Experimental Section

Experimental procedures were as reported earlier.[2] Formamidinesulfinic acid was obtained from Eastman Organic Chemicals, Rochester, N.Y. Optical rotations were measured on a high-precision polarimeter No. 80 (O.C. Rudolph and Sons). The (+)-3-bromocamphor was obtained from Aldrich Chemicals Co., Inc., Milwaukee, Wis.

Reduction of Dihydropseudocodeinone (6) to Dihydropseudocodeine (7). A solution of 114 mg (0.38 mmol) of the free base 6 was dissolved in EtOH (20 mL). This solution was stirred under a current of nitrogen. A solution of FSA (164 mg, 1.52 mmol) and NaOH (121.6 mg, 3.04 mmol) in H_2O (15 mL) was added, and the reaction mixture was heated on a water bath at 80–85 °C for 2 h. It was next cooled and EtOH was carefully removed by evaporation. The white precipitate formed on chilling was collected by suction filtration and washed with ice cold water. The product, **7**, mp 152–155 °C (lit.[15] mp 155 °C), weighed 60 mg (52%): IR (KBr disk) 3380, 3170, 2940, 1605, 1625, 1500 cm^{-1}; ^1H NMR (220 MHz, $CDCl_3$, Me_4Si 6.7 (q, 2 H, aromatic), 4.54 (m, 1 H, 8α-H), 3.86 (s, 3 H, OCH_3), 3.49 (broad s, 1 H, 5β-H), 2.42 (s, 3 H, NCH_3); mass spectrum (70 eV) *m/e* 301 (M^+).

Reduction of (+)-3-Bromocamphor. To a solution of (+)-3-bromocamphor (11.55 g, 0.05 mol) in 95% EtOH (50 mL) was added NaOH (16 g, 0.4 mol) in H_2O (16 mL) and FSA (21.6 g, 0.2 mol). The reaction mixture was stirred under a current of nitrogen at 80–85 °C, as in the previous experiment, for 2 h; it was cooled and then concentrated to half its volume and extracted with $CHCl_3$ (50 mL), the organic layer was washed with water, dried (Na_2SO_4), and evaporated in vacuo to give 5 g of (+)-camphor (66%): mp 179.5 °C; $[\alpha]^{20}_D$ +44.2° (*c* 10, $CHCl_3$).

Acknowledgment. We thank Mr. Charles H. Strom for obtaining NMR and mass spectra. One of us (N.C.) is thankful to Dr. Ralph A. Stephani for his helpful discussions and encouragement. Supported in part by Grants No. DA-00297. We are thankful to Mr. Henry Reha for his assistance in preparing illustrations.

Registry No.—**6**, 5056-91-7; **7**, 3883-12-3; (+)-3-bromocamphor, 55057-87-9; (+)-camphor, 46449-3; FSA, 1758-73-2; dihydrocodeinone, 125-29-1; dihydrothebainone, 847-86-9.

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(10) (a) This sample, from the collection of the late L. F. Small, was kindly furnished by Dr. E. L. May. (b) Our product **3** in the form of its free base has a mp 134–136 °C (lit.[9] mp 139–143 °C); IR ($CHCl_3$) 3525, 3025, 2950, 1710, 1480, 1440, and 1280 cm^{-1}; ^1H NMR ($CDCl_3$, Me_4Si) δ 2.44 (s, 3 H, NCH_3), 3.85 (s, 3 H, OCH_3), 4.28 (distorted d, J = 14 Hz, 1 H).
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N,N-Dialkyl-2-oxocycloalkanonecarboxamide Photochemistry. Possible δ-Hydrogen Abstraction in 2-Substituted Cycloalkanones

