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# Photochemical Syntheses of 2-Aza- and 2-Oxabicyclo[2.1.1]hexane Ring Systems[1]

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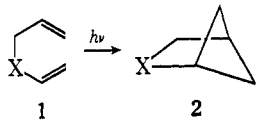
Irradiation of N-substituted 3-allylamino- and 3-allyloxy-5,5-dimethyl-2-cyclohexen-1-ones gives 2-aza- and 2-oxabicyclo[2.1.1]hexane derivatives, respectively, whose structures are assigned on the basis of the NMR spectral and chemical evidence. The photocycloaddition reaction of the *N*-methyl, *N*-allyl, and *N*-phenyl substituted allylamino and allyloxy derivatives produces exclusively or predominantly the thermodynamically unstable isomers, while the *N*-acetyl allylamino derivative gives a ca. 1:1 mixture of two possible isomers. It is suggested that the lone-pair electrons of the heteroatom play an important role in deciding the stereochemical course of this cycloaddition reaction.

Photochemical transformation of 1,5-hexadienes (**1**, X = $CH_2$) to bicyclo[2.1.1]hexanes (**2**, X = $CH_2$) has been extensively studied.[2] Several years ago, we initiated a photochemical study on 1,5-hexadienes containing a heteroatom (**1**, X = a heteroatom) with the hope that the reaction might be extended to the syntheses of the 2-heterobicyclo[2.1.1]hexane systems (**2**, X = a heteroatom). We now report the syntheses of the then unknown 2-azabicyclo[2.1.1]hexane ring system (**2**, X = NR)[3] from N-substituted 3-allylamino-5,5-dimethyl-2-cyclohexen-1-ones and the 2-oxabicyclo[2.1.1]hexane ring system (**2**, X = O)[4] from 3-allyloxy-5,5-dimethyl-2-cyclohexen-1-one. In addition, some chemical transformation reactions of the new heterocycles are described.

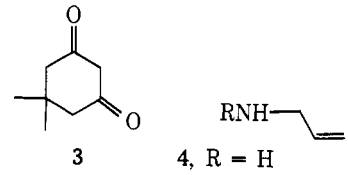


**1** **2**

## Results

3-Allylamino-2-cyclohexen-1-ones (**8–11**) were readily obtained from dimedone (**3**) and the corresponding allylamines (**4–7**) in 75, 71, 46, and 64% yields, respectively. Acetylation of **8** with acetic anhydride and pyridine gave *N*-acetate **12** (43%), *C*-acetate **13** (8%), and an unidentified product (11%). The structural assignments of **8–13** are consonant with elemental analyses and ir, uv, NMR, and mass spectral data (see Experimental Section).

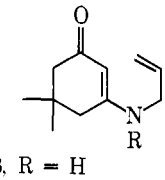
Irradiation of a 0.02 *M* cyclohexane solution of **9** with a 350-W high-pressure mercury lamp through a Pyrex filter for 10 hr resulted in the disappearance of **9** and the concomitant formation of a single photoproduct. The progress of the reaction was conveniently followed by TLC examination. The other aprotic solvents such as ether, benzene, acetone, and methylene chloride could be equally used, but the use of alcoholic solvents such as methanol or ethanol did not give a clear-cut result. The resulting photoproduct was isolated in 50–60% yield as a crystalline solid, mp 48.5–49.5°, by passing through a short alumina column after removal of the cyclohexane.



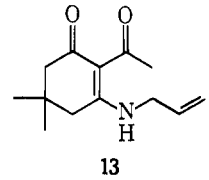
**3**



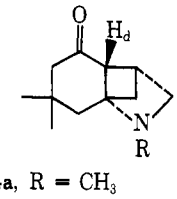
**4**, R = H
**5**, R = $CH_3$
**6**, R = $CH_2CH{=}CH_2$
**7**, R = $C_6H_5$



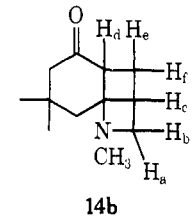
**8**, R = H
**9**, R = $CH_3$
**10**, R = $CH_2CH{=}CH_2$
**11**, R = $C_6H_5$
**12**, R = $COCH_3$



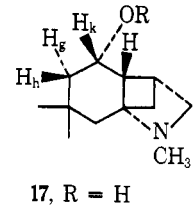
**13**



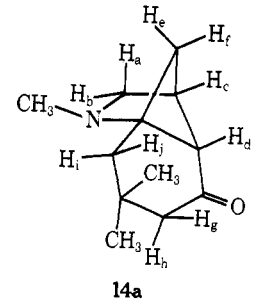
**14a**, R = $CH_3$
**15**, R = $CH_2CH{=}CH_2$
**16**, R = $C_6H_5$



**14b**



**17**, R = H
**18**, R = $COCH_3$



**14a**

The photoproduct was shown to be isomeric with **9** by elemental analysis and mass spectrometry. The ir (an absorption at 1710 $cm^{-1}$ typical of a six-membered ketone) and NMR (no olefinic proton signal) spectrum show no unsaturation, and thus it must be tricyclic. It formed a crystalline hydrochloride, indicating the presence of a basic nitrogen. The lithium aluminum hydride reduction in ether

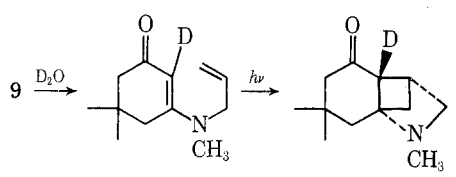
**Table I**
**NMR Data[a] for 2-Aza- and 2-Oxabicyclo[2.1.1]hexanes**

| Compd | Chemical shift,[b] τ | | | | | | Coupling constant, Hz | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ | $J_{ef}$ | $J_{ce}$ | $J_{cf}$ | $J_{ab}$ | $J_{de}$ |
| **14a** | 7.81 (d) | 6.60 (dd) | 7.10 (bs) | 7.53 (bs) | 8.29 (dd) | 8.47 (ddd) | 7.0 | 1.5 | 2.6 | 8.0 | 0 |
| 15 | 7.86 (bd) | 6.75 (dt) | 7.16 (bs) | 7.61 (bs) | 8.36 (dd) | 8.51 (ddd) | 7.0 | 1.0 | 2.6 | 8.5 | 0 |
| 16 | 5.99 (d) | 7.16 (d) | 6.99 (bs) | 7.41 (bs) | 8.21 (s) | 8.21 (s) | | | | 7.5 | 0 |
| 17 | 7.74 (d) | 6.38 (dd) | 7.17 (bs) | 8.61 (bs) | 8.40 (dd) | 8.79 (ddd) | 7.0 | 1.5 | 2.5 | 8.0 | 0 |
| 27 | 7.50 (d) | 7.07 (dd) | 7.03 (bs) | 7.60 (bs) | 8.51 (t) | 8.16 (ddd) | 8.5 | 0 | 3.0 | 8.0 | 8.5 |
| 31 | 6.26 (bd) | 6.77 (dt) | 6.95 (m) | 7.48 (bs) | 8.50 (dd) | 8.13 (ddd) | 7.0 | 1.5 | 2.5 | 7.5 | 0 |
| 32 | 6.59 (s) | 6.59 (s) | 6.88 (dt) | 7.51 (bs) | 8.59 (t) | 7.85[c] | 8.5 | 1.2 | 3.0 | | 8.5 |
| 37a | 6.05 (d) | 6.35 (d) | 6.81 (dt) | 7.49 (bs) | 8.35 (dd) | 8.21 (dd) | 7.5 | 0 | 2.7 | 6.0 | 1.5 |

[a] Spectra were determined with a Varian HA-100 (100 MHz). Other signals are given in the Experimental Section. [b] Chemical shifts relative to $Me_4Si$ in $CDCl_3$, s = singlet, d = doublet, t = triplet, m = multiplet, bs = broad singlet, bd = broad doublet, dd = doublet of doublets, ddd = doublet of double doublets. [c] Splitting pattern of this signal is uncertain because of its overlapping with other signals.

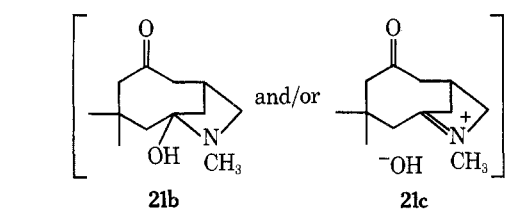
gave an oily secondary alcohol **17**,[5] which could be acetylated by treatment with acetic anhydride and pyridine to give an oily acetate **18**.

