Photochemical Reactivity of Keto Imino Ethers. Determination of the Stereochemistry of the Type I Rearrangement of 2-Ethoxypyrrolin-5-ones by Natural Abundance ^{13}C and ^{15}N Nuclear Magnetic Resonance Spectroscopy[1,2]

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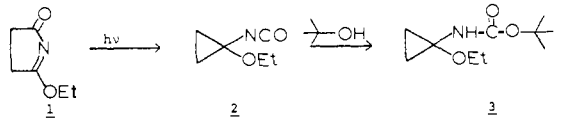
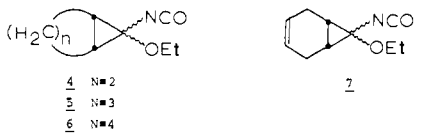
Abstract: The stereochemistry of the photochemical rearrangement of 2-ethoxypyrrolin-5-ones to ethoxycyclopropylisocyanates is described. *cis*- and *trans*-3,4-dimethyl-2-ethoxypyrrolin-5-ones (**10** and **11**, respectively) rearrange to 2,3-dimethylethoxycyclopropylisocyanates, isolated and characterized as methyl carbamates **14a**, **14b**, and **15**, with 98% retention of stereochemistry at carbon 4 of the pyrrolinones. The methyl *N*-(*cis*-2,3-dimethylethoxycyclopropyl)carbamates (**14a** and **14b**) are formed stereoselectively in a ratio of 3.3 to 1.0. Similar stereoselectivity occurs in formation of the bicyclic systems **4**, **5**, **6**, and **7**. Stereochemical assignments were made from γ steric shifts observed in the natural abundance ^{13}C and ^{15}N NMR spectra. This represents the first application of a γ steric shift in natural abundance ^{15}N NMR for stereochemical assignment. *cis*-Piperylene (0.10 M) had no effect on the stereospecificity of the photorearrangement of **11** within experimental error. The reaction mechanism is discussed in terms of the intermediacy of a σ,π-type diradical formed via α cleavage of the n,π^* singlet state of 2-ethoxypyrrolin-5-ones.

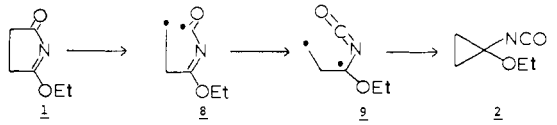
We have reported that 2-ethoxypyrrolin-5-one (**1**) photorearranges to ethoxycyclopropyl isocyanate (**2**) in tetrahydrofuran solvent in 78% isolated yield and to the *tert*-butyl carbamate (**3**) in *tert*-butyl alcohol solvent in 70% isolated



yield.[3] Subsequently we have shown that the photorearrangement is of general synthetic utility for the preparation of bicyclo[*n*.1.0]alkanes (**4**, **5**, and **6**) and bicyclo[4.1.0]hep-



tene (**7**), all functionalized at the one-carbon bridge.[2] The photorearrangement of **1** occurs with a quantum yield of 0.31 from the n,π^* singlet state in *tert*-butyl alcohol. Intersystem crossing to the triplet state occurs with an efficiency of 0.19, and the triplet state appears to be photostable. In view of the facility with which ketones in their n,π^* states α cleave, a Norrish type I mechanism was proposed.[4,5]

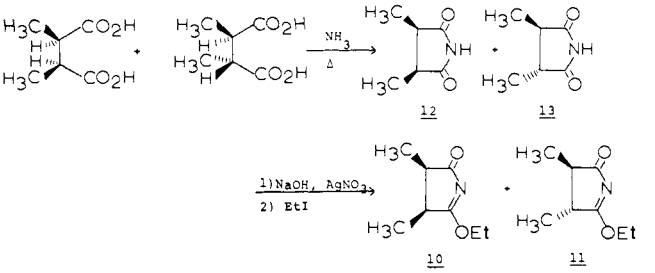


We have now examined the stereospecificity of the photorearrangement as a possible test for the intermediacy of biradicals such as **8** and/or **9**.

Results

The stereospecificity of the photorearrangement of pyrrolin-5-ones was examined with *cis*- and *trans*-3,4-dimethyl derivatives (**10** and **11**). Dimethyl derivatives rather than dideuterio derivatives were ultimately selected for this investigation because of difficulty with hydrogen–deuterium exchange during the synthesis of the required 3,4-dideuteriopyrrolin-5-ones.

