(s, 2, 6-H), 7.84 (s, 2, 4-H), 8.25 and 8.33 (s × 2, 3 × 2, $CH{=}C(CH_3)_2$], 8.95 [s, 6, $CH_2C(CH_3)_2$]; mass spectrum m/e 208 (M^+).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.64; H, 9.47.

4,4-Dimethyl-9-isopropenyl-7-oxabicyclo[4.3.0]nonan-2-one (5). A solution of 265 mg of **4** in 40 ml of cyclohexane was irradiated for 15 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 182 mg (69%) of **5** as a colorless oil: bp 85–90 °C (bath temperature) (0.03 mm); ir ($CHCl_3$) 3080, 1710, 1645, 1060, 900 cm^{-1}; NMR ($CDCl_3$, 100 MHz) τ 5.16 (s, 2, $C{=}CH_2$), 5.56 (dt, 1, J = 7.0 and 5.6 Hz, 6-H), 5.94 (t, 1, J = 8.0 Hz, 8-H), 6.42 (t, 1, J = 8.0 Hz, 8-H), 6.64 (td, 1, J = 8.0 and 6.0 Hz, 9-H), 7.28 (dd, 1, J = 7.0 and 6.0 Hz, 1-H), 7.77 (center of AB q, 2, J = 14.0 Hz, 3-H), 8.17 (d, 2, J = 5.6 Hz, 5-H), 8.26 [t, 3, J = 2.0 Hz, $C(CH_3){=}CH_2$], 8.97 and 8.99 [s × 2, 3 × 2, $C(CH_3)_2$]; mass spectrum m/e 208 (M^+).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.47.

2-(1-Hydroxymethyl-2-methyl-2-propenyl)-5,5-dimethyl-2-cyclohexen-1-one (6). A solution of 100 mg of **5** and 10 mg of sodium methoxide in 2 ml of methanol was refluxed for 1 h. After the solvent was removed, anhydrous ether was added. The insoluble material was filtered off, and the filtrate was dried ($MgSO_4$) and concentrated. The residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C) as solvent to give 64 mg (64%) of **6** as a colorless oil: ir ($CHCl_3$) 3450, 1660, 900 cm^{-1}; uv max (EtOH) 235 nm (log ϵ 3.91) (calcd for 2-alkyl-2-cyclohexen-1-one, 237 nm); NMR ($CDCl_3$) τ 3.30 (t, 1, J = 5 Hz, 3-H), 5.05 and 5.22 (bs × 2, 2, $C{=}CH_2$), 6.20–6.50 (m, 3, $CHCH_2OH$), 7.73 (s, 2, 6-H), 7.79 (s, 1, OH), 8.15–8.40 [m, 5, 4-H and $CH_2{=}C(CH_3)$], 9.00 [s, 6, $C(CH_3)_2$]; mass spectrum m/e 208 (M^+).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.66; H, 9.47.

Ethyl Dimethylacrylate-*3,3-d*$_6$. The procedure of Fodor and Tömösközi[10] was employed. A mixture of 1.92 g of acetone-d_6 and 10.44 g of ethoxycarbonylmethylenetriphenylphosphorane was heated in a sealed tube at 120 °C for 24 h. To the reaction mixture was added anhydrous petroleum ether and insoluble triphenylphosphine oxide was filtered off. The filtrate was concentrated and distilled to give 860 mg (21%) of ethyl dimethylacrylate-*3,3-d*$_6$: bp 62–63 °C (30 mm); ir ($CHCl_3$) 2200, 1705, 1640, 1165 cm^{-1}; NMR ($CDCl_3$) τ 4.36 [s, 1, $CH{=}C(CD_3)_2$], 5.88 (q, 2, CH_2CH_3), 8.77 (t, 3, CH_2CH_3); mass spectrum m/e 134 (M^+).

Dimethylallyl-*3,3-d*$_6$ Alcohol. A solution of 700 mg of ethyl dimethylacrylate-*3,3-d*$_6$ in 3 ml of anhydrous ether was slowly added to a suspension of 200 mg of lithium aluminum hydride in 5 ml of anhydrous ether. The reaction mixture was refluxed for 12 h. After an usual work-up procedure, dimethylallyl-*3,3-d*$_6$ alcohol was obtained in 48% yield (250 mg): bp 55–60 °C (15 mm); ir ($CHCl_3$) 3580, 2200, 1660 cm^{-1}; NMR ($CDCl_3$) τ 4.60 [t, 1, J = 7.0 Hz, $CH{=}C(CD_3)_2$], 5.90 (d, 2, J = 7.0 Hz, CH_2OH), 8.00 (s, 1, OH); mass spectrum m/e 92 (M^+).

