, 2 H), 2.18 (s, 2 H), 1.84–1.96 (m, 2 H), 1.07 (s, 6 H). ^{13}C NMR: CH_3 (28.07), CH_2 (50.13, 43.35, 43.08, 33.27, 32.11, 23.11), CH (126.49, 94.94), C (196.49, 163.62, 139.17, 32.56). MS: calcd for $C_{14}H_{21}NO$ 219.1618, found 219.1624; fragments (intensity) 219 (90), 204 (70), 191 (80), 190 (56), 163 (20), 135 (100). IR (KBr) cm^{-1}: 3420 (NH), 3220 (NH), 3050 (C=CH), 2960 (CH), 1595 (vin. amide), 1560 (vin. amide), 1540 (vin. amide).

3-[(Cyclohexenylmethyl)methylamino]-5,5-dimethyl-2-cyclohexen-1-one (7): 2.8 g of 3-[(cyclohexenylmethyl)-amino]-5,5-dimethyl-2-cyclohexen-1-one (6),[10b] 960 mg of NaH (60% suspension in oil), 1.5 mL of methyl iodide, 150 mL of dry dioxane. The vinylogous amide 6 and NaH were placed in dry dioxane, refluxed for 1 h, and then cooled to room temperature. Methyl iodide then was added by means of a dropping funnel. After the addition was complete the solution was refluxed again for 2 h. The solution was concentrated under vacuum and the residue dissolved in methylene chloride whereupon a white precipitate formed. The solid was removed by filtration, the solution dried over magnesium sulfate, and the methylene chloride removed to provide an orange-brown crystalline compound. Recrystallization from diethyl ether yielded 1.66 g (56%) of 7, mp 96 °C. ^1H NMR: 5.40 (m, 1 H), 5.16 (s, 1 H), 3.73 (s, 2 H), 2.89 (s, 3 H), 2.27 (s, 2 H), 2.16 (s, 2 H), 1.92–2.03 (m, 2 H), 1.69–1.85 (m, 2 H), 1.55–1.67 (m, 4 H), 1.06 (s, 6 H). ^{13}C NMR: CH_3 (28.57, 38.16), CH_2 (22.22, 22.31, 24.78, 26.01, 40.31, 49.30, 57.39), CH (97.32, 122.98), C (32.77, 132.00, 194.05, 196.24). MS: calcd for $C_{16}H_{25}NO$ 247.1932, found 247.1928; IR (KBr) cm^{-1}: 2940 (CH), 1600 (vin. amide), 1550 (vin. amide), 1500 (vin. amide).

Photochemistry of Vinylogous Amides. After dissolving the vinylogous amide in 600 mL of freshly distilled solvent (acetonitrile, unless otherwise stated), the solution was degassed with oxygen-free argon for 0.5 h and then photolyzed until TLC indicated no further reaction. After removal of the solvent the residue was chromatographed on silica with solvent systems as indicated below.

Photolysis of 3-[(2-cyclohexenylethyl)amino]-2-cyclohexen-1-one (1): 2.5 g of 1, solvent acetonitrile; reaction time 8 h; workup by flash chromatography on silica; methylene chloride/ethyl acetate 3:2 as solvent; yield 1.75 g (70%) of **10a**. ^1H NMR: 3.65 (m, 2 H), 3.3 (dd, 1 H), 2.6–2.0 (m, 9 H), 1.97 (dd, 1 H), 1.9–1.2 (m, 8 H). ^{13}C NMR: CH_2 (56.20, 43.76, 43.76, 37.90, 32.09, 30.17, 29.97, 26.23, 22.98, 20.94), CH (37.25), C (215.00, 183.02, 56.13). MS: calcd for $C_{14}H_{21}NO$ 219.1623, found 219.1624; fragments (intensity) 219 (100), 191 (16), 162 (20), 150 (22), 124 (32), 109 (90), 108 (74). IR (KBr) cm^{-1}: 2960 (CH), 2875 (CH), 1715 (C=O), 1630 (C=N).

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Photolysis of 3-[(2-cyclohexenylethyl)amino]-6,6-dimethyl-2-cyclohexen-1-one (2): 400 mg of **2**, solvent acetonitrile; reaction time 14 h; workup by chromatography on silica; methylene chloride/ethyl acetate 3:2 as solvent; yield 240 mg (60%) of **10b**; mp 103–105 °C (diethyl ether). ^{1}H NMR: 3.7–3.4 (m, 3 H), 2.85 (m, 1 H), 2.45 (m, 2 H), 2.2–2.0 (m, 3 H), 1.9 (ddd, 1 H), 1.8–1.6 (m, 6 H), 1.4–1.3 (m, 3 H), 1.13 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR: CH_3 (29.28, 20.53), CH_2 (55.33, 38.92, 38.02, 36.21, 31.36, 30.05, 26.05, 21.94, 20.85), CH (36.11), C (216.71, 182.18, 55.56, 47.10). MS: calcd for $C_{16}H_{25}NO$ 247.1947, found 247.1942; fragments (intensity) 247 (62), 219 (10), 204 (36), 191 (64), 176 (18), 154 (64), 149 (56), 43 (100). IR (KBr) cm^{-1}: 2920 (CH), 2860 (CH), 1690 (C=O), 1610 (C=N).