A mixture of **10** and **11** was prepared by O-alkylation with ethyl iodide of the silver salts of a mixture of *cis*- and *trans*-3,4-dimethylsuccinimides (**12** and **13**). The procedure is



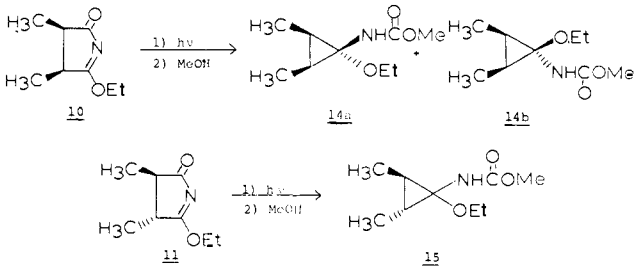
analogous to that reported by Comstock and Wheeler for the preparation of **1**.[3] The mixture of dimethylsuccinimides was synthesized by reaction of a commercially available mixture of *meso*- and *dl*-dimethylsuccinic acids with ammonia at elevated temperature. The *cis*- and *trans*-3,4-dimethyl-2-ethoxypyrrolin-5-ones (**10** and **11**) were separated by preparative gas–liquid chromatography and characterized by their spectrosopic properties (Experimental Section). The stereochemistry was assigned from the relative chemical shifts of the methyl groups in the ^{13}C NMR spectra (Table I). The chemical shifts for the *cis*-methyl substituents appear ~3–4 ppm higher field than the chemical shifts for the *trans*-methyl substituents in the succinimides (**12** and **13**) and the pyrrolinones (**10** and **11**). This is consistent with the steric shift predicted for the more crowded methyls of the cis isomers.[6,7]

10 gave almost exclusively two diastereoisomeric methyl *N*-(2,3-dimethylethoxycyclopropyl)carbamates (**14a** and **14b**) in a ratio of 3.3:1.0 in 58% total isolated yield, and **11** gave almost exclusively one methyl *N*-(2,3-dimethylethoxycyclopropyl)carbamate (**15**) in 60% isolated yield. The carbamates were characterized from spectral and analytical data (Experimental Section). The stereochemistry of the methyl substituents was again established from the ^{13}C NMR spectra (Table I). From a steric shift of ~6 ppm for the methyl absorptions of **14a** and **14b** relative to the methyl absorptions of

Table I. ^{13}C NMR Spectral Data

Compd	C=O	Methine	Chemical shifts[a] Methyl	C=N	OEt	Quaternary	OMe
13	180.62	44.27	14.63				
12	181.73	39.57	11.32				
11	196.43[b]	44.71, 47.43	15.07, 15.59	193.93[b]	67.66, 14.19		
10	197.54[b]	39.71, 42.14	11.03, 12.21	194.96[b]	67.59, 14.19		
15	[c]	28.24, 29.96	13.39, 12.47		62.95, 15.48	72.90	52.56
14a,b	158.13	22.93	7.81		62.28, 15.62	72.12	52.76[d]
	158.13	21.95	6.84		62.90, 15.62	72.12	52.76

[a] ^{13}C NMR spectra were obtained by Fourier transform NMR in $CDCl_3$, and chemical shifts are reported in parts per million from internal TMS. Assignments were made from splitting patterns in off-resonance decoupled spectra. [b] Carbonyl and imine carbons could not be unambiguously assigned. [c] The carbonyl carbon could not be distinguished from noise in the base line. [d] Major isomer, **14a**.

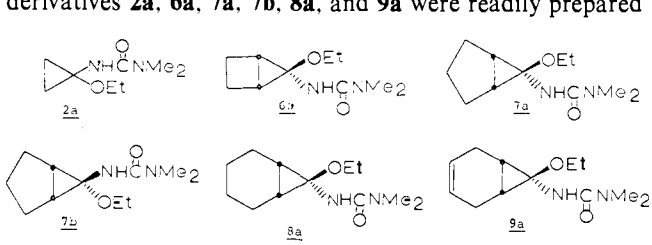


15, diastereoisomers **14a** and **14b** were assigned *cis*-dimethyl stereochemistry and **15** was assigned *trans*-dimethyl stereochemistry.

The stereochemistry of the carbamate and ethoxy substituents of the cis isomers **14a** and **14b** could not be assigned from ^1H or ^{13}C NMR spectra. Similarly, the stereochemistry of the isocyanato and ethoxy substituents of the previously reported bicyclic photoproducts **4**, **5**, **6**, and **7** could not be assigned.[2]

Roberts and co-workers have recently shown that natural abundance ^{15}N NMR spectra of amines,[8] hydrazines,[9] and lactams,[10] among other nitrogen-containing compounds,[11] can be readily obtained most recently using Fourier transform techniques.[10,11] They have shown that nitrogen chemical shifts are susceptible to the same kinds of electronic and steric influences as ^{13}C shifts. In particular, a γ carbon results in an upfield shift of 2.7 ppm in acyclic primary amines, and the shift appears to be sterically induced.[8] A dominant γ steric effect is also given as the simpliest interpretation for the observation that *cis*-1,2-diaminocyclobutane absorbs at 13.5 ppm higher field than *trans*-1,2-diaminocyclobutane; however, stereoelectronic and hydrogen-bonding effects are also thought to be important.[8] These results suggest that it should be possible to assign the stereochemistry of the nitrogen substituent relative to the carbon substituents of the photoproducts from ^{15}N NMR chemical shifts. The ^{15}N chemical shifts, especially for stereoisomers **14a** and **14b**, should differ predominantly by the magnitude of the steric shift of two γ carbons.