3-(Dimethylallyloxy-*3,3-d*$_6$)-5,5-dimethyl-2-cyclohexen-1-one (8). A solution of 80 mg of dimedone and 160 mg of dimethylallyl-*3,3-d*$_6$ alcohol in 5 ml of benzene containing of 3 mg of *p*-toluenesulfonic acid was refluxed for 7 h using a Dean-Stark water separator. After removal of the solvent, the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (1:1) as solvent to give 70 mg (57%) of **8** as a colorless oil: ir ($CHCl_3$) 2230, 2180, 1640, 1605 cm^{-1}; NMR ($CDCl_3$) τ 4.58 [t, 1, J = 7.0 Hz, $CH{=}C(CD_3)_2$], 4.64 (s, 1, 2-H), 5.65 (d, 2, J = 7.0 Hz, OCH_2), 7.77 (s, 2, 6-H), 7.84 (s, 2, 4-H), 8.95 [s, 6, $C(CH_3)_2$]; mass spectrum m/e 214 (M^+).

Irradiation of 8. A solution of 60 mg of **8** in 10 ml of cyclohexane was irradiated for 12 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 37 mg (62%) of **9** as a colorless oil: ir ($CHCl_3$) 2180, 2120, 1710, 1605 cm^{-1}; NMR ($CDCl_3$) τ 6.00 (t, 1, J = 8.0 Hz, 8-H), 6.44 (t, 1, J = 8.0 Hz, 8-H), 6.70 (ddd, 1, J = 8.0, 8.0, and 6.0 Hz, 9-H), 7.35 (d, 1, J = 6.0 Hz, 1-H), 7.81 (s, 2, 3-H), 8.23 (s, 2, 5-H), 9.04 [s, 6, $C(CH_3)_2$]; mass spectrum m/e 214 (M^+).

3-(*N*,3-Dimethyl-2-butenylamino)-5,5-dimethyl-2-cyclohexen-1-one (10). A solution of 140 mg of dimedone and 220 mg of *N*,3-dimethyl-2-butenylamine in 5 ml of benzene was heated in a sealed tube at 100 °C for 7 h. The solvent was removed and the residual liquid distilled to give 206 mg (93%) of **10** as a yellow oil: bp 160–170 °C (bath temperature) (0.08 mm); ir ($CHCl_3$) 1605, 1550 cm^{-1}; NMR ($CDCl_3$) τ 4.47–5.38 [m, 1, $CH{=}C(CH_3)_2$], 4.88 (s, 1, 2-H), 6.18 (bd, 2, J = 7.0 Hz, $CH_2CH{=}$), 7.18 (s, 3, NCH_3), 7.79 (s, 2, 6-H), 7.91 (s, 2, 4-H), 8.30 and 8.36 [bs × 2, 3 × 2, $CH{=}C(CH_3)_2$], 8.97 [s, 6, $C(CH_3)_2$]; mass spectrum m/e 221 (M^+).

Anal. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.71; H, 10.55; N, 6.10.

4,4,7-Trimethyl-9-isopropenyl-7-azabicyclo[4.3.0]nonan-2-one (11). A solution of 102 mg of **10** in 25 ml of cyclohexane was irradiated for 5 h. The solvent was removed and the residual liquid was submitted to preparative TLC using petroleum ether (bp 30–60 °C)–ether (3:2) as solvent to give 67 mg (66%) of **11** as a colorless oil: ir ($CHCl_3$) 3080, 1705, 1640, 895 cm^{-1}; NMR (CCl_4, 100 MHz) τ 5.30 (bs, 2, $C{=}CH_2$), 6.60–6.85 (m, 1, 9-H), 6.93 (t, 1, J = 8.0 Hz, 8-H), 7.32 (td, 1, J = 7.5 and 4.8 Hz, 6-H), 7.53 (dd, 1, J = 7.5 and 5.0 Hz, 1-H), 7.82 (s, 3, NCH_3), 7.87 (s, 2, 3-H), 8.00 (t, 1, J = 8.0 Hz, 8-H), 8.30 [bs, 3, $C(CH_3){=}CH_2$], 8.33 (d, 2, J = 4.8 Hz, 5-H), 8.96 and 8.98 [s × 2, 3 × 2, $C(CH_3)_2$]. Spin decoupling experiments show the following results. Irradiation of 6-H at τ 7.32 caused the doublet of 5-H at τ 8.33 to collapse to a singlet, and irradiation of the multiplet of 9-H converted the doublet of doublets of 1-H at τ 7.53 to the doublet, J = 7.5 Hz, and triplets of 8-H at τ 6.93 and 8.00 to doublets, J = 8.0 Hz. Irradiation of 1-H converted the signal of 9-H to a broad triplet, J = 8.0 Hz; mass spectrum m/e 221 (M^+).

