Acknowledgment. This work was supported by the National Science Foundation under Grants GH32766 and GH17926 for which we are grateful.

Registry No.—**2,** 15068-65-2; **3** uncoordinated, 4529-26-4; **3** coordinated, 7800-63-7; **14,** 59318-44-4; **18,** 59318-45-5; **19,** 1117-89-1; **20** uncoordinated, 59318-46-6; **20** coordinated, 59350-20-8; **23,** 13369-16-9; **25,** 59318-47-7; **27** uncoordinated, 59318-48-8; **27** coordinated, 59350-19-5; **29** uncoordinated, 59318-49-9; **29** coordinated, 59368-11-5; **30** uncoordinated, 59318-50-2; **30** coordinated, 59349-70-1; **31** uncoordinated, 59318-51-3; **31** coordinated, 59368-12-6; **32** uncoordinated, 59318-52-4; **32** coordinated, 59350-26-4; **33** uncoordinated, 59318-53-5; **33** coordinated, 59350-25-3; **34** uncoordinated, 59318-54-6; **34** coordinated, 59350-24-2; **35** uncoordinated, 59318-55-7; **35** coordinated, 59350-23-1; **36** uncoordinated, 59318-56-8; **36** coordinated, 59350-22-0; **37** uncoordinated, 59318-57-9; **37** coordinated, 59368-09-1; **38** uncoordinated, 59318-58-0; **38,** coordinated, 59350-21-9; **39,** 4529-23-1; **40,** 59318-59-1; **41,** 59318-60-4; **42,** 59318-61-5; **43,** 59318-62-6; **44,** 59318-63-7; aniline, 62-53-3; 4-bromo-1-butene, 5162-44-7; *p*-bromo-*N,N*-diallylaniline, 30438-95-0; triethylamine, 121-44-8; diethylphenylborane, 56797-48-9; *N,N*-diallylaniline, 6247-00-3; *N,N,N',N'*-tetrallyl-*p*-phenylenediamine, 59318-64-8; *p*-phenylenediamine, 106-50-3; 3-bromopropene, 106-95-6; *p*-chloro-*N,N*-diallylaniline, 30438-94-9; *p*-chlorophenylborane triethylamine, 59318-65-9; *p*-methylphenylborane triethylamine, 59318-66-0; *p*-methyl-*N,N*-diallylaniline, 3480-96-4; *p*-ethoxyphenylborane triethylamine, 59318-68-2; *p*-methoxyphenylborane triethylamine, 59318-69-3; *p*-methoxy-*N,N*-diallylaniline, 59318-70-6.

Supplementary Material Available. Tables of physical constants and experimental details on syntheses (16 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Taken from the Ph.D. Dissertation of C. L. McCormick, Department of Chemistry, University of Florida, June 1973.
(2) G. L. Statton and G. B. Butler, *J. Am. Chem. Soc.*, **86,** 518 (1964).
(3) G. B. Butler, G. L. Statton, and W. S. Brey, *J. Org. Chem.*, **30,** 4194 (1965).
(4) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962, p 13.
(5) B. M. Mikhailov and F. B. Tutorskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* 1158 (1961).
(6) E. C. Ashby, *J. Am. Chem. Soc.*, **81,** 4791 (1959).
(7) G. B. Butler and R. L. Bunch, *J. Am. Chem. Soc.*, **71,** 3120 (1949).
(8) See paragraph at end of paper regarding supplementary material.

Investigations on the Photochemical Ring Expansion of Ring Fused β-Lactams

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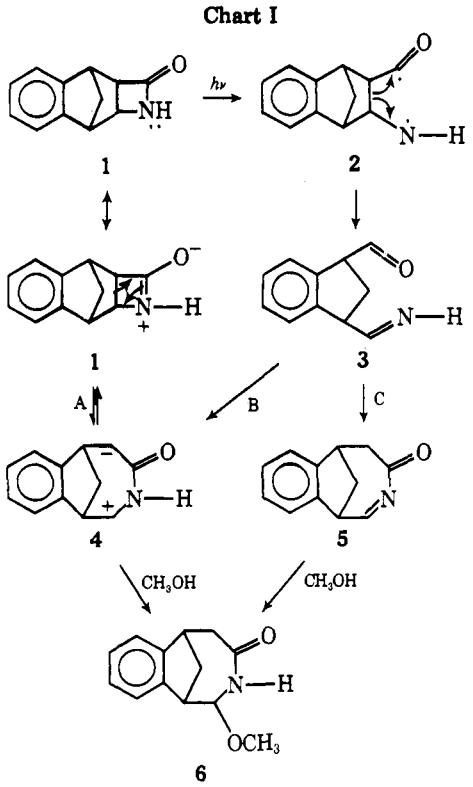
The photochemical ring expansion of *exo*-3-aza-4-ketobenzotricyclo[4.2.1.$0^{2,5}$]non-7-ene (**1**) in the presence of methanol to *exo*-2-methoxy-3-aza-4-keto-7,8-benzobicyclo[4.2.1]nonene (**6**) was studied. Data on the relative quantum yields for product (**6**) formation and starting material (**1**) disappearance as a function of methanol concentration suggest a dipolar intermediate in the reaction. A variety of other ring fused β-lactams were subjected to the reaction conditions and, of materials studied, only those β-lactams fused to the bicyclo[2.2.1]heptane ring system were found to undergo the rearrangement.