The natural abundance ^{15}N spectra were obtained with carbamates **14a**, **14b**, and **15** and the *N,N*-dimethylurea derivatives of isocyanates **2**, **4**, **5**, **6**, and **7**. The dimethylurea derivatives **2a**, **6a**, **7a**, **7b**, **8a**, and **9a** were readily prepared



from the isocyanates as described previously[2] or as described in the Experimental Section. Carbamate and dimethylurea derivatives were employed to facilitate handling and to achieve a nuclear Overhauser enhancement from broad-band proton decoupling.[8,9] In most cases the ^{15}N resonance of the unprotonated dimethylamino nitrogen of the ureas could also be observed, although the signal was substantially smaller.

Table II. ^{15}N NMR Spectral Data

Compd		Chemical shifts[a] NH	NMe_2
2		19.8	50.3
15		22.2[b,c]	
14a	Major product	28.0[b,c]	
14b	Minor product	15.2[b,c]	
6a	Major product[d]	31.3	50.5
7a	Major product	27.2	50.1
7b	Minor product	16.6	Not observed
8a	Major product[d]	27.2	50.0
9a	Major product[d]	30.0	49.8

[a] ^{15}N NMR spectra were obtained by Fourier transform NMR, in $CDCl_3$ except as noted, and chemical shifts are reported in parts per million upfield from internal 2-pyrrolidone. The δ (^{15}N) for 2-pyrrolidone is reported to be 259.3 ppm upfield from external ^{15}N-enriched HNO_3.[10] [b] Spectra were obtained with a known unequal mixture of stereoisomers. [c] Acetone-d_6 was used as the internal locking solvent. [d] Sufficient quantities of the minor stereoisomer could not be obtained for natural abundance ^{15}N NMR spectroscopy.

The ^{15}N chemical shifts are reported in Table II in parts per million upfield from the internal reference 2-pyrrolidone. 2-Pyrrolidone was selected as an internal standard because it is unreactive with the carbamates and ureas, its natural abundance ^{15}N resonance is easily observed, and the chemical shift is known relative to external ^{15}N-enriched nitric acid.[10]

Based upon the work of Roberts which suggests that the γ shift in ^{15}N NMR is sterically induced, the spectral shifts clearly establish the stereochemistry of the nitrogen substituent with respect to the carbon substituents. For the stereoisomeric *cis*-2,3-dimethylethoxycyclopropylcarbamates **14a** and **14b** the ^{15}N resonances differ by 12.8 ppm, and the stereoisomer with the higher field ^{15}N resonance was assigned the stereochemistry of the nitrogen substituent syn to the methyl substituents consistent with the predicted steric shift. The steric shift per methyl substituent is 6.4 ppm. Methyl *trans*-2,3-dimethylethoxycyclopropylcarbamate (**15**) bears one sterically interacting methyl substituent, and its nitrogen should have a chemical shift ~6.4 ppm higher field than the chemical shift of the nitrogen of **14b**. The calculated chemical shift of **15**, equal to 21.8 ppm, is in good agreement with the observed chemical shift (Table II). The chemical shifts for the cyclopropyl-substitued nitrogens of the bicyclic ureas **7a** and **7b** differ by 10.6 ppm and the stereoisomer **7a** with the higher field ^{15}N resonance was similarly assigned the stereochemistry of the nitrogen syn to the carbon substituents. The other bicyclic ureas (**6a**, **8a**, and **9a**) gave high field ^{15}N resonances and were assigned the syn stereochemistry. To our knowledge this represents the first application of natural abundance ^{15}N NMR

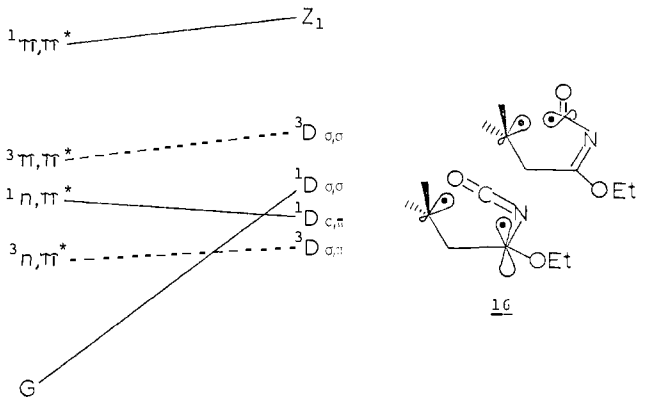


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Figure 1. State correlation diagram for the α cleavage of 2-ethoxypyrrolin-5-one. The ordering of $D_{\sigma,\sigma}$ singlet and triplet states is uncertain and will depend upon nonorthogonality through-bond interactions, etc.[20]

spectroscopy for the assignment of the stereochemistry of a nitrogen substituent relative to a carbon substituent.