It formed a picrate, mp 142–143 °C (from EtOH).

Anal. Calcd for $C_{20}H_{26}N_4O_8$: C, 53.33; H, 5.82; N, 12.44. Found: C, 53.76; H, 6.06; N, 12.53.

Registry No.—**4,** 57969-26-3; **5,** 57969-27-4; **6,** 57969-28-5; **7,** 53439-16-0; **8,** 57969-29-6; **9,** 57969-30-9; **10,** 57969-31-0; **11,** 57969-32-1; **11** picrate, 57969-33-2; dimedone, 126-81-8; 1-bromo-3-methyl-2-butene, 870-63-3; ethyl dimethylacrylate-*3,3-d*$_6$, 53439-15-9; *N*,3-dimethyl-2-butenylamine, 29151-30-2.

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(4) Energy transfer experiments using piperylene showed that the reaction **4** → **5** was not quenched even by high concentration. For example, when a solution of 0.1 M of piperylene and 0.01 M of **4** in ether was irradiated, product **5** was obtained at a similar rate to that of the reaction without piperylene. The result is in contrast to the case of the formation of **3** (X = NMe),[1] and suggests that this reaction involves a singlet excited state of the enone **4**.

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Photochemical Studies on Alkyl Amides

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Although there are numerous studies reported on the photochemistry of aldehydes and ketones,[2] there have been only a few reports on the photochemistry of esters[3] and amides.[4–6] In the case of amides in particular the two major reports are contradictory.

Booth and Norrish[4] studied the photochemistry of a series of alkyl amides by examination of the gaseous products from the reaction in dioxane and hexane. They observed alkenes from the C_4, C_5, and C_6 amides and inferred that they were ethylene, propene, and butene. On the basis of these results they suggested that the type II process (eq 1) was the major one occurring. Chemical tests indicated that primary amines but no aldehydes or diketones were present, and, although CO was isolated in all instances, no methane was obtained from acetamide. These workers suggested that α-cleavage processes (eq 2 and 3) were not important.

$$\mathrm{RCH_2CH_2CH_2CONH_2} \xrightarrow{h\nu} \mathrm{RCH{=}CH_2} + \mathrm{CH_3CONH_2} \qquad (1)$$

$$\mathrm{RCONH_2} \xrightarrow{h\nu} \cdot\mathrm{CONH_2} + \mathrm{R}\cdot \xrightarrow[\text{solvent}]{\sim\mathrm{H}} \mathrm{RH} \qquad (2)$$

$$\mathrm{RCONH_2} \xrightarrow{h\nu} \cdot\mathrm{NH_2} + \mathrm{RCO}\cdot \xrightarrow[\text{solvent}]{\sim\mathrm{H}} \mathrm{RCHO} \qquad (3)$$

$$\mathrm{RCONH_2} \xrightarrow{h\nu} \mathrm{RNH_2} + \mathrm{CO} \qquad (4)$$

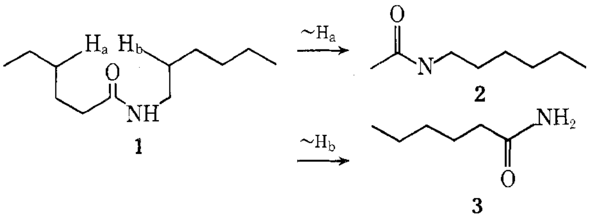
Nicholls and Leermakers[5] subsequently reexamined the photochemistry of a number of amides at 254 nm and noted that prolonged irradiation of primary and secondary amides resulted in no disappearance of starting material but that tertiary amides did decompose under those conditions (Φ = 0.10–0.16). Although the reaction mixture was complex, GLC analysis showed that no type II products (e.g., *N*,*N*-dimethylacetamide from *N*,*N*-dimethylbutyramide) were formed. They suggested that the α-cleavage (type I) reaction (eq 3) was occurring.

