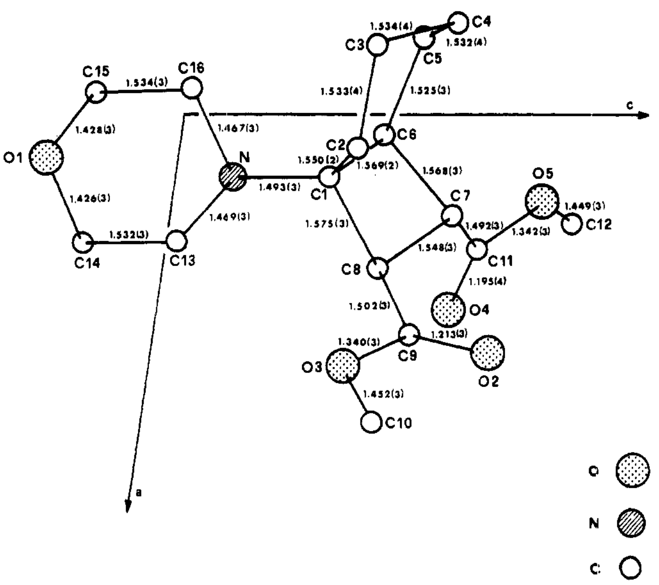

Figure 1. A projection of the molecule along the *b* axis reporting the numbering scheme for the atoms and the bond lengths.

formation of the trans-fused compound **4** might be attributed to the greater stability of **2a** compared with **2b**, owing to the well-known Johnson strains.[11] Obviously the reaction is assumed to be under kinetic control, even if no isomerization of **3** is possible because of its great instability.[10] On the other hand, provided that the Curtin–Hammett principle cannot be applied in this case, one can assume that the collapse of the carbon anion onto C1 may be faster than the formation of **2b**. In any case the cis-fused system is the reaction product.

The spectroscopic data relative to **3** indicate that it probably exists as the single conformation **a**, both in solution and in the solid state. Its NMR spectrum in fact is identical with that of the analogous biased compound, thus indicating that no conformational equilibrium **3a** ⇌ **3b** is present. On the other hand, strong interactions between the group at C8 and the axial hydrogens of the cyclohexane ring would be present in **3b**. A considerably important 1,3-diaxial interaction between the morpholine ring and the group at C7 would further increase the energy of **3b**.

Acknowledgment. This work was supported by C.N.R., Rome, Italy.

Registry No.—**1**, 670-80-4; **3**, 62532-82-5; DMM, 624-48-6; DMF, 624-49-7.

Supplementary Material Available. Tables of temperature factors and torsion angles (3 pages). Ordering information is given on any current masthead page.

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(6) The agreement indices R_1 and R_2 are defined as follows:

$$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

The function minimized was $\Sigma w(k|F_o| - |F_c|)^2/\Sigma w|F_o|^2$, where the weighting factor w was in the form $1/(3.1 + |F_o| + 0.0074|F_o|^2)$. The constants were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and sin ϑ/λ. Atomic scattering factors were from F. H. Moore, *Acta Crystallogr.*, **16,** 1169 (1963).

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(12) See paragraph at end of paper regarding supplementary material.

Synthetic Aspects of the Photochemistry of Keto Imino Ethers.[1,2] A Facile Synthesis of Functionalized Bicyclo[*n*.1.0] Systems

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A general method for the synthesis of bicyclo[*n*.1.0]alkanes functionalized at the one-carbon bridge is described. Bicyclo[*n*.1.0]alkanes **20–24** were prepared by photorearrangement of keto imino ethers **16–19** in THF solvent. The products were isolated in satisfactory yield as isocyanates (**21, 23,** and **24**) or as the dimethylurea derivatives of the isocyanates (**20** and **22**). The required keto imino ethers were prepared by O-alkylation of the silver salts of the corresponding imides **12–15**. The products of the photorearrangement are cyclopropanone derivatives and as such should be useful synthetic intermediates.

We have reported that irradiation of 2-ethoxypyrrolin-5-one (**1**), prepared by O-alkylation of succinimide, gave in good isolated yield 1-ethoxycyclopropyl isocyanate (**2**) or the *tert*-butyl carbamate (**3**).[3] The reaction has been shown to occur from the n,π* singlet state of **1**, and a Norrish type I cleavage mechanism has been proposed.