Prior to workup, product ratios from irradiation of **10** and **11** were carefully measured four times by analytical gas chromatography, and the results are presented in Table III. Product ratios from irradiation of **10** were corrected for 2% impurity of **11** in the starting material. Both diastereoisomeric pyrrolinones (**10** and **11**) gave 98 ± 1% retention of stereochemistry at carbon 4.

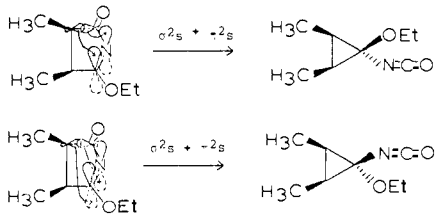
Irradiation of **11** in the presence of 0.10 M *cis*-piperylene gave cyclopropane product, with 97 ± 1% retention of stereochemistry. The *cis*-piperylene was partially isomerized to *trans*-piperylene during the photoreaction.

Discussion

The results of the stereochemistry experiments indicate that the photorearrangement is highly stereospecific with respect to carbon 4 and stereoselective with respect to carbon 2. The triplet quenching experiment with *cis*-piperylene is consistent with reactivity from the n,π^* singlet state and intersystem crossing to an unreactive but quenchable triplet state.[3,12] The results of the quenching experiment are completely analogous to the results reported in detail for the parent system **1**.[3]

There are two reasonable interpretations of the stereospecificity at carbon 4 of the pyrrolinones (**10** and **11**). The reaction could be completely stereospecific and occur by a symmetry-allowed concerted [$_\sigma 2_s + {}_\pi 2_s$] pathway (Scheme I),[13] equivalently via a Hückel four-electron transition state,[14]

Scheme I



or via a short-lived singlet diradical intermediate which ring closes by a rate more than an order of magnitude faster than the rate for bond rotation. The stereoselectivity at carbon 2 of the pyrrolinones is probably governed by steric interactions in the transition states for ring closure via either mechanism. The concerted pathway is analogous to the mechanism proposed for the singlet-state 1,3-sigmatropic rearrangement of β,γ-unsaturated ketones,[15] and the diradical mechanism is analogous to the diradical mechanism proposed for the photochemical ring expansion of cyclobutanones [16-18] Both of these reactions also show a high degree of stereospecificity.[15,16,18] Because the photorearrangement of **10** and **11** does not appear

Table III. Stereospecificity of the Photorearrangement

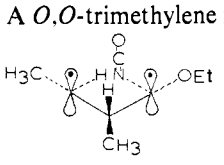
Reagent	Product yields, %	
	trans-**15**	*cis*-**14a,b**
10[a]	2 ± 1	98 ± 1[b]
11	98 ± 1	2 ± 1

[a] Yields were corrected for 2% **11** contaminant in **10**. [b] The ratio of **14a**/**14b** was 3.3.

to be completely stereospecific and because the orbitals involved are approximately orthogonal, at least in the ground state, we tend to favor a mechanism with a diradical intermediate. High stereospecificity and a diradical intermediate are compatible in terms of the hot molecule effect described by Stephenson and Brauman.[19]

The diradical mechanism can be further described in terms of a Salem state correlation diagram[20] as shown in Figure 1. The ordering of the excited states and diradical states was chosen to explain the observed photochemistry and photophysics and is quite similar to the Salem diagrams for analogous α cleavage of 2,4-cyclohexadienones[20] and alkanones.[17,20] The ultraviolet absorption spectrum[2,3] establishes the order of ^{1}n,π^* and $^1\pi,\pi^*$ states. The lack of reactivity of **1** in the [2 + 2] photocycloaddition reaction of alkenes to the carbon–nitrogen double bond of **1** is consistent with an n,π^* configuration for the lowest energy triplet state.[21] The σ,π diradical states were placed below the σ,σ diradical states because of π-delocalization effects in the former.[20] With this arrangement of states (Figure 1), the n,π^* singlet state smoothly correlates with the singlet σ,π diradical state. Inefficiency in the singlet manifold can possibly be explained by the crossing of the ^{1}n,$\pi^* \rightarrow {}^1D_{\sigma,\pi}$ potential energy surface with the surface connecting the ground state with $^1D_{\sigma,\sigma}$. Decay of the n,π^* singlet state by a mechanism of this type should give starting material without a change in stereochemistry as observed.[20] The reactivity of the ^{3}n,π^* state is probably a function of the relative energies of the ^{3}n,π^* and $^3D_{\sigma,\pi}$ states. With the relative energies shown, intersystem crossing of the ^{3}n,π^* to the ground state may be quite competitive with cleavage.