Photolysis of 3-[(2-Cyclopentenylethyl)amino]-2-cyclohexen-1-one (3): 3.0 g of **3**, solvent acetonitrile; reaction time 8 h; workup by flash chromatography on silica; methylene chloride/ethyl acetate 3:2 as the solvent; yield 2.25 g (75%) of **11a**. ^{1}H NMR: 3.8–3.7 (ddd, 1 H), 3.6–3.45 (ddd, 1 H), 2.86 (dd, 1 H), 2.6–1.4 (m, 16 H). ^{13}C NMR: CH_2 (56.29, 45.59, 43.44, 41.55, 33.87, 32.02, 29.69, 26.25, 22.70), CH (44.77), C (214.22, 181.68, 62.59). MS: calcd for $C_{13}H_{19}NO$ 205.1461, found 205.1464; fragments (intensity) 205 (40), 177 (12), 162 (8), 150 (15), 148 (16), 135 (16), 124 (24), 109 (32), 96 (46), 95 (100), 94 (74). IR (KBr) cm^{-1}: 2960 (CH), 2880 (CH), 1715 (C=O), 1635 (C=N).

Photolysis of 3-[(2-cyclopentenylethyl)amino]-5,5-dimethyl-2-cyclohexen-1-one (4): 2.7 g of **4**, solvent acetonitrile; reaction time 8 h; workup by flash chromatography on silica; methylene chloride/ethyl acetate 1:1 as the solvent; yield 2.16 g (80%) of **11b**; mp 65–68 °C (diethyl ether). ^{1}H NMR: 3.70 (ddd, 1 H), 3.55 (ddd, 1 H), 2.6 (dd, 1 H), 2.43 (AB, 1 H), 2.37 (AB, 1 H), 2.20 (AB, dd, m, 3 H), 1.90 (AB, 1 H), 1.70–1.85 (ddd, 1 H), 1.3–1.7 (m, 7 H), 1.00 (s, 3 H), 0.90 (s, 3 H). ^{13}C NMR: CH_3 (29.60, 28.38), CH_2 (56.02, 51.78, 46.84, 40.08, 39.13, 33.37, 31.26, 19.94), CH (45.50), C (211.44, 177.88, 62.53, 34.08). MS: calcd for $C_{15}H_{23}NO$ 233.1774, found 233.1777; fragments (intensity) 233 (32), 218 (12), 205 (10), 192 (14), 178 (20), 150 (34), 136 (24), 135 (29), 109 (72), 96 (100). IR (KBr) cm^{-1}: 2950 (CH), 2880 (CH), 2860 (CH), 1690 (C=O), 1615 (C=N).

Photolysis of 3-[(cyclopentenylmethyl)amino]-5,5-dimethyl-2-cyclohexen-1-one (5): 800 mg of **5**, solvent acetonitrile; reaction time 14.5 h; yield 280 mg of **5**, 320 mg of **12**; separation was accomplished by flash chromatography; solvent system methylene chloride/ethanol 9:1. **12**: oil. ^{1}H NMR: 4.97 (bs, 1 H), 4.92 (m, 1 H), 4.66 (m, 1 H), 4.06 (m, 1 H), 2.41 (m, 2 H), 2.27 (s, 2 H), 2.23 (dd, 2 H), 1.78–1.85 (m, 2 H), 1.58–1.67 (m, 2 H), 1.08 (s, 3 H), 1.04 (s, 3 H). ^{13}C NMR: CH_3 (27.69, 28.27), CH_2 (104.95, 50.21, 44.0, 32.65, 29.92, 24.38), CH (39.47), C (195.15, 158.44, 151.57, 108.4, 31.86). MS: calcd for $C_{14}H_{21}NO$ 219.1618, found 219.1621; fragments (intensity) 219 (100), 204 (16), 190 (22), 176 (44), 162 (22), 140 (42), 135 (90). IR (KBr) cm^{-1}: 3340 (NH), 3200 (NH), 3080 (R_2C=CH_2), 2960 (CH), 2880 (CH), 1650 (vin. amide), 1610 (vin. amide), 1550 (vin. amide).