In an earlier report[1] on the photochemical ring expansion of the β-lactam **1**, in alcoholic solution, to the lactam ether **6** a number of mechanistic possibilities were suggested (Chart I). We now report investigations directed at further elucidating the mechanism of this reaction and studies of a series of β-lactams designed to delineate the scope of the reaction.

Chart I



Results and Discussion

The three logical mechanistic routes for the reaction center on the formation of two intermediates (**4** and **5**), one of which, (**4**), is common to two of the routes (A and B). Routes B and C are initiated by C(O)–N bond cleavage[2] to biradical **2** followed by β-bond cleavage to afford the imine ketene[3] **3** which can react either by addition of the N–H across the ketene[4] moiety to afford acylimine **5** or by collapse to zwitterion[5] **4**. A third alternative (path A) involves electrocyclic ring opening to **4**,[7] a route which is difficult to distinguish from path B which we favor. In either case[4,5a,6] addition of methanol to **4** or **5** would afford the observed product. Our discussions will center on path B although it should be kept in mind that path A remains a viable, but perhaps indistinguishable, alternative.

Our first attempt at differentiating paths B and C was based on the fact that, in the formation of acylimine **5**, the N–H must add across the C=C of the ketene moiety, i.e., a proton is transferred from N to C. We reasoned that N-alkylation of **1** would block this path and that the formation of N-alkylated

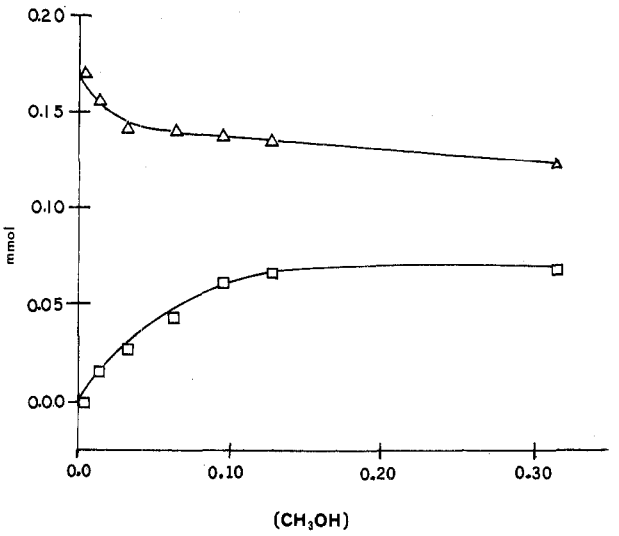
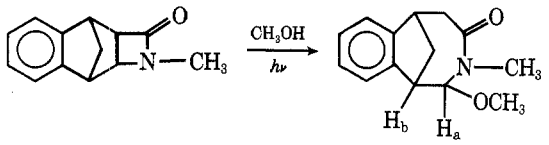


Figure 1. Plot showing dependence of product **6** (□) formation and starting material **1** (△) disappearance on methanol concentration. Unirradiated samples contained 0.216 mmol of **1** in acetonitrile.

product would be convincing evidence that pathway C was not operative.

The required N-methylated derivative **7** was prepared by NaH/DMF/CH_3I alkylation of **1**. Irradiation of **7** in methanol afforded product as evidenced by a doublet at δ 4.6 (H_a in **8**) in the ^1H NMR. Alumina chromatography workup gave material whose NMR and ir spectra were entirely consistent with those expected for a ~60:40 mixture of **8:7**. Thus, in addition to peaks assigned to **7** the spectrum showed resonances at δ 2.7 (NCH_3), 3.4 (OCH_3) and a doublet at δ 4.6 (J = 7 Hz, H_a) assigned to **8**. The infrared spectrum showed carbonyl absorptions at 1735 (from **7**) and 1620 cm^{-1} (from **8**) clearly indicating that **8** was a product of the reaction. Unfortunately,



7 **8**

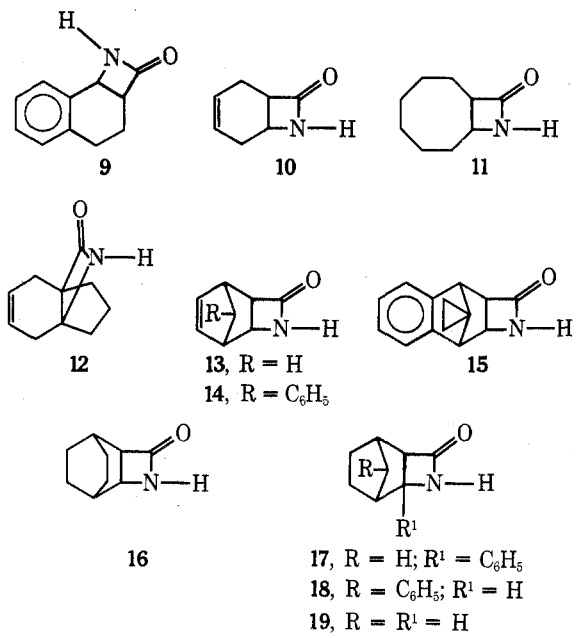
this evidence is inconclusive since repeated purification attempts caused extensive decomposition of the product and we were unable to obtain a pure sample of **8**.[8]

Our second approach was based on the prediction that path B (and A) will be reversible, i.e., intermediate **4** can easily collapse back to starting material (**1**), and methanol addition to give **6** will compete with this reversion to starting material and all other decay processes for **4**. Thus, if the reaction proceeds by either of these routes, the quantum yields for formation of **6** and for the disappearance of **1** should be a function of methanol concentration. Conversely, there is no apparent route for **5** to easily revert to **1** and path C should again show a dependence of product (**6**) quantum yield on methanol concentration but disappearance of **1** should be independent of methanol concentration.

