88% formic acid. It was lyophilized again to give a brown resinous residue from which 22 mg of amorphous solid was obtained after trituration with a few drops of methanol. This was passed through a short column of silica gel (Brinkmann Instrument 70–325 mesh) and eluted with 1% formic acid in ethanol. The middle fractions afforded 5 mg of amorphous solid whose UV spectrum and TLC analysis (Kodak silica gel sheet; chloroform–isopropyl alcohol–88% formic acid, 1:2:0.2) were identical with those of an authentic sample of 6-hydroxynicotinic acid.

**C. With *tert*-Butylamine.** A mixture of 56 mg of **2a** and 1 mL of *tert*-butylamine was stirred at room temperature for 1 h. Dilution with 5 mL of ice water gave a pale yellow precipitate which was crystallized from methanol to yield 40 mg of *N-tert*-butyl-$\alpha$-aminomethyleneglutaconic anhydride (**2d**), mp 185–188 °C.

**Crystallographic Data:** $C_6H_5NO_3$; mol wt, 139.1; monoclinic; $a = 3.7284$ (4) Å; $b = 14.118$ (1) Å; $c = 11.065$ (1) Å; $\beta = 91.44$ (1); $V = 582.25$ Å$^3$; $Z = 4$; space group, $P2_1/c$ (No. 14); $d_{calcd} = 1.586$ g cm$^{-3}$, $d_{measd} = 1.57$ g cm$^{-3}$. Cell dimensions were obtained by least-squares analysis using reflections measured at $\pm\theta$ on a diffractometer (Cu K$\alpha$ radiation, $\lambda = 1.5418$ Å).

**Data Collection.** The crystal used was a platelet approximately 0.25 × 0.25 × 0.15 mm$^{-3}$ and was mounted along a diagonal of the largest face. Intensities were measured with a computer-controlled diffractometer (Nonius CAD-4) using graphite-monochromatized Cu K$\alpha$ radiation. There were 1149 unique reflections, 951 of which had $I_0 > \sigma(I_0)$. Lorentz and polarization corrections were applied but not absorption corrections. There was no indication of significant radiation damage during data collection.

**Registry No.**—**1b**, 67598-05-4; **1c**, 67598-06-5; **2a**, 67598-07-6; **2b**, 67598-08-7; **2c**, 67598-09-8; **2d**, 67598-10-1; **2e**, 67598-11-2; **2f**, 67598,12-3; **4**, 67598-13-4; methyl coumalate, 6018-41-3; coumalyl chloride, 23090-18-8; ethylenimine, 151-56-4; aniline, 62-53-3; benzylamine, 100-46-9; *tert*-butylamine, 75-64-9; diethylamine, 109-89-7; pyrrolidine, 123-75-1.

## References and Notes

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(2) There are a few reports of coumalamides in patents [(a) H. Martin, W. Baumann, H. Zaeslin, and H. Gysin, U.S. Patent 2 364 304, 1944; *Chem. Abstr.*, **39,** P4196 (1945); (b) J. R. Geigy, A.-G. Swiss Patent 215 240, 1941; *Chem. Abstr.*, **42,** P3782f (1948); (c) J. R. Geigy, A.-G. British Patent 586 135, 1947; *Chem. Abstr.*, **42,** P2272d (1948); (d) J. R. Geigy, A.-G. Swiss Patent 222 387, 1942; *Chem. Abstr.*, **43,** P821h (1949); and (e) J. R. Geigy, A.-G. Swiss Patents 220 966–9, 1942; *Chem. Abstr.*, **43,** P2239h (1949)], but these are mainly amides of 4,6-dimethylcoumalic acid (isodehydroacetic acid).

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(11) (a) K. Ezumi, H. Nakai, S. Sakata, K. Nishikida, M. Shiro, and T. Kubota, *Chem. Lett.*, 1393 (1974); (b) J. Bernstein, *J. Chem. Soc., Perkin Trans. 2,* 946 (1972); (c) H. B. Burgin and J. D. Dunitz, *Helv. Chim. Acta*, **53,** 1747 (1970).

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(14) R. S. Mulliken, *J. Chem. Phys.*, **23,** 1833 (1955).