Photolysis of 3-[(cyclohexenylmethyl)amino]-5,5-dimethyl-2-cyclohexen-1-one (6): 1.0 g of **6**;[10b] solvent acetonitrile; reaction time 18 h. After filtration over alumina with diethyl ether/ethanol (18:1), the resulting oily material was chromatographed under medium pressure on silica with ligroin/methylene chloride/ethanol (16:2:1). The resulting two fractions were further purified by HPLC using the same solvent system: yield 30 mg of **13**, 35 mg of **15**, 174 mg of starting material, 40 mg of unresolved mixture. **13**: oil. ^{1}H NMR: 4.74 (m, 1 H), 4.55 (bs, 2 H), 4.45 (m, 1 H), 3.92 (m, 1 H), 2.20–2.50 (m, 6 H), 1.2–1.9 (m, 6 H), 1.07 (s, 3 H), 1.02 (s, 3 H). ^{13}C NMR: CH_3 (28.67, 27.54), CH_2 (107.44, 50.15, 44.31, 35.82, 29.63, 27.45, 26.60), CH (37.17), C (195.02, 157.98, 146.68, 111.00, 31.88). MS: calcd for $C_{15}H_{23}NO$ 233.1780, found 233.1777; fragments (intensity) 233 (72), 218 (100), 216 (20), 204 (30), 201 (32), 191 (18), 190 (32), 152 (24), 83 (52). IR ($CHCl_3$) cm^{-1}: 3360 (NH), 3240 (NH), 3100 (R_2C=CH_2), 2960 (CH), 2880 (CH), 1715 (vin. amide), 1650 (vin. amide), 1620 (vin. amide), 1560 (vin. amide). **15**: oil. ^{1}H NMR: 3.76 (d, 1 H), 3.38 (d, 1 H), 2.75 (d, 1 H), 2.38 (dd, 1 H), 2.25 (dd, 1 H), 2.21 (m, 1 H), 2.16 (m, 1 H), 2.11 (m, 1 H), 2.00 (dd, 1 H), 1.55–1.77 (m, 8 H), 1.19 (s, 3 H), 1.11 (s, 3 H). ^{13}C NMR: CH_3 (33.60, 26.01), CH_2 (58.54, 50.23, 49.50, 42.67, 34.20, 30.16, 25.73, 22.92), CH (36.27), C (209.95, 198.24, 56.01, 36.91). MS: calcd for $C_{15}H_{23}NO$ 233.1780, found 233.1777; fragments (intensity) 233 (14), 218 (14), 205 (14), 204 (14), 190 (20), 177 (20), 176 (26), 148 (34), 124 (42), 109 (100), 94 (94). IR ($CHCl_3$) cm^{-1}: 2930 (CH), 2860 (CH), 1700 (C=O), 1640 (C=N).

Photolysis of 3-[(cyclohexenylmethyl)methylamino]-5,5-dimethyl-2-cyclohexen-1-one (7): 600 mg of **7**, solvent cyclohexane/*tert*-butyl alcohol (6:1); reaction time 10 h. After crude separation by flash chromatography on silica with methylene chloride/ethyl acetate (7:3), the nonpolar fraction was chromatographed with a medium pressure pump and a gradient solvent system with methylene chloride/ethyl acetate (95:5 changing to 70:30): yield 56 mg of **17**, 10 mg of **16**, 409 mg of starting material. **16**: oil. ^{1}H NMR: 4.86 (m, 1 H), 4.71 (m, 1 H), 4.39 (m, 1 H), 3.95 (m, 1 H), 2.91 (d, 3 H), 2.39 (m, 1 H), 2.37 (AB, 2 H), 2.32 (s, 2 H), 2.15 (m, 1 H), 1.74–1.84 (m, 2 H), 1.50–1.70 (m, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H). ^{13}C NMR: CH_3 (29.85, 29.01, 27.97), CH_2 (107.55, 49.86, 39.46, 35.77, 29.69, 27.44, 26.63), CH (37.12), C (193.48, 160.17, 147.04, 107.55, 31.48). MS: calcd for $C_{16}H_{25}NO$ 247.1936, found 247.1934; fragments (intensity) 247 (50), 232 (100), 218 (24), 204 (40), 201 (22), 190 (20). IR ($CHCl_3$) cm^{-1}: 3400 (NH), 3340 (NH), 3080 (R_2C=CH_2), 2940 (CH), 2860 (CH), 1705 (vin. amide), 1650 (vin. amide). **17**: oil. ^{1}H NMR: 3.30 (d, 1 H), 2.78 (bs, 1 H), 2.26 (s, 3 H), 2.0–2.19 (AB, 4 H), 1.91 (d, 1 H), 1.5–1.9 (m, 4 H), 1.5–1.3 (m, 3 H), 1.30 (s, 3 H), 1.1 (s, 3 H). ^{13}C NMR: CH_3 (36.66, 34.11, 31.30), CH_2 (58.94, 53.61, 34.97, 26.16, 23.88, 22.55, 22.02), CH (52.16, 45.02), C (209.84, 74.58, 49.32, 38.07). MS: calcd for $C_{16}H_{25}NO$ 247.1936, found 247.1932. The compound decomposes very rapidly.

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