Accordingly, a series of samples of **1** in acetonitrile[9] containing varying amounts of methanol were irradiated in parallel and analyzed via quantitative HPLC for **1** and **6**. The results (Figure 1) indicate a clear dependence of product formation and starting material disappearance on methanol concentration, i.e., they are only consistent with a reaction occurring via path B (or A) and inconsistent with path C.

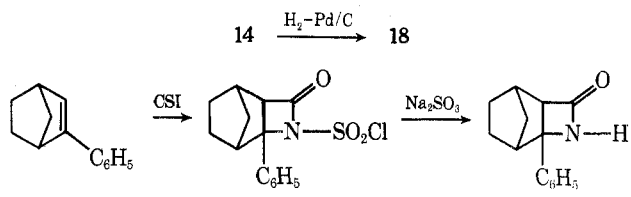
Scope of the Photorearrangement. Since the formation of **6** occurs with reasonable efficiency it was of interest to determine the scope of this reaction since broad applicability would provide a useful synthetic sequence for the formation of a series of novel ring expanded polycyclic lactams. We wished to investigate two major points concerning the reaction: (1) was the aromatic chromophore necessary to the rearrangement, and (2) was there a ring structural requirement which might limit the potential synthetic utility of the reaction? To this end we investigated the photochemistry of the series of fused β-lactams **9**–**19**[10–15] shown in Chart II.

Chart II



9 **10** **11** **12** **13**, R = H; **14**, R = C_6H_5 **15** **16** **17**, R = H; R^1 = C_6H_5; **18**, R = C_6H_5; R^1 = H; **19**, R = R^1 = H

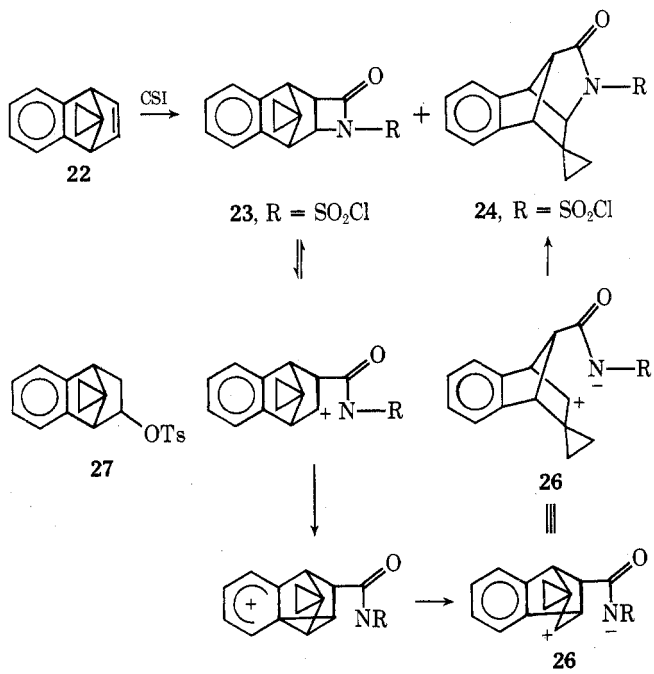
Preparation of β-Lactams. With three exceptions the desired starting materials were prepared by reported routes. Compound **18** was prepared by simple hydrogenation of **14**[14,15] whereas **17** was prepared in 68% overall yield by chlorosulfonyl isocyanate (CSI) addition[16] to **20** followed by removal of the SO_2Cl group according to the procedure of Durst and O'Sullivan.[17] The structures of **17** and **18** follow from their method of synthesis and spectral comparison with the known parent system **19**.[13]



20 **21** **17**

The preparation of **15**, however, was not straightforward. Addition of CSI to **22**[18] in ether gave a 68% yield of a solid material whose infrared spectrum showed absorption at 1825 and 1780 cm^{-1} characteristic of *N*-chlorosulfonyl-β- and γ-lactams,[19d] respectively. Attempts to isolate the desired **23** via silica gel chromatography or crystallization only afforded material enriched with the 1780-cm^{-1} component suggesting that it was being formed by rearrangement of **23**.

An enriched sample (90%) of the rearrangement product was prepared by stirring a sample of the CSI adduct mixture with a slurry of silica gel in chloroform for 24 h. Recrystallization from ether gave pure material which was identified as γ-lactam **24** on the basis of its NMR and ir spectra and those of its reduction product **25**. The NMR spectrum of **24** showed two-proton multiplets centered at δ 0.4 and 1.2 for the cyclopropyl protons and at δ 4.1 (H_d and H_b), 3.65 (H_c), and 2.95 (H_a) in addition to the aromatic resonance at 7.5–7.1 (see structure **25a**, R = SO_2Cl).