Careful examination of the NMR spectra (Table I) prompted us to assign structure **14a** rather than **14b** to the photoproduct. The spectrum (100 MHz) revealed an ABX pattern consisting of a broad signal (X part) at τ 7.10 ($H_c$), a doublet of doublets at 8.29 ($H_e$) ($J_{ef}$ = 7.0 and $J_{ce}$ = 1.5 Hz), a doublet of double doublets at τ 8.47 ($H_f$) ($J_{ef}$ = 7.0, $J_{cf}$ = 2.6, and $J_{bf}$ = 1.5 Hz[6]), and an AB pattern consisting of a doublet with a small splitting at τ 6.60 ($H_b$) ($J_{ab}$ = 8.0 and $J_{bf}$ = 1.5 Hz) and a doublet at τ 7.81 ($H_a$) ($J_{ab}$ = 8.0 Hz). These assignments were confirmed by decoupling and deuterium labeling experiments and experiments using a shift reagent, $Eu(DPM)_3$.[7] Irradiation of $H_b$ caused the doublet of $H_a$ to collapse to a singlet and the signal of $H_f$ into a doublet of doublets of $J$ = 7.0 and 2.6 Hz, and irradiation of $H_c$ converted the broad signal of $H_d$ into a sharp singlet and the signal of $H_f$ into a doublet of doublets of $J$ = 7.0 and 1.5 Hz. In the NMR spectrum of deuterated compound **20** prepared by irradiation of **19** which, in turn, was obtained by shaking a methylene chloride solution of **9** with deuterium oxide for 3 min, the signal of $H_d$ disappeared and the broad signal of $H_c$ was sharpened but the signals due to $H_e$ and $H_f$ remained unchanged. This result also eliminates the possibility of alternative structure **14b**. Addition of $Eu(DPM)_3$ to a solution of **14a** in deuteriochloroform caused significant low-field shifts of the signals due to $H_b$, $H_d$, $H_g$, and $H_h$, as a result of complexation of the shift reagent with the carbonyl oxygen atom. The observed coupling constants ($J_{ef}$ = 7.0, $J_{cf}$ = 2.6, and $J_{ce}$ = 1.5 Hz) are in good agreement with those reported for the bicyclo[2.1.1]hexane system.[8]

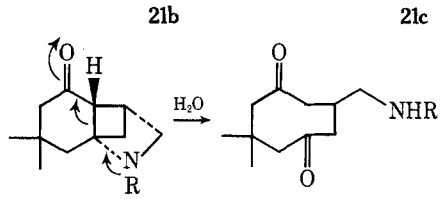



**19** **20**

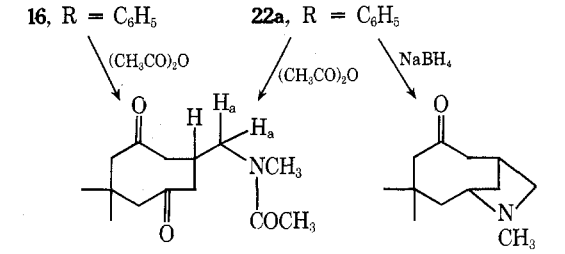
Final confirmation of structure **14a** was given by the chemical transformation. Compound **14a** was found to be labile in water and thus refluxing in water gave a crystalline compound **21** in 94% yield. On the basis of the spectral data (see Experimental Section), taken along with the following chemical evidence, this compound was shown to exist as an equilibrium mixture of the tautomeric isomers (**21a, 21b,** and/or **21c**).[9] Reduction of **21** with sodium borohydride afforded a new amino ketone **23,** whose ir spectrum shows the carbonyl absorption at 1680 $cm^{-1}$. This relatively low-frequency shift of the carbonyl band suggests the occurrence of a well-known transannular interaction between the nitrogen and the carbonyl group.[10] This was confirmed by converting it into the perchlorate **24** in which disappearance of the ir carbonyl band and the appearance of a new strong hydroxylic absorption were observed. On the other hand, acetylation of **21** with acetic anhydride gave the *N*-acetate **25a,** which was also obtained directly from **14a** upon similar treatment with acetic anhydride.



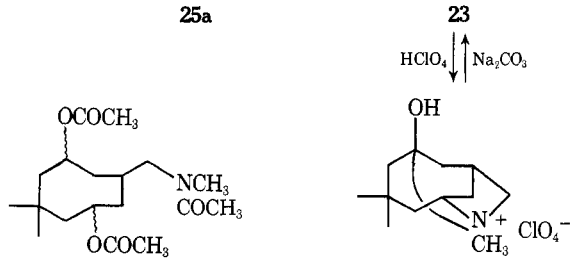

**21b** **21c**



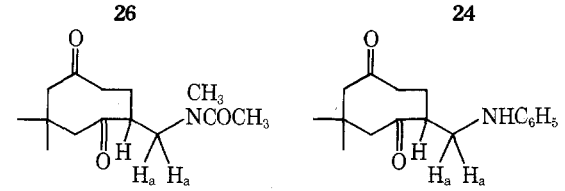

**14a**, R = $CH_3$ **21a**, R = $CH_3$
**16**, R = $C_6H_5$ **22a**, R = $C_6H_5$




**25a** **23**



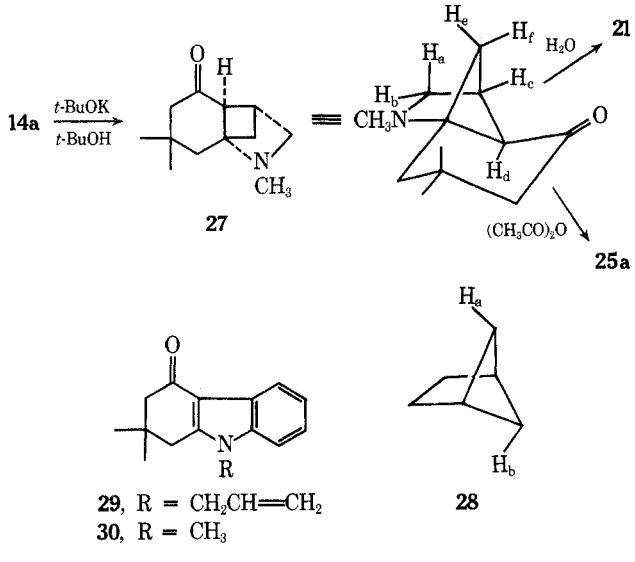

**26** **24**




**25b** **22b**

The mass spectrum of **25a** shows a base peak at *m/e* 86, corresponding to $CH_2{=}N^+(CH_3)COCH_3$. The structure assignment rests largely on the basis of the spectral data (see Experimental Section), a sodium borohydride reduction followed by acetylation to triacetate **26**, and the following deuterium exchange experiment. The *N*-acetate **25a** underwent facile incorporation of deuterium atoms at the four methylene groups adjacent to the carbonyl groups upon heating with deuterium oxide in the presence of sodium deuterioxide. The NMR spectrum showed that the doublet at $\tau$ 6.65 ascribable to two $H_a$'s remained unchanged, in accordance with the expectation based on structure **25a**. In contrast, if the photoproduct were **14b**, the *N*-acetate should be **25b**, in which the two $H_a$'s would be nonequivalent and appear as an AB part of an ABX pattern[11] which should become an AB quartet after deuterium exchange.

The stereochemistry of **14a** was confirmed by isolation of the epimer at $H_d$. Thus, treatment of **14a** with potassium *tert*-butoxide in *tert*-butyl alcohol gave an oily new basic substance **27**, whose structure was readily assigned on the basis of the NMR spectral (Table I) and chemical evidence. The most striking feature of the NMR spectrum is the long-range coupling between endo $H_e$ and endo $H_d$ ($J$ = 8.5 Hz). Such large coupling has been known to occur only if two protons ($H_a$ and $H_b$) in bicyclo[2.1.1]hexane (**28**) are in W configuration.[8] In comparison, this coupling was not observed in **14a**, in which $H_d$ has the exo configuration. Compound **27** was also transformed to **21** and **25a**.

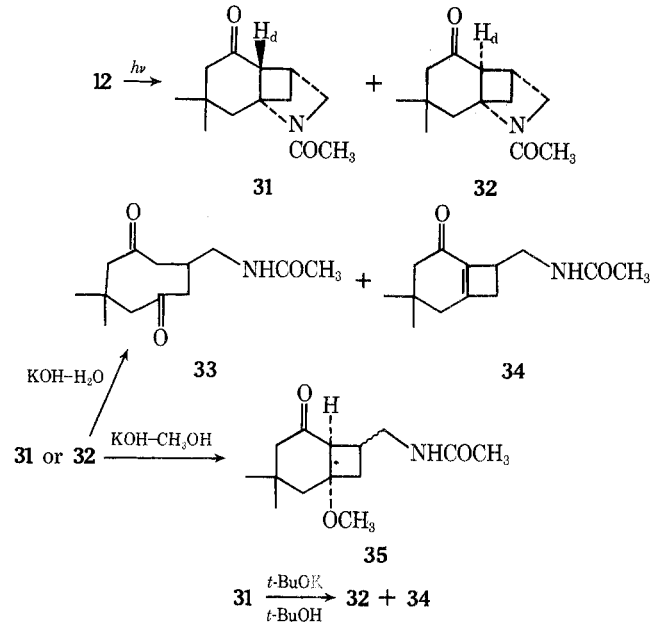



In a similar manner, irradiation of a 0.02 *M* cyclohexane solution of **10** gave a single crystalline product, mp 44–44.5°, in 63% yield, which showed a similar NMR spectrum (Table I) to that of **14a** except for the presence of signals due to an *N*-allyl group instead of the *N*-methyl singlet, thus establishing the structure as **15**.

On the other hand, irradiation of an ethereal solution of **11** gave two products in 39 and 6% yields. The structure of the major product **16**, mp 99–100°, was assigned on the basis of the NMR spectrum (Table I) and transformation to **22a**. Treatment of **16** with potassium hydroxide in aqueous methanol gave a cyclooctane-1,5-dione **22a** in 60% yield, whose ir and NMR spectra (see Experimental Section) suggested that **22a** exists as a diketo form. Deuterium exchange study of **22a** revealed that the doublet at $\tau$ 6.68 ascribed to two $H_a$'s remained unchanged, eliminating alternate structure **22b** from consideration. The stereochemical assignment of **16** was again deduced on the base of the NMR spectral examination which indicated the absence of the long-range coupling between $H_e$ and $H_d$.