Our interest in the photochemistry of amides[6b,c] and lactams led us to reexamine this problem to see if isolation and characterization of some of the solvent derived products formed might provide a clue to resolve these apparently contradictory results.

Results

Irradiation of primary and secondary amides with λ >250 nm indicated that no photodegradation was occurring, but starting material did disappear when irradiation was carried out through Vycor or with an unfiltered (quartz) source.

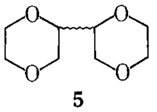
Preliminary investigations were conducted in a number of solvents on *N*-hexylhexanamide (**1**). Irradiations were conducted in methanol, acetonitrile, diisopropyl ether, dioxane, and cyclohexane and, although GLC traces were complex, especially in the latter two solvents, peaks corresponding to type II products **2** and **3** were detected in all cases, but in no case was the sum of the yields of **2** + **3** >3% based on starting material disappearance.

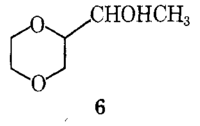


We demonstrated that the products (**2** and **3**) were not undergoing an (unexpected) preferential reaction by irradiating known mixtures of **1**, **2**, and **3**.

Product Isolation. Dioxane Solvent. A number of amides (**4a–f**) were irradiated in dioxane solution and the reaction mixtures analyzed by GLC. In all cases the formation of four products was noted. These products were isolated (preparative GLC) from a photolysis of **1** and characterized as a pair of diastereomeric dioxane dimers[7] (**5**) and the diastereomeric solvent derived alcohols (**6**).[8] The formation of **5** is a clear indication that free-radical processes are occurring whereas the formationf **6** suggests that acetaldehyde is formed and subsequently undergoes photoreduction in dioxane.[8,9] Butene and *n*-pentane were also detected in the reaction mixture from **1** and infrared analysis of the head space gases indicated the presence of carbon monoxide.

RCONHR′
4a, R = $\mathrm{CH_3}$; R′ = $\mathrm{C_6H_{13}}$
b, R = $\mathrm{C_7H_{15}}$; R′ = $\mathrm{C_6H_{13}}$
c, R = $\mathrm{C_5H_{11}}$; R′ = H
d, R = $\mathrm{C_5H_{11}}$; R′ = $\mathrm{CH_3}$
e, R = $\mathrm{C_7H_{15}}$; R′ = H
f, R = $\mathrm{C_2H_5}$; R′ = H
g, R = $\mathrm{C_2H_5}$; R′ = $\mathrm{C_6H_{13}}$


5

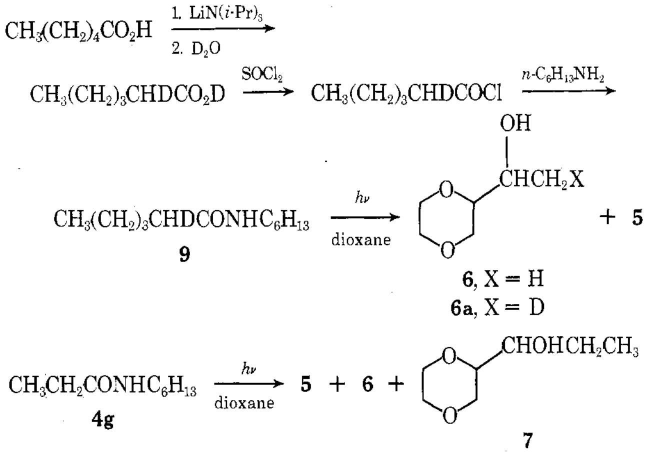


6

Since we had demonstrated that **6** is a product of the direct irradiation of dioxane,[8] although it appears to be generated with much greater efficiency in the present instance, it was necessary to show that **6** was at least partially amide derived. Two experiments were performed addressing this question.