Removal of the chlorosulfonyl group[17] gave **25** whose structural assignment is based on ir absorptions at 3420 and 1700 cm^{-1} indicating the presence of a γ-lactam and its ^1H NMR spectrum which showed the expected aromatic, cyclopropyl, and N–H (at δ 6.6) resonances and a unique set of one-proton multiplets (Figure 2) for the ring protons. The

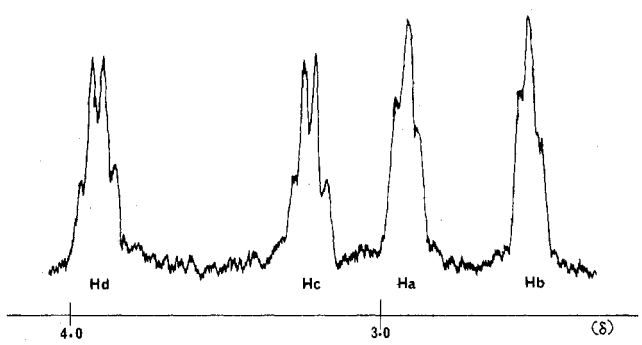
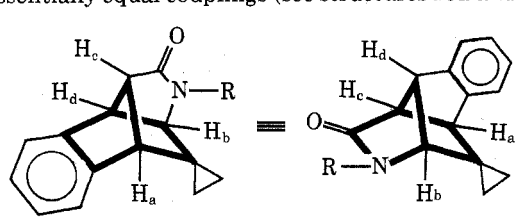


Figure 2. A portion of the NMR spectrum of **25** showing resonances for protons H_a–H_d.

symmetry of the spectrum indicates that there are two pairs of protons with nearly identical couplings. Furthermore, when a decoupling experiment was carried out it was found that irradiation of any of the multiplets caused changes in the other three, i.e., the protons are mutually coupled. These data uniquely fit structure **25.** Protons H_a–H_d are all on the bridgehead positions of bicyclo[2.2.1]heptane systems so that angle factor contributions to couplings should be similar, and they should form two equivalent sets, $H_a + H_b$ and $H_c + H_d$, with essentially equal couplings (see structures **25a** and **25b,**



25a **25b**

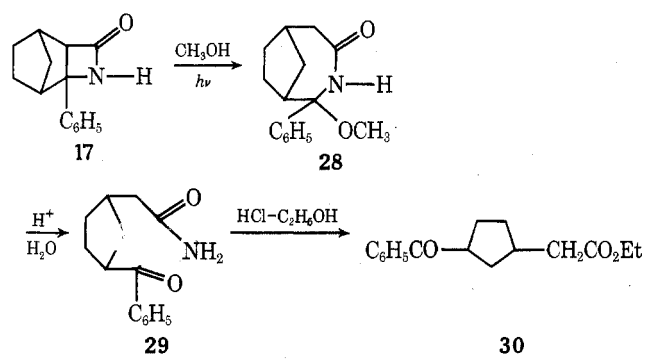
R = H). H_a is vicinally coupled to H_c and W-coupled[20] to H_a and H_d whereas H_b is vicinally coupled to H_d and W-coupled to H_a and H_c. H_c and H_d are vicinally coupled to two protons ($H_a + H_d$ and $H_b + H_c$, respectively) and W-coupled to one proton, H_c to H_b and H_d to H_a. The assignment of H_a to the resonance at δ 2.7 follows from spectral changes occurring on conversion of **24** to **25;** i.e., on removal of the strongly electron-withdrawing chlorosulfonyl group the two-proton multiplet at δ 4.1 in **24** is replaced by a single-proton multiplet at δ 3.9 for H_d and a new multiplet at δ 2.7 for H_b.

There are several analogies to the rearrangements of *N*-chlorosulfonyl-β-lactams[19,21] and the corresponding solvolytic rearrangement of the tosylate **27** has been reported.[22] Apparently, stabilization via the incipient cyclopropylcarbinyl cation in **26** is crucial to the rearrangement since similar treatment of the *N*-chlorosulfonyl derivative of **1** affords no rearranged product.[1]

Finally, reduction of the initial reaction product after careful workup gave the desired β-lactam **15** whose structure was established by comparison of spectral properties with those of **1**.[1]

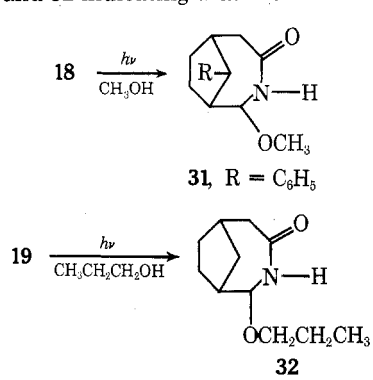
Photolysis of Lactams. Preliminary experiments were run by irradiating the appropriate β-lactam in methanol, carefully evaporating solvent, and examining the ^1H NMR spectrum for a methoxy peak (δ ~3.5) and the proton α to N (H_a in **8** at δ 4.5). Under these conditions **9–16** showed no evidence for the occurrence of the ring expansion reaction.[23]

Examination of the photolysate of **17** showed a methoxy methyl resonance at δ 3.1 consistent with ring expansion to **28.** Attempted workup of the reaction mixture by silica gel chromatography afforded a new material, obviously a degradation product of **28.** Analysis of the spectral data suggested that this material was the keto amide **29** and this was established by refluxing this material in ethanol–HCl to convert it to the known keto ester **30**.[24] Presumably **29** arises via acid-catalyzed loss of methanol from **28.**



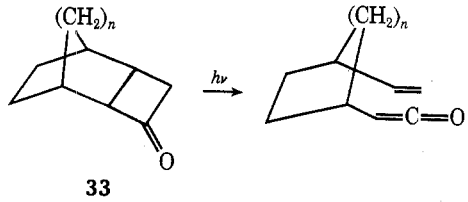
Careful workup of the photolysis mixture by chromatography on neutral alumina gave a 40% yield of **28.** When a sample of **28** was stirred in chloroform containing silica gel it was converted to **29** as expected.

