38 (10), 37 (7); IR (gas phase) 1975 cm^{-1}. Although starting material was recovered, none was present in the volatile samples examined by IR and NMR. The NMR spectra of both isomers were consistent with published data,[29] as were the mass spectra.[30,31]

FVP of [*o*-(Trimethylsiloxy)phenyl]-1-propyne (42). (i) Compound **42** (150.4 mg), distilled (1×10^{-5} torr) from a bath heated from 60 to 80 °C over a 20-min period, was pyrolyzed at 700 °C. Only starting material was present in the pyrolysate (140.9 mg, 93.7%).

(ii) Pyrolysis of compound **42** (127.9 mg) at 800 °C (2×10^{-4} torr) produced ten minor products in addition to recovered starting material which accounted for approximately two-thirds of the total recovered pyrolysate (127.9 mg, 82.6%).

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. **4**, 5101-44-0; **6**, 271-89-6; **7**, 81787-62-4; **9**, 93782-14-0; **10**, 61547-39-5; **11**, 60981-57-9; **15**, 75213-96-6; **17**, 17869-75-9; **20**, 4071-85-6; **22**, 38053-91-7; **23**, 767-91-9; **25**, 254-04-6; **26**, 4265-25-2; **27**, 66021-98-5; **28**, 3131-63-3; **31**, 40230-91-9; **32**, 2170-06-1; **34**, 93782-16-2; **35**, 93782-17-3; **36**, 14583-74-5; *cis*-**37**, 93782-18-4; *trans*-**37**, 93782-21-9; **40**, 3685-19-6; **42**, 93782-20-8; PhC≡CH, 536-74-3; $Me_3SiC{\equiv}C{-}Et$, 62108-37-6; PhC≡CMe, 673-32-5; β,β-dibromo-*o*-(trimethylsiloxy)styrene, 93782-13-9; carbon tetrabromide, 558-13-4; *o*-(trimethylsiloxy)benzaldehyde, 1078-31-5; *n*-butyllithium, 109-72-8; 3-bromobenzofuran, 59214-70-9; [*o*-(trimethylsiloxy)(trimethylsilyl)phenyl]acetylene, 93782-15-1; β,β-dibromo-*o*-methoxystyrene, 90585-32-3; *o*-anisaldehyde, 135-02-4; (trimethylsilyl)propargyl alcohol, 5272-36-6; acetonitrile, 75-05-8; 3-bromo-2-metylbenzofuran, 58863-48-2; 3-lithio-2-methylbenzofuran, 93782-19-5; 4,5-dihydrofuran, 1191-99-7; cyclopropanecarboxaldehyde, 1489-69-6; *trans*-crotonaldehyde, 123-73-9; *o*-methylstyrene, 611-15-4; *m*-methylstyrene, 100-80-1; *p*-methylstyrene, 622-97-9; indene, 95-13-6; 1-butyne, 107-00-6; 1,2-butadiene, 590-19-2; *cis*-crotonaldehyde, 15798-64-8; trimethylchlorosilane, 75-77-4.

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(31) Mass spectra were also matched using the Finnigan INCOS National Bureau of Standards mass spectral data base.

Photochemistry of 4-Pyrimidinones: Isolation of Dewar Isomers

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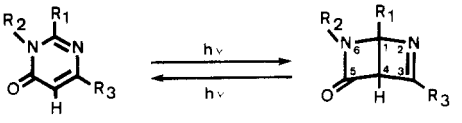
The 1,3,6-trialkyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-enes (Dewar 4-pyrimidinones) **2a–d** which are formed in the photolysis of 2,3,6-trialkyl-4-pyrimidinones **1a–d** were isolated in yields of 16–24%. When 6-[(alkoxycarbonyl)methyl]-4-pyrimidinones **3a–c** were irradiated, 3-[(alkoxycarbonyl)methylene]-2,6-diazabicyclo[2.2.0]hexan-5-ones **4a–c** were formed. The *E* and *Z* isomers of **4** were isolated in total yields of 24–26%. The physical properties of the compounds were measured.

The photoisomerization of diazines and diazinones has been shown to result from transposition of ring nitrogen atoms and has been explained in terms of the valence-bond isomers.[1] However, very few valence-bond isomers of diazines and diazinones have been isolated.[2-4] Recently,[5c-e] spectroscopic evidence (IR, ^1H and ^{13}C NMR) was reported for the formation of the Dewar 4-pyrimidinone **2** as a transient intermediate in the photochemical reactions of 4-pyrimidinone **1** in protic solvents.[5] We now report the successful isolation of the interesting reactive molecular species.