(15) A U.S. patent[2a] describes a compound, *N,N*-diethyl-1,2-pyrone-5-carboxamide [bp 100–105 °C (0.35 mm)], which is quite different from compound **2e.** We were unable to isolate from our reaction any product corresponding to the reported property. The UV spectrum of the reaction mixture before workup showed only absorption due to compound **2e.**

(16) N. Pashusherina, N. D. Dmitrieva, E. A. Luk'yanets, and R. Ya. Levina, *Russ. Chem. Rev.* (*Engl. Transl.*), **36,** 175 (1967).

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(24) One other case of such a small coupling constant was observed by Dudek and Dudek[23] for *N*-methyl-2-hydroxy-1-naphthaldehydimine-$^{15}N$.

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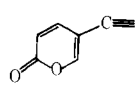
(29) The *m/e* 123 peak is prominent in this spectrum as well as those of methyl coumalate and *N*-coumalylaziridine (**1b**). It is probably due to the ion i and



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can be considered as the characteristic peak for coumalate derivatives. In contrast, in all of the spectra of the anhydrides (**2a–f**), the *m/e* 123 peak is either missing or present in less than 2%.

(30) H. von Pechmann [*Justus Liebigs Ann. Chem.*, **273,** 180 (1893)] described a compound, $C_{12}H_9NO_3$, mp 220–223 °C, of unknown constitution arising from aniline and coumalic acid followed by treatment with acetic anhydride. We have repeated von Pechmann's experiment and established that this unknown compound was identical in every respect with **2c.**

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# Intramolecular Photochemistry of Vinylogous Imides. An Efficient Photochemical Ene Reaction

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Pyrex filtered irradiation of a vinylogous imide derivative of dimedone was found to produce intramolecular ene products rather than the expected cycloaddition product. The stereochemistry of the products was determined using chemical and spectroscopic techniques.

In recent years the photochemistry of vinylogous imides has been studied by several groups. Early examples of vinylogous imide photocycloaddition were provided by Wiesner, who produced cyclobutanes using methyl acrylate[1] and allene[1,2] as the olefin components in intermolecular reactions and a terminal allene in an intramolecular reaction.[3] Likewise, Cantrell[4] reported successful photocycloaddition of cyclopentene to a vinylogous imide. More recently, Tamura[5] has described the production of 2 and 3 by irradiation of 1. In analogy with these previous reports, it was anticipated that 5 would undergo intramolecular 2 + 2 cycloaddition when submitted to Pyrex filtered irradiation. It was found, however,

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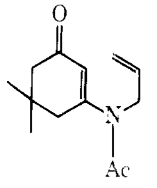

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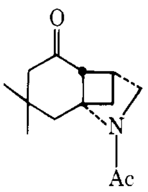

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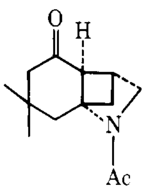

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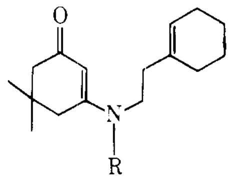
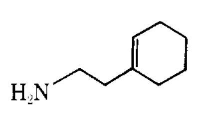


4, R = H
5, R = Ac



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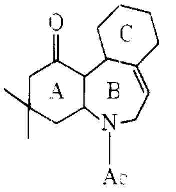
that no cyclobutanes were produced by photolysis of **5**.

Pyrex filtered irradiation of a dilute cyclohexane solution of **5**, produced by condensation of amine **6** and dimedone followed by acetylation of the resulting vinylogous amide **4**, resulted in complete disappearance of the vinylogous imide in 1.7 h. The solvent was evaporated and the residue recrystallized from ether to provide a 78% yield of two compounds which have thus far proved to be inseparable using a variety of chromatographic techniques. Although most resonances in the $^{1}$H NMR spectrum of the mixture were at least partially overlapping, integration indicated a ratio of approximately 4:1. Likewise, integration of similar carbon resonances in the $^{13}$C NMR spectrum of the crude reaction mixture or of crystallized material provides the same estimate.