Irradiations of **18** and **19** also proceeded to give the desired products **31** and **32** indicating that the aromatic ring or any



particular orientation of it is not crucial to the ring expansion reaction, i.e., **19** as well as **1, 17,** and **18** gives product. Con-

versely our results indicate that the reaction occurs only when the β-lactam is fused to a bicyclo[2.2.1] system, e.g., it even fails in the closely related [2.2.2] system **16**. This behavior is reminiscent of that observed by Miller and Abraitys[3d] in the corresponding cyclobutanones, e.g., they observed that members of the bicyclo[2.2.1] system (**33**) (n = 1) were effi-



33

ciently converted to ketene derived products whereas the homologue (n = 2) gave poor yields of those products. They reasoned that the strain inherent to the [2.2.1] system was necessary to cleavage of the second cyclobutanone C–C bond after the initial photochemical α-cleavage reaction. It appears that these considerations also pertain to our system and, in fact, lend further support to the intermediacy of the ketene imine.

Experimental Section

Microanalyses were performed by Dr. Franz Kasler of the Department of Chemistry, University of Maryland. The NMR spectra were obtained on a Varian A-60D or XL-100 NMR spectrophotometer with tetramethylsilane as internal standard. Infrared spectra were obtained as a Perkin-Elmer 337 grating infrared spectrometer or a Beckman IR8 infrared spectrometer in a 0.1-mm cell. Mass spectra were determined on a Du Pont 492 spectrometer at 70 eV. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected.

Relative Quantum Yields as a Function of Methanol Concentration. Analyses of photolysis mixtures were carried out on a Du Pont 830 liquid chromatograph with a uv (254 nm) detector at 875 psi column pressure and ambient temperature. A 25 cm × 2.1 mm Zorbax SIL column and a solvent system consisting of 500 parts methylene chloride, 100 parts water, and 15 parts isopropyl alcohol at a flow rate of 0.5 ml/min was employed. Concentrations were calculated from areas obtained by peak integration (disk) using response factors and internal standards. Benzamide was used as an internal standard added to an aliquot of the reaction mixture after irradiation to avoid competition of the standard for the light. Samples were prepared by dilution of a stock solution containing 4.00 g of **1** in 100 ml of the appropriate solvent. Aliquots of 5 ml of this solution were made up to 25 ml by addition of solvent and methanol. Aliquots (5 ml) (40 mg, 0.216 mmol) of these mixtures were placed in 10 × 1 cm quartz tubes sealed with rubber serum caps and purged with pure nitrogen for 5 min before irradiation. Samples were irradiated in a "merry-go-round", in triplicate, for 390 min using a circular bank of ten GE G15T8 lamps. After irradiation 1-ml aliquots were removed and an aliquot of a standard (benzamide) solution added before HPLC analysis.

3-Methyl-*exo*-4-oxo-3-azabenzotricyclo[4.2.1.0^{2,5}]non-7-ene (7). A solution of 1.5 g of **1** in 20 ml of dry DMF was added dropwise to a slurry of 1.5 g of 50% NaH (pentane washed) in 20 ml of DMF. The mixture was stirred under nitrogen at 100 °C for 11 h. The reaction mixture was allowed to cool and the water condenser replaced with a dry ice condenser. Methyl iodide (5.7 g) was added dropwise, the reaction mixture stirred for 30 min, 100 ml of water added, and the mixture extracted with ether. The organic phase was washed with water and dried ($MgSO_4$) and solvent was evaporated. The residual solid was recrystallized from petroleum ether to give 0.7 g (43%) of **7**: mp 114–115 °C; ir ($CHCl_3$) 3000 and 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.9–7.3 (m, 4, aromatic), 3.4–3.6 (broad s, 3, H–C–N and bridgehead H), 3.1 (m, 1, H–C–C=O), 2.85 (s, 3, NCH_3), 1.8–2.0 (m, 2, $-CH_2$).

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.50; H, 6.66; N, 7.13.

Addition of CSI to Spiro[2,3-benzonorbornadiene-7,1′-cyclopropane] (22). To a stirred solution of 4.0 g (0.024 mol) of **22** in 40 ml of anhydrous ethyl ether at −40 °C was added 4 g (0.028 mol) of CSI in 20 ml of ether. The reaction mixture was allowed to warm to room temperature and was stirred for 15 h and then slowly added to 30 g of ice and 20 ml of saturated $NaHCO_3$. Layers were separated and the aqueous phase extracted with three 40-ml portions of ether. The combined organic layer was dried ($MgSO_4$) and the ether evaporated to give 5 g (68%) of a yellow solid, mp 90–100 °C dec.

The infrared spectrum ($CDCl_3$) of the reaction product had two carbonyl absorptions at 1825 and 1780 cm^{-1} due to the presence of **23** and **24**.

The mixture was heated in $CHCl_3$ at 50 °C in the presence of 10 g of silica gel for 24 h. After filtration and evaporation of $CHCl_3$ the resulting solid contained approximately 90% rearrangement product as determined by NMR integration. Recrystallization from ether gave a white solid, mp 165–167 °C, identified as 2-spirocyclopropane-4-chlorosulfonyl-5-oxo-*exo*-4-azabenzotricyclo[4.3.0^{1,6}.0^{3,7}]non-8-ene (**24**): ir 3090, 3010, 1780, 1400, 1280, 1190, 1040 cm^{-1}.

Anal. Calcd for $C_{14}H_{12}NO_3SCl$: C, 54.28; H, 3.87; N, 4.52. Found: C, 54.02; H, 3.93; N, 4.56.