Irradiation of 4-pyrimidinones **1a–e** in liquid NH_3–ether solution at −40 °C or in methanol[6] at −18 °C gave a mixture of 5-oxo-2,6-diazabicyclo[2.2.0]hex-2-enes (Dewar 4-pyrimidinones) **2a–e** (30–25% estimated by ^1H NMR) and starting materials **1a–e**. The separation of **1** and **2** was carried out by chromatography on Sephadex LH-20 at 17–19 °C with chloroform–hexane (80:20 v/v %) as an

Chart I



1 2

Table I. Isolated Yields and IR Spectral Data for Dewar 4-Pyrimidinones 2

					IR (in $CHCl_3$), cm^{-1}	
no.	R^1	R^2	R^3	yield, %	ν (C=O)	ν (C=N)
2a	CH_3	CH_3	CH_3	24	1750[a]	1605
2b	CH_3	CH_3	*t*-Bu	21	1750	1595
2c	$PhCH_2$	CH_3	*t*-Bu	17	1750	1590
2d	$-(CH_2)_4-$		*t*-Bu	16	1745	1595
2e	H	CH_3	CH_3	0[b]	1750[c]	nd[d]

[a] Reference 5c. [b] A pale yellow polymeric compound (21 w/w %) was obtained and the starting material **1e** (68%) was recovered. [c] Reference 5d. [d] Not determined.

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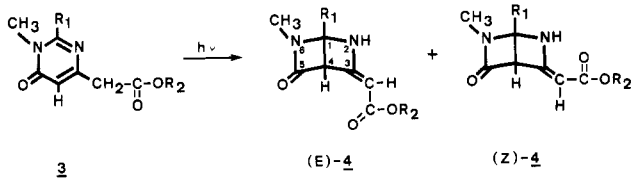
(6) Irradiation of **1e** was carried out in methanol at −18 °C.[5d]

0022-3263/85/1950-0166$01.50/0

Chart II



3 (E)-4 (Z)-4

Table II. Isolated Yields and IR and ^{1}H NMR Spectral Data for Dewar 4-Pyrimidinones 4

					IR (KBr) ν (amide C=O), cm^{-1}	^{1}H NMR ($CDCl_3$), δ	
no.	R^1	R^2	isomer	yield, %		4-H	NH
4a	CH_3	CH_3	*Z*	17	1760	4.28	7.20
			E	9	1735	4.68	6.00
4b	CH_3	C_2H_5	*Z*	19	1750	4.27	7.23
			E	5	1735	4.63	6.36
4c	H	CH_3	*Z*	15	1750	4.50	7.07
			E	9	1740	4.93	6.03

eluant. The Dewar 4-pyrimidinones **2a–d** were isolated as the crystalline compounds in 16–24% yields. The isolated yields and IR data of **2a–d** are listed in Table I. The isolation of **2e** was unsuccessful because of the instability of **2e**. The structures were confirmed by the spectral data and chemical methods. The IR spectra ($CHCl_3$) showed a β-lactam C=O at 1750–1745 cm^{-1} and a C=N stretching band at 1605–1590 cm^{-1}. The UV spectra (CH_3CN) exhibited two peaks at 256 ± 2 (sh, ϵ 1600–470) and 297 ± 4 nm (sh, ϵ 1500–170). The ^{1}H NMR spectra of **2b–d** were similar to that of **2a** which was previously reported.[5c] The C=N stretching band of **2a–d** is analogous to that in the azetines,[7] but is about 60 cm^{-1} lower than the C=N band in the six- and seven-membered monocyclic imines[8] at 1665–1660 cm^{-1}. The shift to lower frequency may be due to the lowered π-overlap in the strained double bond.