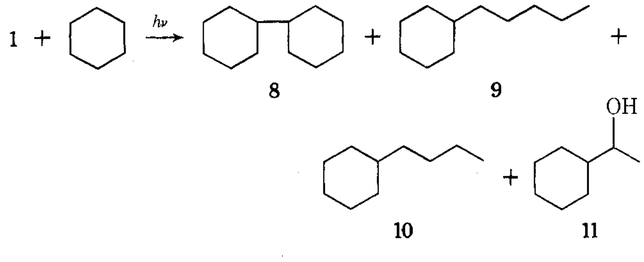
α-Deuterio-*N*-hexylhexanamide (**9**, 28% α-d_1) was prepared from the labeled acid[10] (Chart I), irradiated in dioxane solution, and the alcohols **6** and **6a** were isolated by preparative GLC. Mass spectral analysis showed a **6**/**6a** ratio of 23, indicating that approximately 85% of the product was solvent derived and only 15% was the direct result of amide photolysis.

Chart I



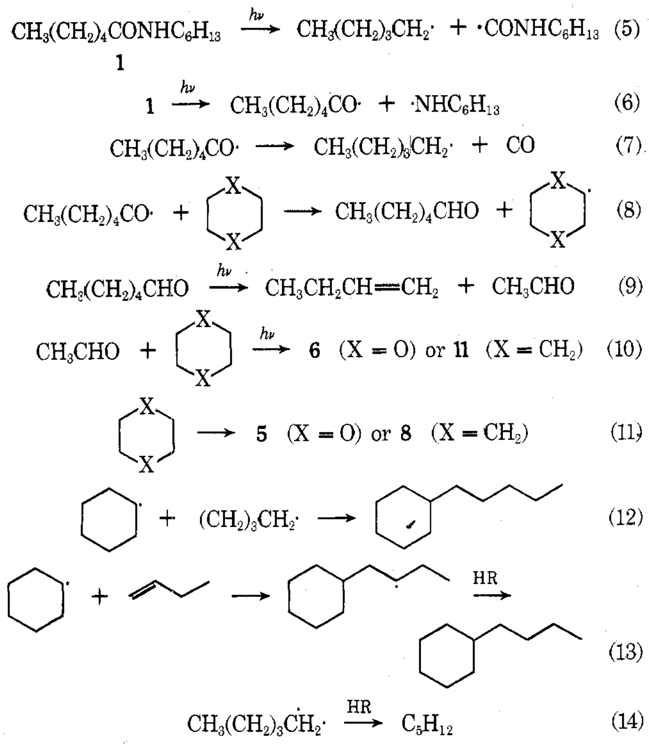
In a second experiment, irradiation of **4g** in dioxane afforded, in addition to **5** and **6**, alcohols **7**. Clearly **7** is an amide-derived product since it is not produced from dioxane alone but presumably arises via the intermediate formation of propionaldehyde.

Cyclohexane Solvent. In view of the reactivity of dioxane under the photolysis conditions, a study was conducted in cyclohexane. The GLC trace of the **1**–cyclohexane photolysate was exceedingly complex, consisting of one major and numerous minor peaks.[11] Four of these were isolated in pure form and identified as butylcyclohexane (**10**), pentylcyclohexane (**9**), bicyclohexyl (**8**), and α-methylcyclohexanemethanol (**11**). *n*-Pentane was detected (GLC) but hexylcyclohexane was shown to be absent. A sample of **1** was irradiated in the presence of an internal standard and the yields of **8** (33%), **9** (5%), **10** (2%), and **11** (1%) determined.[12]



The complexity of the amide photolysis has already been noted. Although no primary products were isolated and it is difficult to relate the yields of secondary products to the efficiencies of the primary photochemical acts,[12] several conclusions can be reached. We suggest the sequence outlined in Scheme I to explain the observed products. The formation of radical initiated products **5** and **6** and the appearance of **2** and **3** as only minor products indicates that type I cleavages (eq 5 and/or 6) are the major processes occurring.

