(rel intensity) 191 ($M^{+\cdot}$ –I, 14), 105 ($PhCO^+$, 100), 106 ($PhCHO^+$, 9), 60 (CH_3COOH^+, 9), 43 (CH_3CO^+, 9).

3-Iodo-2-oxopropyl Benzoate. The reaction was carried out in 2-mmol scale. The crude product was purified on TLC to give unreacted allyl benzoate (55 mg, 17%), and the title compound was obtained (229 mg, 49%): mp 77–77.5 °C (hexane); IR (nujol) 1735 (vs, –O–C=O), 1715 cm^{-1} (vs, C=O); NMR ($CDCl_3$) 3.96 (s, 2 H, CH_2ICO–), 5.20 (s, 2 H, –OCH_2CO–), 7.50–7.80 (m, 3 H, aromatic), 8.21–8.35 ppm (m, 2 H, aromatic); MS *m/e* (rel intensity) 304 ($M^{+\cdot}$ 2), 177 ($M^{+\cdot}$ –I, 16), 169 (CH_2ICO^+, 1), 135 ($M^{+\cdot}$ –$COCH_2I$, 4), 106 ($PhCHO^+$, 11), 105 ($PhCO^+$, 100), 77 (Ph^+, 46).

α-Iodo-δ-valerolactone. The reaction was carried out in 2-mmol scale using 1.2 equiv of iodine, and the crude product was purified on TLC to give the title compound (175 mg, 39%): bp 80–82 °C/1.5 mm; IR (neat) 1730 cm^{-1} (vs, C=O); NMR (CCl_4) 1.70–2.45 (m, 4 H, –CH_2–), 4.37–4.64 (m, 2 H, –OCH_2–), 4.86 ppm (t, 1 H, J = 5 Hz, –CHICO–); MS *m/e* (rel intensity) 226 ($M^{+\cdot}$ 28), 196 ($M^{+\cdot}$ –CH_2O), 11), 127 (I^+, 32), 99 ($M^{+\cdot}$ –I, 20), 55 ($COCHCH_2^+$, 100).

Registry No.—**2**, 63641-54-3; **6**, 63641-55-4; silver chromate, 19247-15-5; iodine, 7553-56-2.

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(9) The structure of **6** was inferred on the basis of its spectral properties: IR (neat) 1725 cm^{-1} (vs, C=O); NMR (CCl_4) 0.80–2.30 (m, 10 H), 2.55 (t, 2 H, J = 6 Hz), 3.20–3.70 (m, 3 H), 3.75–4.30 (m, 1 H), 9.80 ppm (br s, 1 H); MS *m/e* (rel intensity) 296 ($M^{+\cdot}$ 1), 267 (1), 252 (2), 209 (4), 169 (3), 87 (24), 71 (100), 57 (9), 43 (56), 29 (17).

(10) The role of pyridine is presumably that of facilitating the formation of the supposed hypoiodous–chromic acid mixed anhydride: In fact, an addition of pyridine to the silver chromate–iodine mixture caused an immediate change of color.

(11) To ensure dryness of silver chromate, the use of molecular sieves is preferable.

(12) Because of the less stable nature of the product, both a short column and rapid elution are recommendable.

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Photochemistry of a Ketone with a Reportedly High Circular Dichroism Using Circularly Polarized Light

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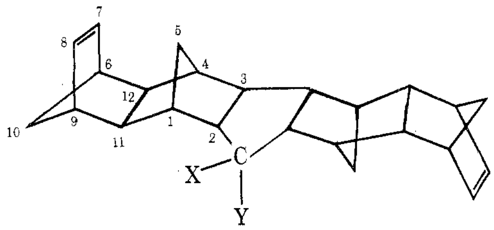
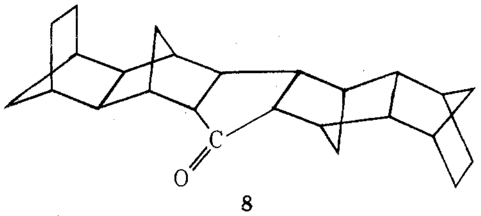
Partial photoresolution with circularly polarized light (CPL) is useful in the determination of the anisotropy factor (*g* factor = Δε/ε) of chiral compounds. This easily available test led us to reinvestigate the previously described[1] chiroptical properties of ketone 1.