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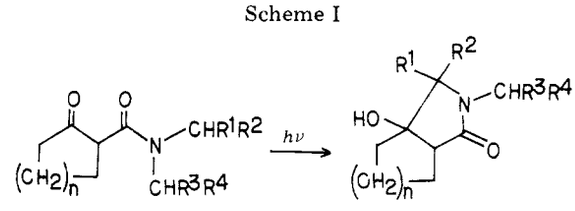
The Norrish types I and II reactions of ketones are the most widely studied of photochemical processes.[1] Cyclic ketones bearing γ hydrogens can undergo both reactions.[2] The rate of the type I reaction (α cleavage) is enhanced by a substituent on the α carbon, and reducing the size of the ring increases the rate of α cleavage.[2a,b] Consequently, little hydrogen abstraction is observed from 2-substituted cyclopentanones because the rate constant for γ-hydrogen abstraction is not fast enough to compete with the rate of α cleavage.[2a,b] It is well-known that the rate of δ-hydrogen abstraction is much slower than that of γ-hydrogen abstraction.[3] Therefore, there is no example of δ-hydrogen abstraction of 2-substituted cyclopentanones or cyclohexanones. We previously reported the photocyclization of acyclic β-oxo amides to pyrrolidin-2-ones[4] and now wish to report that of *N,N*-dialkyl-2-oxocycloalkanonecarboxamides to bicyclic lactams via an unprecedented δ-hydrogen abstraction in simple 2-substituted cycloalkanones.

Irradiation of a benzene solution of *N,N*-dibenzyl-2-oxocyclopentanecarboxamide (**1a**) in a Pyrex vessel under nitrogen with a high-pressure mercury lamp gave the bicyclic lactam **2a**, mp 116–117 °C, in 64% yield (see Scheme I). The structure of the lactam **2a** was elucidated by spectral data and elemental analysis. The IR spectrum of **2a** showed characteristic hydroxy (3400 cm^{-1}) and five-membered lactam carbonyl (1670 cm^{-1}) absorptions. The NMR spectrum showed a singlet at δ 4.17, attributable to the C-4 methine proton. These results indicate that only one stereoisomer was produced exclusively from the oxo amide **1a**. The C-4 phenyl group seems to be trans to the C-6 methylene group by analogy to pyrrolidin-2-ones.[4b] This configuration would be expected to be the more thermally stable. Similarly, irradiation of *N,N*-diisopropyl-2-oxocyclopentanecarboxamide (**1b**) and 2-oxocyclohexanecarboxamide (**1c**) under the same conditions also afforded the corresponding bicyclic lactams **2b** and **2c**, respectively. The structures of the lactams were determined by IR and NMR spectra and by elemental analyses. The ring-fusion stereochemistry of **2a**, **2b**, and **2c** was presumed

Scheme I



	1					2					
	n	R^1	R^2	R^3	R^4	*n*	R^1	R^2	R^3	R^4	yield, %
a,	1	H	Ph	H	Ph	1	H	Ph	H	Ph	64
b,	1	Me	Me	Me	Me	1	Me	Me	Me	Me	41
c,	2	Me	Me	Me	Me	2	Me	Me	Me	Me	46
d,	1	H	H	H	H	1	H	H	H	H	0
e,	2	H	H	H	H	2	H	H	H	H	0
f,	1	H	Ph	H	H	1	H	Ph	H	H	18

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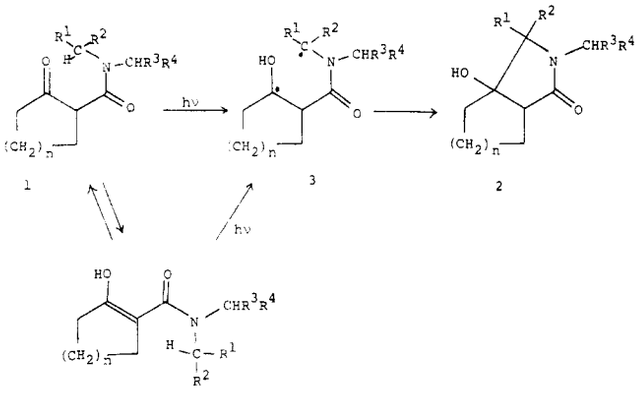

Figure 1. The process of δ-hydrogen abstraction through a seven-membered transition state.

to be cis because the alternative trans ring juncture would be energetically unfavorable.[5] The α-cleavage products could not be detected in photolysis of **1a**, while ca. 25% of the products (unsaturated aldehydes) were produced in the case of **1b**[6] and **1c**. But they were not completely purified. On the other hand, photolyses of *N,N*-dimethylcarboxamides **1d** and **1e** did not give lactams but only polymeric intractable material.