When 6-[(methoxycarbonyl)methyl]-2,3-dimethyl-4-pyrimidinone (**3a**) was photolyzed in acetonitrile solution under argon through quartz at −14 °C and the reaction mixture was chromatographed on Sephadex LH-20 with acetone as an eluant, (*E*)- and (*Z*)-3-[(methoxycarbonyl)-methylene]-1,6-dimethyl-2,6-diazabicyclo[2.2.0]hexan-5-one (enamine Dewar 4-pyrimidinone) (**4a**) were ioslated in the yields of 9% and 17%, respectively. Analogous photolysis of **3b** and **3c** gave the corresponding (*E*)- and (*Z*)-**4b** and (*E*)- and (*Z*)-**4c**, and no imine-type Dewar isomer was isolated.[9] The isolated yields and characteristic spectral data are shown in Table II. All compounds showed λ_{max} (CH_3CN) at 270 ± 1 nm (ϵ 18 000). The infrared spectra (KBr) in each case showed four peaks of 3370–3300 (NH), 1760–1735 (β-lactam C=O), 1700–1680 (conjugated ester C=O), 1655–1620 cm^{-1} (C=C). The ^{1}H NMR ($CDCl_3$) spectra indicated the presence of one methine proton, one olefinic proton, and a secondary amine. From these data, the structure was assigned to the enamine Dewar 4-pyrimidinone. The stereochemistry about the double bond of **4a–c** was determined by comparison of the ^{1}H NMR data with those of α-(aminoalkylidene)-β-alkoxy β-lactams[5a] and amino vinyl ketones.[10]

The substitution of an (alkoxycarbonyl)methyl group at the 6-position of 4-pyrimidinone for the methyl group leads to the formation of the enamine Dewar isomer. The initial photoproduct should be the imine Dewar isomer which tautomerizes to the thermodynamically stable enamine Dewar.

The quantum yields of the reactions **1b** to **2b** and **2b** to **1b** at 254 nm in acetonitrile under argon atmosphere at 20–21 °C were 0.043 at 5.1% conversion and 0.94 at 3.6% conversion, respectively. The results indicate an efficient photoreverse reaction of **2** to **1**[5c,d] (Chart I).

Experimental Section

Melting points were measured with a Yanako melting point apparatus and were uncorrected. The spectroscopic measurements were carried out with the following instruments: IR, JASCO IRA-1; UV, Hitachi Model 200-10; mass spectra (MS), JEOL OISG-2 at 70 eV; NMR (^{1}H and ^{13}C), Varian EM-390 and Varian XL-200, chemical shifts were reported in parts per million on the δ scale relative to a Me_4Si internal standard. High-pressure liquid chromatography (HPLC) was performed on a Waters Analytical HPLC equipped with an M-45 pumping system, M-U6K injector, and M-440 UV spectrometer with μBondapak NH_2 as the stationary phase.

Materials. 6-*tert*-Butyl-2-methyl-4(3*H*)-pyrimidinone, 2-benzyl-6-*tert*-butyl-4(3*H*)-pyrimidinone, 6-[(methoxycarbonyl)-methyl]-2-methyl-4(3*H*)-pyrimidinone, and 6-[(ethoxycarbonyl)methyl]-2-methyl-4(3*H*)-pyrimidinone were synthesized from the corresponding amidine hydrochlorides[11] and β-keto esters[12] as described in the literature.[13] 2-Mercapto-6-[(methoxycarbonyl)methyl]-4(3*H*)-pyrimidinone was prepared by condensation of thiourea with methyl acetonedicarboxylate as described in the literature.[13a,14] Desulfurization of 2-mercapto-6-[(methoxycarbonyl)methyl]-4(3*H*)-pyrimidinone with Raney Ni(W-4) in methanol gave 6-[(methoxycarbonyl)methyl]-4-(3*H*)-pyrimidinone. The melting points, molecular ion, and analytical data for the compounds are shown in Table III (supplementary material).

2,3,6-Trimethyl-4(3*H*)-pyrimidinone (**1a**),[5a] 6-*tert*-butyl-2,3-dimethyl-4(3*H*)-pyrimidinone (**1b**), 2-benzyl-6-*tert*-butyl-3-methyl-4(3*H*)-pyrimidinone (**1c**), 3,6-dimethyl-4(3*H*)-pyrimidinone (**1e**),[5d] 6-[(methoxycarbonyl)methyl]-2,3-dimethyl-4(3*H*)-pyrimidinone (**3a**), 6-[(ethoxycarbonyl)methyl]-2,3-dimethyl-4-(3*H*)-pyrimidinone (**3b**), and 6-[(methoxycarbonyl)methyl]-3-methyl-4(3*H*)-pyrimidinone (**3c**) were prepared from iodomethane and the corresponding 4(3*H*)-pyrimidinones in alcoholic solutions containing base at 65–80 °C.