The minor product, mp 146–147°, has the molecular formula $C_{17}H_{19}ON$ (elemental analysis and mass spectrometry). In agreement with the assigned structure **29**, this photoproduct exhibits an ir band at 1640 $cm^{-1}$. Its uv spectrum (see Experimental Section) was similar to that reported for carbazole **30**.[12] The final confirmation was given by the NMR spectrum, which shows four aromatic protons and signals characteristic of an allyl group. The formation of the carbazole **29** must be a result of the presence of the phenyl group which comprises a divinylamine system. Oxidative photocyclizations of the divinylamine system are well known.[13]

Irradiation of a 0.02 *M* ethereal solution of **12** under similar conditions was found to cause the rapid disappearance of the starting material (within 1 hr) and the concomitant formation of two photoproducts in a ratio of 1.07:1 (by NMR spectroscopy). The products could be isolated by preparative TLC to give **31**, mp 38–39°, and **32**, mp 69–70°, in 31 and 25% yields, respectively. The structures of **31** and **32** were apparent from the following spectral data and several interconversions. The principal features of the mass and ir spectra of both compounds **31** and **32** were markedly similar. The ir spectra of **31** and **32** show two strong carbonyl absorptions at 1715 and 1650 $cm^{-1}$. Heating of **31** or **32** in aqueous potassium hydroxide solution gave the same diketo acetate **33** accompanied by enone **34**, and treatment with potassium hydroxide in methanol resulted in the formation of the same methanol adduct **35**. Treatment of **31**



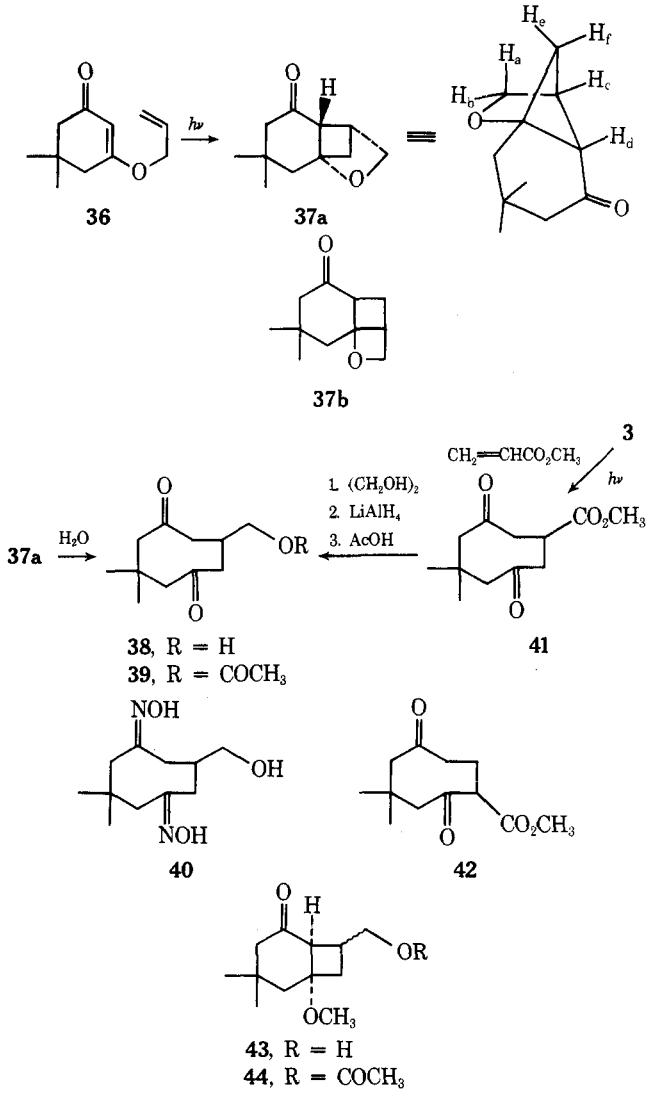

with potassium *tert*-butoxide in *tert*-butyl alcohol gave **32** in addition to **34**, while **32** was recovered unchanged under the similar conditions. Evidence for the structures of **33**, **34**, and **35** are given in the Experimental Section. The stereochemistry of **31** and **32** was firmly confirmed by examination of the NMR spectra; the long-range coupling between $H_d$ and $H_e$ ($J$ = 8.5 Hz) was observed in **32**, while **31** did not show such a coupling.

Irradiation of **8** in various solvents was attempted but the reaction proceeded only very slowly to give an unstable product in low yield accompanied by polymeric substance. Prolonged irradiation led to polymer formation.

Irradiation of a 0.02 *M* cyclohexane solution of **36** led to complete disappearance of starting material after 10 hr and appearance of a new spot on TLC. Evaporation of the solvent followed by submitting to preparative TLC on alumina gave a colorless oil in a yield greater than 72%. Although

TLC or GLC analyses indicated that it consists of a single component, its NMR spectrum clearly showed it to contain a trace amount of an unidentified product in addition to a major product.[14] Attempts to isolate the photoproducts in a pure form were unsuccessful. However, careful examination of the ir (1710 $cm^{-1}$) and NMR (Table I) spectra prompted us to assign structure **37a** rather than **37b** to the major product. The exo configuration of $H_d$ was suggested on the basis of the absence of a large long-range coupling between $H_d$ and $H_e$.

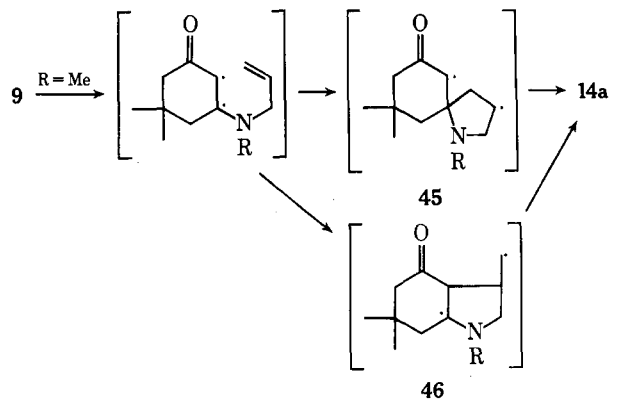
Confirmation of structure **37a** was given by the following chemical evidence. When the photoproduct was refluxed in water, a diketo alcohol **38** was obtained in 53% yield, which gave *O*-acetate **39** by treatment with acetic anhydride and pyridine, and dioxime **40** by treatment with hydroxylamine. The structure of **38** was established by an independent synthesis from dimedone (**3**). Thus, according to the procedure of de Mayo and coworkers,[15] we obtained diketo ester **41** in poor yield by irradiation of **3** and a large excess of methyl acrylate in cyclohexane. The ir spectrum of **41** (1735 and 1710 $cm^{-1}$) clearly excluded an alternative $\beta$-keto ester structure **42**. Ketalization of **41** followed by lithium aluminum hydride reduction and treatment with 90% acetic acid gave a diketo alcohol, which was identical with **38** in all respects.



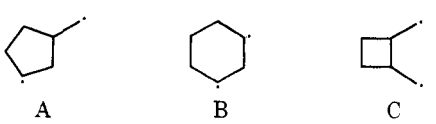

In order to obtain some supporting evidence on the stereochemistry of **37a**, epimerization of **37a** was attempted but without success. Thus, treatment with potassium *tert*-butoxide in *tert*-butyl alcohol gave a complex mixture, and treatment with sodium methoxide in methanol resulted in the addition of methanol to give 52% yield of an oily compound **43**. The structure of **43** was assigned on the basis of spectral (see Experimental Section) and chemical evidence. Thus, it gave *O*-acetate **44** upon treatment with acetic anhydride and pyridine, and afforded **38** upon treatment with hydrochloric acid in methanol.

## Discussion

In an attempt to clarify the reactive species in this photocycloaddition reaction, energy transfer experiments were carried out on **9** and **12**. The reaction (**9** → **14a**) was found to be effectively sensitized by acetophenone and benzophenone, and quenched by phenanthrene, naphthalene, and piperylene. Figure 1 shows a plot of the reciprocal of the relative quantum yield for the cycloaddition reaction of **9** against piperylene concentration. The linearity of the Stern–Volmer plot as well as sensitizing experiments confirms that the cycloaddition reaction (**9** → **14a**) occurs via the triplet excited state. Taking into account the results of earlier studies on the intermolecular[16] and intramolecular[2] photocycloaddition of $\alpha,\beta$-unsaturated ketones to alkenes, it would appear that the most likely initial step of the reaction of **9** would involve the n → $\pi^*$ excitation of the enone group,[17] raising the enone portion to an excited triplet state. The excited enone can undergo a cross addition to the double bond via either diradical intermediate **45** or **46**, leading to 2-azabicyclo[2.1.1]hexanes (e.g., **14a**).




There was no evidence for the formation of the parallel addition products [2-azabicyclo[2.2.0]hexanes (i.e., **14b**)]. The preference for forming cross addition products (bicyclo[2.1.1]hexanes) over parallel addition products (bicyclo[2.2.0]hexanes) in the photocycloaddition reaction of 1,5-hexadienes [1, (X = $CH_2$)] is a well-known phenomenon but still a disputable problem. Recently, it has been suggested that the formation of the five-membered ring intermediate (A) leading to bicyclo[2.1.1]hexanes is preferred to the other possible six- (B) or four-membered ring intermediates (C) in terms of strain and entropy factors;[2c,18] apparently, the stability of the diradical is not an important factor.