Cyclopropanes **2** and **3** are derivatives of cyclopropanone, and derivatives of this type have been used as precursors for a variety of compounds.[4] For instance, the bicyclo[4.1.0]heptane **4**[5] has been converted to the β-lactam **5**,[6] the cyclobutanone **6**,[7] amino ethers **7**,[6] the cyclopropanol **8**,[5] and further derivatives.[5–7] Photoproducts **2** and **3** have been hydro-

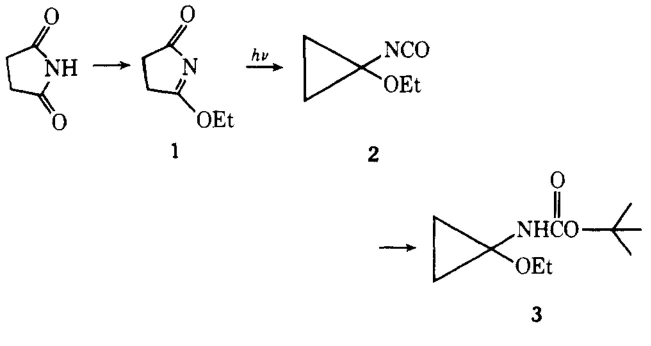
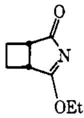
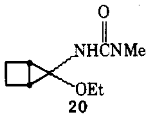
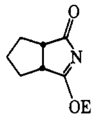
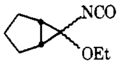
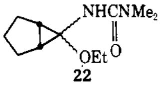
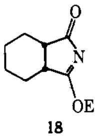
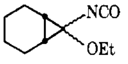
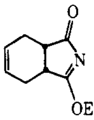
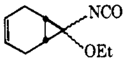
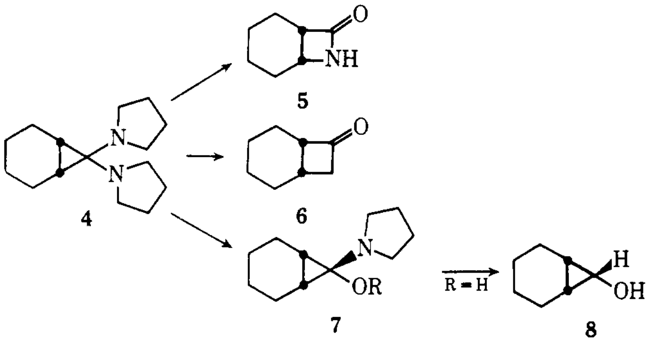


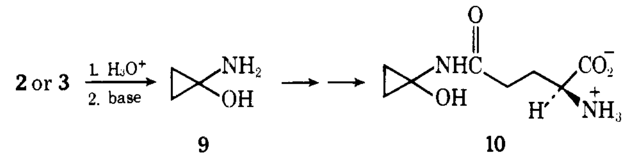
Table I. Product Yields and Ultraviolet Spectral Data

Registry no.	Keto imino ether (isolated yield)	UV absorption, nm (THF)	Photoproduct or derivative (isolated yield)
62505-92-4	 (84)[a] 16	274 (ε 64)	 (43) 20
62505-93-5	 (59) 17	273 (ε 50)	 (76) 21  (56) 22
62505-94-6	 (89) 18	258 (ε 50)	 (64) 23
62505-95-7	 (74) 19	257 (ε 64)	 (53) 24

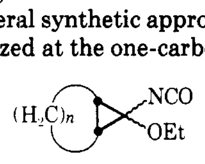
[a] The yield was corrected for recovered starting material.



lyzed to 1-aminocyclopropanol (**9**) which has subsequently been converted to the unusual natural product coprine (**10**).[8]



Because of the availability of cyclic imides, the facility of the photorearrangement of **1**, and the utility of the cyclopropanone derivatives, it seemed desirable to develop the photoreaction as a general synthetic approach to bicyclo[*n*.1.0]alkanes functionalized at the one-carbon bridge (**11**).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Results and Discussion

The keto imino ethers for the photorearrangement reaction were prepared by O-alkylation of the silver salts of the corresponding imides (**12–15**). The silver salts were prepared by a procedure analogous to that reported by Schwartz and Lerner for the preparation of silver maleimide,[9] and the silver salts were alkylated with ethyl iodide in refluxing chloroform solvent.[10] The yields for the overall conversion are fair to good as shown in Table I. In one case there was some difficulty in the alkylation step. On workup, the reaction mixture from alkylation of the silver salt of cyclobutane dicarboximide (**12**) with ethyl iodide consistently gave considerable quantities of recovered **12** in addition to the desired product **16**. We suspect that this reflects some difference in the basicity of the imide anions, and that elimination effectively competes with substitution in this case. Significant differences in the pK_a of imides as a function of structure have been reported.[11]