2-*tert*-Butyl-6,7,8,9-tetrahydro-4*H*-pyrido[1,2-*a*]pyrimidin-4-one (**1d**) was synthesized by condensation of 2-amino-3,4,5,6-tetrahydropyridine hydrochloride with ethyl trimethylacetoacetate[12c] as described for the preparation of related compounds.[5a]

The compounds **1b–d** and **3a–c** showed λ_{max} (MeOH) 275 ± 1 (ϵ 5000) and 224 ± 1 nm (ϵ 6000).

For **1b**: mp 81–81.5 °C; IR (nujol) 1670, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 9 H), 2.57 (s, 3 H), 3.52 (s, 3 H), 6.30 (s, 1 H); MS, *m/e* 180 (M^+).

For **1c**: mp 46–48 °C; IR ($CHCl_3$) 1665, 1585 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.27 (s, 9 H), 3.40 (s, 3 H), 4.13 (s, 2 H), 6.37 (s, 1 H), 7.28 (s, 5 H); MS, *m/e* 256 (M^+).

For **1d**: mp 72–73 °C; IR ($CHCl_3$) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (s, 9 H), 1.70–2.17 (m, 4 H), 2.93 (t, J = 6 Hz, 2 H), 3.97 (t, J = 6 Hz, 2 H), 6.33 (s, 1 H); MS, *m/e* 206 (M^+).

For **3a**: mp 74–76 °C; IR (KBr) 1740, 1675, 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.55 (s, 3 H), 3.53 (s, 3 H), 3.53 (s, 2 H), 3.75, (s, 3 H),

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6.32 (s, 1 H); MS, m/e 196 (M^+).

For **3b**: mp 47–49 °C; IR (KBr) 1730, 1670, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3 H), 2.53 (s, 3 H), 3.52 (s, 2 H), 3.55 (s, 3 H), 4.23 (q, J = 7 Hz, 2 H), 6.35 (s, 1 H); MS, m/e 210 (M^+).

For **3c**: mp 69–71 °C; IR (KBr) 1720, 1680, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.47 (s, 3 H), 3.53 (s, 2 H), 3.72 (s, 3 H), 6.40 (s, 1 H), 8.10 (s, 1 H); MS, m/e 182 (M^+).

The analytical data are listed in Table IV (supplementary material).

General Procedures for the Irradiation of 4-Pyrimidinones. The 4-pyrimidinone (1.2–2.2 g) was dissolved in 280 mL of liquid NH_3-ether at −40 °C or acetonitrile at −20 to −14 °C in a reaction cell. The solution was irradiated under an argon atmosphere with a 100-W high-pressure mercury lamp. The reaction progress was routinely followed by the ^1H NMR spectra.

General Procedures for the Isolation of the Photoproducts. After irradiation, the solvent was evaporated under vacuum and the reaction mixture was chromatographed. When the reaction mixture of **1** and **2** was passed through a column of Sephadex LH-20 (Pharmacia Fine Chemcials AB) with chloroform–hexane, the Dewar 4-pyrimidinone **2** was concentrated in the first fractions of eluant (10–30 mL). The ratio of **1** and **2** in the first eluant(s) varied with the amount of Sephadex LH-20, the size of column, the flow rate, temperature, and solvent. A vareity of conditions were investigated and the following set of conditions was found to lead consistently to the first eluant(s) containing pure substance **2**: A solution of 1.1–2.2 g of the reaction mixuture in 5–10 mL of chloroform–hexane (4:1 v/v) was adsorbed on a column (150 × 2.5 cm) made from a slurry of Sephadex LH-20 (180 g of dry gel) previously swelled in chloroform. The column was then eluted with chloroform–hexane (4:1 v/v, each fraction 10 mL) at a flow rate of 1.7–2.8 mL per minute at 17–19 °C. The reaction mixture of **3** and the Dewar isomers **4** was chromatographed on a column (150 × 2.5 cm) of Sephadex LH-20 (280 g of dry gel) with distilled acetone as an eluant (each fraction 10 mL, flow rate 2.2–2.5 mL per minute) at 20–25 °C.