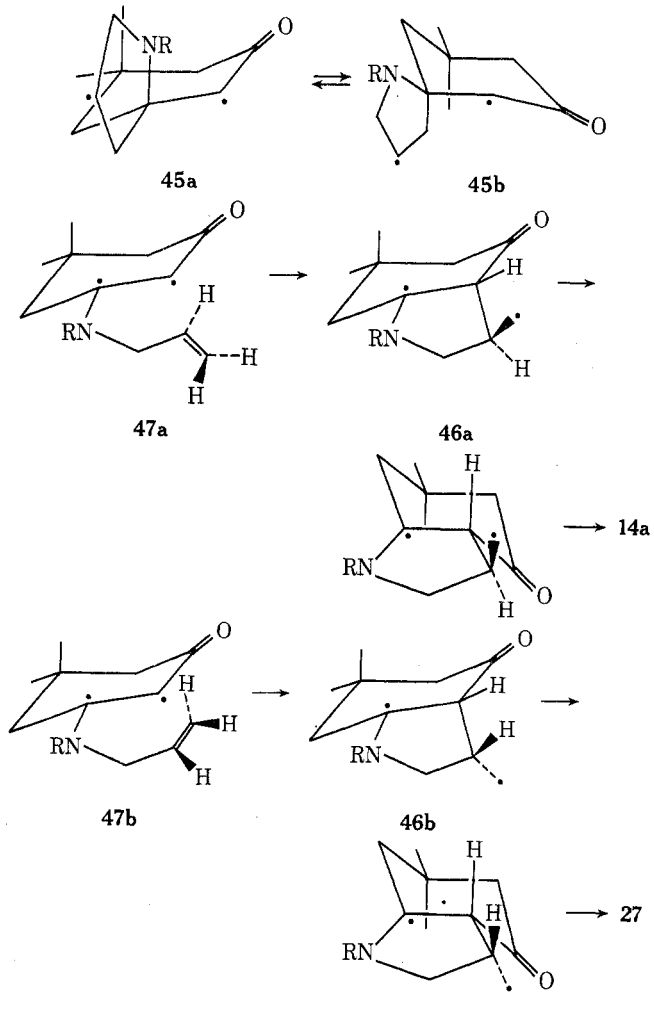



It should be emphasized here that the cycloaddition reaction of **9–11** and **36** produces exclusively or predominantly the thermodynamically unstable isomers,[19] while **12** gave a ca. 1:1 mixture of two possible stereoisomers. In addition, it is noteworthy that the reaction is significantly faster with the *N*-acetyl derivative **12** than with the *N*-methyl **9** or *N*-allyl derivative **10**. These observations suggest that the

lone-pair electrons of the heteroatom play important role in deciding the stereochemical course of this cycloaddition reaction.

The formation of the trans-fused 6–4 ring system from the reaction of **9–11** and **36** is formally related to the intermolecular cycloaddition reactions of cyclohexenones to alkenes in which thermodynamically unstable trans-fused bicyclo[4.2.0]octanones are predominatly produced.[16] However, it has not yet been clarified why the trans adducts should be formed in the latter reaction, although a few interpretations are presented.[16]

Although some interpretations for the stereospecific formation of **14a** from **9** may also be possible (for example, see ref 2c), our interpretation is based on the stereochemical arguments. Thus, if the reaction of **9** is assumed to proceed through intermediate **45** (mechanism a), two conformations **45a** and **45b** may be considered. However, examination of molecular models using $sp^2$-hybridized carbons for the radical center reveals no marked steric effects which would favor the formation of **14a** over **27** from either conformers; thus, if this reaction is kinetically controlled, the formation of both isomers **14a** and **27** is expected by this mechanism. On the other hand, if alternative intermediate **46** is involved (mechanism b), the initial bond formation may produce two configurational isomers **46a** (leading to the observed product **14a**) and **46b** via the corresponding transition states **47a** and **47b**. Examination of models suggests that approach of the olefinic bond to the radical center at the $\alpha$ position to the ketone as shown in **47b** would be expected to be severely hindered as a result of eclipsing of the double bond with the $C^2H$–$C^1$=O bond.[20] Nonbonded interactions of this type are not involved in the transition state **47a**, and thus formation of **46a** would be favored.



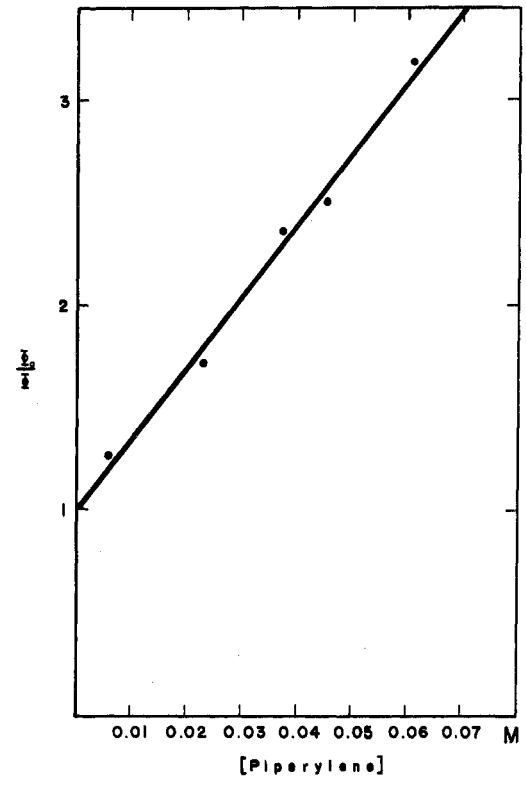




**Figure 1.** Stern–Volmer plot of quenching of photocycloaddition of **9** (0.009 *M*) by piperylene in ether. The identity and yield of the product **14a** were determined by GLC analysis at 150° and SE-30.

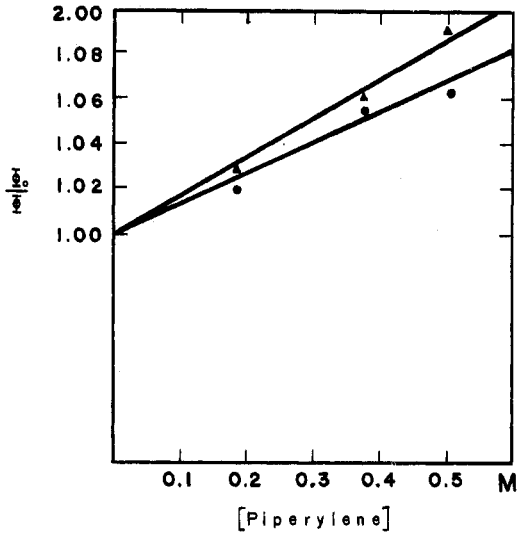



**Figure 2.** Stern–Volmer plot of quenching of photocycloaddition of **12** (0.01 *M*) by piperylene in ether: ●, **31**; ▲, **32**. The identity and yield of the products **31** and **32** were determined by GLC analysis at 150° on 15% BSP.

The lack of stereospecificity in the cycloaddition of **12**, however, can not be explained by mechanism b, unless it is assumed that the different excitation processes in **12** and the nonacylated compounds **9–11** and **36** operate. In fact, energy transfer experiments of **12** suggested the participation of a different precursor from that of **9**: the reaction (**12** → **31** and **32**) was not sensitized by benzophenone and the slope of the Stern–Volmer plots[21] for the quenching of the isomerization of **12** by piperylene (Figure 2) is about 20 times lower than that of **9**. Assuming that the quenching is diffusion controlled, this indicates the difference of the magnitude in the lifetime of the reacting species of **12** and **9**. Thus, whereas it is clear that compound **9** reacts via the

triplet state, the reaction of **12** may involve a different excited state from that of **9**, presumably a singlet or a triplet pathway; this could also be responsible for the rapid reaction rate of **12**. As one possibility, one can imagine the intermediate **45** (R = acetyl) being involved in the reaction of **12**. However, until more suitable evidence is available, further speculation concerning mechanistic problems must be postponed.

## Experimental Section

Melting points are uncorrected. Unless otherwise stated, NMR spectra were determined with an Hitachi R-20A spectrometer (tetramethylsilane as internal standard). Ir spectra were recorded with an Hitachi EPI-G2 spectrophotometer, and uv spectra with an Hitachi 124 spectrophotometer. Mass spectra were obtained with an Hitachi RMU-6D with a direct inlet system operating at 70 eV. Preparative TLC was carried out on Merck alumina $PF_{254}$. Unless otherwise stated, the petroleum ether used was the fraction having bp 30–60°. Uv irradiation were carried out in a Pyrex vessel at room temperature, using an Eikosha 350-W high-pressure mercury lamp.

**3-Allylamino-5,5-dimethyl-2-cyclohexen-1-one (8).** A solution of 7 g of dimedone (**3**) and 5 g of allylamine (**4**) in 40 ml of benzene was heated in a sealed tube at 100° for 7 hr. After the solvent was removed, the residual oil was distilled [bp 146° (0.08 mm)] to give 6.72 g (75%) of **8**, which solidified on standing: mp 75–75.5° (from $Et_2O$); ir ($CHCl_3$) 3440, 1590 $cm^{-1}$; uv max (EtOH) 289 nm (log $\epsilon$ 4.43); NMR ($CDCl_3$) $\tau$ 3.85–4.45 (m, 1, $-CH{=}CH_2$), 4.50 (br, 1, NH), 4.60–4.95 (m, 2, $-CH{=}CH_2$), 4.92 (s, 1, 2-H), 6.28 (br, 2, $J$ = 5.5 Hz, $-CH_2CH{=}CH_2$), 7.79 (s, 2, 6-H), 7.86 (s, 2, 4-H), 8.96 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 179 ($M^+$).

Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.83; H, 9.69; N, 7.68.

