Photochemical Cyclization of Olefinic N-Chloroamides

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Chlorination of olefinic N-monoalkylamide lithium derivatives with N-chlorosuccinimide provided N-chloroamides. Irradiation of these in benzene solution with a 450-W high pressure mercury arc through a Corex filter led to bridged and unbridged C-chloro-N-acylpyrrolidines and C-chloro-γ-lactams. No six-membered-ring formation was found but selectivity was shown for double bonds with increased substitution.

Intramolecular addition of amino radicals ($R_2N\cdot$) and aminium radicals ($R_2HN\cdot^+$) to double bonds is well established and has been shown to lead only to the formation of five-membered rings.[1-9] In these studies nitrogen radicals were generated by decomposition of tetrazenes, or from N-nitroso- or N-chloroamines in neutral or acidic solutions, by irradiation or by treatment with titanium trichloride. Since the analogous cyclization of olefinic carbon radicals can be diverted from a kinetically favored five-membered-ring formation to generation of six-membered rings by placing strong radical-stabilizing substituents on the acyclic carbon radical,[10-17] or by steric constraints in the cyclopentane formation,[18,19] it was of interest to see if amide radicals would show divergence from the cyclization of amine radicals. As no cyclizations of olefinic amide radicals were known until the latter part of our investigation, their demonstration as a new method for formation of lactams or N-heterocyclic amides was of particular interest as a model study for alkaloid syntheses.[20]

An electron spin resonance study has shown that the amide radical is best described with location of the radical centered on nitrogen in a 2p orbital[21] and intramolecular hydrogen abstraction[22-26] seems to take place preferentially with transfer of hydrogen to nitrogen rather than oxygen.[24] The photolysis of saturated N-chloroamides thus leads to γ- and δ-chloroamides, which usually cyclize to γ- and δ-iminolactones.[22,23] N-Alkylation has, however, been found in the generation of some bicyclic lactams, where the usual O-alkylation would require bridgehead iminolactones.[26]

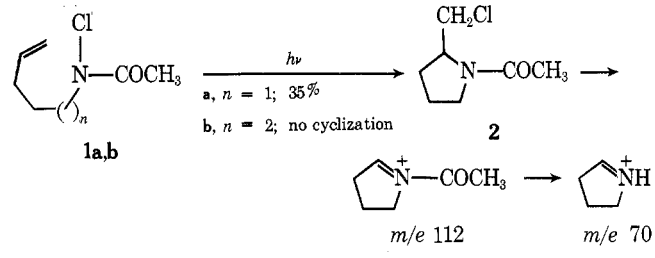
Attempted intermolecular photochemical reactions of N-alkyl-N-chloroamides with a variety of olefins had failed[23] when our intramolecular reaction studies were started but such reactions have now been described for N-chloroacetamide and chlorinated N-chloroacetamides.[20a]

The following examples demonstrate the formation of five-membered lactams or N-heterocyclic amides as main products in the photochemical reactions of olefinic N-alkyl-N-chloroamides and limitations of this new reaction. The product yields which are shown were often obtained from very small scale reactions with high percentage losses in purifications. Higher preparative yields may be possible and the isolation of minor products remains for further investigation.

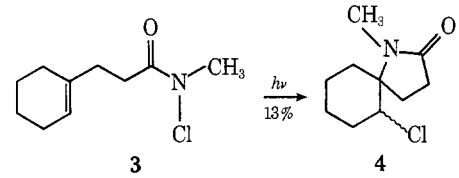
Two general types of N-chloroamides were used in this study. The compounds were either acetamides of olefinic amines or N-methylamides of olefinic acids. The N-chloro derivatives were obtained in 40–70% yields from reactions of these amides with n-butyllithium and N-chlorosuccinimide.

Irradiation of N-chloro-N-(4-n-penten-1-yl)acetamide (**1a**) in benzene solution with a 450-W high-pressure mercury arc, filtered through Corex, gave the N-acetyl-2-chloromethylpyrrolidine **2**. This product was particularly characterized by its mass spectrum, which showed a fragment at *m/e* 70 arising from an initial loss of CH_2Cl to give an *m/e* 112 ion and subsequent loss of CH_2CO, as seen from a metastable peak (*m/e* 43.8) corresponding to the *m/e* 112 to 70 fragmentation.

In contrast to this cyclization, the next higher homolog, N-chloro-N-(5-n-hexen-1-yl)acetamide (**1b**), yielded a mixture of at least seven components containing primarily the parent N–H amide when irradiated in benzene and only that major compound when irradiated in cyclohexane.

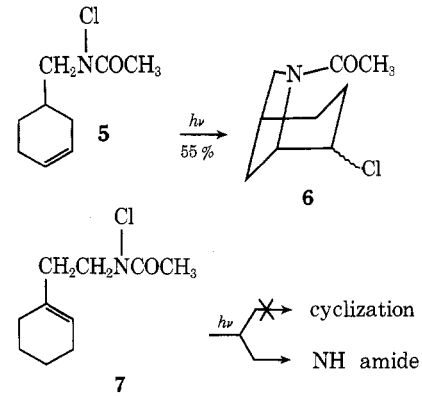


When N-chloro-N-methyl-3-(cyclohex-1-en-1-yl)propionamide (**3**) was subjected to photolysis, only the spirolactam **4** with characteristic ir absorption at 1690 cm^{-1} and an NMR multiplet at δ 4.0 for the proton adjacent to chlorine could be isolated and no perhydroquinolone was obtained.



3 **4**

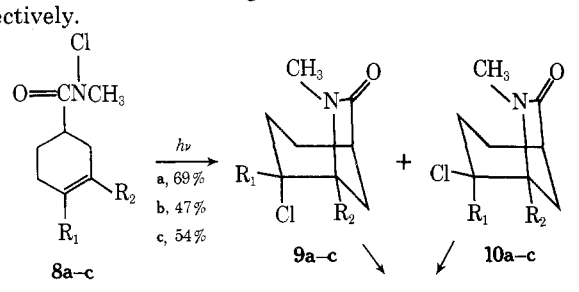
Irradiation of N-chloro-N-[(3-cyclohexen-1-yl)methyl]-acetamide (**5**) gave bicyclic product **6** to which a [3.2.1] bridged structure could be assigned on the basis of the remarkable overlap of its mass spectrum with that of authentic 6-acetyl-6-azabicyclo[3.2.1]octane, prepared by reduction of m-aminobenzoic acid[27] and acetylation.[28] On the other hand, no monomeric cyclization product was obtained from irradiation of N-chloro-N-[2-(1-cyclohexen-1-yl)ethyl]acetamide (**7**), where only the parent amide was isolated.



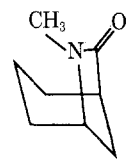
These findings are consistent with the usual preference for five-membered-ring formation and steric facilitation of olefinic radical cyclizations when the double bond and radical centers are separated by three atoms.