The photorearrangement reaction of pyrrolinones can be compared with other reactions which also presumably occur via 1,3 diradicals. Two thermal methods for the generation of 1,3 diradicals are the pyrolysis of pyrazolines and the pyrolysis of cyclopropanes. Varying degrees of stereospecificity have been observed in these reactions. Two highly stereospecific thermal cyclopropane cis–trans isomerizations have been reported by Berson and co-workers.[22] The reaction mechanism is thought to be conrotatory ring opening to a *O,O*-trimethylene[23] followed by conrotatory ring closure to starting material or isomerized cyclopropane. *O,O*-Trimethylene diradicals plus 1,3 diradicals structurally different from *O,O*-trimethylenes have been implicated as intermediates from pyrolysis of pyrazolines.[24] The number and type of 1,3-diradical intermediates is probably a function of substitution and reaction conditions.[25] If 1,3 diradicals are intermediates in the photorearrangement of pyrrolinones **10** and **11**, the diradicals must have structures different from the *O,O*-trimethylene structure such as **17**. A *O,O*-trimethylene intermediate would



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randomize the stereochemistry at carbon 4, independent of the mode of ring closure, conrotatory or disrotatory. Ring closure of a σ,π type diradical such as **16** prior to rotation, however, would give the observed stereospecificity.

In summary we have reported evidence which indicates that the photorearrangement of 2-ethoxypyrrolin-5-ones (**10** and **11**) is highly stereospecific at carbon 4 and occurs almost exclusively with retention of configuration. The rearrangement is also stereoselective at carbon 2 of the pyrrolinones and yields predominantly the stereoisomer with the isocyanate functional group syn to the carbon substituents. A reaction mechanism involving the intermediacy of a σ,π-type diradical is favored.

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 Mat CH-5 spectrometers were used to determine IR and mass spectra, respectively. ^1H and ^{13}C NMR spectra were recorded with Varian T60A and JEOL PFT-100 spectrometers, respectively, and chemical shifts are reported in δ units from internal tetramethylsilane. GLC analyses and isolations were performed with a Wilkins Model 200 gas chromatograph equipped with a thermal conductivity detector, and peak areas were measured as peak height times width at half height. Microanalyses were performed by Atlantic Microlab, Atlanta, Ga.

***cis* and *trans*-2,3-Dimethylsuccinimides (12 and 13).** To a long-neck 50-mL round bottom flask, equipped with a side arm and a cold finger condenser with a cup at the bottom, was added 2.01 g (13.8 mmol) of 2,3-dimethylsuccinic acid (mixture of meso and *dl* isomers). With magnetic stirring, ammonia gas was introduced through the side arm while the flask was slowly heated to 190 °C with an oil bath. The reaction mixture was heated at 190 °C until the contents of the flask began to reflux on the sides of the flask. The flask was then allowed to cool to room temperature and the solid product was dissolved in a mixture of water, ethanol, and benzene. Rotary evaporation of the water–ethanol–benzene azeotrope yielded a tan solid which upon vacuum sublimation at 50 °C (0.02 Torr) gave 1.53 g (88%) of a 4:1 mixture of *trans*- and *cis*-2,3-dimethylsuccinimide, mp 87–93 °C (lit. melting point of trans isomer 107–109 °C; cis isomer 45–47 °C).[26] The mixture of stereoisomers gave the following spectroscopic data: IR (KBr) 3.14, 3.37, 5.86 μ; NMR ($CDCl_3$), trans isomer, δ 1.40 (d, J = 7 Hz, 6 H), 2.25–2.80 (m, 2 H), 8.27 ppm (br, 1 H); NMR, cis isomer, δ 1.25–1.55 (m, 6 H), 2.80–3.35 (m, 2 H), 8.27 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 127 (25), 99 (10), 84 (11), 56 (base), 41 (42).