The site of imide alkylation was established from spectral properties. As is the case with 2-ethoxypyrrolin-5-one (**1**),[3] all the keto imino ethers (**16–19**) exhibit carbonyl and carbon–nitrogen double bond stretching bands at ca. 5.7 and 6.4 μ, respectively, in the IR spectra and methylene quartets at δ 4.2–4.5 ppm in the ^1H NMR spectra. Analogous *N*-ethyl imides give methylene quartets at about 1 ppm higher field. The UV spectra of compounds **16–19** compare favorably with those of similar keto imino ethers prepared in this laboratory (Table I).[3,12]

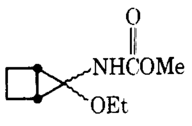
Our initial photochemical experiments were conducted with keto imino ethers **18** and **19**. Irradiation in *tert*-butyl alcohol solvent did not yield the expected carbamates but rather the isocyanates **23** and **24**, respectively. Irradiation of **18** and **19** in THF solvent allowed easy isolation of isocyanates **23** and **24** in moderate but useful yields (Table I). Isocyanate **23** was also not easily derivatized with methanol. The reaction was slow, required acid catalysis, and gave a low yield of carbamate product.

Irradiation of **16** in THF solvent gave a product which was an isocyanate as shown by IR spectroscopy but was unstable to isolation. Again derivatization with methanol was very slow and required acid catalysis. The two major components of the reaction mixture after treatment with acidic methanol were imperfectly separated by preparative GLC and the mixture characterized by ^1H NMR spectroscopy as the desired carbamate **25** and a carbamate **26** in which the ethoxy group was

Table II. ^{13}C NMR Spectral Data[a]

Registry no.	Compd	Chemical shifts						
		C=O	OEt	NMe	Quaternary	Methine	Methylene	Olefinic
62505-96-8	21 major	125.37 (s)	62.88 (t) 15.15 (q)		78.77 (s)	31.70 (d)	26.18[b] 25.00	
62505-97-9	21 minor	125.37 (s)	63.84 15.15 (q)		78.77 (s)	33.22 (d)	26.18 25.00	
62505-98-0	23 major	*c*	62.73 (t) 15.22 (q)		78.47 (s)	20.52 (d)	20.96 (t) 18.75 (t)	
62505-99-1	23 minor	*c*	63.25 15.22 (q)		78.47 (s)	20.52 (d)	22.36 18.31	
62506-00-7	24 major	123.11 (s)	62.88 (t) 15.15 (q)		76.71 (s)	19.27 (d)	18.75 (t)	123.11 (d)
62506-01-8	24 minor	123.11 (s)	62.88 (t) 15.15 (q)		76.71 (s)	19.27 (d)	18.17	122.38 (d)
62506-02-9	20 major[d]	158.04 (s)	62.76 (t) 15.63 (q)	36.45 (q)	74.02 (s)	27.62 (d)	19.71 (t)	
62506-03-0	22 major[d]	157.36 (s)	61.64 (t) 15.58 (q)	36.45 (q)	71.74 (s)	31.36 (d)	26.21 (t) 24.85 (t)	

[a] ^{13}C NMR spectra were obtained by Fourier transform NMR on a ca. 1 M solution in $DCCl_3$, and chemical shifts are reported in parts per million from internal Me_4Si. Splitting patterns were observed in off-resonance decoupled spectra. [b] Splitting patterns could not be unambiguously determined in some cases. [c] The carbonyl resonance could not be distinguished from noise in the baseline. [d] The minor stereoisomers were not present in the samples used.



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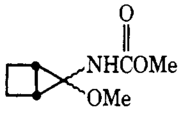

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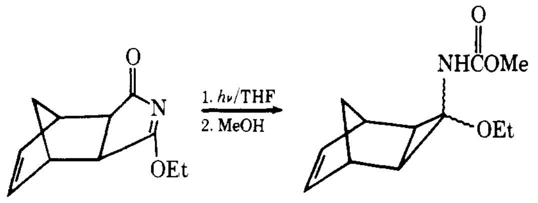
exchanged for methoxy. Facile exchange of hydroxy and alkoxy groups in cyclopropanone derivatives has been described.[4] For instance, aminocyclopropanol hydrochloride gives methoxyaminocyclopropane hydrochloride on treatment with methanol and ethoxyaminocyclopropane hydrochloride on treatment with ethanol.[8] Addition of an excess of dimethylamine to an irradiated solution of **16** gave a satisfactory yield of the crystalline dimethylurea derivative **20**.

When keto imino ether **17** was irradiated in THF solvent, the isocyanate **21** was isolated in 76% yield. Although consistent spectra were obtained for this photoproduct, a satisfactory elemental analysis was not. The isocyanate was, therefore, analyzed as its dimethylurea derivative (**22**).