Bridged [3.2.1] bicyclic products (**9a** and **10a**) were also obtained from irradiation of *N*-chloro-*N*-methylcyclohex-3-enecarboxamide (**8a**). The product mixture, containing about equal amounts of epimeric chlorolactams, could be separated by absorption chromatography, yielding the less polar axial chloro compound **9a** with an *N*-methyl NMR signal at δ 2.96 and the more polar equatorial chloro epimer **10a** with the *N*-methyl signal at δ 3.16. Reduction of these compounds with tri-*n*-butylstannane gave the lactam **11**, which could be compared with the methylation product of 6-azabicyclo[3.2.1]octan-7-one.[27]

The presence of methyl substituents at either end of the double bond (**8b,c**) did not divert the cyclization reaction from formation of bridged γ-lactams (**9b,c, 10b,c**). Thus the 4-methyl chloroamide **8b** yielded a separable 1:1 mixture of chloro epimers **9b** and **10b**, which showed analogous NMR differences and equivalent mass spectra. Since the 3-methyl chloroamide **8c** could not be completely freed from the 4-methyl isomer **8b**,[30] a mixture of four products was obtained from that reaction. Chromatographic separation into the two sets of axial and equatorial chlorolactams and subtraction of the NMR spectra of pure isomers **9b** and **10b** gave spectra of the isomers **9c** and **10c**, showing protons on carbon bearing chlorine at δ 4.08 and 3.95, respectively.



a, $R_1 = R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$



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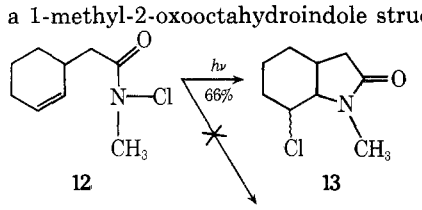
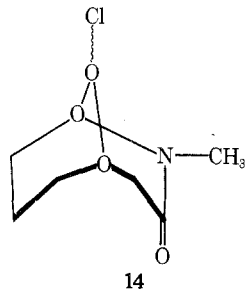
The occurrence of the perhydroindole skeleton in several alkaloid classes prompted an examination of the photochemical cyclization of *N*-chloro-*N*-methyl-2-cyclohexen-1-yl acetamide (**12**). The resultant product could be assigned a 1-methyl-2-oxooctahydroindole structure **13** with exclusion of the alternative bicyclic lactam **14** by its NMR spectrum. The ring juncture proton next to nitrogen was seen as a triplet at δ 3.42, which collapsed to a doublet (J = 7.5 Hz) by decoupling from the proton next to chlorine at δ 3.90.



12 **13**



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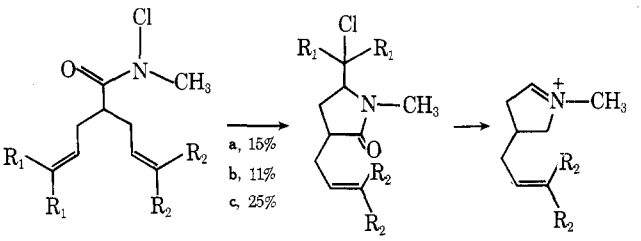
The analogous *N*-3,4-dimethoxybenzyl chloroamide did not yield any cyclization product on irradiation but gave instead the *N*-acylimine by loss of a hydrogen from the benzylic substituent. Since cyclization would have provided facile synthetic access to alkaloids with the lycorane skeleton, the alternative dimethoxyphenylacetic acid amide of 2-(cyclohex-2-en-1-yl)ethylamine was prepared, but it could not be converted to the required *N*-chloroamide.



15a–c **16a–c**

	m/e (100%)
a, $R_1 = CH_3$, $R_2 = H$	**17a**, 138
b, $R_1 = R_2 = H$	b, 138
c, $R_1 = R_2 = CH_3$	c, 166

The above examples show that olefinic chloroamides undergo intramolecular reactions with double bonds at various levels of substitution. In order to learn if there is any selectivity associated with the degree of substitution, the allyl-3,3-dimethylallyl chloroamide **15a** was irradiated. Only the cyclization product **16a**, derived from reaction of the more substituted double bond, could be detected. A characteristic vinyl multiplet in the NMR spectrum and a mass spectral base peak **17a** at *m/e* 138 due to loss of the chloropropenyl group (with no *m/e* 166 peak from loss of chloromethylene) could be compared and contrasted with corresponding spectra derived from cyclization of the symmetric diene chloroamides **15b** and **15c**. Since the unsubstituted double bond did not react at all in the mixed diene **15a** but reacted in the diallyl compound **15b** and since highest yields were found from the fully substituted diene **15c**, selectivity for more substituted double bonds is indicated in this reaction. While this selectivity implies some stability for amide radicals, one does not, however, find formation of *N*-acylpiperidine rather than *N*-acylpyrrolidine products corresponding to cyclizations of stabilized olefinic carbon radicals. The difference may be due to a smaller compression barrier and less ring strain in formation of the intermediate *N*-acylpyrrolidine radical.

Experimental Section

Preparation of Amides. *N*-(4-*n*-Penten-1-yl)acetamide. To 1.1 g (0.029 mol) of lithium aluminum hydride in 125 ml of ether, 2.45 g (0.029 mol) of 4-pentenonitrile was added dropwise in an equal volume of ether so as to maintain a steady reflux. The mixture was refluxed overnight, then 0.28 ml of water followed by 0.28 ml of 15% sodium hydroxide followed by 0.84 ml of water was added. The ether layer was filtered and cooled, and 2.94 g (0.0288 mol) of acetic anhydride was added dropwise with stirring. The solution was stirred for 1.5 hr, then 20 ml of 15% sodium hydroxide was added and the mixture was stirred overnight. The ether layer was separated, dried over magnesium sulfate, filtered, and concentrated to yield a colorless liquid which was distilled to give 2.5 g (68%) of a colorless oil: bp 70–71° (0.02 mm); ir 1650, 1550 cm^{-1}; NMR δ 1.65 (q, 2 H), 1.98 (s, 3 H), 2.10 (m, 2 H), 3.25 (q, 2 H), 4.85–6.00 (m, 3 H), 6.65 (m, 1 H).

Anal. Calcd for $C_7H_{13}NO$: C, 66.1; H, 10.3; N, 11.0. Found: C, 66.3; H, 10.5; N, 11.1.

N-(5-*n*-Hexen-1-yl)acetamide was prepared similarly from 5-hexenonitrile,[32] giving 74% of colorless liquid: bp 84–85° (0.07 mm); ir 1550, 1650 cm^{-1}; NMR δ 1.95 (s, 3 H), 3.25 (q, 2 H), 4.8, 5.1, 5.8 (3 m, 4 H).

Anal. Calcd for $C_8H_{15}NO$: C, 68.0; H, 10.7; N, 9.9. Found: C, 68.0; H, 10.9; N, 10.1.

***N*-[(3-Cyclohexen-1-yl)methyl]acetamide.** To a slurry of 3.58 g (0.094 mol) of lithium aluminum hydride in 200 ml of ether was added 10 g (0.094 mol) of 3-cyclohexenecarbonitrile in an equal volume of dry ether. The mixture was refluxed for 24 hr and cooled, and 0.94 mol of water was added slowly, followed by 0.94 ml of 10% sodium hydroxide solution and 3 ml of water. The resulting white precipitate was removed by filtration. The ether solution was cooled to 0° and 7.8 g (0.076 mol) of acetic anhydride dissolved in an equal volume of ether was added dropwise. The resulting solution was slurried for 3 hr at room temperature; 10 ml of 10% sodium hydroxide was added and the solution was stirred for an additional 45 min. The aqueous layer was separated and the ether layer was dried over potassium carbonate, filtered, and concentrated to a colorless oil. Distillation yielded 10.7 g (75%): bp 88–95° (0.07 mm); ir 1650 cm^{-1}; NMR δ 1.9 (s, 3 H), 3.1 (t, 2 H), 5.6 (s, 2 H), 7.8 (br, 1 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.6; H, 9.9; N, 9.1. Found: C, 70.6; H, 10.0; N, 9.0.