***cis* and *trans*-3,4-Dimethyl-2-ethoxypyrrolin-5-one (10 and 11).** To a 250-mL round-bottom flask was added 1.85 g (14.6 mmol) of a 4:1 mixture of *trans*- and *cis*-2,3-dimethylsuccinimide dissolved in 62 mL of absolute ethanol followed by 2.60 g (15.3 mmol) of silver nitrate in 12 mL of distilled water. The flask was covered with aluminum foil, and 44 mL of a 0.325 M ethanolic sodium hydroxide solution was added dropwise with stirring over a period of 30 min. The reaction mixture was stirred at ambient temperature for 21 h. Benzene was added to the flask and the benzene–ethanol–water azeotrope rotary evaporated in the dark. The flask was then covered with aluminum foil and the light brown crystals were vacuum dried for 48 h at 25 °C (0.02 Torr). The silver succinimides were then alkylated by adding 92 mL of dry chloroform and 4.84 g (31 mmol) of ethyl iodide and refluxing for 24 h in the aluminum foil covered flask. The silver iodide was removed by vacuum filtration and the solvent by rotary evaporation. The resulting yellow oil was vacuum distilled at 60–70 °C (0.02 Torr) to yield 1.98 g (88%) of a mixture of *trans*- and *cis*-3,4-dimethyl-2-ethoxypyrrolin-5-one. The cis and trans isomers were separated by preparative GLC using a 2 m by 0.64 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 137 °C (He 55 mL/min). The trans isomer gave the following spectral data: IR (neat) 3.38, 5.72, 6.38 μ; NMR ($CDCl_3$) δ 1.15 (d, J = 7 Hz, 3 H), 1.17 (d, J = 7 Hz, 3 H), 1.21 (t, J = 7 Hz, 3 H), 1.80–2.75 (m, 2 H), 4.33 (q, J = 7 Hz, 2 H); mass spectrum (70 eV) m/e (rel intensity) 155 (29), 140 (24), 127 (35), 113 (base), 84 (24), 70 (41), 69 (21), 56 (76), 55 (35), 43 (24), 41 (35); UV λ_{max} (THF) 271 nm (ϵ 46). The cis isomer gave the following spectral data: IR (neat) 3.39, 5.73, 6.39 μ; NMR ($CDCl_3$) δ 1.08 (d, J = 7 Hz, 3 H), 1.10 (d, J = 7 Hz, 3 H), 1.38 (t, J = 7 Hz, 3 H), 2.40–3.30 (m, 2 H), 4.45 (q, J = 7 Hz, 2 H); mass spectrum (70 eV) m/e (rel intensity) 155 (27), 140 (20), 127 (38), 113 (base), 84 (24), 70 (42), 69 (22), 56 (89), 55 (33), 43 (56), and 41 (42); UV λ_{max} (THF) 270 nm (ϵ 64). The pyrrolinones were insufficiently stable to moisture for accurate elemental analysis.

Irradiation of 11. To a micro irradiation apparatus, consisting of a 15 cm × 1 cm i.d. quartz test tube with a 14,9 cm × 0.6 cm o.d. Pyrex cold finger, was added 106 mg (0.85 mmol) of **11** in 3.0 mL of dry tetrahydrofuran (distilled from lithium aluminum hydride). The solution was degassed for 30 min with nitrogen and irradiated external to a Vycor filtered, 450-W mercury lamp for 2 h with continuous nitrogen degassing. At this time 97% of the starting material was destroyed as indicated by GLC with a 2 m × 0.64 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 137 °C (He 55 mL/min). At this time 1.0 mL of dry methanol (distilled from magnesium methoxide) was added and the nitrogen degassing continued for 31 h in the dark. The solvent was partially removed by rotary evaporation, and the carbamate product ratios were measured four times by GLC with a 2 m × 0.64 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 117 °C (He 55 mL/min). The mixture of methyl *N*-(*trans*-2,3-dimethylethoxycyclopropyl)carbamate (**15**) and the two methyl *N*-(*cis*-2,3-dimethylethoxycyclopropyl)carbamate diastereoisomers (**14a** and **14b**) was 49.0 ± 0.5 to 1.0 ± 0.5. The remaining solvent was then removed by rotary evaporation. The trans carbamate (77 mg, 60%) was isolated by preparative GLC, using the column and conditions described above, as a colorless oil with the following spectral properties: IR (neat) 3.03, 3.40, 5.82 μ; NMR ($CDCl_3$) δ 0.6–1.25 (m, 8 H), 1.18 (t, J = 7 Hz, 3 H), 3.60 (q, J = 7 Hz, 2 H), 3.73 (s, 3 H), 5.75 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 187 (7), 158 (60), 84 (73), 76 (73), 69 (base).

Anal. Calcd for $C_9H_{17}O_3N$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.49; H, 9.17; N, 7.39.

Irradiation of 10. Using the same procedure as described for irradiation of the trans isomer **11**, 110 mg (0.87 mmol) of a 44:1.0 mixture of *cis*- and *trans*-3,4-dimethyl-2-ethoxypyrrolin-5-one was irradiated for 2 h. After reaction of the photoproducts with anhydrous methanol, the solvent was partially removed by rotary evaporation and the carbamate product ratios measured four times by GLC as described above. The mixture of **14a** plus **14b** and **15** was 22.7 ± 0.2 to 1.0 ± 0.5 and the ratio of the two *cis*-dimethylcyclopropylcarbamates (**14a** and **14b**) was 3.3:1.0. The remaining solvent was then removed by rotary evaporation, and 77 mg (58%) of **14a** plus **14b** was isolated by preparative GLC using the 2-m FS-1265 column (vide supra). They gave the following physical and spectral data. Major isomers **14a**: mp 80–82 °C; IR (KBr) 3.04, 3.45, 5.87 μ; NMR (*o*-dichlorobenzene, 60 °C) δ 0.85–1.60 (m, 8 H), 1.20 (t, J = 7 Hz, 3 H). 3.65 (q, J = 7 Hz, 2 H), 3.73 (s, 3 H), 5.35 (br, 1 H); mass spectrum m/e (rel intensity) 187 (6), 158 (73), 84 (81), 76 (77), 69 (base). Minor isomer **14b**: mp 55–60 °C; IR (KBr) 3.08, 3.43, 5.87 μ; NMR (*o*-dichlorobenzene, 60 °C) δ 0.85–1.60 (m, 8 H), 1.23 (t, J = 7 Hz, 3 H), 3.66 (q, J = 7 Hz, 2 H), 3.71 (s, 3 H), 5.57 (br, 1 H); mass spectrum m/e (rel intensity) 187 (9), 158 (73), 84 (90), 76 (79), 69 (base).