The gross structure of the major and minor products was readily determined from spectroscopic data and simple chemical transformations. The infrared spectrum of the mixture contained absorptions at 5.85 and 6.15 μm (CHCl$_3$), demonstrating the presence of saturated ketone and amide units. Furthermore, the similarity of shifts in the $^{13}$C NMR spectrum of the mixture implied a close structural relationship between the two products. In addition to ketone and amide carbon resonances, both compounds displayed trisubstituted double-bond resonances (major, δ 150.0 (C), 115.9 (CH); minor, δ 146.9 (C), 117.6 (CH)). Finally, treatment of the mixture with potassium hydroxide in methanol provides a single enone in 83% yield. Thus, the photoproducts are diastereomers of structure **7** and the enone has structure **8**. The double-bond position is fully supported by $^{1}$H NMR spectra of **7** and **8**. In the spectrum of the photoproduct mixture, the olefinic proton resonance of the major isomer completely obscures that of the minor isomer and appears as a doublet of doublets at δ 5.46 ($J$ = 3.5 and 7.0 Hz), whereas the side chain olefinic proton resonance in **8** appears as a broad triplet at δ 5.31 ($J$ = 7.5 Hz). Furthermore, irradiation of the olefinic resonance in the photoproduct mixture perturbs a broad multiplet at δ 3.8, which must be due to allylic methylene protons next to nitrogen.



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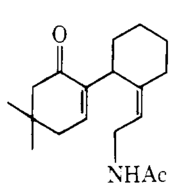

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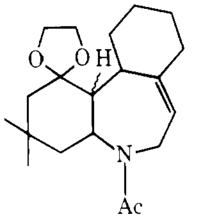
The photoproducts were shown to differ only in the stereochemistry of the methine proton next to the carbonyl. Ketalization of the photomixture led to a mixture of two ketals **9** in approximately equal amounts as judged from the $^{13}$C NMR spectrum of the reaction mixture. This change in ratio of products is easily accounted for by acid-induced epimerization during or after the ketalization process. Acid hydrolysis of the ketal mixture produced the original 4:1 ratio of photoproducts. Furthermore, base treatment of enone **8** also provided the original photomixture.

The assignment of the relative stereochemistry in the photoproducts rests on analysis of $^{1}$H NMR spectra of the original mixture and deuterated derivatives thereof. Exposure of the photomixture to potassium carbonate in refluxing deuterium oxide–tetrahydrofuran produced trideuterio derivatives **10**, while sodium deuterioxide treatment provided the pentadeuterio derivatives **11**, presumably via the deuterated derivative of enone **8**, which was also isolated from the reaction. The amido methine proton of the major product, which appears as an eight line resonance at δ 4.78 ($J$ = 5.0, 10.5, and 13.0 Hz) in the $^{1}$H NMR spectrum, collapses to a four line pattern ($J$ = 5.0 and 10.5 Hz) in the spectrum of **10** and to a broad singlet in **11**. The loss of such a large coupling constant in **10** implies a trans diaxial relationship of the bridgehead protons; hence, the AB ring fusion must be trans in the major photoproduct and cis in the minor. The remaining stereochemical point, namely, the allylic methine center, has been tentatively assigned (vide infra) as shown in structures **12** and **13** for the major and minor photoproducts, respectively.



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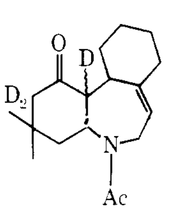

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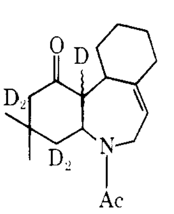

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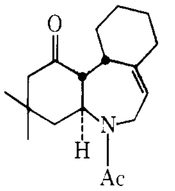

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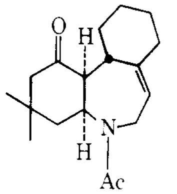

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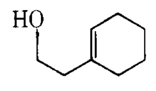
The final stereochemical assignment rests on the assumption that the allylic methine proton resonance of **12** can be fully identified in the NMR spectrum of the photomixture. In the δ 2.4–3.2 region there are several resonances partially overlapping what appears to be a broad doublet centered at δ 2.72 ($J$ = 13.0 Hz). In the spectrum of **10** this region is completely clean except for the δ 2.72 doublet which appears unchanged. Thus, there must be no significant coupling between the allylic proton in **12** and its neighbor which is replaced in **10**. The required dihedral angle of 90° can only be accommodated by a cis relationship of the two protons.