Formation of the bicyclic lactams can be explained in terms of photocyclization involving δ-hydrogen abstraction by the ketone carbonyl through a seven-membered transition state (see Figure 1). Another route which involves hydrogen abstraction by the olefinic carbon (C-2) of the enol form of 1 through a five-membered transition state seems to be improbable because (a) *N,N*-dibenzyl-2,2-dimethylbenzoylacetamide, which carries no enolizable hydrogens, also undergoes the cyclization[4b] and (b) hydrogen abstraction by an olefinic carbon through a five-membered transition state is a rarely observed process.[7]

The process of hydrogen abstraction through a seven-membered transition state is a surprisingly rare event in the photochemistry of cycloalkanones. The hydrogen abstraction in 2-oxocycloalkanonecarboxamides seems to be remarkably affected by substituents on the nitrogen atom. Substituents which stabilize the 1,5 biradical (**3**) apparently enhance the abstraction. This fact is further supported by the regioselectivity in the photoreaction of *N*-benzyl-*N*-methyl-2-oxocyclopentanecarboxamide (**1f**).

Irradiation of the oxo amide **1f** under the same conditions gave an *N*-methyl bicyclic lactam in 18% yield, which was produced through benzylic hydrogen abstraction by the ketone carbonyl. No *N*-benzyl bicyclic lactam, which would be formed through methyl hydrogen abstraction, was isolated. These results are consistent with the regioselectivity usually observed in the photochemistry of ketones[8] and seems to indicate that 2-oxocycloalkanonecarboxamides undergo photocyclization through the typical biradical intermediate.

Effective quenching of the photocyclization of the oxo amide **1a** by 0.1 M piperylene was not observed. This result indicates that the cyclization of the 2-oxocycloalkanonecarboxamide, like most cycloalkanones,[9] mainly proceeds from the n,π* singlet state of the oxxo amide, although a rapid triplet-state reaction is not necessarily eliminated from the available data.

A mechanism involving initial electron transfer from the amide nitrogen to the ketone carbonyl and subsequent δ-proton transfer[10] is also conceivable because intramolecular photoreactions via electron transfer are usually unquenchable[10] (see Figure 2). However, it is known that photoreduction of ketones by amines via electron or charge-transfer interaction does not show such regioselectivity as described above.[11] Davidson and Lambeth reported that the benzylic

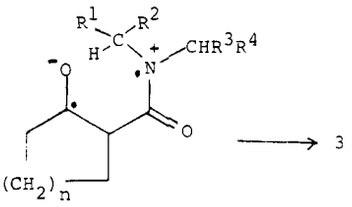

Figure 2. A mechanism involving an initial electron transfer from the amide nitrogen to the ketone carbonyl and subsequent δ-proton transfer.

C–H bond was less reactive than the methyl C–H bond in the photoreduction of benzophenone by N-alkylated diphenylamines.[12] Therefore, the mechanism involving electron transfer seems to be less probable, although the possibility can not be excluded.

In conclusion, the photocyclization of the *N,N*-dialkyl-2-oxocycloalkanonecarboxamides can be most reasonably explained in terms of δ-hydrogen abstraction from the n,π* singlet (or triplet) state. This indicates that δ-hydrogen abstraction is unusually fast. Such a rapid rate, however, is not unreasonable for the structure. The enhancement by a nitrogen atom is expected since atoms with lone pairs of electrons stabilize radicals.[8] Furthermore, **1a–c** have to rotate only two bonds to achieve the favored geometry for hydrogen abstraction because the α bond and the CO–N bond are fixed during the photoprocess. The frozen rotation in these cyclic oxo amides should further enhance the rate of the intramolecular hydrogen abstraction. Lewis et al. reported the remarkable rate enhancement in type II cyclization of conformationally restricted molecules.[13] Finally, these results indicate that δ-hydrogen abstraction in 2-substituted cyclopentanones or cyclohexanones occurs only when the δ hydrogens are strongly activated by substituents, and the abstraction is further enhanced by conformational factors.

Experimental Section

IR spectra were recorded with a Hitachi EPI-2 spectrometer and NMR spectra with a Hitachi R-20 spectrometer (tetramethylsilane as an internal standard). An Ushio 450-W high-pressure mercury lamp was used as the irradiation source.