Partial photodecomposition of a racemic mixture with CPL was first realized by Kuhn.[2] We reinvestigated this field in 1974 and gave a kinetic treatment permitting the prediction of the optical purity of the remaining material (characterized by its *g* factor) for a given fraction of destruction.[3] With *dl*-camphor (g = 0.09, λ 310 nm) 99% destruction allowed us to recover optically active camphor with 20% enantiomeric excess (e.e.).

Scheme I



1, X = Y = O
6, X = H, Y = OH
7, X = H, Y = OCO_2(−)Menthyl



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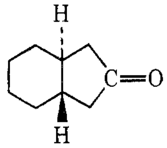

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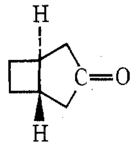
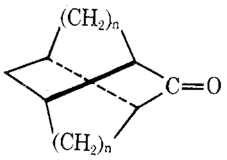


3



4, n = 1
5, n = 2

This method can be useful for obtaining, for the first time, a chiral compound if classical resolution methods fail but, of course, either a high *g* factor or a high degree of photodestruction is necessary if reasonable optical purities are needed. Therefore, very little of the unphotolyzed starting material is obtained, and it must be separated and purified from a huge mass of photodecomposition products. In addition, we pointed out[3] that with a few independent experiments it should be possible to calculate the *g* factor and specific rotation of the optically pure compound.[4]

Our attention was drawn by a report[1] describing the resolution and chiroptical properties of ketone 1. From the published data, *g* factor values can be calculated at several wavelengths: g = 0.77 (322 nm), g = 0.70 (312 nm), and g = 0.65 (301 nm). These values can be compared with those of all known polycyclic ketones and even with other organic compounds.[5] For example, some of the highest known *g* factor values are 0.24 (313 nm), 0.20 (311 nm), 0.12 (286 nm), and 0.30 (288 nm) for the chiral twisted ketones 2–5,[6–9] respectively.

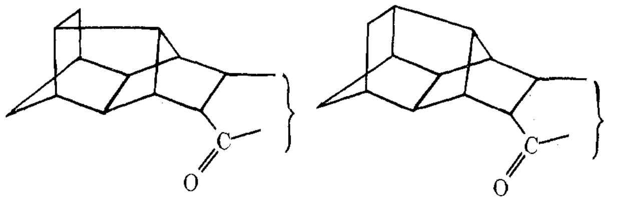
It thus appears that for 1 the CD and *g* values are exceptionally high. This might be the consequence of high twist of the cyclopentanone unit, as shown by a recent report about ketones 2 and 3.[10]

These considerations led us to investigate the promising photochemistry of ketone 1 with CPL. Computations with g = 0.80 showed that 90% and 99% decomposition should allow the recovery of 1 in 81% and 99% e.e.,[3] respectively, making this method very competitive with the previously described resolution involving formation of diastereomers.[1]

Results and Discussion

The partial photoresolution with CPL of ketone 1 is very disappointing; enantiomeric enrichment is smaller than expected and is in agreement with an average *g* factor of 0.10. Photoproducts[11] could possibly arise from an energy transfer mechanism which would change the basis of our previous calculations (Scheme II).[3] Before considering this hypothesis, we reinvestigated the chiroptical properties of ketone **1**. LAH reduction of *dl*-1 quantitatively gave *dl*-**6**. Treatment by

Scheme II



9a 9b

(−)-menthyl chloroformate in the presence of pyridine in benzene yielded the mixture of diastereomeric carbonates **7**. Two crystallizations of the crude material in hexane afforded a pure diastereomer in excellent yield (as shown by GLC analysis on a 4% OV1 column which permitted a nice separation of the two diastereomers). LAH treatment of the latter diastereomer in THF and purification gave alcohol (−)-**6**: $[\alpha]_D$ −12 ± 1° (c 0.40, cyclohexane) which was optically pure. Oxidation[12] of (−)-**6** gave (−)-**1**, purified by chromatography on silica and crystallized from hexane. Optically pure **1** (as shown by GLC analysis on **7**) has the following properties: $[\alpha]_D$ −270 ± 10° (*c* 0.104, cyclohexane; *c* 0.066, ether), $[\alpha]_D$ −244 ± 10° (*c* 0.390, benzene).