The high efficiency of this photochemical process suggested that extension to larger rings might be possible; hence, the photochemistry of **17** was briefly investigated. Alcohol **14** was converted to amine **15** by tosylation, cyanide displacement, and lithium aluminum hydride reduction. Condensation of dimedone and amine **15** followed by acetylation provided the



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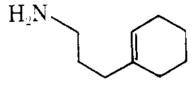

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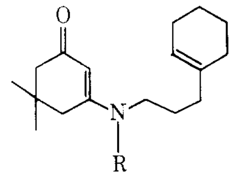
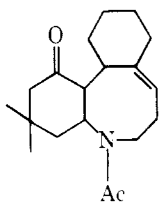
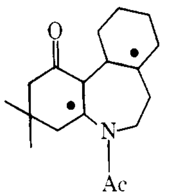


16, R = H
17, R = Ac



**18**



**19**

vinylogous imide **17**. Irradiation of this material as a dilute cyclohexane solution for 2.5 h provided a 57% yield of crystalline product. The IR and $^1$H NMR spectra of this material are in accord with structure **18**. The $^{13}$C NMR spectrum is in agreement, and the spectrum of crude material indicates the presence of minor impurities; however, these were not investigated.

The overall photochemical transformation described for **5** and **17** corresponds to an ene reaction. Analogous processes have been reported as significant side reactions in previously described intermolecular photochemical additions of enones.[6] The present cases can be rationalized as proceeding via intermediates such as **19**, which can provide the observed products by hydrogen atom transfer.[7] The alternative process, hydrogen abstraction followed by ring closure, seems less likely since only seven-membered ring products are produced from **5**.

## Experimental Section

Melting points were measured on a Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer and UV spectra on a Cary-17 spectrophotometer. Unless otherwise noted, $^1$H and $^{13}$C NMR spectra were obtained on deuteriochloroform solutions. Proton spectra were recorded on Varian T60A and HA-100 spectrometers, and chemical shifts are reported in parts per million downfield from internal Me$_4$Si. Carbon spectra were recorded on a Nicolet TT-14 spectrometer, and chemical shifts, reported in parts per million downfield from Me$_4$Si, were determined using the solvent signal as an internal standard.

Photochemical reactions were carried out using a Pyrex immersion well and a Hanovia 450 W medium pressure lamp. All experiments requiring anhydrous conditions were conducted under a positive pressure of dry nitrogen in glassware that had been flamed in a dry nitrogen stream. Tetrahydrofuran was distilled from lithium aluminum hydride immediately prior to use. Combustion analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

**Vinylogous Amide 4.** A solution of 23.5 g of dimedone and 21.3 g of amine **6**[8] in 250 mL of benzene was refluxed for 5 h with continuous removal of water. The benzene was then evaporated at reduced pressure, and the resultant yellow solid was recrystallized three times from benzene–ligroine (2:1) to yield 37.6 g of colorless plates: mp 146–146.5 °C; IR (CHCl$_3$) 2.95, 3.08, 6.31–6.62 (vs) $\mu$m; UV (methanol) $\lambda_{max}$ 292 nm ($\epsilon$ 60 000); $^1$H NMR $\delta$ 1.05 (s, 6 H), 1.42–2.10 (m, 10 H), 2.12 (s, 2 H), 2.20 (s, 2 H), 3.18 (q, 2 H, $J$ = 8.0 Hz), 5.08 (s, 1 H), 5.46 (br s, 1 H), 5.82 (br s, 1 H). $^{13}$C NMR: CH$_3$ carbons at $\delta$ 28.1 (2 C); CH$_2$ carbons at $\delta$ 22.1, 22.8, 25.1, 27.8, 36.5, 40.1, 43.4, and 50.3; CH carbons at $\delta$ 95.3 and 123.8; C carbons at $\delta$ 32.6, 134.0, 162.5, and 196.3. Anal. Calcd for C$_{16}$H$_{25}$NO: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.63; H, 10.12; N, 5.63.