Anal. Calcd for $C_9H_{17}O_3N$ (mixture): C, 57.73; H, 9.15; N, 7.48. Found: C, 57.78; H, 9.17; N, 7.48.

Irradiation of 11 in the Presence of *cis*-Piperylene. To the micro irradiation apparatus was added a solution of 92 mg (0.72 mmol) of a 43:1 mixture of **11** and **10** and 27 mg (0.40 mmol) of *cis*-piperylene in 4.0 mL of dry THF. The solution was irradiated as described above to 57% destruction of **11** as indicated by GLC. The photoproduct was then reacted with ~2 mL of dry methanol. Isomerization of *cis*-piperylene was measured by GLC using a 4 m by 0.64 cm 25% β,β-oxydipropionitrile on 80/100 mesh Chromosorb P column at ambient temperature (He 60 mL/min). The ratio of *cis*- to *trans*-piperylene was 12.4. A portion of the solvent was then removed by rotary evaporation and the carbamate product ratios were determined four times by GLC (vide infra). After correction of peak areas for the small amount of **10** in the starting material, 97 ± 1% of the carbamate product was **15** and 3 ± 1% was a mixture of **14a** and **14b**.

^{15}N NMR Spectra. The ^{15}N NMR spectra were obtained at a frequency of 10.13 MHz with a JEOL PFT-100 pulse spectrometer using an 11-μs pulse (20° flip angle) with a pulse repetition of 1.1 s. All spectra were broad band proton decoupled, and all resonances exhibited a negative nuclear Overhauser effect.[8,9] Spectra of **2a**, **6a**, **7a**, **8a**, **and 9a** were obtained using 2 mL of a solution 1 M in compound and 1 M in 2-pyrrolidone reference in $CDCl_3$ solvent employed as an internal lock. A spectrum of a mixture of **7a** and **7b** was obtained using a $CDCl_3$ solution 0.5 M in **7a**, 0.5 M in **7b**, and 1 M in 2-pyrrolidone. The resonances of **14a**, **14b**, and **15** were observed with a 3-mL sample 0.4 M in **14a**, 0.2 M in **14b**, 4.2 M in **15**, and 1 M in 2-pyrrolidone

containing ~10% acetone-d_6 employed as an internal lock. The average accumulation time was ~20 h.

Preparation of *N,N*-Dimethylurea Derivatives. Derivatives **6a**, **7a**, and **7b** were prepared as previously described.[1] Derivative **2a** was obtained in 77% yield from addition of gaseous dimethylamine to the product of irradiation of 2.0 g of **1** in THF solvent as described previously.[3] Derivatives **8a** and **9a** were prepared in 65 and 95% yields, respectively, by addition of gaseous dimethylamine to a solution containing 1.0 g of the respective isocyanates in 10 mL of dry THF until GLC analysis using a 2 m × 0.64 cm column of 5% FS-1265 on 60/80 mesh Diatoport S at 100 °C (He 55 mL/min) indicated complete destruction of starting material.

***N,N*-Dimethyl-*N'*-(1-ethoxycyclopropyl)urea (2a).** An analytical sample obtained by recrystallization from acetonitrile had mp 113–113.5 °C and the following spectral properties: IR (CH_2Cl_2) 2.90, 3.41, 6.00, 6.65 μ; NMR ($CDCl_3$) δ 0.87–1.20 (m, 4 H), 1.13 (t, J = 7 Hz, 3 H), 2.93 (s, 6 H), 3.70 (q, J = 7 Hz, 2 H), 5.50–5.83 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 73 (11), 72 (100), 44 (16).

***N,N*-Dimethyl-*N'*-[7-(7 ethoxybicyclo[4.1.0]heptyl)]urea (8a).** An analytical sample obtained by recrystallization from acetonitrile had mp 140–140.5 °C and the following spectral properties: IR (CH_2Cl_2) 2.91, 3.41, 5.98, 6.65 μ; NMR ($CDCl_3$) δ 0.87–2.20 (m, 10 H), 1.12 (t, J = 7 Hz, 3 H), 2.98 (s, 6 H), 3.65 (q, J = 7 Hz, 2 H), 5.15–5.38 ppm (br, 1 H); mass spectrum (70 eV) m/e (rel intensity) 226 (0.76), 197 (76), 144 (13), 109 (37), 88 (12), 80 (15), 72 (100), 46 (11), 44 (15).