***N*-Methyl-3-cyclohexenylcarboxamide.** A solution of 5.0 g (0.039 mol) of 3-cyclohexencarboxylic acid in 125 ml of dry benzene was cooled to 0°, and 7.0 g (0.059 mol) of oxalyl chloride was added slowly with stirring. After 3 hr at room temperature the benzene and excess oxalyl chloride were evaporated, 150 ml of dry benzene was added to the residue, and excess anhydrous methylamine was bubbled through the solution. Evaporation of the solvent, solution in ether, washing with 10% hydrochloric acid, and concentration and crystallization from pentane gave 4.8 g (89%) of white solid: mp 89–90°; ir 1660 cm^{-1}; NMR δ 2.2 (m, 6 H), 2.8 (d, 3 H), 5.7 (s, 2 H), 6.1 (br, 1 H).

Anal. Calcd for $C_8H_{13}NO$: C, 69.0; H, 9.4; N, 10.1. Found: C, 69.2; H, 9.5; N, 9.8.

3- and 4-Methyl-3-cyclohexenecarboxylic Acid. A sealed glass tube containing 11.3 g (0.166 mol) of isoprene and 12.0 g (0.166 mol) of acrylic acid was heated to 120° for 8 hr. Then the tube was cooled and the semisolid contents were washed with cold hexane to give 10.8 g (46%) of white solid: mp 88–92°,[30] 97–99°; ir 1700 cm^{-1}; NMR δ 1.64 (s, 3 H), 2.1 (m, 7 H), 5.30 (s, 1 H), 11.19 (s, 1 H). Dehydrogenation over palladium on charcoal at 215° gave *p*-toluic acid, indicating the solid acid to be the 4-methyl isomer.

The liquid portion was distilled to give 8.2 g (35%) of colorless liquid: bp 60–62° (0.01 mm); ir 1700 cm^{-1}; NMR δ 1.64 (s, 3 H), 2.1 (m, 7 H), 5.30 (s, 1 H), 11.2 (s, 1 H). This was taken to be the 3-methyl isomer.

4- and 3-Methyl-*N*-methyl-3-cyclohexenecarboxamide. In analogy to the above preparation of the cyclohexenecarboxamide, the 4-methyl-substituted compound was prepared in 93% yield: mp 111–112°, crystallized from hexane; ir 1650 cm^{-1}; NMR δ 1.60 (s, 3 H), 2.68 (d, 3 H), 5.04 (s, 1 H), 5.84 (br, 1 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.6; H, 9.9; N, 9.1. Found: C, 70.7; H, 10.0; N, 9.0.

From 2.5 g (0.017 mol) of 3-methyl-3-cyclohexenecarboxylic acid was prepared 2.3 g (86%) of *N*-methylamide, crystallized from hexane–benzene: mp 51–56°; ir 1650 cm^{-1}; NMR δ 1.56 (s, 3 H), 2.64 (d, 3 H), 5.08 (s, 1 H), 5.64 (br, 1 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.6; H, 9.9; N, 9.1. Found: C, 70.8; H, 10.0; N, 8.9.

***N*-Methyl-2-(2-cyclohexen-1-yl)acetamide.** To 50 g (0.036 mol) of 2-(2-cyclohexen-1-yl)acetic acid[33] in 12.5 ml of benzene, 0.45 g (0.035 mol) of oxalyl chloride was added at 0°. The mixture was stirred overnight at room temperature, benzene and excess oxalyl chloride were evaporated, and the crude acid chloride was added dropwise to 125 ml of benzene, saturated at 0° with methylamine. The solution was stirred for 1 hr; then water was added and the organic layer was separated, washed with 10% hydrochloric acid, and dried over magnesium sulfate. The solvent was evaporated and the residue was crystallized from pentane to give 4.5 g (80%) of white needles: mp 58–58.5°; ir 1650 cm^{-1}; NMR δ 2.72 (d, 3 H), 5.50 (m, 2 H), 6.10 (m, 1 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.5; H, 9.9; N, 9.1. Found: C, 70.4; H, 9.8; N, 9.3.

2-Allyl-*N*,5-dimethyl-4-hexenamide. To 125 ml of dry ethyl ether and 0.129 mol of sodium hydride (6.2 g, 50% dispersion in mineral oil, from which the oil was removed by washing with pentane) was added dropwise 17 g (0.086 mol) of ethyl 2-acetyl-5-methyl-4-hexenoate.[33] The slurry was stirred for 15 min; then 10.4 g (0.086 mol) of allyl bromide dissolved in an equal volume of dry ether was added dropwise. This mixture was refluxed overnight, then filtered, washed with water, and dried over magnesium sulfate. The ether solvent was evaporated to give 14.6 g (71%) of ethyl 2-acetyl-2-allyl-5-methyl-4-hexenoate: bp 67–72° (0.02 mm); ir 1650, 1720, 1750 cm^{-1}; NMR δ 1.28 (t, 3 H), 1.64 (s, 3 H), 1.72 (s, 3 H), 2.16 (s, 3 H), 2.62 (d, 4 H), 4.24 (q, 2 H), 4.78–6.00 (m, 4 H).

To a solution of 2.0 g (0.087 mol) of sodium in 150 ml of methanol, 14.6 g (0.061 mol) of ethyl 2-acetyl-2-allyl-5-methyl-4-hexenoate was added, and the solution was refluxed overnight. Half of the methanol was evaporated, water was added, and the mixture was quickly extracted with ethyl ether. The ether solution was dried over magnesium sulfate, concentrated, and the residual oil distilled to yield 7.6 g (69%) of methyl 2-allyl-5-methyl-4-hexenoate: bp 104–106° (26 mm); ir 1650, 1750 cm^{-1}; NMR δ 1.64 (s, 3 H), 1.72 (s, 3 H), 2.32 (m, 5 H), 3.76 (s, 3 H), 5.0–6.2 (m, 4 H).

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.5; H, 10.0. Found: C, 72.7; H, 10.1.

Hydrolysis of 9.2 g (0.039 mol) of methyl 2-allyl-5-methyl-4-hexenoate in 150 ml of methanol and 20 ml of water with 3.5 g (0.087 mol) of sodium hydroxide at room temperature (2 hr) was followed by removal of half of the solvent, addition of more water, and extraction with ether. To the aqueous layer 10% hydrochloric acid was added until the pH was about 4, and this solution was extracted with ether. The acidic ether extracts were dried over magnesium sulfate, concentrated, and the residual liquid distilled to give 3.66 g (58%) of colorless oil: bp 73–76° (0.05 mm); ir 1720 cm^{-1}; NMR δ 1.68 (s, 3 H), 1.72 (s, 3 H), 2.41 (m, 5 H), 5.09–6.16 (m, 4 H), 12.0 (s, 1 H).

To 125 ml of dry benzene and 3.7 g (0.023 mol) of 2-allyl-5-methyl-4-hexenoic acid, cooled in an ice bath, 4.3 g (0.034 mol) of oxalyl chloride was added dropwise. The solution was stirred overnight at room temperature. Benzene and excess oxalyl chloride were evaporated, and the crude acid chloride was added dropwise to 125 ml of dry benzene saturated with methylamine. The solution was stirred for 1 hr, water was added, and the benzene layer was separated and dried over magnesium sulfate. Concentration and distillation gave 3.6 g (82%) of colorless oil: bp 84–86° (0.02 mm); ir 1650 cm^{-1}; NMR δ 1.64 (s, 3 H), 1.72 (s, 3 H), 2.26 (m, 5 H), 2.86 (d, 3 H), 5.00–6.20 (m, 5 H).

Anal. Calcd for $C_{11}H_{19}NO$: C, 72.9; H, 10.6; N, 7.7. Found: C, 73.1; H, 10.8; N, 7.7.