The ^{1}H NMR spectrum ($CDCl_3$) of **23** was obtained by subtracting the resonances due to **24** from the spectrum of the mixture: δ 7.4–7.1 (m, 4, aromatic), 4.45–4.35 (d, J = 4 Hz, 1, H–C–N–SO_2Cl), 3.65–3.50 (d, J = 4 Hz, 1, H–C–C=O), 3.45 (s, 1, bridgehead), 3.1 (s, 1, bridgehead), 1.3–0.1 (m, 4, cyclopropane).

2-Spirocyclopropyl-5-oxo-4-aza-8,9-benzotricyclo[4.3.0^{1,6}.0^{3,7}]non-8-ene (25). To a solution of 0.250 g (0.0081 mol) of **24** in 20 ml of $CHCl_3$ was added 5 ml of 25% Na_2SO_3 solution. The reaction mixture was allowed to stir for 3 h while the pH was adjusted at 7–9 using KOH. The layers were separated and the $CHCl_3$ layer was washed with 30 ml of water, dried ($MgSO_4$), and evaporated. Recrystallization of the resulting solid from THF–petroleum ether gave 85 mg (50% yield) of reduction product **25**, mp 183–185 °C: ir ($CDCl_3$) 3420, 3010, and 1700 cm^{-1}.

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.30; H, 6.38; N, 6.43.

***exo*-4-Oxo-9-spirocyclopropyl-*exo*-3-azabenzotricyclo-[4.2.1.0^{2,5}]non-7-ene (15).** Similar treatment of 6 g of the crude CSI–**22** addition product with Na_2SO_3–KOH gave 1.7 g (42%) of **15**, mp 190–192 °C after recrystallization from MeOH–H_2O: ir ($CHCl_3$) 3400 and 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.1 (m, 4, aromatic), 6.8–6.4 (broad, 1, N–H), 3.7 (d, J = 9 Hz, 1, HC–N), 3.4–3.2 (m, 1, HC–C=O), 3.0–2.8 (m, 2, bridgehead), 1.2–0.1 (m, 4, cyclopropane).

Anal. Calcd for $C_{14}H_{13}NO$: C, 79.60; H, 6.20; N, 6.63. Found: C, 79.31; H, 6.41; N, 6.40.

***endo*-2-Phenyl-3-chlorosulfonyl-*exo*-4-oxo-*exo*-3-azatricyclo[4.2.1.0^{2,5}]nonane (21).** A solution of 2.9 g (20.5 mmol) of CSI in 15 ml of anhydrous ethyl ether was added dropwise to a stirred solution of 3.5 g (20.5 mmol) of 2-phenyl-2-norbornene in 15 ml of anhydrous ethyl ether cooled in an ice water bath. After completion of the addition the reaction mixture was allowed to stir for 1 h. The solid was filtered and washed with cold ether, giving 5.3 g of **21** (85% yield). Recrystallization from ethyl ether gave a white solid, mp 114–116 °C: ir ($CDCl_3$) 3000, 1810, 1410, 1180, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.6–7.3 (m, 5, aromatic ring), 3.5 (s, 1, H–C–C=O), 3.4 (m, 1, bridgehead), 2.7 (m, 1, bridgehead), 2.2–1.0 (m, 6).

Anal. Calcd for $C_{14}H_{14}NO_3ClS$: C, 53.94; H, 4.49; N, 4.49. Found: C, 53.71; H, 4.60; N, 4.52.

***endo*-2-Phenyl-*exo*-4-oxo-3-azatricyclo[4.2.1.0^{2,5}]nonane (17).** Treatment of 1 g (0.0032 mol) of **21** with Na_2SO_3 in the usual manner gave a white solid which was recrystallized from CH_2Cl_2 affording 0.5 g (74%) of **17**, mp 171–172 °C: ir ($CDCl_3$) 3420, 2990, 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3 (s, 5, aromatic), 6.7–6.5 (broad, 1, NH), 3.2 (m, 1, H–C–C=O), 2.7–2.5 (m, 2, bridgehead), 2.2–1.0 (m, 6).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.88; H, 7.04; N, 6.57. Found: C, 78.93; H, 7.24; N, 6.54.

Photolysis of *endo*-2-Phenyl-*exo*-4-oxo-3-azatricyclo-[4.2.1.0^{2,5}]nonane (17) in Methanol. A mixture of 4 g (0.0188 mol) of **17** in 1800 ml of absolute MeOH in a N_2 atmosphere was irradiated for 29 h through a Vycor filter with a 450-W Hanovia medium-pressure mercury lamp. The inner surface of the reaction vessel was coated with a polymeric film after irradiation. Removal of the solvent gave a yellow oil which was dissolved in 1:1 CCl_4–$CHCl_3$ and applied to a neutral alumina column (120 g) and eluted with CCl_4. Fraction 1 (100 ml) contained an unidentified yellow oil. Fraction 2–3 (200 ml each) and fractions 4–6 (1:3-$CHCl_3$–CCl_4, 200 ml) contained product **28**. Fraction 7 contained a mixture of **17** and **28** whereas fractions 8–11 contained only **17**. Recrystallization of **28** from ethyl ether gave 1.43 g (40% based upon recovered starting material), mp 118–120 °C, of *endo*-2-phenyl-*exo*-2-methoxy-4-oxo-3-azabicyclo[4.2.1]nonane (**28**): ir ($CDCl_3$) 3410, 2960, 1650, 1450, 1380, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.16–7.2 (broad s, 5, aromatic), 6.4–6.2 (broad s, 1, NH), 3.1 (s, 3, –OMe), 2.7–2.5 (m, 3, bridgehead + CH_2C=O), 2.5–2.2 (m, 3), 2.0–1.4 (m, 4).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.15; H, 7.87; N, 5.36.