Further evidence of the utility of this reaction has previously been shown in this laboratory. Irradiation of the tricyclic molecule **27** followed by trapping with methanol gave the carbamate **28** in 54% isolated yield.[12]

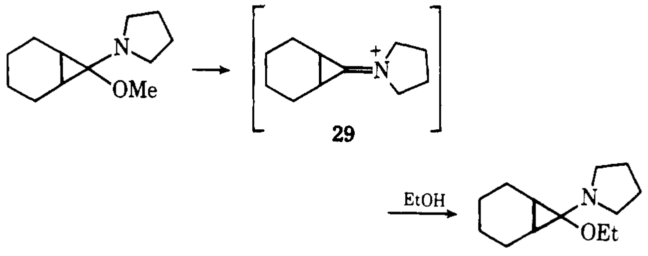


27 **28**

Structures for photoproducts **21**, **23**, and **24** were assigned from IR and ^{1}H NMR spectral data (Experimental Section) in comparison with spectral data for the parent system **2**. The spectra of the dimethylurea derivatives **20** and **22** were as anticipated. Further confirmation of structures comes from ^{13}C NMR spectra of all products (Table II) which clearly show the symmetry of the molecules.

The ^{13}C NMR spectra for the isocyanates and the ^{1}H NMR spectra for isocyanates **21** and **23** and ureas **20** and **22** indicate that the products are a mixture of two stereoisomers. The ratio of stereoisomers varies from about 3:1 to 10:1 depending upon structure. The stereochemistry at the one-carbon bridge cannot be unambiguously assigned from the spectral data; however, the low reactivity of the major stereoisomers with alcohol suggests that these stereoisomers have the isocyanate functional group endo.

Formation of stereoisomers in the photoreaction is not viewed as a serious problem when the photoproducts are used as synthetic intermediates. Wasserman[4,6] and others[4] have postulated that substitution reactions of cyclopropyl aminals and amino ethers occur via iminium ion intermediates such as **29**, and hence, the ultimate stereochemistry will be a



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function of the thermodynamics of nucleophilic addition to the iminium ions. Presently the steric control of these substitution reactions has only been established in one case.[5]

In summary we have reported a general synthetic approach to the preparation of bicyclo[*n*.1.0]alkanes functionalized at the one-carbon bridge. Other syntheses of equivalent molecules include addition of amines to cyclopropanones[4] and Favorskii-type rearrangements of α-chloro ketones[5,13] in the presence of amines. These approaches are presently of more limited scope. Work on the development of the functionalized bicyclo[*n*.1.0]alkanes as useful synthetic intermediates is in progress in our laboratories.

Experimental Section

Melting points and boiling points are uncorrected. Melting points were measured with a Fisher-Johns melting point apparatus. Perkin-Elmer 337 and Varian 635 spectrophotometers were used to determine IR and UV spectra, respectively. NMR spectra were recorded with Varian T60A and JEOL PFT-100 spectrometers, and chemical shifts are reported in δ units from internal tetramethylsilane. Mass spectra were measured at 70 eV with Varian MAT CH-5 and CH-7 spectrometers. GLC analyses were performed with Varian Aerograph Model 200 and 1700 gas chromatographs equipped with thermal conductivity detectors. Microanalyses were performed by Atlantic Microlab, Atlanta, Ga.

Preparation of the Imides. *cis*-Cyclobutane-1,2-dicarboximide (**12**) was prepared from the corresponding anhydride (Aldrich) either by passing ammonia gas over a melt of the anhydride or more conveniently by heating an intimate mixture of the anhydride and 1.1 equiv of urea at 170–180 °C until gas evolution ceased. Sublimation (90 °C at 0.05 Torr) followed by recrystallization from water gave imide with mp 137.5–138 °C (lit. mp 134.5–135 °C).[14]

cis-Cyclopentane-1,2-dicarboximide (**13**) was prepared in four steps from 2-carbalkoxycyclohexanone (Aldrich) via *trans*-cyclopentane-1,2-dicarboxylic acid,[15] which was converted in refluxing acetic anhydride to the cis anhydride.[16] The imide was obtained from the anhydride as described above, sublimed (80 °C at 0.01 Torr), and recrystallized from water, mp 85.5–86° (lit. mp 85–87 °C).[17]

cis-Cyclohexane-1,2-dicarboximide (**14**) was prepared as described above from the corresponding anhydride (Aldrich). Imide recrystallized from water melted at 134–135 °C (lit. mp 136–137 °C).[18]

4-Cyclohexene-1,2-dicarboximide (**15**) was commercially available from Aldrich.