2-Allyl-*N*-methyl-4-pentenamide. Following the above procedure, 19.5 g of ethyl 2-acetyl-2-allyl-4-pentenoate[34] was converted to 11.3 g (78%) of methyl 2-allyl-4-pentenoate: bp 64–66° (15 mm); ir 1630, 1730 cm^{-1}; NMR δ 2.32 (m, 5 H), 3.60 (s, 3 H), 4.80–5.88 (m, 6 H). Analogous subsequent reactions gave the *N*-methylamide in 69% yield: mp 54–55°; ir 1640 cm^{-1}; NMR δ 2.20 (m, 5 H), 2.72 (d, 3 H), 4.60–5.90 (m, 7 H).

Anal. Calcd for $C_9H_{15}NO$: C, 70.5; H, 9.9; N, 9.1. Found: C, 70.4; H, 10.0; N, 8.9.

***N*,5-Dimethyl-2-(3-methyl-2-buten-1-yl)-4-hexenamide.** Similarly, 7.74 g (0.0395 mol) of 2-(3-methyl-2-buten-1-yl)-5-methyl-4-hexenoic acid[35] was converted to 6.2 g (75%) of the *N*-methylamide: bp 95–99° (0.01 mm); ir 1670 cm^{-1}; NMR δ 1.58 (s, 6 H), 1.66 (s, 6 H), 2.20 (m, 5 H), 3.26 (s, 3 H), 4.92 (t, 2 H).

Anal. Calcd for $C_{13}H_{23}NO$: C, 74.6; H, 11.1; N, 6.7. Found: C, 74.8; H, 11.2; N, 6.6.

Preparation of *N*-Chloroamides Using Ethyl Ether as Solvent. The procedure for preparation of *N*-chloro-*N*-methyl-3-cyclohexenecarboxamide (**8a**) is representative. To 50 ml of dry ethyl ether and 1.0 g (0.0072 mol) of *N*-methyl-3-cyclohexenylcarboxamide, 4.5 ml (0.0072 mol) of 1.6 *M* *n*-butyllithium in hexane was added. A jelly-like precipitate formed rapidly and the mixture was stirred for 1 hr. To this mixture 1.44 g (0.0108 mol) of *N*-chlorosuccinimide was added all at once and the mixture was refluxed overnight. Water was added, and the ether layer was separated, washed with water, dried over magnesium sulfate, and concentrated. The residual oil was chromatographed on silica gel and eluted with ether. The first fraction gave a light yellow oil which was distilled to yield 0.96 g (76%) of a colorless oil: bp 44–47° (0.1 mm); ir 1675 cm^{-1}; uv λ_{max} (C_2H_5OH) 206 nm (log ϵ 3.66); NMR δ 2.0 (m, 6 H), 3.3 (s, 3 H), 5.78 (s, 2 H).

Anal. Calcd for $C_8H_{12}NOCl$: C, 55.3; H, 7.0; N, 8.1; Cl, 20.4. Found: C, 55.5; H, 7.1; N, 7.9; Cl, 20.4.

***N*-Chloro-*N*-[2-(1-cyclohexen-1-yl)ethyl]acetamide (7).** From 2.0 g (0.00912 mol) of *N*-[2-(1-cyclohexen-1-yl)ethyl]acetamide[36] in 100 ml of ethyl ether was prepared 1.34 g (55%) of *N*-chloro-*N*-(2-(1-cyclohexen-1-yl)ethyl)acetamide: bp 50–55° (0.08 mm); ir 1675 cm^{-1}; NMR δ 1.6 (m, 5 H), 2.0 (m, 5 H), 2.2 (s, 3 H), 3.8 (t, 2 H), 5.5 (br, 1 H).

Anal. Calcd for $C_{10}H_{16}NOCl$: C, 59.6; H, 8.0; N, 6.9; Cl, 17.6. Found: C, 59.3; H, 8.2; N, 6.9; Cl, 17.5.

Preparation of *N*-Chloro-*N*-(5-*n*-hexen-1-yl)acetamide (1b). From 1.0 g (0.0071 mol) of *N*-(5-*n*-hexen-1-yl)acetamide in 50 ml of ethyl ether was prepared 0.60 g (48%) of chloroamide: bp 60–70° (0.07 mm); ir 1675 cm^{-1}; NMR δ 1.55 (m, 6 H), 2.14 (s, 3 H), 3.72 (t, 2 H), 4.85–6.15 (m, 3 H).

Anal. Calcd for $C_8H_{14}NOCl$: C, 54.7; H, 8.0; N, 8.0; Cl, 20.2. Found: C, 55.0; H, 8.1; N, 7.9; Cl, 20.2.

***N*-Chloro-*N*-(4-*n*-penten-1-yl)acetamide (1a).** From 1.0 g (0.0079 mol) of *N*-(4-*n*-penten-1-yl)acetamide in 50 ml of ether was prepared 0.54 g (42%) of *N*-chloroamide: bp 42–43° (0.03 mm); ir 1675 cm^{-1}; NMR δ 1.98 (m, 4 H), 2.27 (s, 3 H), 3.78 (t, 2 H), 4.89–6.00 (m, 3 H).

Anal. Calcd for $C_7H_{12}NOCl$: C, 52.0; H, 7.5; N, 8.7; Cl, 21.9. Found: C, 52.0; H, 7.6; N, 8.5; Cl, 22.0.

***N*-Chloro-*N*,5-dimethyl-2-allyl-4-hexenamide (15a).** From 0.967 g (0.00535 mol) of *N*-methyl-2-allyl-4-hexenamide in 50 ml of ethyl ether was prepared 0.523 g (45%) of *N*-chloroamide: ir 1650 cm^{-1}; NMR δ 1.68 (s, 3 H), 1.76 (s, 3 H), 2.38 (m, 5 H), 3.48 (s, 3 H), 5.04–6.24 (m, 4 H).

Preparation of *N*-Chloroamides using 1,2-dimethoxyethane as a Solvent. The procedure for preparation of *N*-chloro-*N*-[(3-cyclohexen-1-yl)methyl]acetamide (**5**) is representative. To 1.07 g (7.04 mmol) of *N*-[(3-cyclohexen-1-yl)methyl]acetamide and 50 ml of dry 1,2-dimethoxyethane under nitrogen, 4 ml (~8.0 mmol) of *n*-butyllithium in hexane was added. After stirring for 1.5 hr, 1.02 g (8.2 mmol) of *N*-chlorosuccinimide dissolved in 50 ml of dry 1,2-dimethoxyethane was added dropwise and the mixture was stirred for 3 hr at room temperature. Water was added, followed by dichloromethane. The organic layer was separated, washed with saturated sodium chloride, and dried over magnesium sulfate. Concentration and chromatography of the residual yellow oil on silica gel, eluting with ethyl ether, gave 0.48 g (36%) of *N*-chloroamide: ir 1665 cm^{-1}; NMR δ 2.22 (2, 3 H), 3.60 (d, 2 H), 5.62 (s, 2 H).

Anal. Calcd for $C_9H_{14}NOCl$: C, 57.6; H, 7.5; N, 7.5; Cl, 18.9. Found: C, 57.4; H, 7.6; N, 7.6; Cl, 18.6.

***N*-Chloro-*N*-methyl-2-(2-cyclohexen-1-yl)acetamide (12).** From 1.0 g (0.0065 mol) of *N*-methyl-2-(2-cyclohexen-1-yl)acetamide was prepared 0.80 g of *N*-chloroamide: ir 1670 cm^{-1}; NMR δ 1.60 (m, 6 H), 2.50 (m, 3 H), 3.28 (s, 3 H), 5.50 (m, 2 H).