**Vinylogous Imide 5.** A solution of 12.35 g of the vinylogous amide **4** and 20 mL of pyridine in 200 mL of dry tetrahydrofuran was maintained at 0 °C under a nitrogen atmosphere while 7.85 g of acetyl chloride in 25 mL of dry tetrahydrofuran was slowly added. The mixture was stirred at room temperature for 1 h and then filtered to remove precipitated pyridine hydrochloride. The precipitate was washed well with methylene chloride, and the two organic solutions were combined and extracted first with 10% hydrochloric acid and then with water. The organic solution was dried over potassium carbonate and evaporated at reduced pressure to provide an oil which contained diacylated material (O, N) in addition to **5**. The unwanted material was hydrolyzed to the desired compound **5**, without separation of the crude product, by stirring the mixture in a solution of 50 mL of methanol containing 10 mL of 10% hydrochloric acid. After 24 h, methylene chloride was added and the layers separated. The aqueous phase was washed with methylene chloride, and the organic layers were combined and dried over anhydrous potassium carbonate. The solvent was removed at reduced pressure and the resultant oil chromatographed on alumina with benzene–ligroine (1:1) to provide 10.6 g of a colorless oil: IR (CHCl$_3$) 6.01–6.30 $\mu$m (vs); $^1$H NMR $\delta$ 1.13 (s, 6 H), 1.40–2.10 (m, 10 H), 2.10 (s, 3 H), 2.30 (s, 2 H), 2.47 (s, 2 H), 5.40 (br s, 1 H), 5.77 (s, 1 H). $^{13}$C NMR: CH$_3$ carbons at $\delta$ 22.4 and 27.8 (2 C); CH$_2$ carbons at $\delta$ 21.8, 22.5, 24.8, 28.0, 36.4, 42.8, 45.1 and 50.5; CH carbons at $\delta$ 123.4 (2 C); C carbons at $\delta$ 33.1, 133.8, 159.3, 168.8, and 198.6. Anal. Calcd for C$_{18}$H$_{27}$NO$_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.64; H, 9.35; N, 4.99.

**Photoproducts 12 and 13.** A degassed solution containing 0.65 g of vinylogous imide **5** in 800 mL of cyclohexane was irradiated through Pyrex for 1.75 h, at which time the very strong absorption of the vinylogous imide chromophore was no longer visible in the infrared spectrum of a reaction mixture aliquot. The solvent was removed at reduced pressure and the crude product recrystallized from ether to provide 0.51 g of crystalline product, mp 172–173 °C. Although the sharp melting point of the product and its migration as a single spot on TLC under a large variety of conditions implied that a single compound had been obtained, NMR spectra of the material clearly indicated the presence of two products in approximately a 4:1 ratio. Separation of these compounds was attempted using a host of normally successful methods, including fractional crystallization, differential sublimation, gas chromatography, and chromatography on silica gel and alumina using preparative layer and liquid techniques with a wide selection of solvents. In no case was separation or significant enrichment of either isomer obtained.

All spectra and analytical data were obtained on the mixture. Specific absorptions have been assigned to the major (**12**) and minor (**13**) products when reasonable: IR (CHCl$_3$) 5.85, 6.15 $\mu$m; $^1$H NMR $\delta$ 0.95 (s, shoulder, minor), 0.99 (s, major), 1.06 (s, major), 1.10 (s, minor), 1.20–2.30 (m, ~15 H), 2.05 (s, major and minor acetyl methyl), 2.60–3.20 (m, ~2 H), 3.40–4.20 (m, ~2 H), 4.45 (dd, $J$ = 8.0 and 16.0 Hz, minor), 4.78 (ddd, $J$ = 5.0, 10.5, and 13.0 Hz, major), 5.46 (dd, 1 H, $J$ = 3.5 and 7.0 Hz, major and minor). $^{13}$C NMR of **12:** CH$_3$ carbons at $\delta$ 22.1, 25.6, and 31.6; CH$_2$ carbons at $\delta$ 26.3, 30.1, 30.3, 38.3, 40.2, 42.4, and 54.3; CH carbons at $\delta$ 41.6, 49.9, 53.8, and 115.9; C carbons at $\delta$ 32.8, 150.0, 169.1, and 207.8. $^{13}$C NMR of **13:** CH$_3$ carbons at $\delta$ 21.1; CH$_2$ carbons at $\delta$ 36.4, 37.9, 43.9, and 54.0; CH carbons at $\delta$ 54.5 and 117.6; C carbons at $\delta$ 32.5, 146.9, 167.9, and 207.0; and absorptions at $\delta$ 29.6, 29.8, and 32.5 whose multiplicities were unclear in the off-resonance spectrum. Anal. Calcd for C$_{18}$H$_{27}$NO$_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.83; H, 9.41; N, 4.80.