***N,N*-Dimethyl-*N'*-[7-(7-ethoxybicyclo[4.1.0]hept-3-enyl)]urea (9a).** An analytical sample obtained by recrystallization from acetonitrile had mp 141.0–141.5 °C and the following spectral properties: IR (CH_2Cl_2) 2.88, 3.30, 3.44, 5.98, 6.61 μ; NMR ($CDCl_3$) δ 1.13 (t, J = 7 Hz, 3 H), 1.40–1.65 (m, 2 H), 2.07–2.47 (m, 4 H), 2.90 (s, 6 H), 3.70 (q, J = 7 Hz, 3 H), 4.96–5.23 (br, 1 H), 5.38–5.63 (m, 2 H); mass spectrum (70 eV) m/e (rel intensity) 224 (4), 195 (31), 107 (16), 78 (14), 72 (100).

References and Notes

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(2) For the previous paper on the photochemistry of the keto imino ether functional group, see G. C. Crockett and T. H. Koch, *J. Org. Chem.*, **42**, 2721 (1977).
(3) T. H. Koch, R. J. Sluski, and R. H. Moseley, *J. Am. Chem. Soc.*, **95**, 3957 (1973).
(4) C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1504 (1945).
(5) J. C. Dalton, K. Dawes, N. J. Turro, D. W. Weiss, J. A. Barltrop, and J. D. Coyle, *J. Am. Chem. Soc.*, **93**, 7213 (1971), and references therein.
(6) For a discussion of the steric chemical shift, see "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", G. C. Levy and G. L. Nelson, Ed., Wiley-Interscience, New York, N.Y., 1972.
(7) An analogous steric shift has been reported for the methyls of *cis*- and *trans*-1,2-dimethylcyclopentanes: M. Christl, H. J. Reich, and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 3463 (1971).
(8) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 2495 (1972).
(9) R. L. Lichter and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 4904 (1972).
(10) K. L. Williamson and J. D. Roberts, *J. Am. Chem. Soc.*, **98**, 5082 (1976).
(11) V. Markowski, C. R. Sullivan, and J. D. Roberts, *J. Am. Chem. Soc.*, **99**, 714 (1977).
(12) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).
(13) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
(14) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971); H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971).
(15) E. Baggiolini, K. Schaffner, and O. Jeger, *Chem. Commun.*, 1103 (1969).
(16) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Acc. Chem. Res.*, **5**, 92 (1972).
(17) N. J. Turro, W. E. Farneth, and A. Devaquet, *J. Am. Chem. Soc.*, **98**, 7425 (1976).
(18) Quinkert has proposed a concerted mechanism for the photochemical ring expansion of cyclobutanones: W. D. Stohrer, P. Jacobs, K. H. Kaiser, G. Weich, and G. Quinkert, *Top. Curr. Chem.*, **46**, 181 (1974).
(19) L. M. Stephenson and J. J. Brauman, *J. Am. Chem. Soc.*, **93**, 1988 (1971); L. M. Stephenson and T. A. Gibson, *ibid.*, **96**, 5624 (1974).
(20) L. Salem, *J. Am. Chem. Soc.*, **96**, 3486 (1974); W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).
(21) R. M. Rodehorst and T. H. Koch, *J. Am. Chem. Soc.*, **97**, 7298 (1975).
(22) J. A. Berson and L. D. Pederson, *J. Am. Chem. Soc.*, **97**, 238 (1975); J. A. Berson, L. D. Pederson, and B. K. Carpenter, *ibid.*, **97**, 240 (1975).
(23) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
(24) T. C. Clarke, L. A. Wendling, and R. G. Bergman, *J. Am. Chem. Soc.*, **97**, 5638 (1975).
(25) P. B. Dervan and T. Uyehara, *J. Am. Chem. Soc.*, **98**, 1262 (1976).
(26) R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 3722 (1954).

Free-Radical Halogenations. Chlorination of Alkanes by *N*-Chlorophthalimide

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Abstract: The photoinitiated free-radical chlorination of hydrocarbons with *N*-chlorophthalimide, NCP, has been investigated. The product distribution obtained at the completion of the reaction was found to be the result of the equilibration of the initially formed alkyl radicals with the product of the abstraction step, hydrogen chloride. The equilibration of the intermediate alkyl radicals, through reversible hydrogen abstraction from hydrogen chloride, was found to complicate the expected Goldfinger-type mechanism for the reaction of this *N*-chloroimide.

The free-radical chlorination reactions of *N*-chlorophthalimide (NCP), would be expected to be similar to those reported for *N*-chlorosuccinimide (NCS), or other *N*-chloroimides. The mechanism of action of NCS has been reported to involve a free radical chain mechanism with chlorine as the hydrogen atom abstracting species, Scheme I.[1] Based upon a comparison of the relative reactivities for NCP chlorinations of hydrocarbons of different structures with the relative rates of reaction obtained for molecular chlorine, NCP appears to proceed by a mechanism different than that described by Scheme I. These discrepancies have been studied and the

Scheme I