General Procedure for the Preparation of Imide Silver Salts. A procedure similar to that reported by Schwartz and Lerner for the preparation of silver maleimide was employed.[9] To a solution of the imide in absolute ethanol (4 mL/mmol) was added a solution of 0.98 equiv of silver nitrate in dimethyl sulfoxide (0.7 mL/mmol). To this solution with rapid stirring was added dropwise 0.95 equiv of sodium ethoxide in ethanol (ca. 0.4 M, prepared from sodium metal and absolute ethanol, and standardized with 0.10 N hydrochloric acid). Typical addition time was ca. 1.5 h for a 0.3-mol scale. Stirring was continued for 1–2 h, and the resulting slurry was then stored overnight in the freezer to aid aggregation. The solid was collected on filter paper by suction filtration and washed well successively with absolute ethanol, water, absolute ethanol, acetone, and ether. The white to brown powder was sucked dry in the funnel under a rubber dam and further dried overnight in vacuo (<0.05 Torr) at ambient temperature. Without characterization the dry salt was used in the subsequent alkylation step. All manipulations were performed in such a way as to afford a minimum exposure of silver compounds to light.

From 16.9 g (0.135 mol) of imide **12** was obtained 27.9 g (0.120 mol, 94%) of a brown powder.

From 5.0 g (0.036 mol) of imide **13** was obtained 6.3 g (0.026 mol, 71%) of a brown powder.

From 5.0 g (0.033 mol) of imide **14** was obtained 7.8 g (0.030 mol, 97%) of an off-white powder.

From 17.6 g (0.117 mol) of imide **15** was obtained 25.9 g (0.100 mol, 86%) of a tan powder.

General Procedure for the Preparation of Keto Imino Ethers (16, 17, 18, and 19). The procedure is essentially that of Comstock and Wheeler.[10] To a slurry of the imide silver salt in dry chloroform (1 mL/mmol) was added 1.5 equiv of ethyl iodide. The slurry was refluxed with vigorous stirring in the dark for 2 days, cooled, and filtered through Celite to remove silver iodide. The filter cake was washed well with dry chloroform, and the combined filtrates were rotary evaporated. The resulting crude product was distilled (**17** and **18**) or sublimed (**19**). After an initial purification step (vide infra), **16** was also distilled.

2-Ethoxy-3-azabicyclo[3.2.0]hept-2-en-4-one (16). The crude oil, obtained from 27.9 g (0.12 mol) of the silver salt of **12** as described above, was dissolved in a few milliliters of dry ether and cooled in the freezer. The crystals of imide which precipitated were removed by filtration and washed with ether. The ether solvent of the filtrate was removed by rotary evaporation. Distillation of the residual oil at 64–66 °C (0.01 Torr) gave 8.4 g (46%, 84%, based on recovered imide) of a water-white liquid identified as **16**. An analytical sample, prepared by evaporative distillation, had the following spectral properties: IR (CH_2Cl_2) 3.39, 5.75, and 6.42 μ; ^1H NMR ($CDCl_3$) δ 1.42 (t, J = 7 Hz, 3 H), 1.77–2.97 (m, 4 H), 3.00–3.60 (m, 2 H), and 4.55 ppm (q, J = 7 Hz, 2 H); UV (THF) 213 nm (ϵ 4930) and 274 (64); mass spectrum *m/e* (rel intensity), 153 (32), 126 (10), 125 (91), 108 (22), 98 (13), 97 (49), 96 (base), 83 (29), 82 (57), 81 (30), 80 (13), 70 (49), 69 (29), 68 (11), 56 (19), 55 (54), 54 (93), 53 (56), 52 (16), 51 (13), 42 (28), 41 (25), 40 (14), 38 (45).

Anal. Calcd for $C_8H_{11}NO_2$: C, 62.73; H, 7.24; N, 9.14. Found: C, 62.72; H, 7.26; N, 9.12.

2-Ethoxy-3-azabicyclo[3.3.0]oct-2-en-4-one (17). From 5.95 g (0.024 mol) of the silver salt of **13** was obtained 3.37 g (83%) of **17** as a water-white liquid, bp 61–62 °C (0.02 Torr). An analytical sample, prepared by evaporative distillation, had the following spectral properties: IR (CH_2Cl_2) 3.39, 5.72, and 6.38 μ; ^1H NMR ($CDCl_3$) δ 0.95–2.28 (m, 6 H), 1.32 (t, J = 7 Hz, 3 H), 2.88–3.42 (m, 2 H), and 4.42 ppm (q, J = 7 Hz, 2 H); UV (THF) 214 nm (ϵ 3007) and 273 (50); mass spectrum *m/e* (rel intensity) 167 (39), 139 (base), 111 (32), 98 (29), 97 (17), 96 (35), 95 (23), 83 (19), 70 (24), 69 (20), 68 (95), 67 (58), 66 (10), 58 (20), 55 (19), 43 (51), 42 (12), 41 (31), 40 (10), 39 (24), and 31 (16).