These optical rotations are in good agreement with the previous $[\alpha]_D$ value of −261° (solvent not specified).[1] The UV spectrum is identical with that described, while strong disagreement exists concerning the CD spectrum. Our value of $\Delta\epsilon$ (Figure 1) is always much smaller than the published data.[1] From the curves of Figure 1, *g* values could be calculated for several wavelengths. An average *g* value of 0.15 between 290 and 330 nm was obtained, close to that deduced from our partial photoresolution experiment. In addition, reduction of the double bonds in (+)-**1** (53% e.e.) and chromatographic purification yielded the partially resolved ketone **8**. From its rotation and circular dichroism, the optical rotation of the pure ketone **8** was calculated to be $[\alpha]_D$ +250 ± 10° (*c* 0.171, cyclohexane). From the CD and UV spectra, an average *g* factor of 0.16, of the same magnitude as for **1**, was calculated. It is clear that contrary to previous reports[1,13] ketone **1** has no unusual chiroptical properties; its behavior is very similar to that of ketones **2** and **3** which were recently described. Tricyclo[4.4.0.0^{3,8}]decan-2-one (**5**) and *trans*-2-hydrindanone (**2**) remain, to our knowledge, the ketones with the highest anisotropy factor.[14]

Experimental Section

Melting points, uncorrected, were determined on a Reichert apparatus using a microscope hot stage. Infrared spectra were recorded on a Perkin-Elmer 257 spectrophotometer and ultraviolet spectra on a Unicam SP 1800 spectrometer. ^{1}H NMR spectra were determined on a Perkin-Elmer R-32 instrument (90 MHz) (δ, parts per million from Me_4Si), the optical rotations on a Perkin-Elmer 141 polarimeter, and the circular dichroism (CD) on a Roussel-Jouan dichrograph. A Carlo Erba GI chromatograph was used for the GLC experiments (N_2 as carrier gas). Mass spectra were recorded on an AEI MS30 mass spectrometer.

Irradiation of Ketone 1 with Natural Light. A solution of 240 mg (0.7 mmol) of (±)-ketone **1** in 900 mL of cyclohexane was irradiated in a classical photochemical apparatus (Hanovia 450 W) with a Pyrex filter. The progress of the reaction was monitored by GLC analysis using an OV17 4% 2-m column (oven 260 °C). Two photoproducts were detected, the second one coming from a photochemical rearrangement of the first one. At the end of the reaction, a single photoproduct was isolated.[11] Purification by chromatography on silica gel (95:5 hexane–ether) and crystallization from cyclohexane gave 140 mg of white plates (60%): mp 241–242 °C; IR 1715 cm^{-1} (Nujol); NMR ($CDCl_3$) δ 0.4–2.4 (m); UV (cyclohexane) λ_{max} (ϵ) 290, 298, 308 (55), 319, 331 nm; mass spectrum *m/e* 344 (P). Anal. Calcd for $C_{25}H_{28}O$: C, 87.19; H, 8.19. Found: C, 86.95; H, 8.34.

Irradiation of Ketone 1 with Circularly Polarized Light (CPL). A solution of 615 mg (1.8 mmol) of (±)-ketone **1** in 760 mL of cyclohexane was irradiated with right CPL (313 nm) using the apparatus previously described.[3] The progress and the extent of the reaction were measured by GLC analysis using an internal standard (OV 17 4% 2 m, 260 °C). The irradiation was stopped before the disappearance of all of the ketone. The more accurate determination of percent destruction of **1** by GLC is 60 ± 5%. An NMR study by analysis of the H vinylic signals showed a destruction of 65 ± 5%. A first purification by chromatography on silica gel–$AgNO_3$ (10%) followed by two others on silica gel (97:3 hexane–ether) gave a sample of pure ketone **1** $[\alpha]^{25}_D$ +8.20° (*c* 0.3, cyclohexane) e.e. 3%, whereas computation with $g = 0.80$ shows that 60% photodestruction would allow the recovery of **1** in 38% e.e.