**Enone 8.** A solution of 311 mg of the photoproduct mixture of **12** and **13** in 10 mL of methanol containing 10 mL of 10% potassium hydroxide was refluxed for 4 min, cooled, diluted with water, and extracted twice with 15-mL portions of methylene chloride. The organic phase was dried over anhydrous potassium carbonate and evaporated at reduced pressure to provide an oil. This residue was chromatographed on alumina with ether to give 148 mg of oily enone **8** and 132 mg of **12** and **13** as a 4:1 mixture. The yield of enone **8** was 83% based upon recovered starting material: IR (CHCl$_3$) 2.92, 3.02, 6.03 (s) $\mu$m; $^1$H NMR $\delta$ 1.0 (s, 6 H), 1.14–2.22 (m, 16 H), 1.96 (s, 3 H), 3.80 (m, 2 H), 5.31 (t, 1 H, $J$ = 7.5 Hz), 6.20 (br s, 1 H), 6.67 (dt, 1 H, $J$ = 4.5 and 1.5 Hz). $^{13}$C NMR: CH$_3$ carbons at $\delta$ 23.0, 27.7, and 28.2; CH$_2$ carbons at $\delta$ 21.8, 27.9, 29.6, 33.9, 36.4, 40.1, and 52.4; CH carbons at $\delta$ 34.9, 120.7, and 143.4; C carbons at $\delta$ 33.5, 139.3, 142.6, 169.6, and 199.1. Anal. Calcd for C$_{18}$H$_{27}$NO$_2$: C, 74.70; H, 9.40; N, 4.84. Found: C, 74.68; H, 9.50; N, 4.69.

**Ketalization of 12 and 13.** A solution of 1.1 g of the 4:1 mixture of **12** and **13**, 5 mL of ethylene glycol, and 25 mg of $p$-toluenesulfonic acid in 50 mL of benzene was refluxed for 48 h with continuous removal of water. After cooling, the reaction mixture was washed with 10 mL of 10% potassium carbonate solution and then dried over anhydrous potassium carbonate. Evaporation of the benzene left a solid residue which was chromatographed on alumina with ether–benzene (1:5) to provide 1.05 g of **9** as a mixture of diastereomers. The $^{13}$C NMR spectrum clearly indicated that two compounds had been produced in approximately a 1:1 ratio. Furthermore, the ketone absorptions of **12** and **13** were absent, and ketal absorptions were present at $\delta$ 63.9 (4 C), 110.8, and 111.1; IR (CHCl$_3$) 6.14 $\mu$m (s).

**Acid Hydrolysis of 9.** A solution of 400 mg of the ketals **9** and 5 mL of 5% hydrochloric acid in 25 mL of tetrahydrofuran was allowed to stand at room temperature for 48 h. The reaction mixture was then extracted with benzene and the extract dried over potassium carbonate. Removal of the solvent at reduced pressure provided 246 mg of a 4:1 mixture of **12** and **13**, respectively, as shown by $^{13}$C NMR spectroscopy.

**Deuteration of 12 and 13.** A solution containing 116 mg of the **12,13** mixture, 2 mL of deuterium oxide, and 20 mg of anhydrous potassium carbonate in 10 mL of dry tetrahydrofuran was refluxed for 5 h. After the reaction mixture had cooled, it was extracted three times with 5-mL portions of methylene chloride. The extracts were combined, dried over anhydrous potassium carbonate, and evaporated to dryness at reduced pressure. The residue was recrystallized from ether to provide 94 mg of **10** as a mixture of diastereomers. In the $^1$H NMR spectrum, the δ 4.78 resonance of **12** appeared as a doublet of doublets ($J$ = 5.0 and 10.5 Hz) and the δ 2.60–3.20 region was simplified considerably and contained only a broad doublet at δ 2.72 ($J$ = 13.0 Hz).