Anal. Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.80; H, 7.90; N, 8.32.

7-Ethoxy-8-azabicyclo[4.3.0]non-7-en-9-one (18). From 7.81 g (0.030 mol) of the silver salt of **14** was obtained 4.43 g (82%) of **18** as a water-white liquid, bp 70–72 °C (0.01 Torr). An analytical sample, prepared by evaporative distillation, had the following spectral properties: IR (CH_2Cl_2) 3.42, 5.73, and 6.40 μ; ^1H NMR ($CDCl_3$) δ 1.10–2.27 (m, 8 H), 1.40 (t, J = 7 Hz, 3 H), 2.67–3.27 (m, 2 H), and 4.53 ppm (q, J = 7 Hz, 2 H); UV (THF) 220 nm (ϵ 2300) and 258 (50); mass spectrum *m/e* (rel intensity) 181 (53), 153 (73), 152 (12), 124 (29), 112 (37), 111 (10), 110 (10), 109 (11), 98 (18), 83 (15), 82 (64), 81 (56), 79 (15), 70 (23), 68 (22), 67 (44), 55 (22), 54 (21), 53 (22), 41 (39), 39 (18), 32 (19), 31 (12), 29 (37), 28 (base), and 27 (29).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.28; H, 8.36; N, 7.70.

7-Ethoxy-8-azabicyclo[4.3.0]nona-3,7-dien-9-one (19). The crude product from 25.9 g (0.100 mol) of the silver salt of **15** was sublimed at 50 °C (0.01 Torr) to give 15.5 g (86%) of **19** as white needles, mp 51.5–56.5 °C. An analytical sample prepared by resublimation at 40–45 °C (0.015 Torr) had the following spectral properties: IR (CH_2Cl_2) 3.38, 5.73, and 6.38 μ; ^1H NMR ($CDCl_3$) δ 1.40 (t, J = 7 Hz, 3 H), 2.17–2.63 (m, 4 H), 2.77–3.13 (m, 2 H), 4.15 (q, J = 7 Hz, 2 H), and 5.57–6.17 ppm (m, 2 H); UV (THF) 208 nm (ϵ 6320) and 257 (64); mass spectrum *m/e* (rel intensity) 180 (12), 179 (base), 151 (31), 122 (18), 108 (16), 81 (38), 80 (72), 79 (90), 78 (16), 77 (37), 72 (10), 70 (22), 66 (15), 54 (11), 53 (11), 39 (18), 29 (30), 28 (54), and 27 (29).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.90; H, 7.34; N, 7.87.

Irradiation of Keto Imino Ethers 16 and 17. The respective keto imino ether (5.0 g) was dissolved in 100 mL of dry THF in a quartz immersion well apparatus. The solution was stirred magnetically and degassed with nitrogen for 0.5 h. The solution was irradiated (ca. 2.5 h) with a Hanovia 450-W mercury lamp through a Vycor filter until gas chromatographic analysis at 150 °C with a 2.1 m by 0.63 cm column of 5% FS-1265 on 60/80 mesh Diatoport S (He 60 mL/min) showed the starting material to be greater than 90% destroyed. The reaction could also be monitored by disappearance of the C=N stretching band at 6.4 μ in the IR spectrum and appearance of the isocyanate stretching band at 4.42 μ. Anhydrous dimethylamine (Eastman) was then bubbled into the solution with stirring until gas chromatographic analysis with the same column at 100–110 °C indicated no further loss in peak height for the product. Several byproducts were observed, with retention times similar to that of the photoproduct from **17**, which complicated determination of the end point of the trapping reaction. The solvent was removed by rotary evaporation and the crude product isolated as described below.