***N*-Chloro-*N*-methyl-3-(1-cyclohexen-1-yl)propionamide (3).** From 0.319 g (1.90 mmol) of *N*-methyl-3-(1-cyclohexen-1-yl)propionamide was prepared 0.162 g (42%) of *N*-chloroamide: ir 1670 cm^{-1}; NMR δ 0.76 (m, 12 H), 3.36 (s, 3 H), 5.44 (s, 1 H).

***N*-Chloro-*N*,5-dimethyl-2-(3-methyl-2-buten-1-yl)-4-hexenamide (15c).** From 1.11 g (0.0053 mol) of *N*,5-dimethyl-2-(3-methyl-2-buten-1-yl)-4-hexenamide was prepared 0.76 g (57%) of *N*-chloroamide: ir 1670 cm^{-1}; NMR δ 1.58 (s, 6 H), 1.66 (s, 6 H), 2.20 (m, 5 H), 3.26 (s, 3 H), 4.42 (t, 2 H).

Preparation of *N*-Chloro-*N*-methyl-2-allyl-4-pentenamide (15b). From 1.0 g (0.0062 mol) of *N*-methyl-2-allyl-4-pentenamide was prepared 0.55 g (47%) of *N*-chloroamide: ir 1660 cm^{-1}; NMR δ 2.24 (m, 5 H), 3.24 (s, 3 H), 4.72–5.80 (m, 6 H).

***N*-Chloro-*N*,3-dimethyl- and *N*,4-dimethyl-3-cyclohexenecarboxamide (8c and 8b).** From 1.0 g (0.0065 mol) of *N*,3- and -4-dimethyl-3-cyclohexenecarboxamide was prepared 0.71 g (58%) of *N*-chloroamide: ir 1660 cm^{-1}; NMR δ 1.64 (s, 3 H), 2.0 (m, 6 H), 3.28 (s, 3 H), 5.24 (s, 1 H).

***N*-Chloro-*N*,4-dimethyl-3-cyclohexenecarboxamide (8b).** From 1.0 g (0.0065 mol) of *N*,4-dimethyl-3-cyclohexenecarboxamide was prepared 0.80 g (65%) of *N*-chloroamide: ir 1660 cm^{-1}; NMR δ 1.64 (s, 3 H), 2.0 (m, 6 H), 3.29 (s, 3 H), 5.23 (s, 1 H).

Photolysis of *N*-Chloroamides. *N*-Chloroamides were irradiated in benzene under a nitrogen atmosphere using a Hanovia 450-W high-pressure mercury arc with a Corex filter, unless otherwise stated. The photolysis apparatus consisted of a Pyrex cylinder (55 mm. i.d. and 298 mm long) with a 60/50 ground joint on top, into which a water-jacketed quartz lamp housing was fitted. A no. 2 stopcock 70 mm from the top of the ground joint was connected to a mercury seal gas trap during the irradiations.

Photolysis of *N*-Chloro-*N*-methyl-3-cyclohexenecarboxamide (8a). The following procedure for the photolysis of *N*-chloro-*N*-methyl-3-cyclohexenecarboxamide is representative. To 190 ml of dry benzene in the photolysis apparatus was added 0.55 g of *N*-chloroamide. Nitrogen was bubbled through the solution for 5 min, and the solution was then irradiated for 15 min. Benzene was evaporated and ether was added to the light brown oil to give a brown precipitate and colorless solution. The ether solution was separated and concentrated to yield 0.50 g of light brown oil. The oil was distilled to yield 0.38 g (69%) of colorless oil: bp 60–62° (0.01 mm); ir 1700 cm^{-1}; NMR δ 2.0 (m, 7 H), 2.92 (s, 1.5 H), 3.16 (s, 1.5 H), 3.76 (t, 0.5 H), 3.92 (d, 0.5 H), 4.16 (m, 0.5 H), 4.40 (s, 0.5 H); a mixture of isomers **9a** and **10a**.

Anal. Calcd for $C_8H_{12}NOCl$: C, 55.3; H, 7.0; N, 8.1; Cl, 20.4. Found: C, 55.1; H, 7.2; N, 7.9; Cl, 20.1.

The isomers were separated as follows. Onto a chromatographic column containing 100 g of silica gel was placed 0.168 g of the mixture and this was eluted with ethyl ether. A solvent gradient, starting with 1% ethanol and 2.5% increments using 200 ml each, was brought to 10% ethanol, when fractions were obtained.

Fraction 1 was distilled to yield 0.070 g: bp 60–61° (0.01 mm); ir 1700 cm^{-1}; NMR δ 2.0 (m, 7 H), 2.96 (s, 3 H), 3.76 (t, 1 H), 4.40 (s, 1 H).

Fraction 2 was distilled to yield 0.053 g: bp 60–61° (0.01 mm); ir 1700 cm^{-1}; NMR δ 2.0 (m, 7 H), 3.16 (s, 3 H), 3.88 (d, 1 H), 4.10 (m, 1 H).

The mass spectra of the isomers were identical: *m/e* 173 (34), 138 (48), 110 (100), 96 (57), 42 (61).

Fraction 1 was assigned as 6-methyl-4-*exo*-chloro-6-azabicyclo-[3.2.1]octan-7-one (**10a**), and fraction 2 was assigned as 6-methyl-4-*endo*-chloro-6-azabicyclo[3.2.1]octan-7-one (**9a**) on the basis of the position of the methyl singlet (NMR) and polarity.

Photolysis of *N*-Chloro-*N*-[(3-cyclohexen-1-yl)methyl]acetamide (5). Irradiation of 0.476 g (2.55 mmol) of *N*-chloro-*N*-[(3-cyclohexen-1-yl)methyl]acetamide in 190 ml of dry benzene for 20 min gave 0.405 g of a light brown oil, distilled to yield 0.268 g (55%) of colorless liquid (**6**): bp 80–90° (0.01 mm); ir 1620 cm^{-1}; NMR δ 2.20 (s, 3 H), 3.52 (m, 2 H), 4.05 (m, 1 H), 4.32 (m, 1 H); mass spectrum *m/e* (rel intensity) 187 (M^+, 28), 152 (7), 145 (9), 110 (75), 68 (100).

Anal. Calcd for $C_9H_{14}NOCl$: C, 57.6; H, 7.5; N, 7.5; Cl, 18.9. Found: C, 57.8; H, 7.7; N, 7.5; Cl, 18.8.

Photolysis of *N*-Chloro-*N*-[2-(1-cyclohexen-1-yl)ethyl]acetamide (7). A solution of 1.3 g (0.0065 mol) of chloroamide in 150 ml of dry benzene was irradiated until the solution did not darken a potassium iodide solution in aqueous acetic acid (1.25 hr). The mixture was worked up as described above to yield 0.11 g of a light yellow oil which was found to be identical with *N*-[2-(1-cyclohexen-1-yl)ethyl]acetamide.

Photolysis of *N*-Chloro-*N*-(5-*n*-hexen-1-yl)acetamide (1b). An irradiated solution of 0.60 g (0.0034 mol) of the chloroamide in 150 ml of dry benzene was checked every 30 min with potassium iodide in aqueous acetic acid. After 1.5 hr the test solution no longer turned dark when added to a small amount of the photolysis mixture, indicating absence of active chlorine. The mixture was worked up as above and the oil was distilled to give 0.11 g of a material which contained seven components on TLC (Eastman silica gel sheet developed with ethyl ether). The NMR of the crude product was very similar to that of *N*-(5-*n*-hexen-1-yl)acetamide.

Irradiation of 0.213 g (0.00122 mol) of *N*-chloro-*N*-(5-*n*-hexen-1-yl)acetamide in 150 ml of dry cyclohexane for 1 hr and distillation gave 0.18 g (90%) of *N*-(5-*n*-hexen-1-yl)acetamide, bp 80–85° (0.03 mm).