A solution of 247 mg of the **12,13** mixture and 3 mL of 10% sodium deuterioxide in 10 mL dry tetrahydrofuran was allowed to stir at room temperature for 36 h. The solution was then extracted twice with methylene chloride, and the extracts were combined, dried over potassium carbonate, and evaporated to dryness under reduced pressure. The residue was recrystallized from ether to give 124 mg of **11**. Evaporation of the mother liquor followed by chromatography of the residue on alumina with ether provided 98 mg of deuterio enone **8**. The $^{13}$C NMR spectrum of **11** was the same as that of the original mixture of **12** and **13** except for the absence of peaks at δ 42.4, 53.8, 54.3 (major, **12**) and δ 43.9, 54.0, 54.5 (minor, **13**). The δ 4.78 resonance in the $^1$H NMR spectrum of the original mixture of **12** and **13** appeared as a very broad singlet. The deuterio derivative of enone **8** was identified by the absence of absorptions at δ 40.1 and 52.4 in the $^{13}$C NMR spectrum and at δ 2.26 in the $^1$H NMR spectrum.

**Conversion of Enone 8 to 12 and 13.** A solution of 56 mg of enone **8** in 5 mL of dry tetrahydrofuran was added to 8.4 mg of a 57% oil dispersion of sodium hydride, and the mixture was stirred in a dry nitrogen atmosphere at room temperature for 2 days. The reaction was terminated by addition of 2 mL of water and 15 mL of tetrahydrofuran. The resulting solution was dried with anhydrous potassium carbonate, and after removal of solvent at reduced pressure 54 mg of product was obtained. The $^1$H NMR spectrum of this material indicated an approximately 1:1 mixture of **8** and the original mixture of products **12** and **13**.

**3-Cyclohexenyl-1-propylamine (15).** A pyridine solution of 55.2 g of alcohol **14**[9] was treated with *p*-toluenesulfonyl chloride and then sodium cyanide according to literature procedures[10] to produce 52 g of the corresponding unsaturated nitrile. A solution of 52 g of the nitrile in 100 mL of ether was added to 20 g of lithium aluminum hydride in 200 mL of dry ether at room temperature. After 2 h, water was cautiously added and the resulting precipitate was filtered and washed with three 100-mL portions of ether. The combined organic solutions were extracted three times with 100-mL portions of 10% hydrochloric acid, and these aqueous extracts were combined, made strongly alkaline with potassium hydroxide, and extracted four times with ether. The combined ether extracts were dried over potassium carbonate, and the ether was removed at reduced pressure. The resulting liquid residue was distilled at reduced pressure to provide 45 g of amine **15**: bp 95–99 °C (15 torr); IR (neat) 2.96, 3.02, 6.01 μm; $^1$H NMR δ 1.42–2.11 (m, 14 H), 3.33 (br s, 2 H), 5.60 (br s, 1 H).

**Vinylogous Amide** 16. A solution of 45 g of amine **14** and 50.4 g of dimedone in 250 mL of benzene was refluxed for 5 h with continuous removal of water. The resulting solution was evaporated under reduced pressure to provide a tan residue which was recrystallized twice from benzene–ligroine (1:1) to yield colorless crystals: mp 145–146 °C; IR ($CHCl_3$) 2.90, 3.05, 6.30–6.57 (vs) μm; $^1$H NMR δ 0.97 (s, 6 H), 1.40–2.10 (m, 12 H), 2.16 (s, 2 H), 2.26 (s, 2 H), 3.05 (br q, 2 H, $J$ = 7 Hz), 5.05 (s, 1 H), 5.38 (br s, 1 H), 6.88 (br s, 1 H). $^{13}$C NMR: $CH_3$ carbons at δ 27.9 (2 C); $CH_2$ carbons at δ 22.2, 22.6, 24.9, 26.0, 27.9, 35.1, 42.4, 43.0, and 50.2; CH carbons at δ 94.4 and 121.5; C carbons at δ 32.4, 136.1, 163.5, and 196.0. Anal. Calcd for $C_{17}H_{27}NO$: C, 78.11; H, 10.41; N, 5.36. Found: C, 78.31; H, 10.50; N, 5.23.