***N,N*-Dimethyl-*N'*-5-(5-ethoxybicyclo[2.1.0]pentyl)urea (20).** Ether was added to the oily residue left from evaporation of the solvent (vide supra) and the mixture was stirred well. A white, crystalline powder (2.4 g) separated, and was collected by filtration. The residue from rotary evaporation of the filtrate was sublimed at 70 °C (0.01 Torr) to give a thick oil. Trituration of this material with ether gave an additional 0.4 g of white crystals (total yield of **20**, 2.8 g, 43%). The combined crystalline product was one pure stereoisomer by ^1H NMR and ^{13}C NMR spectroscopy. A sample recrystallized from acetonitrile melted at 151.5–152 °C. An analytical sample prepared by sublimation of the recrystallized material at 65 °C (0.01 Torr) had the following spectral properties: IR (CH_2Cl_2) 2.91, 3.39, 3.42, 6.00, and 6.66 μ; ^1H NMR ($CDCl_3$) δ 1.12 (t, J = 7 Hz, 3 H), 1.17–1.63 (m, 2 H), 1.70–2.40 (m, 4 H), 3.00 (s, 6 H), 3.72 (q, J = 7 Hz, 2 H), and 5.37–5.63 ppm (broad, 1 H); mass spectrum *m/e* (rel intensity) 198 (0.5), 169 (19), 111 (10), 83 (14), 82 (15), 72 (base), 44 (11), and 28 (15).

Anal. Calcd for $C_{10}H_{18}N_2O_2$: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.60; H, 9.16; N, 14.13.

^1H NMR analysis of the ether-soluble oil left from the second crop of crystals indicated that it contained a mixture of the two stereoisomers of **20** plus some impurities. Medium pressure liquid chromatography of the oil was performed with a 2.54 by 61 cm column of Woelm 0.032–0.063 mm silica gel eluting with 5% methanol in ethyl acetate at 9 mL/min and 5-mL fractions were collected. Fractions 54–80 yielded 0.40 g (6%) of a light green oil that appeared by ^1H NMR spectroscopy to be an impure mixture of the two stereoisomers of **20**. The isomers were present in a ratio of 2.3:1 estimated from the peak heights of the NMe resonances. The minor isomer was identified as the previously isolated stereoisomer of **20** by the position of the NMe resonance (δ 3.00 ppm). The major isomer present in this sample gave an NMe resonance at δ 2.92 ppm. No further attempt was made to isolate or characterize the minor stereoisomer since it constituted less than 4% of product.

***N,N*-Dimethyl-*N'*-6-(6-ethoxybicyclo[3.1.0]hexyl)urea (22).** Rotary evaporation of the solvent from the reaction mixture (vide supra) afforded a white solid which was dissolved in ca. 15 mL of hot acetonitrile. On cooling, 2.3 g of white crystals were isolated. Rotary evaporation of the solvent from the mother liquor followed by addition of enough ether to effect solution (ca. 5 mL) and storage in the freezer for 5 days yielded an additional 0.9 g of white crystals (total yield 3.2 g, 50%). The combined product was one stereoisomer of **22** by ^{1}H NMR and ^{13}C NMR analysis. A sample of the product recrystallized from acetonitrile melted at 138–138.5 °C. An analytical sample of **22** prepared by sublimation at 65 °C (0.01 Torr) of the recrystallized material gave the following spectral absorptions: IR (CH_2Cl_2) 2.93, 3.40, 3.42, 6.02, and 6.68 μ; ^{1}H NMR ($CDCl_3$) δ 0.77–2.17 (m, 8 H) 1.13 (t, J = 7 Hz, 3 H), 2.95 (s, 6 H), 3.65 (q, J = 7 Hz, 2 H), and 5.07–5.47 ppm (broad, 1 H); mass spectrum *m/e* (rel intensity) 212 (0.5), 183 (54), 95 (24), 73 (11), 72 (base), 67 (14), 57 (11), 46 (12), 44 (16), and 41 (11).

Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20. Found: C, 62.14; H, 9.52; N, 13.22.

Sublimation at 65 °C (0.01 Torr) of the residue from the ether crystallization produced a viscous oil which was chromatographed on 85 g of silica gel using ethyl acetate as eluent. Four 100-mL fractions were collected. The third and fourth fractions contained an oil which was shown by ^{1}H NMR analysis to consist of an unidentified impurity and a mixture of the stereoisomers of **22**. Medium-pressure liquid chromatography of the oil was performed as described above for **20**. Fractions 54–70 contained a light green oil (0.38 g, 6%) which ^{1}H NMR analysis showed to be a mixture of approximately equal amounts of the two stereoisomers of **22**. The new stereoisomer gave the following ^{1}H NMR resonances: ($CDCl_3$) δ 1.10 (t, J = 7 Hz, 3 H), 0.77–2.17 (m, 8 H), 2.92 (s, 6 H), and 3.69 ppm (q, J = 7 Hz, 2 H).

Irradiation of Keto Imino Ethers 17, 18, and 19. The keto imino ether (2–10 g) was dissolved in 110 mL of dry THF in the immersion well apparatus, degassed, and irradiated (vide supra). Reaction progress was monitored by disappearance of the 6.4 μ IR band of the keto imino ether, and the irradiation was stopped at greater than 90% destruction of starting material. The solvent was removed by rotary evaporation and the product was isolated by vacuum distillation.