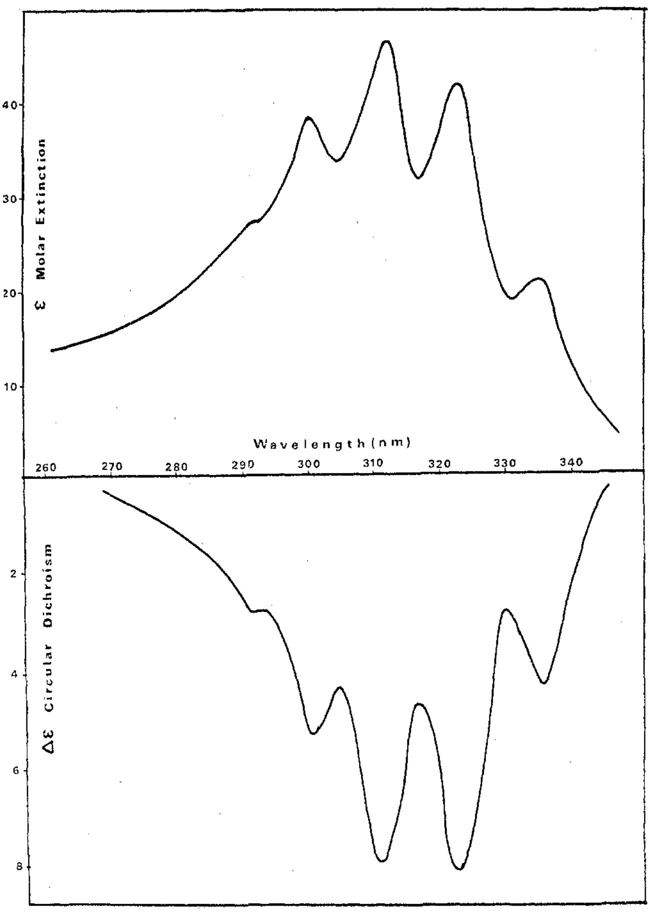


Figure 1. UV and CD spectra of ketone 1 in cyclohexane.

Diastereomeric Carbonates 7. (−)-Menthyl chloroformate (0.7 g (3.2 mmol)) was added to a solution of 1.07 g (3.1 mmol) of (±)-alcohol **6**[15] in 30 mL of benzene with a few drops of pyridine. The mixture was stirred at room temperature for 24 h. Then 20 mL of chloroform was added and the solution was washed once with 1 N NaOH and twice with NaCl saturated solution. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness. The solid residue was recrystallized from 45 mL of hexane to give 430 mg of (−)-carbonate **7** (81% e.e.): mp 212 °C. A new recrystallization in hexane gave 320 mg of (−)-carbonate **7** optically pure (checked by GLC analysis on a OV 1 4% 1.70-m column): mp 217–218 °C; $[\alpha]^{25}_D$ −76° (*c* 1.24, $CHCl_3$), $[\alpha]^{25}_D$ −65° (*c* 0.89, C_6H_6); IR (Nujol) 3040 (=CH), 1725 (C=O), 1285 (CO), 775, 755 cm^{-1}; NMR ($CDCl_3$) δ 0.30–2.10 (m, 28, CH menthyl + cycle), 2.80 (s, 4 H, allylic), 4.50 (m, -CHOCOOCH-), 5.88 (s, 4, -HC=CH-). Column chromatography of the residue obtained from the mother liquor on 100 g of silica gel with hexane as eluent gave 1.15 g of (+)-carbonate **7** (53% e.e.). The enantiomeric excess was determined by GLC (column OV1 4%, 250 °C).