Photolysis of *N*-Chloro-*N*-(4-*n*-penten-1-yl)acetamide (1a). From 0.55 g of *N*-chloroamide in 150 ml of dry benzene, irradiation for 1 hr and distillation gave 0.19 g (35%) of colorless liquid (**2**): bp 75–80° (0.03 mm); ir 1670 cm^{-1}; NMR δ 2.1 (m, 7 H), 3.6 (m, 5 H); mass spectrum *m/e* (rel intensity) 161 (M^+, 10), 126 (11), 112 (33), 70 (100), 43 (55), metastable peak at 43.8.

Photolysis of *N*-Methyl-*N*-chloro-2-(2-cyclohexen-1-yl)-acetamide (12). From 0.80 g (0.0043 mol) of *N*-chloroamide in 150 ml of benzene, 15-min irradiation, and distillation, 0.53 g (66%) of **13** was obtained as a colorless liquid: bp 70–75° (0.01 mm); ir 1690 cm^{-1}; NMR δ 1.55 (m, 7 H), 2.16 (d, 2 H), 2.54 (m, 1 H), 2.92 (s, 3 H), 3.42 (t, 1 H), 3.90 (m, 1 H); mass spectrum *m/e* (rel intensity 187 (16), 110 (100), 97 (11), 42 (16), 41 (9), 39 (8). A high-resolution spectrum was taken: *m/e* 187.067 (M^+), 110.072 (P^+).

Anal. Calcd for $C_9H_{14}NOCl$: C, 57.6; H, 7.5; N, 7.5; Cl, 18.9. Found: C, 57.6; H, 7.5; N, 7.5; Cl, 18.7.

Photolysis of *N*-Chloro-*N*-methyl-3-(1-cyclohexen-1-yl)-propionamide (3). From 162 mg (0.805 mmol) of **3** in 190 ml of benzene and irradiation for 25 min, 148 mg of a brown oil was obtained. Distillation gave 48 mg (30%) of a colorless liquid, bp 90–100° (0.01 mm). The liquid was chromatographed on silica gel in chloroform, and 25-ml fractions were collected. Fraction 14 contained, after distillation, 22 mg of **4** as a colorless liquid: bp 90–95° (0.01 mm); ir 1690 cm^{-1}; NMR δ 1.0–2.5 (m, 12 H), 2.76 (s, 3 H), 4.00 (m, 1 H); mass spectrum *m/e* (rel intensity) 201 (M^+, 19) 166 (27), 124 (100), 111 (29), 73 (29).

Photolysis of *N*-Chloro-*N*,5-dimethyl-2-allyl-4-hexenamide (15a). From 0.523 g (0.00224 mol) of *N*-chloroamide in 180 ml of

benzene and irradiation for 20 min, 0.51 g of dark oil was obtained. TLC of 100 mg on silica gel with ether gave one major fraction (R_f 0.29–0.32). This fraction was distilled to yield 15 mg (15%) of colorless liquid **16a:** ir 1630, 1680 cm^{-1}; NMR δ 1.48 (s, 3 H), 1.59 (s, 3 H), 2.99 (s, 3 H), 3.60 (t, 1 H), 4.80–5.84 (m, 3 H); mass spectrum *m/e* (rel intensity) 215 (M^+, 5), 138 (100), 110 (76), 96 (50), 81 (84), 55 (45), 39 (76), 42 (65).

Photolysis of *N*-Chloro-*N*-methyl-2-allyl-4-pentenamide (15b). From 0.55 g (0.0029 mol) of *N*-chloroamide in 190 ml of benzene and 20-min irradiation, 0.50 g of oil was obtained. TLC of 100 mg on silica gel with ethyl ether gave a fraction (R_f 0.1–0.2) which was distilled to give 11 mg (11%) of **16b** as colorless liquid: bp 60–80° (0.05 mm); ir 1680 cm^{-1}; NMR δ 2.80 (s, 3 H), 3.56 (m, 3 H), 4.80–5.84 (m, 3 H); mass spectrum *m/e* (rel intensity) 187 (M^+, 19), 138 (100), 110 (37), 96 (52), 81 (30), 42 (72), 39 (47).

Photolysis of *N*-Chloro-*N*,5-dimethyl-2-(3-methyl-2-buten-1-yl)-4-hexenamide (15c). From 0.76 g of *N*-chloroamide in 170 ml of benzene and irradiation for 15 min, 0.75 g of brown oil was obtained. TLC of 130 mg on silica gel with ethyl ether gave a fraction (R_f 0.14–0.36) which was distilled to give 32 mg (25%) of colorless oil (**16c**): bp 80–90° (0.02 mm); ir 1685 cm^{-1}; NMR δ 1.46, 1.56, 1.58, 1.66 (4 s, 12 H), 2.98 (s, 3 H), 3.58 (m, 1 H), 4.92 (m, 1 H); mass spectrum *m/e* (rel intensity 243 (M^+, 24), 166 (100), 110 (61), 98 (99), 41 (89).

Photolysis of a Mixture of *N*-Chloro-*N*,3- and -4-dimethyl-3-cyclohexenecarboxamide (8c and 8b). Irradiation of 0.63 g (0.0034 mol) of *N*-chloroamides in 180 ml of benzene for 20 min gave 0.54 g of crude photoproduct, which was distilled to give 0.334 g (54%): bp 60–70° (0.001 mm); ir 1690 cm^{-1}; NMR, a series of eight methyl singlets at δ 1.36, 1.42, 1.60, 1.70, 2.68, 2.88, 2.90, and 3.04.

The mixture was chromatographed on a high-pressure liquid chromatograph using Porasil A–chloroform, yielding two fractions. Fraction 1 was a mixture of 4-*exo*-chloro-6,4-dimethyl- and -6,5-dimethyl-6-azabicyclo[3.2.1]octan-7-one (**9b,c**): ir 1680 cm^{-1}; NMR δ 1.39 (s, 1.8 H), 1.67 (s, 1.2 H), 2.75 (s, 1.8 H), 3.00 (s, 1.2 H), 3.52 (d, 1.4 H), 4.08 (s, 0.6 H). Fraction 2 was a mixture of 4-*endo*-chloro-6,4-dimethyl- and -6,5-dimethyl-6-azabicyclo[3.2.1]octan-7-one (**10b,c**): ir 1680 cm^{-1}; NMR δ 1.52 (s, 1.8 H), 1.74 (s, 1.2 H), 2.97 (s, 1.8 H), 3.14 (s, 1.2 H), 3.65 (d, 0.4 H), 3.95 (m, 0.6 H). The mass spectra of the two fractions were identical; *m/e* 187 (M^+, 36), 124 (79), 110 (100), 56 (53), 42 (53).

Photolysis of *N*-Chloro-*N*,4-dimethyl-3-cyclohexenecarboxamide (8b). From 0.78 g (0.0042 mol) of *N*-chloroamide in 190 ml of benzene and irradiation for 20 min, 0.76 g of light brown oil was obtained and distilled to give 0.366 g (47%) of **9b** and **10b:** bp 70° (0.01 mm); ir 1700 cm^{-1}; NMR, four methyl singlets at δ 1.70, 1.76, 3.05, and 3.20.

High-pressure liquid chromatography using Porasil A–chloroform gave two fractions. Fraction 1 (**9b**) was crystallized from hexane: mp 117°; ir 1700 cm^{-1}; NMR δ 1.66 (s, 3 H), 2.98 (s, 3 H), 3.50 (d, 1 H). Fraction 2 (**10b**) was a liquid and distilled: bp 60° (0.01 mm); ir 1700 cm^{-1}; NMR δ 1.70 (s, 3 H), 3.10 (s, 3 H), 3.60 (d, 1 H). The mass spectra of the isomers were identical: *m/e* (rel intensity) 42 (100), 187 (M^+, 37), 152 (58), 110 (82), 109 (70), 42 (100).