**3-(*N*-Methylallylamino)-5,5-dimethyl-2-cyclohexen-1-one (9).** A solution of 2.9 g of **3** and 1.9 g of allylmethylamine (**5**) in 50 ml of benzene was heated in a sealed tube at 100° for 5 hr. After evaporation of the solvent, distillation of the residual oil [bp 116° (0.08 mm)] gave 2.75 g (71%) of **9** as a yellow, viscous oil: ir ($CHCl_3$) 1600, 1550 $cm^{-1}$; uv max (EtOH) 299 nm (log $\epsilon$ 4.48); NMR ($CDCl_3$) $\tau$ 3.9–4.6 (m, 1, $-CH{=}CH_2$), 4.6–5.2 (m, 2, $-CH{=}CH_2$), 4.85 (s, 2-H), 6.0–6.4 (m, 2, $-CH_2CH{=}CH_2$), 7.05 (s, 3, $NCH_3$), 7.70 (s, 2, 6-H), 7.84 (s, 2, 4-H), 8.92 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 193 ($M^+$).

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.54; H, 9.91; N, 7.25. Found: C, 74.12; H, 9.99; N, 7.01.

**3-Diallylamino-5,5-dimethyl-2-cyclohexen-1-one (10).** A solution of 2.8 g of **3** and 2.95 g of diallylamine (**6**) in 50 ml of benzene was heated in a sealed tube at 100° for 7 hr. After removal of the solvent, distillation of the residual oil [bp 146–152° (0.45 mm)] gave 2.85 g (46%) of **10**: ir ($CHCl_3$) 1595, 1550 $cm^{-1}$; uv max (EtOH) 301 nm (log $\epsilon$ 4.50); NMR ($CDCl_3$) $\tau$ 3.85–4.5 (m, 2, 2-$CH{=}CH_2$), 4.6–5.1 (m, 4, 2-$CH{=}CH_2$), 4.75 (s, 1, 2-H), 6.15 (br d, 4, $J$ = 5.5 Hz, 2-$CH_2CH{=}CH_3$), 7.70 (s, 2, 6-H), 7.83 (s, 2, 4-H), 8.92 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 219 ($M^+$).

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.27; H, 9.77; N, 6.51.

**3-(*N*-Allylanilino)-5,5-dimethyl-2-cyclohexene-1-one (11).** A solution of 1 g of **3** and 1 g of *N*-allylaniline (**7**) in 50 ml of toluene was refluxed in the presence of 1 drop of sulfuric acid in a flask equipped with a Dean-Stark trap for 20 hr. The solvent was removed and the residue was chromatographed on alumina. Elution with benzene–ethyl acetate (7:3) gave 1.16 g (64%) of **11** as a colorless oil, which solidified on standing: mp 64–65° (from *n*-hexane); ir ($CHCl_3$) 1605, 1555 $cm^{-1}$; uv max (EtOH) 302 nm (log $\epsilon$ 4.51); NMR ($CDCl_3$) $\tau$ 2.30–2.97 (m, 5, aromatic), 3.75–4.45 (m, 1, $-CH{=}CH_2$), 4.71 (s, 1, 2-H), 4.70–5.10 (m, 2, $-CH{=}CH_2$), 5.85 (dt, 2, $J$ = 5.0 and 1.5 Hz, $-CH_2CH{=}CH_2$), 7.91 (s, 2, 6-H), 7.96 (s, 2, 4-H), 9.06 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 255 ($M^+$).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.04; H, 8.36; N, 5.40.

**3-(*N*-Allylacetamido)-5,5-dimethyl-2-cyclohexen-1-one (12) and 2-Acetyl-3-allylamino-5,5-dimethyl-2-cyclohexen-1-one (13).** A solution of 1 g of **8** in 0.6 ml of pyridine and 4 ml of acetic anhydride was refluxed for 1 hr. After removal of the solvent in vacuo, the residual oil was chromatographed on alumina using petroleum ether–ether (3:7) as solvent to give 525 mg (43%) of **12** as a colorless oil: ir ($CHCl_3$) 1650, 1580 $cm^{-1}$; uv max (EtOH) 282 nm (log $\epsilon$ 4.02); NMR ($CDCl_3$) $\tau$ 3.84–4.96 (m, 1, $-CH{=}CH_2$), 4.20 (s, 1, 2-H), 4.70–5.05 (m, 2, $-CH{=}CH_2$), 5.83 (dt, 2, $J$ = 5.0 and 1.5 Hz, $-CH_2CH{=}CH_2$), 7.55 (s, 2, 6-H), 7.78 (s, 2, 4-H), 7.88 (s, 3, $COCH_3$), 8.94 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 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, 8.71; N, 6.10.

Further elution with the same solvent gave 104 mg (8%) of **13**: mp 40–41° (from petroleum ether); ir ($CHCl_3$) 1630, 1570 $cm^{-1}$; uv max (EtOH) 260 nm (log $\epsilon$ 4.11), 292 (4.14); NMR ($CDCl_3$) $\tau$ −2.7 (br, 1, NH), 3.78–4.90 (m, 1, $-CH{=}CH_2$), 4.55–5.00 (m, 2, $-CH{=}CH_2$), 6.03 (m, 2, $-CH_2CH{=}CH_2$), 7.51 (s, 3, $COCH_3$), 7.61 (s, 2, 6-H), 7.76 (s, 2, 4-H), 8.99 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 221 ($M^+$).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.34; H, 8.78; N, 6.73.

Further elution with the same solvent gave 138 mg of an unstable oily product which was not further examined.

**Irradiation of 9.** A solution of 4 g of **9** in 1 l. of cyclohexane was irradiated for 10 hr. The solvent was removed and the residue was chromatographed on alumina. Elution with petroleum ether–ether (10:1) gave a solid which was recrystallized from petroleum ether to give 2.0–2.4 g (50–60%) of **14a**: mp 48.5–49.5°; ir ($CHCl_3$) 1710 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.70 (s, 3, $NCH_3$), 7.86 (s, 2, $H_g$ and $H_h$), 8.12 (center of AB q, 2, $J$ = 14.0 Hz, $H_i$ and $H_j$), 8.66 and 8.86 [2 s, 6, $-C(CH_3)_2$]. The NMR spectrum of 38 mg of **14a** in 0.4 ml of $CDCl_3$ in the presence of 15 mg of $Eu(DPM)_3$ showed the following signals: $\tau$ 6.38 (dd, 1, $H_b$), 7.05 (br s, 1, $H_c$), 7.37 (br s, 1, $H_d$), 7.65 (s, 2, $H_g$ and $H_h$), 7.70 (s, 3, $NCH_3$), 7.80 (d, 1, $H_a$), 8.08 (s, 2, $H_i$ and $H_j$), 8.27 (dd, 1, $H_e$), 8.45 (ddd, 2, $H_f$), 8.64 and 8.86 [2 s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 193 ($M^+$).

Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.25; H, 9.86; N, 7.37.

The hydrochloride was prepared by passing dry hydrogen chloride into an anhydrous ethereal solution of **9**. The precipitated white solid was collected and recrystallized from ethyl acetate: mp 139–140.5°; ir ($CHCl_3$) 2100–2600, 1720 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{20}NOCl{\cdot}H_2O$: C, 58.17; H, 8.95; N, 5.65. Found: C, 58.04; H, 8.92; N, 5.80.

**Reduction of 14a.** A solution of 728 mg of **14a** in 10 ml of anhydrous ether was added to a suspension of 230 mg of lithium aluminum hydride in 10 ml of anhydrous ether and the mixture was stirred at room temperature overnight. After an usual work-up procedure, distillation [bp 75–85° (bath temperature) (0.2 mm)] afforded 621 mg (85%) of **17**: ir ($CHCl_3$) 3660 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.04 (q, 1, $J$ = 3.0 Hz, $H_k$), 7.68 (s, 3, $NCH_3$), 8.19 (dd, 1, $H_g$, $J$ = 3 and 14 Hz), 8.32 (center of AB q, 2, $J$ = 13.5 Hz, $H_i$ and $H_j$), 8.66 (m, 1, $H_h$), 8.70 and 9.08 [2 s, 6, $-C(CH_3)_2$].

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.33; H, 10.82; N, 7.24.

**Acetylation of 17.** A mixture of 275 mg of **17** in 0.5 ml of pyridine and 0.5 ml of acetic anhydride was allowed to stand at room temperature overnight. The solvent was removed, the residue was dissolved in benzene, and the solution was washed ($Na_2CO_3$, NaCl) and dried ($MgSO_4$). After evaporation of the solvent, the residual oil was distilled [bp 100–110° (bath temperature) (0.25 mm)] to give 113 mg (34%) of **18**, ir ($CHCl_3$) 1720 $cm^{-1}$.

Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.70; H, 9.70; N, 5.75.

**3-(*N*-Methylallylamino)-2-deuterio-5,5-dimethyl-2-cyclohexen-1-one (19).** A solution of 564 mg of **9** in 2 ml of methylene chloride and 1 ml of deuterium oxide was well shaken for 3 min and concentrated to give a crude oil of **19**. The NMR spectrum indicated the absence of 2-H.

**Irradiation of 19.** A solution of 503 mg of **19** in 300 ml of cyclohexane was irradiated for 10 hr. The solvent was removed and the residue was distilled [bp 80–90° (bath temperature) (0.1 mm)] to give 243 mg (48%) of **20**, whose NMR spectrum indicated the absence of $H_d$.