(−)-Alcohol 6 from (−)-Carbonate 7. To a magnetically stirred mixture of 40 mg (1 mmol) of LAH in 20 mL of dry THF was added slowly a solution of 300 mg (0.57 mmol) of (−)-carbonate **7** in 20 mL of THF. The mixture was boiled under reflux for 1 h. After hydrolysis by 1 M H_2SO_4, the organic layer was washed (5% $NaHCO_3$ and NaCl saturated solutions). After drying (Na_2SO_4) and evaporation of the solvent, the menthol was removed by sublimation (120 °C (0.1 mm), 3 h). A sample of (−)-alcohol **6** was obtained. 170 mg (87%): mp 208 °C: $[\alpha]^{25}_D$ −12° (*c* 0.39, cyclohexane) (lit.[1] $[\alpha]_D$ −14°, solvent not specified).

(−)-Ketone 1 from (−)-Alcohol 6. A solution of 160 mg of optically pure (−)-alcohol 6 in 2 mL of benzene was added to a mixture of 2 drops of CH_3COOH, 4 drops of H_2SO_4, 30 mg of $Na_2Cr_2O_7$, and 0.5 mL of water. The mixture was stirred for 1 h at room temperature and then washed ($NaHCO_3$ and water). The organic layer was dried (Na_2SO_4) and evaporated. A recrystallization in hexane gave 140 mg (87%) of optically pure (−)-ketone **1:** mp 266–267 °C; $[\alpha]^{25}{}_D$ −270° (*c* 0.104, cyclohexane), $[\alpha]^{25}{}_D$ −244° (*c* 0.39, benzene); CD λ_{max} ($\Delta\epsilon_{max}$) 300.5 (−5.33), 311.5 (−7.91), 323 (−8.17), 336 nm (−4.37) (*c* 3.02 mmol/L, cyclohexane); UV (cyclohexane) λ_{max} (ϵ_{max}) 301 (37.2), 312 (45.8), 323 (41.0), 335 nm (20.6).

(+)-Ketone 8 from (+)-Ketone 1. The (+)-ketone 1 (53% e.e.) was prepared from (+)-carbonate 7 (53% e.e.) according to the method previously described. A catalytic hydrogenation of ketone 1[15] on Pd/C gave the saturated ketone 8 (53% e.e.): mp 281–282 °C, $[\alpha]^{25}{}_D$ +132° (*c* 0.17, cyclohexane) which gives $[\alpha]^{25}{}_D$ max calcd +250°; CD (corrected for 100% e.e.) λ_{max} ($\Delta\epsilon_{max}$) 301 (4.14), 311.5 (6.13), 324 (6.39), 336.5 (3.37); UV (cyclohexane) λ_{max} (ϵ_{max}) 302 (40.8), 312 (49), 324 (44.2), 337 (24.3) nm.

Acknowledgment. We thank CNRS for financial support.

Registry No.—(±)-**1**, 63864-54-0; **1** isomer 1, 63864-55-1; **1** isomer 2, 54383-73-2; (±)-**6**, 63864-56-2; (−)-**6**, 63864-57-3; **7** isomer 1, 63784-77-0; **7** isomer 2, 63814-62-0; (+)-**8**, 63864-58-4; **9a**, 63784-78-1; **9b**, 63784-79-2; (−)-menthyl chloroformate, 14602-86-9.

References and Notes

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(4) Recently an accurate kinetic treatment of a photoresolution allowed Rau et al.[4a] to calculate the *g* factor, and molar ellipticity of a tetraazaspirane. A special case of photoresolution was developed by Nelander and Norden[4b] by working in an iced matrix. Thus the dithiane itself (which is a stable racemic mixture at 77 K) was resolved for the first time and its chiroptical properties studied at 77 K; (a) R. Blume, H. Rau, and O. Schuster, *J. Am. Chem. Soc.*, **98**, 6583 (1976); (b) B. Nelander and B. Norden, *Chem. Phys. Lett.*, **28**, 384 (1974).
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(11) Two photoproducts were detected during photolysis of **1** and their structures were investigated by spectrometric methods (IR, MS, NMR). One and two double bonds disappear, the cyclopentanone ring is not cleaved, and the molecular weight remains unchanged. These data led us to consider two possible internal hydrogen abstractions (cyclization C_5–C_8 or C_5–C_7). Two structures, **9a** and **9b**, satisfy these data. Further work is needed to decide between the two possibilities. For a previously described similar photoreaction see (a) W. Herz and M. G. Nair, *J. Am. Chem. Soc.*, **89**, 5474 (1967); (b) W. Herz, V. S. Iyer, M. G. Nair, and J. Saltiel, *ibid.*, **99**, 2704 (1977).
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An Alternative Synthesis of (±)-α- and (±)-γ-Lycoranes