Anal. Calcd for $C_9H_{14}NOCl$: C, 57.6; H, 7.5; N, 7.5; Cl, 18.9. Found for fraction 1: C, 57.3; H, 7.7; N, 7.7; Cl, 18.8. Found for fraction 2: C, 57.9; H, 7.7; N, 7.6; Cl, 18.6.

6-Methyl-6-azabicyclo[3.2.1]octan-7-one (11). A. A mixture of 0.44 g (0.0035 mol) of 6-azabicyclo[3.2.1]octan-7-one,[27] 0.40 g (0.0088 mol) of 90% sodium amide, and 10 ml of toluene was refluxed for 4 hr, then 2.5 ml of methyl iodide was added and the mixture was refluxed overnight. Cooling, filtration, and distillation gave 0.38 g (78%) of colorless liquid; bp 38–40° (0.1 mm). This material was identical with the compound obtained from the following dechlorination by ir and NMR.

B. A mixture of 5 ml of dry benzene, 0.42 g (0.0024 mol) of 6-methyl-4-chloro-6-azabicyclo[3.2.1]octan-7-one (**9a** and **10a**), 0.77 g (0.0026 mol) of tri-*n*-butylstannane, and a few crystals of azabisisobutyronitrile was refluxed overnight; then 10% hydrochloric acid was added followed by water. The benzene layer was separated, dried over magnesium sulfate, and concentrated, and the colorless liquid was chromatographed on silica gel with pentane to remove tri-*n*-butyltinchloride. Benzene was added to the column followed by benzene–ethyl ether followed by benzene-ethyl ether–ethanol in a 40:50:10 ratio to give a light brown oil. The oil was distilled to yield 0.122 g (37%) of colorless liquid: bp 37–40° (0.1 mm); ir 1695 cm^{-1}; NMR δ 1.65 (m, 9 H), 2.80 (s, 3 H), 3.56 (m, 1 H).

Anal. Calcd for $C_8H_{13}NO$: C, 69.0; H, 9.4; N, 10.1. Found: C, 68.9; H, 9.6; N, 9.8.

6-Acetyl-6-azabicyclo[3.2.1]octane. A solution of 1.6 g (12.8 mmol) of 6-azabicyclo[3.2.1]octan-7-one[27] in 25 ml of 1,2-dimethoxyethane was added dropwise to 0.49 g (12.8 mmol) of lithium aluminum hydride in 50 ml of 1,2-dimethoxyethane. The mixture was refluxed overnight and cooled, and 0.13 ml of water was added, followed by 0.13 ml of 15% sodium hydroxide, followed by 0.4 ml of water. The slurry was stirred for 30 min, filtered, and cooled, and 3 ml of acetic anhydride was added dropwise. The solution was stirred for 3 hr; then 15 ml of 10% sodium hydroxide was added. The mixture was stirred for 1 hr. The organic layer was separated, dried over potassium carbonate, concentrated, and distilled to give 1.7 g (86%) of a colorless liquid: bp 70–75° (0.01 mm); ir 1625 cm^{-1}; NMR δ 2.04 (s, 3 H), 2.40 (br, 1 H), 3.36 (m, 2 H), 3.92 (t, 0.5 H), 4.32 (t, 0.5 H); mass spectrum *m/e* (rel intensity) 153 (M^+, 27), 110 (55), 68 (100), 43 (23).

Anal. Calcd for $C_9H_{15}NO$: C, 70.5; H, 9.9; N, 9.1. Found: C, 70.5; H, 9.8; N, 9.0.

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Registry No.—1a, 54385-04-5; **1b,** 54385-05-6; **2,** 54385-06-7; **3,** 54385-07-8; **4,** 54385-08-9; **5,** 54385-09-0; **6,** 54385-10-3; **7,** 54385-11-4; **8a,** 36393-98-3; **8b,** 54385-12-5; **8c,** 54385-13-6; **9a,** 36394-04-4; **9b,** 54385-39-6; **9c,** 54385-40-9; **10a,** 36394-03-3; **10b,** 54385-41-0; **10c,** 54385-42-1; **11,** 24173-53-3; **12,** 54385-43-2; **13,** 54385-14-7; **15a,** 54385-15-8; **15b,** 54385-16-9; **15c,** 54385-17-0; **16a,** 54385-18-1; **16b,** 54385-19-2; **16c,** 54385-20-5; *N*-(4-*n*-penten-1-yl)acetamide, 54385-21-6; 4-pentenonitrile, 592-51-8; *N*-(5-*n*-hexen-1-yl)acetamide, 54385-22-7; 5-hexenonitrile, 5048-19-1; *N*-[(3-cyclohexen-1-yl)methyl]acetamide, 54385-23-8; 3-cyclohexenecarbonitrile, 100-45-8; *N*-methyl-3-cyclohexenylcarboxamide, 54385-24-9; 3-cyclohexenecarboxylic acid, 4771-80-6; 3-methyl-3-cyclohexenecarboxylic acid, 54385-25-0; 4-methyl-3-cyclohexenecarboxylic acid, 4342-60-3; isoprene, 78-79-5; acrylic acid, 79-10-7; 4-methyl-*N*-methyl-3-cyclohexenecarboxamide, 54385-26-1; 3-methyl-*N*-methyl-3-cyclohexenecarboxamide, 54446-42-3; *N*-methyl-2-(2-cyclohexen-1-yl)acetamide, 54385-27-2; 2-(2-cyclohexen-1-yl)acetic acid, 3675-31-8; 2-allyl-*N*,5-dimethyl-4-hexenamide, 54385-28-3; ethyl 2-acetyl-5-methyl-4-hexenoate, 1845-52-9; allyl bromide, 106-95-6; ethyl 2-acetyl-2-allyl-5-methyl-4-hexenoate, 54385-29-4; methyl 2-allyl-5-methyl-4-hexenoate, 54385-30-7; 2-allyl-5-methyl-4-hexenoic acid, 54385-31-8; 2-allyl-*N*-methyl-4-pentenamide, 54385-32-9; ethyl 2-acetyl-2-allyl-4-pentenoate, 3508-77-8; methyl 2-allyl-4-pentenoate, 54385-33-0; *N*,5-dimethyl-2-(3-methyl-2-buten-1-yl)-4-hexenamide, 54385-34-1; 2-(3-methyl-2-buten-1-yl)-5-methyl-4-hexenoic acid, 54385-35-2; *N*-chlorosuccinimide, 128-09-6; *N*-[2-(1-cyclohexen-1-yl)ethyl]acetamide, 51072-38-9; *N*-methyl-2-allyl-4-hexenamide, 54385-36-3; *N*-methyl-3-(1-cyclohexen-1-yl)propionamide, 54385-37-4; 6-azabicyclo[3.2.1]octan-7-one, 6142-56-9; 6-acetyl-6-azabicyclo[3.2.1]octane, 54385-38-5.