Rearrangement of *endo*-2-Phenyl-*exo*-2-methoxy-4-oxo-3-azabicyclo[4.2.1]nonane (28). To a solution of 650 mg of **28** in 40 ml of $CHCl_3$ was added 30 g of silica gel and 1 ml of water; the mixture was allowed to stir at room temperature for 2 days and filtered, and the silica gel was washed with 300 ml of $CHCl_3$. Evaporation of solvent gave a white solid which was recrystallized from ether to give 200 mg (33%) of 2-(3-benzoylcyclopentyl)acetamide (**29**), mp 108–110 °C: ir ($CDCl_3$) 3550, 3440, 2950, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.1–7.8 (m, 2, aromatic), 7.6–7.2 (m, 3, aromatic), 6.7–5.8 (broad s, 2, NH_2), 4.1–3.6 (m, 1, H–C–C=O), 2.6–1.2 (m, 9, cyclopentane CH_2C=O).

This material was identical with the product obtained via workup of the original photolysis mixture by silica gel chromatography.

A solution of 200 mg (0.87 mmol) of **29** in 15 ml of ethyl alcohol and 5 drops of concentrated HCl was allowed to stir for 2 days at 70 °C. The mixture was filtered and removal of solvent gave a brown solid. The solid was taken up in CCl_4 and unreacted starting material crystallized. The mother liquid was evaporated to give a yellow oil identified as **30**: ir (CCl_4) 2900, 1740, 1680 cm^{-1}; ^1H NMR δ 8.2–7.8 (m, 2, aromatic), 7.6–7.3 (m, 3, aromatic), 4.3–4.0 (q, 2, OCH_2), 4.0–3.7 (m, C-1), 2.7–1.5 (m, 9, cyclopentane CH_2C=O), 1.5 –1.3 (t, 3, CH_3). Treatment of the oil with 2,4-dinitrophenylhydrazine reagent gave organge-red crystals which were recrystallized three times from ethyl alcohol to give the 2,4-DNP derivative of mp 81–82 °C (lit. mp 83–85 °C).[24]

The infrared spectrum (KBr) had absorption at 3280, 2960, 1740, 1620, 1595, 1345, 1300, and 1260 cm^{-1}.

***anti*-9-Phenyl-*exo*-4-oxo-3-azatricyclo[4.2.1.$0^{2,5}$]nonane (18).** **14** (4.6 g, 0.022 mol) in 70 ml of ethyl acetate was hydrogenated over 10% palladium on powdered charcoal at an initial pressure of 50 psi in a Parr shaker apparatus. After 5 h the reaction mixture was filtered, solvent removed, and the resulting solid recrystallized from methylene chloride–cyclohexane to give 4.0 g (86%) of **18**, mp 150–152 °C: ir (KBr) 3200, 2970, 2955, 1710, 1335, 1175, 720, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3–7.1 (s, 5, aromatic), 6.3–6.1 (broad, 1, N-H), 3.6–3.5 (d, J = 5 Hz, 1, H–C–N), 3.25–3.1 (s, 1, H–C–C=O), 3.4–3.35 (m, 1, benzylic), 2.9–2.7 (m, 2, bridgehead), 1.65–0.85 (m, 4).

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.56. Found: C, 78.91; H, 7.20; N, 6.47.

Photolysis of 18. A mixture of 600 mg of **18** in 450 ml of absolute MeOH was irradiated for 27 h. Approximately 225 ml of the reaction mixture was evaporated giving a yellow oil. This oil was applied to a dry column of alumina (20 × 1 in.) and eluted with 100 ml of THF. Four bands resulted. The band with R_f ~0.4 was cut from the column, eluted, and recrystallized from THF and petroeum ether (bp 40–60 °C) to give 20 mg of ring-expanded product identified as *exo*-2-methoxy-4-oxo-*anti*-9-phenyl-3-azabicyclo[4.2.1]nonane (**31**), mp 140–141 °C: ir ($CDCl_3$) 3530, 3410, 2950, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9–7.6 (broad s, 1, NH), 7.4–7.1 (s, 4, aromatic), 4.3–4.1 (t, J = 8 Hz, 1, H–C–OMe), 3.7 (s, 1, benzylic), 3.6–3.4 (s, 3, OMe), 2.8–2.5 (m, 4, bridgehead and CH_2C=O), 2.2–1.6 (m, 4).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.25; H, 7.71; N, 5.48.

Photolysis of 19. A solution of 3 g of **19** in 430 ml of 1-propanol was irradiated for 20.5 h. The residue from evaporation of the photolysate was chromatographed on 250 g of alumina with 3:1 benzene–chloroform and 150-ml fractions taken. Fractions 26–34 were combined and chromatographed on 125 g of silica gel (4:1 benzene–chloroform). Product (**32**, 50 mg) obtained from fraction 23 as an oil showed ir 3400 and 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (s, 1, NH), 4.2 (t, 1, J = 5 Hz, H–C–O–), 3.1–3.8 (m, 2, OCH_2) 2.8–1.4 (m, 12), 0.95 (t, 3, $-CH_3$).

Anal. Calcd for $C_{11}H_{19}NO_2$: N, 7.10. Found: N, 7.59, 6.96.