**3-Methylaminomethyl-7,7-dimethylcyclooctane-1,5-dione (21a).** A mixture of 1 g of **14a** and 30 ml of water was refluxed with stirring. After 3 hr, **14a** was completely dissolved in water. After removal of water, the residual solid was recrystallized from petroleum ether to give 1.03 g (94%) of **21a**: mp 79.5–80.5°; ir (KCl) 3300, 1685 $cm^{-1}$; ($CHCl_3$) 1700 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.2–7.5 (m, 8), 7.54 (s, 3, $NCH_3$), 7.66–8.06 (m, 4), 8.90 [s, 6, $-C(CH_3)_2$]; ($H_2O$) $\tau$ 7.00 (m, 1, 3-H), 7.44 (center of AB q, 4, $J$ = 12.0 Hz, 6-H and 8-H), 7.46 (d, 2, $J$ = 6.0 Hz, $-CHCH_2N$), 7.67 (s, 3, $NCH_3$), 7.35–8.15 (m, 4, 2-H and 4-H), 8.88 and 8.98 (2 s, 6, $-C(CH_3)_2$]; in the NMR spectrum in $D_2O$ the signals due to 2-H and 4-H disappeared. This may be a result of the occurrence of an intramolecular abstraction of the 2-H and 4-H by the amino group, since the *N*-

acetate **25a** did not show such a deuterium exchange; mass spectrum *m/e* 193 (M − 18).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.31; H, 10.15; N, 6.49.

Its hydrochloride: mp 155–156° dec (from EtOH); ir (KCl) 3370, 2430, 1700, 1630 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{22}NO_2Cl$: C, 58.17; H, 8.95; N, 5.65. Found: C, 58.08; H, 8.66; N, 5.74.

**3-(*N*-Allylacetamido)-5,5-dimethyl-2-cyclohexen-1-one (12) and Dione (25a).** A solution of 100 mg of **21** in 3 ml of acetic anhydride was refluxed for 4.5 hr. The solvent was removed and the residue was recrystallized from ligroin to give 103 mg (86%) of **25a:** mp 130°; ir (KCl) 1700, 1640 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.65 (d, 2, $J$ = 7.0 Hz, $-CHCH_2N$), 6.92 (s, 3, $NCH_3$), 6.97 (br, 1, 3-H), 7.56 (center of AB q, 4, $J$ = 12.0 Hz, 6-H and 8-H), 7.55–7.88 (m, 4, 2-H and 4-H), 7.87 (s, 3, $COCH_3$), 8.98 [s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* (rel intensity) 253 ($M^+$, 2), 86 (100, $CH_2{=}N^+(CH_3)COCH_3$).

Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.48; H, 9.37; N, 5.43.

**Deuteration of 25a.** A solution of 30 mg of **25a** in 0.5 ml of deuterium oxide containing 3 mg of NaOD and a small amount of sodium 3-trimethylsilylpropanesulfonate as internal reference was heated at 80° for 10 min. The NMR spectrum was then recorded. The signals due to the four methylene groups adjacent to the carbonyl groups disappeared.

**3-(*N*-Acetylmethylaminomethyl)-1,5-diacetoxy-7,7-dimethylcyclooctane-1,5-dione (26).** To a solution of 141 mg of **25a** in 1.5 ml of ethanol was added 142 mg of sodium borohydride, and the mixture was stirred at room temperature for 2 hr. After the excess hydride was decomposed by acetic acid, the solution was made alkaline with saturated sodium bicarbonate and extracted with ether. The dried extract was concentrated and the residue was dissolved in 1 ml of acetic anhydride and 1 ml of pyridine. The mixture was allowed to stand overnight at room temperature. The solvent was removed and the residue was recrystallized from petroleum ether–ether to give 32 mg (17%) of **26:** mp 83–86°; ir ($CHCl_3$) 1725, 1630 $cm^{-1}$.

Anal. Calcd for $C_{18}H_{31}NO_5$: C, 63.31; H, 9.15; N, 4.10. Found: C, 63.19; H, 9.18; N, 4.13.

**5,5,8-Trimethyl-8-azabicyclo[5.2.1]decan-3-one (23).** To a solution of 150 mg of **21** in 1.5 ml of ethanol was added 11 mg of sodium borohydride and the mixture was stirred at room temperature overnight. After the excess hydride was decomposed with acetic acid, the solution was made alkaline with saturated sodium bicarbonate and extracted with ether. After the extract was dried ($MgSO_4$) and concentrated, the residue was distilled [bp 100–110° (bath temperature) (0.1 mm)] to give 101 mg (70%) of **23,** which solidified on standing: mp 61–62° (from petroleum ether); ir ($CHCl_3$) 1680 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.22 (d, 2, $J$ = 12.0 Hz), 8.06 (d, 2, $J$ = 12.0 Hz), 7.34–7.48 (m, 6), 7.84 (s, 3, $NCH_3$), 8.25 (dd, 1, $J$ = 15.0 and 6.0 Hz), 8.58 (d, 1, $J$ = 15.0 Hz), 8.85 (s, 3), 9.08 (s, 3); mass spectrum *m/e* 195 ($M^+$).

Anal. Calcd for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 73.65; H, 11.01; N, 7.06.

Its perchlorate **24** was prepared by adding 70% perchloric acid to an ethereal solution of **23.** The precipitated crystals were recrystallized from EtOH: mp 280° dec; ir (KCl) 3380, 1100–1080 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{22}NO_5Cl$: C, 48.73; H, 7.50; N, 4.73. Found: C, 48.67; H, 7.62; N, 4.60.

An aqueous solution of 65 mg of the perchlorate **24** was made alkaline with saturated $Na_2CO_3$ and extracted with ether and the extract was dried ($MgSO_4$). Evaporation of the solvent gave 33 mg of **23,** mp 61–62°.

**Epimerization of 14a.** A solution of 130 mg of **14a** and 25 mg of potassium *tert*-butoxide in 5 ml of *tert*-butyl alcohol was warmed at 50–60° for 5 min with stirring. After removal of the solvent in vacuo, anhydrous ether was added to the residue and insoluble material was removed by filtration. Removal of the solvent followed by distillation [bp 75–85° (bath temperature) (0.1 mm)] gave 84 mg (65%) of **27:** ir ($CHCl_3$) 1705 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.12 (s, 3, $NCH_3$), 7.85 (center of AB q, 2, $H_g$ and $H_h$, $J$ = 13.5 Hz), 8.29 (center of AB q, 2, $H_i$ and $H_j$, $J$ = 14.0 Hz), 8.87 and 8.94 (2 s, 6, $-C(CH_3)_2$]; the mass spectrum was identical with that of **14a.**

Its hydrochloride was prepared by passing dry hydrogen chloride into an ethereal solution of **27:** mp 139–140° (from ethyl acetate); ir (KCl) 3490, 3420, 2700–2200, 1720 $cm^{-1}$.

Anal. Calcd for $C_{12}H_{20}NOCl{\cdot}H_2O$: C, 58.17; H, 8.95; N, 5.65. Found: C, 58.31; H, 9.10; N, 5.65.

**Transformation of 27 to 21.** A mixture of 65 mg of **27** in 1 ml of $H_2O$ was allowed to stand overnight, and removal of the solvent gave a quantitative yield of **21,** mp 79.5–80.5°.

**Transformation of 27 to 25a.** A solution of 75 mg of **21** in 3 ml of acetic anhydride was heated at 80° for 1 hr. The solvent was removed and the residue was recrystallized from ligroin to give 71 mg (72%) of **25a,** mp 130°.

**Irradiation of 10.** A solution of 200 mg of **10** in 20 ml of cyclohexane was irradiated for 7 hr and the solvent was removed. Distillation [bp 115–140° (bath temperature) (0.1 mm)] of the residue gave 125 mg (63%) of **15** as a colorless oil, which crystallized on standing: mp 44–44.5° (from petroleum ether); ir ($CHCl_3$) 1705, 1640 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 3.98–4.44 (m, 1, $-CH{=}CH_2$), 4.70–5.10 (m, 2, $-CH{=}CH_2$), 6.45–6.69 (m, 2, $NCH_2$–), 7.93 (s, 2, $H_g$ and $H_h$), 8.14 (center of AB q, 2, $J$ = 14.0 Hz, $H_i$ and $H_j$), 8.75 and 8.94 [2 s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* 219 ($M^+$).

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.78; H, 9.73; N, 6.62.

**Irradiation of 11.** A solution of 465 mg of **11** in 50 ml of ether was irradiated for 3 hr. Removal of the solvent left a mixture of two compounds which could be separated by preparative tlc using petroleum ether–ether (1:1) as solvent. The fast-moving component was identified as **16.** Recrystallization from petroleum ether gave 180 mg (39%) of white crystals: mp 99–100°; ir ($CHCl_3$) 1705, 1595 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 2.65–3.25 (m, 5, aromatic), 7.50 (center of AB q, 2, $J$ = 14.0 Hz, $H_i$ and $H_j$), 7.86 (s, 2, $H_g$ and $H_h$), 8.94 and 9.02 [2 s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* 255 ($M^+$).

Anal. Calcd for $C_{17}H_{21}NO$: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.16; H, 8.43; N, 5.76.

The slower moving component was identified as **29.** Recrystallization from *n*-hexane afforded 30 mg (6%) of white crystals: mp 146–147°; ir ($CHCl_3$) 1640 $cm^{-1}$; uv max (MeOH) 216 nm (log $\epsilon$ 4.46), 245 (4.27), 267 (4.07), 301 (4.13); NMR ($CDCl_3$) $\tau$ 1.66–1.84 (m, 1), 2.64–2.77 (m, 3), 3.85–4.25 (m, 1), 4.70–5.06 (m, 2), 5.15–5.35 (m, 2), 7.24 (s, 2), 7.55 (s, 2), 8.85 (s, 6); mass spectrum *m/e* 253 ($M^+$).

Anal. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53. Found: C, 80.56; H, 7.84; N, 5.64.