References and Notes

(1) R. S. Neale, *Synthesis*, **1**, 1 (1971).
(2) J. M. Surzur, L. Stella, and P. Tordo, *Tetrahedron Lett.*, 3107 (1970).
(3) J. M. Surzur, L. Stella, and R. Novgulier, *Tetrahedron Lett.*, 903 (1971).
(4) R. S. Neale, *J. Org. Chem.*, **32**, 3263 (1967).
(5) R. S. Neale and N. L. Marcus, *J. Org. Chem.*, **32**, 3273 (1967).
(6) R. S. Neale and N. L. Marcus, *J. Org. Chem.*, **33**, 3457 (1968).
(7) Y. L. Chow, R. A. Perry, B. C. Menon, and S. C. Chen, *Tetrahedron Lett.*, 1545 (1971).
(8) Y. L. Chow, R. A. Perry, and B. C. Menon, *Tetrahedron Lett.*, 1549 (1971).
(9) J. Surzur and L. Stella, *Tetrahedron Lett.*, 2191 (1974).
(10) M. Julia, *Acc. Chem. Res.*, **4**, 386 (1971).
(11) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).
(12) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Am. Chem. Soc.*, **88**, 5361 (1966).
(13) C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, **94**, 6059 (1972).
(14) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, 434 (1966).
(15) M. Julia and M. Maumy, *Bull. Soc. Chim. Fr.*, 1603 (1968).
(16) C. Walling and A. Cioffari, *J. Am. Chem. Soc.*, **94**, 6064 (1972).
(17) C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).
(18) A. L. J. Beckwith, I. A. Blair, and G. Phillipou, *Tetrahedron Lett.*, 2251 (1974).
(19) M. E. Kuehne and R. E. Damon, *J. Org. Chem.*, in press.
(20) Similar investigations have since provided results consistent with our own: (a) D. Touchard and J. Lessard, *Tetrahedron Lett.*, 4425 (1971); (b) Y. L. Chow and R. A. Perry, ibid., 531 (1972); (c) E. Flesia, A. Croatto, P. Tordo, and J. M. Surzur, ibid., 535 (1972).

(21) W. C. Danen and R. W. Gellert, *J. Am. Chem. Soc.*, **94**, 6853 (1972).
(22) A. L. J. Beckwith and J. E. Goodrich, *Aust. J. Chem.*, **18**, 747 (1965).
(23) R. S. Neale, N. L. Marcus, and R. G. Shepers, *J. Am. Chem. Soc.*, **88**, 3051 (1966).
(24) Y. L. Chow and T. C. Joseph, *Chem. Commun.*, 490 (1969).
(25) Y. L. Chow, N. S. Tam, and A. C. H. Lee, *Can. J. Chem.*, **47**, 2441 (1969).
(26) O. E. Edwards, J. M. Paton, M. H. Benn, R. E. Mitchell, C. Watanada, and K. W. Vohra, *Can. J. Chem.*, **49**, 1648 (1971).
(27) F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 2767 (1955).
(28) It may be noted that acylation of 2-azatricyclo[2.2.2.$0^{2,6}$]octane yields instead predominantly bicyclo[2.2.2]amides.[29]
(29) W. Nagata, S. Hirai, K. Kawata, and T. Aoki, *J. Am. Chem. Soc.*, **89**, 5045, 5046 (1967).
(30) These compounds were obtained from Diels–Alder addition of acrylic acid to isoprene, separation of the resultant acids,[31] and subsequent conversions to the chloroamides.
(31) A. Manjarrex, T. Rios, and A. Guzman, *Tetrahedron*, **20**, 333 (1964).
(32) F. B. LaForge, N. Green, and W. A. Gersdorff, *J. Am. Chem. Soc.*, **70**, 3707 (1948).
(33) M. Mousseron and F. Winternitz, *Bull. Soc. Chim. Fr.*, 604 (1946).
(34) C. Wolff, *Justus Liebigs Ann. Chem.*, **201**, 45 (1880).
(35) H. Machleidt, *Justus Liebigs Ann. Chem.*, **667**, 24 (1963).
(36) W. Schneider and M. Muller, *Arch. Pharm. (Weinheim)*, **294**, 360 (1961).

Ultraviolet Photoelectron Spectra of Some Substituted Triarylphosphines

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The photoelectron spectra of a series of triarylphosphines, containing various ring substituents, have been investigated. The spectra show a band due to ionization from the phosphorus lone pair (IP_1), followed by one or more bands assigned to ionizations of the phenyl π electrons. The values of IP_1 are sensitive to the nature of the ring substituents and reflect the influence of the substituents on the charge density at the ring position adjacent to the phosphorus. The number of observed IP's in the region assigned to the phenyl π electrons are generally the same as the number of IP's for the corresponding monosubstituted benzene. Moreover the IP values are generally close to the IP's found for the monosubstituted benzenes. The observed results are explained by a lack of substantial resonance interaction between the phosphorus and the π orbitals of the aryl system. The variation of phosphorus lone pair IP values is discussed in terms of charge stabilization in the radical cation produced by ionization of a lone-pair electron.

Several recent articles on the ultraviolet photoelectron spectra (pes) of monosubstituted benzenes have discussed the effect of substitution on ionization from the $e_g\pi$ orbitals of benzene.[1-7] The resonance effect of certain substituents (OR,[3] CH_3[4,7]) on the b_1 orbital[8] appears to raise its energy (lower ionization potential) from that of the a_2 orbital,[8] and thus the first ionization potential (IP) can be assigned to ionization from the b_1 orbital. The second ionization is then from the a_2 orbital and appears unchanged from the corresponding ionization in benzene (9.24 eV). Other substituents (F,[4] Cl[6]) show the same resonance effect, but an electron-withdrawing inductive effect is apparently also present. Thus the first two IP's are assigned as before, but the IP values are somewhat larger. In monosubstituted benzenes containing a third class of substituents (*tert*-butyl,[9] $(CH_3)_3Si$,[9] CF_3[9]) the ionizations from the a_2 and b_1 orbitals are close in energy and are either poorly resolved or not at all. The band envelopes are raised or lowered in energy from that of benzene, depending on whether the substituent is electron donating or withdrawing.

b_1 a_2

In the present study we have investigated the pes of a series of triarylphosphines containing these ring substituents. Schäfer and Schweig[10] have interpreted the pes of dimethylphenylphosphine in terms of a complete lack of interaction between the aryl group and the trivalent phosphorus atom. The energies of ionization from the phosphorus lone pair and phenyl π orbitals remain virtually the same as in $(CH_3)_3P$ and benzene, respectively. Debies and Rabalais[11] observed in the pes of $C_6H_5PH_2$ a stabilization of the phenyl π orbitals and a splitting of the a_2 and b_1 components, along with a destabilization of the phosphorus lone pair. It was suggested that this is due to delocalization of charge from phenyl π orbitals into the d orbitals on phosphorus. (The IP of the phenyl π electrons in $(C_6H_5)_3P$ is the same as in benzene, however, and no splitting of the components was observed.)

Results and Discussion

The pes of the substituted triarylphosphines (Table I) show one or more peaks in the region assigned to ionization of the phenyl π electrons in the corresponding monosubstituted benzenes (Table II). In most cases the number of IP's observed in this region corresponds to the number of IP's observed for the monosubstituted benzene. In addition to these, a low IP band is observed in each of the spectra, which is readily assigned, as by the previous authors,[10,11] to ionization from the lone pair of electrons on phosphorus.

Although the complexity of the molecules studied appears to inhibit the use of vibrational fine structure in assigning the bands in the phenyl region, it seems likely that the band assignments for the triarylphosphines generally correspond to the assignments made for the monosubstituted benzenes. The following reasons are apparent.

(1) In almost all cases, and independent of the nature of the substituent, the IP's assigned to the phenyl electrons in $aryl_3P$ correspond closely to the IP's found for the monosubstituted benzene. Particularly in the case of $aryl_3P$ substituted with methoxy and dimethylamino groups, the separation of ionizations from the a_2 and b_1 orbitals is so large that it is unlikely that the assignments could be reversed upon substitution into the phosphino system, with one energy level raised and the other lowered from the value in the monosubstituted benzene.