The 2-oxocycloalkanonecarboxamides were prepared according to previously described methods.[14]

General Procedure for Photoreactions of 2-Oxocycloalkanonecarboxamides. A solution of the 2-oxocycloalkanonecarboxamide (1, 500 mg) in 80 mL of benzene was irradiated in a Pyrex vessel under nitrogen with a high-pressure mercury lamp. The solvent was removed in vacuo, and the residue was chromatographed on silica gel. Elution with benzene–ethyl acetate afforded the bicyclic lactams **2**.

(i) 3-Benzyl-5-hydroxy-4-phenyl-3-azabicyclo[3.3.0]octan-2-one (2a). Mp 116–117 °C; IR (KBr) 3400, 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.4–1.2 (m, 6 H, CH_2), 2.7 (m, 1 H, 1-CH), 2.8 (brd s, 1 H, OH), 3.39 and 5.18 (AB q, 2 H, J = 15.0 Hz, CH_2Ph), 4.17 (s, 1 H, 4-CH), 6.0–7.45 (m, 10 H, aromatic).

Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.18; H, 6.84; N, 4.46.

(ii) 5-Hydroxy-3-isopropyl-4,4-dimethyl-3-azabicyclo-[3.3.0]octan-2-one (2b). Mp 114–115 °C; IR (KBr) 3350, 1660 cm^{-1}; NMR ($CDCl_3$) δ 1.22 (s, 6 H, 4-CH_3), 1.40 (d, 6 H, J = 6.0 Hz, $CH(CH_3)_2$), 1.5–2.1 (m, 6 H, CH_2), 2.6 (m, 1 H, 1-CH), 2.95 (s, 1 H, D_2O exchangeable), 3.30 (sep, 1 H, J = 6.0 Hz, $CH(CH_3)_2$).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.38; H, 9.85; N, 6.59.

(iii) 5-Hydroxy-3-isopropyl-4,4-dimethyl-3-azabicyclo-[4.3.0]nonan-2-one (2c). Mp 147–148 °C; IR (KBr) 3400, 1660 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (s, 6 H, 4-CH_3), 1.3–1.7 (m, 8 H, CH_2), 1.42 (d, 6 H, J = 6.5 Hz, $CH(CH_3)_2$), 2.55 (m, 1 H, 1-CH), 2.60 (s, 1 H, OH, D_2O exchangeable), 3.37 (sep, 1 H, $CH(CH_3)_2$).

Anal. Calcd for $C_{13}H_{23}NO_2$: C, 69.29; H, 10.29; N, 6.22. Found: C, 69.10; H, 10.16; N, 6.05.

(iv) 5-Hydroxy-3-methyl-4-phenyl-3-azabicyclo-[3.3.0]octan-2-one (2f). Mp 149–150 °C; IR (KBr) 3350, 1670 cm^{-1};

NMR ($CDCl_3$) δ 1.5–2.2 (m, 6 H, CH_2), 2.67 (s, 3 H, CH_3), 4.47 (s, 1 H, 1-CH), 7.0–7.4 (m, 5 H, aromatic).

Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.73; H, 7.40. Found: C, 72.72; H, 7.31.

Registry No.—**1a,** 64425-71-4; **1b,** 64425 72-5; **1c,** 64425-73-6; **1f,** 64425-74-7; **2a,** 64425-75-8; **2b,** 64425-76-9; **2c,** 64425-77-0; **2f,** 64425-78-1.

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Reduction of Aromatic Amides by Sodium in Liquid Ammonia

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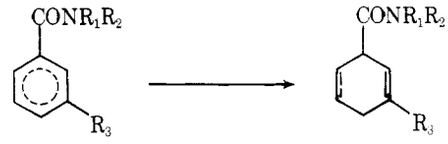
Because of reported variations for Birch reduction[1] of aromatic amides, we undertook a study of the reduction of benzamide (**1**), *m*-methoxybenzamide (**2**), *N*-methylbenzamide (**3**), and *N,N*-dimethylbenzamide (**4**).