Scheme I



The absence of the expected aldehydes in the reaction mixture can be rationalized by the sequence eq 8–10. Under the reaction conditions hexanal, which has its n → π^* absorption at 290 nm, is immediately exposed to light, and undergoes a type II reaction affording acetaldehyde and the previously observed 1-butene. Acetaldehyde then undergoes photoreduction to the alcohol **6**, in which form it is immune to chemical tests for aldehydes whereas at least a portion of the 1-butene appears as **10** in the cyclohexane experiments. These experimental results and the formation of **8**, **9**, and **11** in cyclohexane (eq 10–14) are consistent with those of Booth and Norrish.[4] We observe no aldehyde products since the aldehydes formed undergo secondary photoreduction to give alcohols. We also observe alkenes but our evidence suggests that they arise largely from secondary photochemical reactions of intermediate products (aldehydes) and not directly from type II reactions of amides.

Our conclusions essentially agree with those of Nicholls and Leermakers, i.e., we find that the type II process in amides is quite inefficient with respect to the type I cleavage.

Experimental Section

Infrared (ir) spectra were taken on a Perkin-Elmer 337 or a Beckman IR-8 grating spectrometer. NMR spectra were obtained in $CDCl_3$ solution (unless otherwise noted) on a Varian A-60D spectrometer at ambient temperature. Ultraviolet (uv) spectra were obtained on a Cary 15 spectrophotometer in cyclohexane. Mass spectra were obtained on a Du Pont 492 double focusing spectrometer. GLC work was carried out on a Varian Aerograph Model 1200 gas chromatograph or on a Varian Aerograph Model 90-P. Columns employed in GLC work follow: column A, 6 ft × 0.25 in., 15% DC550 on 80/100 Chromosorb W; column B, 6 ft × 0.125 in., 20% Versamid on 60/80 Chromosorb W; column C, 6 ft × 0.125 in., 15% DC550 on 80/100 Chromosorb W; column D, 6 ft × 0.125 in., 20% XE60 on Chromosorb W. Matheson Coleman and Bell spectrograde dioxane and cyclohexane from freshly opened bottles were used without further purification. Authentic bicyclohexyl, butylcyclohexane, pentylcyclohexane, and hexylcyclohexane were obtained from Chemical Samples Co. Mass spectra were taken by Dr. M. Gay and microanalyses were performed by Dr. Franz Kasler of the University of Maryland.

Photolysis Procedure. Two percent solutions of the amide in an appropriate solvent were purged with nitrogen for a minimum of 30 min and sealed with rubber serum caps. Samples were irradiated with a Hanovia 450-W Type L lamp through quartz for periods of 4–140 h and progress of the reaction was monitored by GLC. In preparative runs solvent was removed by distillation and product mixtures separated from the usual extensive polymeric residue by vacuum distillation. Separation of products was accomplished by preparative GLC.

***N*-Hexylhexanamide (1) in Dioxane.** A solution of 4 g of **1** in 200 ml of spectrograde dioxane was irradiated for 135 h. The solution was cooled in an ice bath. An infrared spectrum of the gas over the solution showed the presence of carbon monoxide. GLC analysis on columns C (35 °C), B (60 °C), and D (60 °C) indicated the presence of *n*-pentane and 1-butene. Work-up by GLC on column A (110 °C) gave the alcohols **6** and the dimers **5** identified by spectral comparison with authentic samples. Irradiation and GLC analysis of samples of **4a–f** indicated that starting material was disappearing and **5** and **6** were produced in all cases.

***N*-Hexylpropionamide in Dioxane.** Irradiation was carried out via the general procedure. GLC work-up gave, in addition to **5** and **6**, the diastereomeric alcohols **7a** and **7b**.[14] The ratio **6**/**7** was estimated to be $\simeq 4$.

7a: NMR δ 1.0 (t, 3), 1.15–1.75 (m, 2), 3.1–4.1 (m, 9); ir (CCl_4) 3600, 3550–3300, 2965, 2910, 2875, 2860, 1450, 1115 cm^{-1}, MS *m/e* 146 (P, 0.2), 128 (0.40), 117 (3.6), 87 (44), 59 (62), 58 (51), 57 (76), 45 (83), 44 (69), 43 (66), 31 (100).

7b: NMR δ 0.98 (t, 3), 1.2–1.8 (m, 2), 3.2–4.1 (m, 9); ir (CCl_4) 3650–3300, 2975, 2930, 2875, 1450, 1115 cm^{-1}; MS *m/e* 146 (P, 1.5), 128 (0.6), 117 (7.1), 87 (62), 59 (100), 58 (24), 57 (56), 45 (88), 44 (82), 43 (56), 37 (91).