**Vinylogous Imide** 17. A solution of 4.43 g of vinylogous amide **16** and 20 mL of triethylamine in 100 mL of dry tetrahydrofuran under an inert atmosphere was stirred at room temperature while 25 mL of tetrahydrofuran containing 10 mL of acetic anhydride was slowly added. The mixture was refluxed for 24 h, cooled, and washed once with 50 mL of 10% hydrochloric acid, three times with 25-mL portions of 10% potassium carbonate solution, and once with water. The solvent was removed under reduced pressure, and the resultant oil was stirred for 24 h with a solution of 25 mL of methanol and 10 mL of 10% hydrochloric acid to destroy diacylated material as in the case of **5** (vide supra). The solution was extracted three times with methylene chloride, and the organic solutions were combined and dried over potassium carbonate. When the solvent was removed under reduced pressure and the oily residue was chromatographed on alumina with ligroine, 3.01 g of a colorless oil was obtained: IR ($CHCl_3$) 5.95–6.32 μm (vs); $^1$H NMR δ 1.10 (s, 6 H), 1.35–2.07 (m, 12 H), 2.15 (s, 3 H), 2.25 (s, 2 H), 2.43 (s, 2 H), 3.60 (m, 2 H), 5.37 (br s, 1 H), 5.77 (s, 1 H). $^{13}$C NMR: $CH_3$ carbons at δ 22.6 and 27.8 (2 C); $CH_2$ carbons at δ 22.2, 22.6, 24.9, 26.1, 27.8, 34.7, 42.9, 46.2, and 50.5; CH carbons at δ 121.5 and 123.3; C carbons at δ 33.2, 135.9, 159.4, 169.1, and 198.6. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.23; H, 10.03; N, 4.53.

**Photoproduct** 18. A degassed solution of 2.58 g of vinylogous imide **17** in 600 mL of cyclohexane was irradiated through Pyrex for 2.5 h, at which time TLC analysis of an aliquot of the reaction mixture indicated complete consumption of the starting material. The solvent was removed under reduced pressure, and the resultant residue was recrystallized from ether–ligroine (1:1) to provide 1.21 g of **18**. The mother liquor was evaporated to provide a syrup which was chromatographed on alumina with ether, and an additional 0.26 g of **18** was obtained. Recrystallization and sublimation of the combined material produced a white solid: mp 178–179 °C; IR ($CHCl_3$) 5.85, 6.12 μm; $^1$H NMR δ 0.97 (s, 3 H), 1.08 (s, 3 H), 1.20–2.60 (m, 15 H), 2.00 (s, 3 H), 2.90 (m, 3 H), 3.50 (m, 3 H), 5.20 (m, 2 H). $^{13}$C NMR: $CH_3$ carbons at δ 23.2, 25.9, and 31.9; $CH_2$ carbons at δ 25.9, 26.5, 28.4, 29.4, 40.5, 41.5, 42.2, and 54.6; CH carbons at δ 40.4, 47.5, 54.8, and 112.3; C carbons at δ 32.3, 146.4, 170.7, and 207.9. Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 75.30; H, 9.81; N, 4.51.

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**Registry No.**—**4,** 67505-54-8; **5,** 67505-55-9; **6,** 3399-73-3; **8,** 67505-56-0; **9** (isomer 1), 67505-57-1; **9** (isomer 2), 67529-67-3; **10** (isomer 1), 67505-58-2; **10** (isomer 2), 67529-68-4; **11** (isomer 1), 67505-59-3; **11** (isomer 2), 67529-69-5; **12,** 67505-60-6; **13,** 67529-70-8; **14,** 3197-68-0; **15,** 13992-93-3; **16,** 67505-61-7; **17,** 67505-62-8; **18,** 67530-29-4; dimedone, 126-81-8.

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