We have found that some ring reduction of **1** to 1,4-dihydrobenzamide (**5**) occurs with sodium and either ethanol or *tert*-butyl alcohol while Kuehne and Lambert[2] report ring reduction with *tert*-butyl alcohol but not with ethanol. However we found *tert*-butyl alcohol more effective than ethanol with reduction proceeding well with 3.42 equiv of sodium regardless of whether the sodium or the *tert*-butyl alcohol was added last.[3]

In contrast ethanol gave poor and erratic results with the amount of **5** varying from reduction to reduction but never exceeding 50% when the procedure of adding sodium last was used. The crude product contained unreduced **1,** tetrahydro products, as well as **5** but not benzaldehyde or toluene. These latter two compounds were sought using GLC and were not found. Nor was any hydrobenzamide (**11**) found. Progressively increasing the sodium from 3.3 equiv to 5.0, 7.0, or 9.0 equiv progressively decreased the amount of unreduced **1,** increased the amount of tetrahydro products, but did not substantially increase **5.** This strongly suggests that **5** is an intermediate in the formation of the tetrahydroproducts. One experiment using 5.0 equiv of sodium plus an equimolar mixture of ethanol and *tert*-butyl alcohol gave no improvement over use of ethanol alone.

Also with *tert*-butyl alcohol, its addition last or sodium addition last made little or no difference. But in the case of ethanol, its addition last gave even less **5** than when sodium was added last.



1, R_1, R_2, R_3 = H
2, R_1, R_2 = H; R_3 = OCH_3
3, R_1, R_3 = H; R_2 = CH_3
4, R_3 = H; R_1, R_2 = CH_3

5, R_1, R_2, R_3 = H
6, R_1, R_2 = H; R_3 = OCH_3
7, R_1, R_3 = H; R_2 = CH_3

If no ammonium chloride was added to neutralize the alkoxide before work-up, then air oxidation of **5** to reform **1** occurred. A control experiment started with a solution of **5** in ammonia containing sodium ethoxide which was similarly exposed to air resulted in reformed **1.** Kuehne and Lambert[2] also report similar base-catalyzed air oxidations.

m-Methoxybenzamide (**2**) was reduced to 1,4-dihydro-3-methoxybenzamide (**6**) with 3.3 equiv of sodium and ethanol at −75 °C. At −33 °C more extensive reduction occurred yielding a mixture which was not separated. When 8.0 equiv of sodium at −33 °C was used, more extensive reduction resulted[4] in formation of 1,4,5,6-tetrahydro-3-methoxybenzyl alcohol (**8**). Kuehne and Lambert[2] report no reduction of **2** with 3.3 equiv of sodium and formation of **6** with 7.6 equiv of sodium.

While we can offer no firm explanation as to why our results[5] with **1** and **2** differ from those of Kuehne and Lambert,[2] it can be noted that the effects of many experimental variables on the Birch reduction are incompletely understood.[6]

Possibly more of their sodium was consumed in a side reaction. Thus reduction of **1** may have been too incomplete to be detected and reduction of **2** would have required more sodium. Such a side reaction might be sodium with alcohol and/or ammonia to produce hydrogen. Since their work, small amounts of colloidal iron, which commonly occur in commercial ammonia, have been reported to catalyze this reaction and affect Birch reductions.[6b-d]

An additional factor must be involved in the reduction of **1** with ethanol as more extensive reduction to tetrahydro products occurs. This consumes additional sodium but also requires formation of a conjugated diene as isolated double bonds are not reduced under these conditions. The conjugated diene could form if the more acidic ethanol is less specific in protonation of the anion intermediate than *tert*-butyl alcohol or by rapid rearrangement of initially formed unconjugated diene. The alkoxide produced in the reduction could catalyze this rearrangement and, as ethanol is reported[6b] to react faster than *tert*-butyl alcohol under these conditions, the more rapidly formed ethoxide could catalyze rearrangement faster than the more slowly formed *tert*-butoxide.

The following two experiments indicate the latter explanation is insufficient to explain the different results with ethanol and *tert*-butyl alcohol. Based on the report of Dryden[6b] that the presence of 0.5 or 1.0 ppm of iron increased the rate of the reaction of *tert*-butyl alcohol and sodium to that comparable to ethanol and sodium, we did a reduction using *tert*-butyl alcohol, adding 3.42 equiv of sodium last and having 1 ppm of iron present. There was a definite increase in the rate of disappearance of the sodium but **5** was still obtained in good yield and without any appreciable tetrahydro product. Another experiment using *tert*-butyl alcohol with 3.42 equiv of *tert*-butoxide initially present with 3.42 equiv of sodium

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