Photolysis of Lactams 9–16. Photolyses were carried out in methanol and monitored by NMR using the prominent H–C–O product resonance to indicate reaction. Compounds **13** and **14** reacted efficiently, presumably via dimerization, as evidenced by the disappearance of olefinic proton resonances. Lactam **15** rapidly disappeared with concomitant decay of the cyclopropyl resonances. Other lactams disappeared slowly with no evidence for product formation.

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References and Notes

(1) H. L. Ammon, P. H. Mazzocchi, W. J. Kopecky, Jr., H. J. Tamburin, and P. H. Watts, Jr., *J. Am. Chem. Soc.*, **95**, 1968 (1973).
(2) There are a number of analogies for C(O)–N bond cleavages in lactams: (a) M. Fisher, *Chem. Ber.* **101**, 2669 (1968); (b) *ibid.*, **102**, 342 (1969); (c) *Tetrahedron Lett.*, 2281, 4295 (1969); (d) P. H. Mazzocchi and J. Thomas, *J. Am. Chem. Soc.*, **94**, 8281 (1972); (e) P. H. Mazzocchi, J. J. Thomas, and F. Danisi, *J. Polym. Sci., Part B*, **13**, 737 (1975); (f) Z. Horii, Y. Hori, and C. Iwata, *Chem. Commun.*, 1424 (1969).
(3) The corresponding cleavage of cyclobutanones to alkene ketenes is also well known: (a) W. Hostettler, *Tetrahedron Lett.*, 687 (1965); (b) G. Buchi and E. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962); (c) J. Hurst and G. Whitman, *J. Chem. Soc.*, 2864 (1960); (d) R. D. Miller and V. Y. Abraitys, *J. Am. Chem. Soc.*, **94**, 664 (1972).
(4) J. F. Banfield, G. M. Brown, F. H. Davey, N. Davies, and T. H. Ramsay, *Aust. J. Sci. Res., Ser. A*, 330 (1948).
(5) (a) H. B. Kagan and J. L. Luche, *Tetrahedron Lett.*, 3093 (1970); (b) A. Gomes and M. M. Joullie, *Chem. Commun.*, 935 (1967); (c) R. Huisgen, B. A. Davis, and M. Mazikawa, *Angew. Chem., Int. Ed. Engl.*, **7**, 826 (1968); (d) W. T. Brady and E. D. Dorsey, *J. Org. Chem.*, **35**, 2732 (1970).
(6) W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959).
(7) The thermal analogy of this ring opening in an imino ether is known: L. A. Paquette, M. T. Wyuratt, and G. R. Allen, *J. Am. Chem. Soc.*, **92**, 1763 (1970).
(8) The instability of lactam ethers similar to **8** has been noted: I. Ninomiya, T. Kiyuchi, and T. Naito, *Chem. Commun.*, 81 (1974).
(9) The dielectric constants of acetonitrile (ϵ 36.2) and methanol (ϵ 32.6) are sufficiently close so that there will be no change in solvent polarity on methanol addition.
(10) E. J. Moriconi and P. H. Mazzocchi, *J. Org. Chem.*, **31**, 1372 (1966).
(11) E. Giovannini and W. Wegmuller, *Helv. Chim. Acta*, **41**, 933 (1958).
(12) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Am. Chem. Soc.*, **93**, 152 (1971).
(13) E. J. Moriconi and W. C. Crawford, *J. Org. Chem.*, **33**, 370 (1968).
(14) Farbwerke Hoechst A.-G, Netherlands Patent Application 6 504 300; *Chem. Abstr.*, **64**, 8135 (1966).
(15) P. H. Mazzocchi, T. Halchak, and H. L. Ammon, Abstracts, First Chemical Congress of North America, Nov 30–Dec 5, 1975, Organic Paper No. 113.
(16) H. Ulrich, *Chem. Rev.*, **65**, 369 (1965).
(17) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).
(18) B. M. Trost, *J. Org. Chem.*, **34**, 3644 (1969).
(19) (a) T. Sasaki, S. Eguchi, and A. Yamada, *J. Org. Chem.*, **38**, 679 (1973); (b) L. A. Paquette and M. J. Broadhurst, *J. Org. Chem.*, **38**, 1886, 1893 (1973); (c) J. R. Malpass, *Tetrahedron Lett.*, 4951 (1972); (d) G. T. Furst, M. A. Wachsman, J. Pieroni, J. G. White, and E. J. Moriconi, *Tetrahedron*, **29**, 1675 (1973), and references cited therein.
(20) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon Press, Oxford, 1969, p 334.
(21) A similar rearrangement product has been reportedly formed in 1.6% yield on treatment of *syn*-6,7-benzotricyclo[3.2.2.$0^{2,4}$]nona-6,8-diene with CSI: W. E. Volz and L. A. Paquette, *J. Org. Chem.*, **41**, 57 (1976).
(22) D. Lenoir, P. v. R. Schleyer, and J. Ipaktschi, *Justus Liebigs Ann. Chem.*, **750**, 28 (1971).
(23) In several cases starting material disappeared rapidly but reaction was apparently proceeding via a competing alternate pathway. Thus the NMR of the photolysate of **13** and **14** showed no olefinic absorption suggesting that dimerization had occurred while that of the photolysate of **15** showed no cyclopropyl protons indicating that an alternative process involving the cyclopropyl ring had taken place.
(24) C. L. Stevens, T. A. Treat, P. M. Pillai, W. Schmonsees, and M. D. Glick, *J. Am. Chem. Soc.*, **95**, 1978 (1973).