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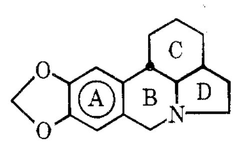
Received April 26, 1977

Although an important stereochemical requirement to build up the skeleton of α-lycorane (1)[1,2] and lycorine (2)[3,4] centers around the construction of the C ring and is successfully fulfilled by application[2,3] of the Diels–Alder reaction, we have searched for another route starting from a cyclohexanone to prepare a lactam (3),[2a] which is already converted into 1. Thus, a cyclic hydroxamic acid (4) is considered as an equivalent synthon for 3 and reaction of an oxime (5) with zinc dust in boiling acetic acid was carried out in view of the fact[5] that the similar reaction of an oxime (6) gives a cyclic hydroxamic acid (7) of a six-membered ring. However, we found that reaction of the oxime (5) gave unsaturated lactams instead of 4. Here, we wish to report on the structures of unsaturated lactams 8, 9, and 10 and on an alternative synthesis of (±)-α-lycorane (1) via unsaturated lactams 10 and 11 and (±)-γ-lycorane (12)[2b,c,6] via 9.



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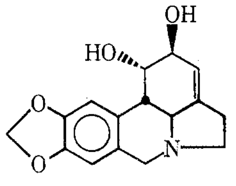

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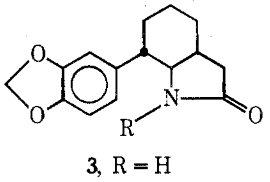

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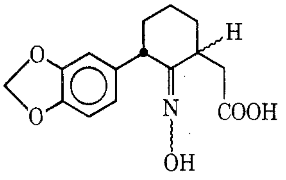
4, R = OH



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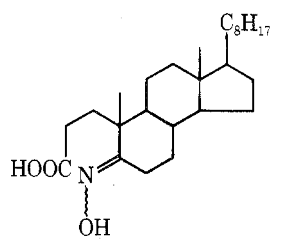

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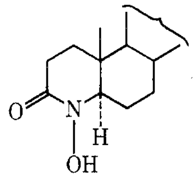

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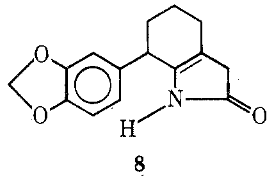

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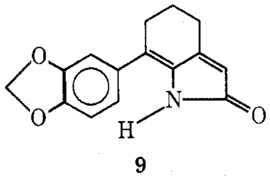

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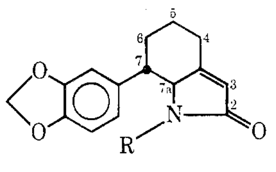
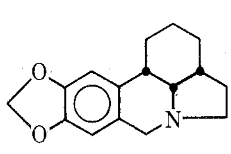


10, R = H
11, R = C_7H_7



12

Grignard reaction of cyclohexanone with 3,4-methylenedioxyphenylmagnesium bromide[7] in tetrahydrofuran followed by dehydration and hydroboration oxidation produced a cyclohexanol (13) whose Jones oxidation gave a cyclohexanone (14).[8] Alkylation of 14 via an enamine and successive alkaline hydrolysis furnished a 2-oxocyclohexylacetic acid (15).

Refluxing with zinc dust in glacial acetic acid of the oxime 5 afforded a mixture of lactams A, B, and C. Mass spectra of the lactams A and C showed the same molecular peak at *m/e* 257, which was two mass units less than that of **3**, while that of the lactam B was at *m/e* 255.

From the spectral data (NMR, IR, and MS), structures of the lactams A, B, and C proved to be **8**, **9**, and **10**, respectively.