6-Isocyanato-6-ethoxybicyclo[3.1.0]hexane (21). From 2.0 g (0.012 mol) of **17** after 2 h irradiation, 1.47 g (76%) of **21** was obtained as a water-white liquid after Kugelrohr distillation at 70–80 °C (0.5 Torr). A sample prepared by evaporative distillation had the following spectral properties: IR (CH_2Cl_2) 4.42, 6.92, and 7.70 μ; ^{1}H NMR ($CDCl_3$) major isomer δ 1.20 (t, J = 7 Hz, 3 H), 1.50–2.17 (m, 8 H), and 3.65 ppm (q, J = 7 Hz, 2 H), minor isomer δ 1.23 (t, J = 7 Hz, 3 H), 1.50–2.17 (m, 8 H), and 3.67 ppm (q, J = 7 Hz, 2 H); mass spectrum *m/e* (rel intensity) 167 (3), 139 (53), 138 (13), 111 (56), 98 (48), 97 (29), 96 (41), 95 (29), 83 (41), 70 (39), 69 (29), 68 (base), 67 (94), 66 (11), 65 (10), 55 (27), 53 (11), 41 (44), 40 (11), and 39 (26). The isocyanate **21** was not sufficiently stable for an acceptable elemental analysis and was therefore analyzed as the dimethylurea derivative **22** (vide supra).

7-Isocyanato-7-ethoxybicyclo[4.1.0]heptane (23). From 10.0 g (0.055 mol) of **18** after 26.5 h of irradiation was obtained 6.42 g (64%) of **23** as a water-white liquid, bp 41–46 °C (0.5 Torr). An analytical sample prepared by evaporative distillation had the following spectral properties: IR (CH_2Cl_2) 4.42, 6.93, and 7.48 μ; ^{1}H NMR ($CDCl_3$) major isomer δ 1.18 (t, J = 7 Hz, 3 H), 1.00–2.18 (m, 10 H), and 3.65 ppm (q, J = 7 Hz, 2 H), minor isomer δ 1.17 (t, J = 7 Hz, 3 H), 1.00–2.18 (m, 10 H), and 3.62 ppm (q, J = 7 Hz, 2 H); mass spectrum *m/e* (rel intensity) 181 (2), 153 (26), 152 (11), 125 (15), 124 (44), 112 (68), 111 (17), 110 (14), 109 (17), 98 (33), 96 (21), 85 (14), 83 (27), 82 (77), 81 (base), 80 (21), 79 (50), 77 (20), 72 (11), 71 (15), 70 (47), 69 (17), 68 (44), 67 (92), 66 (14), 65 (11), 56 (15), 55 (53), 54 (48), 53 (45), 52 (12), and 51 (14).

Anal. Calcd for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.40; H, 8.35; N, 7.66.

7-Isocyanato-7-ethoxybicyclo[4.1.0]hept-3-ene (24). From 10.0 g (0.056 mol) of **19** after 22.5 h irradiation was obtained 5.32 g (53%) of **24** as a water-white liquid, bp 37–39 °C (0.02 Torr). This yield may be low due to the volatility of the product. An analytical sample prepared by evaporative distillation had the following spectral properties: IR (CH_2Cl_2) 4.42, 7.01, and 7.50 μ; ^{1}H NMR ($CDCl_3$) δ 1.20 (t, J = 7 Hz, 3 H), 1.33–1.67 (m, 2 H), 1.80–2.77 (m, 4 H), 3.48 (q, J = 7 Hz, 2 H), and 5.42 ppm (m, 2 H); mass spectrum *m/e* (rel intensity) 179 (3), 151 (19), 122 (12), 108 (14), 81 (28), 80 (68), 79 (base), 78 (18), 77 (43), 72 (10), 70 (23), 67 (11), 66 (14), 53 (13), 52 (11), 51 (15), 43 (12), 40 (20), and 38 (21).

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.10; H, 7.36; N, 7.79.

Registry No.—**12**, 1122-09-4; **12** anhydride derivative, 4462-96-8; **12** Ag(I), 62506-04-1; **13**, 62506-05-2; **13** anhydride derivative, 35878-28-5; **13** Ag(I), 62506-06-3; **14**, 7506-66-3; **14** anhydride, 13149-00-3; **14** Ag(I), 62506-07-4; **15**, 1469-48-3; **15** Ag(I), 62506-08-5; *exo*-**20**, 62532-68-7; *exo*-**22**, 62506-09-6.

References and Notes

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