Irradiation of propionamide in dioxane also gave **5**, **6**, and **7**.

***N*-Hexylhexanamide (1) in Cyclohexane.** A solution of 4 g of **1** in 210 ml of cyclohexane was irradiated for 115 h. Work-up by preparative GLC on column A gave **8**, **9**, **10**, and **11**,[14] identified by comparison of NMR, ir, and mass spectra with those of authentic samples. Yields were determined in a separate experiment in which 0.6646 g of **1** (with hexadecane internal standard) was irradiated and sampled after 4 (20% conversion), 8, and 13 h. Yields were calculated assuming a molar correspondence of **1** reacted and product formed.

Hexanal in Dioxane. A solution of 2.5 g of hexanal in 250 ml of dioxane was irradiated for 1.5 h. GLC analysis (column C, 40 °C) at 30-min intervals showed the rapid disappearance of hexanal and buildup of acetaldehyde, 1-butene, and *n*-pentane. The hexanal had almost completely disappeared after 1.5 h.

Preparation of *N*-Hexylhexanamide-α-d_1 (9). A 45-ml portion of diisopropylamide and 100 ml of dry THF were treated at 0 °C with 25.8 ml of 90% butyllithium and stirred for 0.5 at 0 °C. A mixture of 27 ml of hexamethylphosphoramide, 18.7 ml of freshly distilled hexanoic acid, and 45 ml of dry THF was added slowly at 0 °C to the stirred lithium diisopropylamide. After stirring for 6 h at 0 °C, 20 ml of D_2O was added slowly, and the mixture was stirred overnight, acidified to pH 5, and extracted with anhydrous Et_2O. Distillation of the residue after evaporation yielded 12.9 g of labeled product, bp 108–112 °C (15 mm). NMR indicated that this material was 42% α-d_1.

The acid was converted to acid chloride by conventional treatment with thionyl chloride. A solution of 6.5 g of labeled hexanoyl chloride in 15 ml of THF was added dropwise at 0 °C to a mixture of 5.1 g of hexylamine, 20 ml of THF, and 30 ml of 1% NaOH. The mixture was stirred for 10 h at room temperature, layers were separated, and the aqueous phase was extracted with ether. Work-up of the combined organic phases yielded 8.5 g of **9**, bp 135 °C (2.7 mm). Mass spectral analysis indicated that this material was 28% α-d_1. Compound **9** was irradiated in dioxane as previously described and the alcohols purified by preparative GLC. Deuterium incorporation was measured by comparing the $(P + 1)/[P + (P + 1)]$ ratios for unlabeled alcohol **6** (0.092) vs. that obtained from irradiation of **9** (0.136).

Acknowledgment. This research was partially supported by a grant from the Center for Materials Research of the University of Maryland.

Registry No.—1, 10264-29-6; **4a,** 7501-79-3; **4b,** 57969-34-3; **4c,** 628-02-4; **4d,** 3418-05-1; **4e,** 628-62-6; **4f,** 79-05-0; **4g,** 10264-24-1; **7** isomer 1, 57969-35-4; **7** isomer 2, 57969-36-5; hexanal, 66-25-1.

References and Notes

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(11) All photolysis reactions were accompanied by the formation of extensive amounts of polymeric materials. Irradiation of cyclohexane alone afforded small amounts of **8** as reported previously but no **9**, **10**, or **11**.

(12) The formations of these secondary products is predictably inefficient. For example, the photoreduction of acetone in dioxane[9a] affords the alcohol in only 16% yield. The addition product of 1-octene to dioxane is produced in 5% yield (27% when acetone sensitizer was employed).[13] In our hands irradiation of acetaldehyde in cyclohexane gave a 7% yield of **11** (by GLC).

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Cyclopropane Ring Opening with Pyridine Hydrochloride

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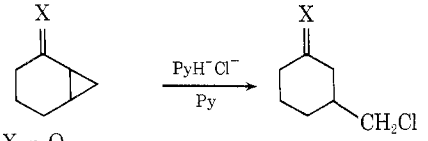
Two electron-withdrawing groups will make a cyclopropane derivative susceptible to suffer ring opening by nucleophilic attack[1–2,] while monosubstituted cyclopropane rings require a strong nucleophile (like mercaptide ion[3]) or very strained systems.[4–6]

We have found that pyridine hydrochloride can produce the ring cleavage of bicyclo[4.1.0]heptan-2-one (**1**) and of its oximes **3**. When **1**[7] was refluxed in dry pyridine in the presence of pyridine hydrochloride for 20 h a high yield of 3-chloromethylcyclohexanone (**2**) was obtained.