**3-Anilinomethyl-7,7-dimethylcyclooctane-1,5-dione (22a).** A mixture of 50 mg of **16** and 400 mg of KOH in 5 ml of 90% methanol was refluxed for 20 hr. The solvent was removed and the residue was extracted with ether. The extract was dried ($MgSO_4$) and concentrated. The residue was purified by preparative TLC using ether as solvent to give 32 mg (60%) of **22a:** mp 109–110° (from petroleum ether); ir ($CHCl_3$) 3320, 1695, 1600 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 2.67–3.55 (m, 5, aromatic), 6.10 (br, 1, NH), 6.90 (d, 2, $J$ = 6.5 Hz, $-CHCH_2N$), 7.24 (br, 1, 3-H), 7.59 (center of AB q, 4, $J$ = 12 Hz, 6-H and 8-H), 7.15–7.95 (m, 4, 2-H and 4-H), 8.90 (s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* 273 ($M^+$).

Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.79; H, 8.53; N, 5.25.

**Deuteration of 22a.** A solution of 30 mg of **22a** in 0.3 ml of deuterium oxide and 0.3 ml of pentadeuteriopyridine containing 5 mg of NaOD and a small amount of sodium 3-trimethylsilylpropanesulfonate as internal reference was heated at 80° for 10 min. The NMR spectrum was then recorded. The signals due to the four methylene groups adjacent to the carbonyl groups disappeared.

**Irradiation of 12.** A solution of 152 mg of **12** in 50 ml of ether was irradiated for 45 min. The solvent was removed and the residue was submitted to preparative TLC using petroleum ether–ether (3:7) as solvent to give 46 mg (31%) of **31** and 37 mg (25%) of **32.** Compound **31** had mp 38–39° (from petroleum ether); ir ($CHCl_3$) 1715, 1650 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.64 and 8.08 (2 d, 2, $H_i$ and $H_j$, $J$ = 14.0 Hz), 7.89 (center of AB q, 2, $J$ = 14.0 Hz, $H_g$ and $H_h$), 8.05 (s, 3, $COCH_3$), 8.97 [s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* 221 ($M^+$).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.73; H, 8.69; N, 6.31.

Compound **32** had mp 69–70° (from petroleum ether); ir ($CHCl_3$) 1715, 1650 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.53 (center of AB q, 2, $J$ = 14.0 Hz, $H_i$ and $H_h$), 7.83 (center of AB q, 2, $J$ = 14.0 Hz, $H_g$ and $H_h$), 7.99 (s, 3, $COCH_3$), 8.86 and 8.98 [2 s, 6, $-C(CH_3)_2$]; mass spectrum *m/e* 221 ($M^+$).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.32; H, 8.68; N, 6.31.

**3-(*N*-Acetylaminomethyl)-7,7-dimethylcyclooctane-1,5-dione (33) and 8-(*N*-Acetylaminomethyl)-4,4-dimethylbicyclo[4.2.0]oct-1-en-2-one (34). A. From 31.** A solution of 80 mg of **31** in 1 ml of 10% aqueous KOH solution was refluxed for 15 min and concentrated. Anhydrous ether was added to the residue and

insoluble material was removed by filtration. Evaporation of the solvent and separation by preparative TLC using ether as solvent gave 45 mg (52%) of **33** and 8 mg (10%) of **34**.

Compound **33**: mp 120.5–121.5° (from petroleum ether); ir ($CHCl_3$) 3440 (NH), 1695 (C=O), 1670 $cm^{-1}$ (NHC=O); NMR ($CDCl_3$) $\tau$ 3.95 (br, 1, NH), 6.79 (d, 2, $J$ = 6.5 Hz, $-CHCH_2N$), 6.89 (br, 1, 3-H), 7.60 (center of AB q, 4, $J$ = 12 Hz, 6-H and 8-H), 7.45–7.92 (m, 4, 2-H and 4-H), 8.01 (s, 3, $COCH_3$), 8.95 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 239 ($M^+$).

Anal. Calcd for $C_{13}H_{21}NO_3$: C, 65.24; H, 8.85; N, 5.85. Found: C, 65.16; H, 8.90; N, 5.75.

Compound **34**: bp 140–150° (bath temperature) (0.13 mm); ir ($CHCl_3$) 3360 (NH), 1670 $cm^{-1}$ ($\alpha,\beta$-unsaturated ketone and amido carbonyl group); uv max (EtOH) 245 nm (log $\epsilon$ 3.93); NMR ($CDCl_3$) $\tau$ 3.35 (br, 1, NH), 5.84–6.16 (m, 2, $-CH_2NH$), 6.60–7.56 (m, 3, cyclobutene), 7.75 (br s, 4), 8.91 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 221 ($M^+$). The uv absorption maximum closely resembles the reported value for bicyclo[4.2.0]oct-1-en-2-one.[15]

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.55; H, 8.65; N, 6.33. Found: C, 70.51; H, 8.83; N, 6.03.

**B. From 32.** Treatment of 184 mg of **32** with aqueous KOH solution as described above gave 64 mg (33%) of **33** and 14 mg (8%) of **34**.

**8-(*N*-Acetylaminomethyl)-6-methoxy-4,4-dimethylbicyclo[4.2.0]octan-2-one (35) A. From 31.** A solution of 115.8 mg of **31** and 10 mg of KOH in 1 ml of methanol was refluxed for 15 min and concentrated. Anhydrous ether was added to the residue and the insoluble material was removed by filtration. Evaporation of the solvent and recrystallization of the residual solid from petroleum ether gave 104.5 mg (77%) of **35**: mp 85°; ir ($CHCl_3$) 3350 (NH), 1690 (C=O), 1665 $cm^{-1}$ (NHCO); NMR ($CDCl_3$) $\tau$ 3.65 (br, 1, NH), 6.20–6.54 (m, 1), 6.75–7.10 (m, 1), 6.85 (s, 3, $OCH_3$), 7.35 (d, 1, $J$ = 7.5 Hz), 7.80 (s, 2), 8.06 (s, 3, $COCH_3$), 8.20 (center of AB q, 2, $J$ = 15.0 Hz), 7.89–8.22 (m, 3, cyclobutane), 8.97 and 9.02 [2 s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 253 ($M^+$). The cis stereochemistry of the ring juncture was assigned on the basis of thermodynamic considerations and the fact that **35** was also produced from **32**.

Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.51, H, 9.25; N, 5.51.

**B. From 32.** Treatment of 129 mg of **32** with KOH in methanol as described above gave 20 mg (14%) of **35**.

**Epimerization of 31.** A solution of 80 mg of **31** and 100 mg of potassium *tert*-butoxide in 1 ml of *tert*-butyl alcohol was allowed to stand at room temperature for 5 min. The solvent was removed, anhydrous ether was added to the residue, and the insoluble material was removed by filtration. After the solvent was evaporated, the residue was separated by preparative TLC using ether as solvent to give 22 mg (27%) of **32** and 27 mg (34%) of **34**.

Upon similar treatment of **32**, only the starting material was recovered unchanged.

**3-Allyloxy-5,5-dimethyl-2-cyclohexen-1-one (36).** According to the known procedure[22] **36** was prepared from dimedone and allyl alcohol in the presence of *p*-toluenesulfonic acid: bp 82° (0.1 mm) [lit.[23] bp 155° (20 mm)]; ir ($CHCl_3$) 1640, 1600 $cm^{-1}$; uv max (EtOH) 250 nm (log $\epsilon$ 4.21); NMR ($CDCl_3$) $\tau$ 3.80–4.50 (m, 1, $-CH=CH_2$), 4.70–5.10 (m, 2, $-CH=CH_2$), 4.65 (s, 1, 2-H), 5.58 (br d, 2, $-CH_2CH=CH_2$, $J$ = 5.5 Hz), 7.71 (s, 2, 6-H), 7.79 (s, 2, 4-H), 8.91 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 180 ($M^+$).

**Irradiation of 36.** A solution of 300 mg of **36** in 50 ml of cyclohexane was irradiated for 10 hr and the solvent was removed. The residue was submitted to preparative TLC using petroleum ether–ether (1:1) as solvent to give 212 mg (72%) of a colorless oil. Although TLC and GLC analyses of the oil indicated that it consists of a single component, its NMR spectrum clearly showed it to contain a trace amount of an unidentified product in addition to a major product (**37a**). Attempts to isolate the photoproducts in a pure form were unsuccessful.

Compound **37a** (containing a trace amount of an unidentified product): ir ($CHCl_3$) 1710 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 7.86 (s, 2, $H_g$ and $H_h$), 8.05 (center of AB q, 2, $J$ = 15.0 Hz, $H_i$ and $H_j$), 8.78 and 8.87 [2 s, 6, $-C(CH_3)_2$]; ms spectrum $m/e$ 180 ($M^+$).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.09; H, 9.31.

**Methyl 7,7-Dimethylcyclooctane-1,5-dione-3-carboxylate (41).** A solution of 2.45 g of **3** and 200 g of methyl acrylate in 350 ml of cyclohexane was irradiated for 8 hr. A large amount of a white polymer was formed. The cyclohexane layer was decanted and the polymer was washed with ether. The combined organic layer was dried ($MgSO_4$). Removal of the solvent and recrystallization of the residual solid from ligroin gave 145 mg of **41**: mp 103.5–105°; ir ($CHCl_3$) 1735, 1705 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.27 (s, 3, $OCH_3$), 7.52 (center of AB q, 4, $J$ = 12.6 Hz, 6-H and 8-H), 6.95–7.65 (m, 5, 2-H, 3-H, and 4-H), 8.90 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 226 ($M^+$).

Anal. Calcd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.38; H, 8.12.

**3-Hydroxymethyl-7,7-dimethylcyclooctane-1,5-dione (38). A. From 37a.** A mixture of 1 g of **37a** and 10 ml of water was refluxed for 3 hr. The water was removed and the residue was recrystallized from benzene–petroleum ether (bp 60–80°) to give 587 mg (53%) of **38**: mp 110–111°; ir ($CHCl_3$) 3610, 3480–3380, 1695 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.47 (d, 2, $J$ = 6 Hz, $-CH_2OH$), 7.58 (center of AB q, 4, $J$ = 12.0 Hz, 6-H and 8-H), 7.65 (s, 1, OH), 7.25–7.90 (m, 5, 2-H, 3-H, and 4-H), 8.89 [s, 6, $-C(CH_3)_2$]; mass spectrum $m/e$ 180 ($M^+ - 18$).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.44; H, 9.32.

**B. From 41.** A solution of 70 mg of **41** and 120 mg of ethylene glycol in 5 ml of benzene was refluxed in the presence of a small amount of *p*-toluenesulfonic acid in a flask equipped with a Dean-Stark trap for 3 hr. The solution was washed with water and dried ($MgSO_4$). After removal of the solvent, 5 ml of anhydrous ether was added. The solution was added dropwise to a suspension of 10 mg of lithium aluminum hydride in 5 ml of anhydrous ether and the reaction mixture was stirred overnight. After an usual work-up procedure, the reduction product was dissolved in 5 ml of 90% acetic acid and the solution was refluxed for 1 hr. After the solvent was evaporated, a residual solid was recrystallized from benzene–petroleum ether (bp 60–80°) to give colorless crystals, mp 109–110°, which were identical with **38** in all respects.

**C. From 43.** A solution of 102 mg of **43** in 3 ml of methanol and 3 ml of 10% hydrochloric acid was allowed to stand at room temperature for 3 hr. The solvent was removed and the residue was recrystallized from benzene–petroleum ether (bp 60–80°) to give 63 mg of colorless crystals, mp 109–110.5°, which were identical with **38** in all respects.

**3-Acetoxymethyl-7,7-dimethylcyclooctane-1,5-dione (39).** A solution of 22.7 mg of **38** in 0.5 ml of acetic anhydride and 0.5 ml of pyridine was allowed to stand at room temperature overnight. The solvent was removed and the residue was recrystallized from petroleum ether (bp 60–80°) to give 24 mg (87%) of **39**: mp 99.5–100°; ir ($CHCl_3$) 1735, 1700 $cm^{-1}$; mass spectrum $m/e$ 240 ($M^+$).

Anal. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.11; H, 8.63.

**3-Hydroxymethyl-7,7-dimethylcylooctane-1,5-dione Dioxime (40).** A solution of 200 mg of **38**, 105 mg of hydroxylamine hydrochloride, and 120 mg of sodium acetate in 5 ml of aqueous ethanol (1:1) was heated at 80° for 1 hr and concentrated to one-third. The precipitated crystals were collected and recrystallized from ethyl acetate to give 211 mg (92%) of **40**: mp 219–220°; ir ($CHCl_3$) 3200–3300 $cm^{-1}$.

Anal. Calcd for $C_{11}H_{20}N_2O_3$: C, 57.87; H, 8.83; N, 12.27. Found: C, 57.73; H, 9.04; N, 12.00.

**4,4-Dimethyl-6-methoxy-8-hydroxymethylbicyclo[4.2.0]octan-2-one (43).** A solution of 870 mg of **37a** and 20 mg of sodium methoxide in 5 ml of methanol was heated at 80° for 5 min. After removal of the solvent, anhydrous ether was added to the residue and the insoluble material was removed by filtration. Evaporation of the solvent and distillation gave 528 mg (52%) of **43**: bp 95–103° (bath temperature) (0.07 mm); ir ($CHCl_3$) 3480, 1690 $cm^{-1}$; NMR ($CDCl_3$) $\tau$ 6.35 (d, 2, $J$ = 5.5 Hz), 6.85 (s, 3), 7.21 (d, 1, $J$ = 8.5 Hz), 7.79 (s, 2), 8.04 (s, 2), 7.70–8.70 (m, 4), 8.95 and 9.04 (2 s, 6); mass spectrum $m/e$ 180 ($M^+ - CH_3OH$). The cis stereochemistry of the ring juncture was tentatively assigned on the basis of thermodynamic considerations; i.e., it was formed under the basic conditions.

Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found; C, 67.62; H, 9.27.

**4,4-Dimethyl-6-methoxy-8-acetoxymethylbicyclo[4.2.0]octan-2-one (44).** A solution of 145 mg of **43** in 2 ml of acetic anhydride and 2 ml of pyridine was allowed to stand at room temperature for 3 days. Removal of the solvent followed by distillation gave 130 mg (82%) of **44**: bp 100–120° (bath temperature) (0.15 mm); ir ($CHCl_3$) 1735, 1695 $cm^{-1}$; mass spectrum $m/e$ 195 ($M^+$).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.56; H, 8.62.

**Energy Transfer Experiments on 9.** Energy transfer experiments were carried out using 0.009 $M$ of **9** and 0.1 $M$ of transfer

agents (acetophenone, benzophenone, phenanthrene, naphthalene, and piperylene) in ether. Each solution was irradiated in a Pyrex tube at room temperature for 70 min and submitted to GLC after removal of solvent. Irradiation of **9** in the presence of acetophenone or benzophenone led to complete disappearance of starting material within 10 min and formation of a new product, which was identical on the GLC retention time with a product obtained from irradiation of **14a** in the presence of acetophenone or benzophenone; thus, the new compound is a secondary product from **14a**. The nature of this compound is presently under investigation. Phenanthrene and naphthalene completely quenched the cycloaddition, and piperylene partially quenched by the concentration used.

**Energy Transfer Experiments on 12.** Energy transfer experiments on **12** using benzophenone and piperylene as transfer agents were carried out in a similar manner described above for **9**. Benzophenone has no effect on the product distribution and yields, and piperylene gave results as shown in Figure 2.

**Registry No.**—**3**, 126-81-8; **4**, 107-11-9; **5**, 627-37-2; **6**, 124-02-7; **7**, 589-09-3; **8**, 55800-10-7; **9**, 55800-11-8; **10**, 55800-12-9; **11**, 55800-13-0; **12**, 55800-14-1; **13**, 55800-15-2; **14a**, 37914-13-9; **14a** HCl, 55869-62-0; **15**, 55869-63-1; **16**, 55800-16-3; **17**, 55800-17-4; **18**, 55869-64-2; **19**, 55800-18-5; **20**, 55869-65-3; **21a**, 37914-12-8; **21a** HCl, 55800-19-6; **22a**, 55800-20-9; **23**, 37910-73-9; **24**, 37910-74-0; **25a**, 37910-75-1; **26**, 55800-21-0; **27**, 37914-08-2; **27** HCl, 37910-76-2; **29**, 55800-22-1; **31**, 55800-23-2; **32**, 55869-66-4; **33**, 55800-24-3; **34**, 55800-25-4; **35**, 55800-26-5; **36**, 31928-99-1; **37a**, 55869-67-5; **38**, 37914-09-3; **39**, 37914-10-6; **40**, 55800-27-6; **41**, 37914-11-7; **43**, 55800-28-7; **44**, 55800-29-8.

## References and Notes


(1) Portions of this work have appeared as preliminary communications; see Y. Tamura, Y. Kita, H. Ishibashi, and M. Ikeda, *Chem. Commun.*, 167 (1971); *Tetrahedron Lett.*, 1977 (1972).
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(3) At the same time, Paquette and coworkers reported a synthesis of 1,4-dimethyl-2-azabicyclo[2.1.1]hexan-3-one by the reaction of 1,3-dimethylbicyclo[1.1.0]butane with chlorosulfonyl isocyanate; see L. A. Paquette, G. R. Allen, Jr., and M. J. Broadhurst, *J. Am. Chem. Soc.*, **93**, 4503 (1971).
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(6) The long-range coupling between $H_b$ and $H_f$ in the bicyclo[2.1.1]hexane system is as yet unrecorded.
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# The Chemistry of Hindered Systems. Syntheses and Properties of Tetramethylazacycloheptanes and Related Acyclic Amines


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Hindered acyclic *N-tert*-butyl amines **1–5** have been synthesized to determine the relative importance of steric and electronic factors in these systems. The syntheses of the acyclic amines, which involved manipulation of a common intermediate, namely tetramethylazacycloheptane acyloin **9**, (formed from diester **1**), are discussed. The reduction of acyloin **9** was studied in detail and the stereochemistry of the critical diol intermediates formed, **12a** and **12b**, was established using chemical and spectroscopic techniques. One of the spectroscopic approaches utilized $^1$H NMR chiral shift reagents to distinguish between the diol meso and *dl* diastereomers. Low-temperature dynamic $^1$H NMR techniques were used to measure $\Delta G^{\ddagger}$ (free energy for inversion–rotation processes about the N–$CH_2$ bonds; e.g., 9.1 kcal/mol for parent amine **4**) for the acyclic amines. Similarities in $\Delta G^{\ddagger}$ for **1–4** indicate that steric factors and not electronic factors best account for the inversion–rotation barrier found in these molecules. Studies of favorable conformations for amines **1–3**, however, suggested that these systems might be capable of some nitrogen–carbonyl interaction. Comparisons of uv spectra obtained for the diketone **3**, dialdehyde **2**, and cyclic ketone **23** provide evidence that interaction (i.e., mixing of the nitrogen and carbonyl orbitals) does occur in the examples cited.


Our reports[1,2] on the synthesis of the hindered *N-tert*-butyl-3,3′-imino diester **1**, and on the possibility that intramolecular 1,4-nitrogen–carbonyl interactions[3,4] resulting as a consequence of preferred conformations[5] might account for some of the unusual properties of this molecule (and other hindered systems we have now synthesized as part of this study), prompted us to synthesize dialdehyde **2** and diketone **3**.