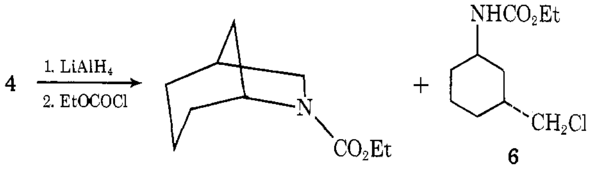


1, X = O
3, X = N〰OH

2, X = O
4, X = N〰OH

Under the same conditions a syn and anti mixture of **3** furnished a syn and anti mixture of **4**. Traces of **2** were also found if the reaction medium was not perfectly dry. Interestingly, only **4** was obtained when the oximation of **1** was accomplished according to the usual procedure using hydroxylamine hydrochloride in ethanolic pyridine solution.

The structure of **4** was deduced from spectral data (ir, NMR, MS). Confirmatively *N*-carbethoxy-6-azabicyclo[3.2.1]octane (**5**) was recognized as one of the two products obtained by the lithium aluminum hydride reduction of **4** followed by treatment with ethyl chlorocarbonate; the other one was the chlorourethane **6**. An authentic sample of **5** was prepared from *m*-aminobenzoic acid according to the reported procedure.[8] **6** and its cis isomer were obtained also by catalytic hydrogenation of **4**.



5

6

We think that at least two features of the compounds **1** and **3** are determinant in the nucleophilic cyclopropane ring opening: the conjugation of the three-membered ring with a π system and the participation of the cyclopropane of a more strained system. According to this assumption bicyclo[4.1.0]heptane was recovered unchanged after an analogous treatment with pyridine hydrochloride in pyridine. In addition we found both cyclopropyl methyl ketone and its oximes to react quite slowly under the conditions used for the cleavage of **1** and **3**.

The peculiarity of pyridine hydrochloride[9] in such a hydrochloric acid addition to a cyclopropane ring appears clearly. Bicyclo[4.1.0]heptane was reported to react with 12 M HCl in equimolar ratio at room temperature. After 6 h a mixture of olefins and chlorides was obtained.[10] Actually we found that both **1** and **3** remained unreacted under the same conditions. However, α-cyclopropyl ketones are known to give ring cleavage in HBr–AcOH at room temperature.[11]

The ring opening is selective. The C_1–C_7 bond cleavage observed is consistent with a previous report according to which this bond is the weakest because of its large orbital overlap with the adjacent π system.[12] This selectivity, the high yield obtained, and the possibility of the hydroxyiminic function preservation can get this sequence of reactions regarded as a useful synthetic route to the azabicycloalkanes.

Experimental Section

General. GC analyses were performed on a Carlo Erba Fractovap GI gas chromatograph equipped with a column of Apiezon L (60 m × 0.25 mm) and on a Carlo Erba Fractovap GV gas chromatograph equipped with a column of 4% OV 17 (2 m × 3 mm). Infrared spectra were obtained on a Perkin-Elmer 257 Infracord instrument. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 90-MHz spectrometer, using Me_4Si as an internal standard. Mass spectra were obtained on an AEI-MS12 spectrometer at an ionization potential of 70 eV. GC–MS spectra were obtained using a column of 2% OV 17 (2 m × 2 mm).

Oximes of Bicyclo[4.1.0]heptan-2-one (3). A solution of 2.2 g (20 mmol) of **1**,[7] 2.1 g (30 mmol) of hydroxylamine hydrochloride, and 3.2 g of $CH_3COONa{\cdot}3H_2O$ in 16 ml of ethanol was heated under reflux for 6 h. To the cooled mixture a saturated NaCl solution was added. Extraction with ether followed by evaporation afforded a residue of 1.9 g (76%) of **3**: mp 83–86 °C (petroleum ether); the GC analysis showed two partially overlapped peaks of similar areas, whose GC–MS spectra were nearly identical; ir (CCl_4) 3600, 3250, 3090, 3010 cm^{-1}; NMR (CCl_4) δ 0.4–1.1 (m, 3