1,3,6-Trimethyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-ene (2a). From 2.248 g (16.28 mmol) of **1a** in liquid NH_3-ether at −40 °C, a mixture of **2a** (30%) and **1a** (70%) was obtained after 5.5 h of irradiation. The reaction mixture was divided into two portions (ca. 1.2 g and 1.1 g) and each portion was chromatographed to give 0.542 g (24%) of pure **2a** (solidifies in the refrigerator). The starting material **1a** (1.198 g, 53%) and a mixture of **1a** and **2a** (0.583 g, 26%) were recovered. The crystalline **2a** was not further purified: mp 22–25 °C; IR ($CHCl_3$) 1750, 1605 cm^{-1}; UV (CH_3CN) λ_{max} 292 nm (sh, ϵ 1480), 258 nm (sh, ϵ 1630), 213 nm (sh, ϵ 3530); ^1H NMR ($CDCl_3$) δ 1.72 (s, 3 H, 1-CH_3), 2.22 (s, 3 H, 3-CH_3), 2.80 (s, 3 H, NCH_3), 4.26 (s, 1 H, 4-H); MS, m/e (relative intensity) 138 (M^+, 6), 97 (52), 85 (18), 83 (29), 82 (48), 56 (100), 42 (34), 39 (26).

3-*tert*-Butyl-1,6-dimethyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-ene (2b). From 2.145 g (11.92 mmol) of **1b** in liquid NH_3-ether at −40 °C, a mixture of **2b** (30%) and **1b** (70%) was obtained after 5 h of irradiation. Column chromatography of the reaction mixture gave 0.443 g (21%) of pure **2b** (solidifies on standing at room temperature). The starting material **1b** (1.661 g, 77%) was recovered. The crystalline **2b** was purified by sublimation at a bath temperature of 40 °C under vacuum to give colorless prisms: mp 36–38 °C; IR ($CHCl_3$) 1750, 1595 cm^{-1}; UV (CH_3CN) λ_{max} 300 nm (sh, ϵ 757), 255 (sh, ϵ 673), 213 (sh, ϵ 2130); ^1H NMR ($CDCl_3$) δ 1.20 (s, 9 H, *t*-Bu), 1.72 (s, 3 H, 1-CH_3), 2.80 (s, 3 H, NCH_3), 4.30 (s, 1 H, 4-H); MS, m/e (relative intensity) 180 (M^+, 13), 179 (11), 165 (14), 138 (10), 124 (5), 110 (3), 97 (53), 82 (31), 67 (8), 56 (100).

1-Benzyl-3-*tert*-butyl-6-methyl-5-oxo-2,6-diazabicyclo[2.2.0]hex-2-ene (2c). From 2.236 g (8.73 mmol) of **1c** in liquid NH_3-ether at −40 °C, a mixture of **2c** (29%) and **1c** (71%) was obtained after 4.5 h of irradiation. Column chromatography of the reaction mixture gave 0.378 g (17%) of the crystalline **2c**. A mixture of **1c** and **2c** (1.654 g, 74%) was recovered. Recrystallization of **2c** from pentane–CCl_4 gave colorless fine needles: mp 101–103 °C; IR ($CHCl_3$) 1750, 1590 cm^{-1}; UV (CH_3CN) λ_{max} 258 nm (sh, ϵ 890), 253 nm (sh, ϵ 900); ^1H NMR ($CDCl_3$) δ 1.10 (s, 9 H, *t*-Bu), 2.77 (s, 3 H, NCH_3), 3.35 (s, 2 H, CH_2), 4.22 (s, 1 H, 4-H), 7.30 (s, 5 H, C_6H_5); MS, m/e (relative intensity) 257 (24), 256 (M^+, 100), 255 (85), 241 (88), 228 (38), 214 (51), 213 (65), 144 (21), 132 (32), 131 (94), 116 (59), 115 (37), 91 (82), 82 (63), 57 (35), 41 (44).

9-*tert*-Butyl-7-oxo-6,10-diazatricyclo[4.4.0.0^{1,8}]dec-9-ene (2d). From 2.014 g (9.77 mmol) of **1d** in liquid NH_3–ether at −40 °C, a mixture of **2d** (25%) and **1d** (75%) was obtained after 5 h of irradiation. The reaction mixture was divided into two portions (ca. 1.2 and 0.8 g) and each portion was chromatographed. Column chromatography gave 0.322 g (16%) of the crystalline **2d**. The starting material **1d** (1.603 g, 80%) and a mixture of **1d** and **2d** (0.091 g, 5%) were recovered. Recrystallization of **2d** from pentane–CCl_4 gave colorless prisms: mp 85–88 °C; IR ($CHCl_3$) 1745, 1595 cm^{-1}; UV (CH_3CN) λ_{max} 306 nm (sh, ϵ 165), 254 nm (sh, ϵ 474); ^1H NMR ($CDCl_3$) δ 1.21 (s, 9 H, *t*-Bu), 1.53–2.43 (m, 6 H, 3 × CH_2), 2.72–3.12 (m, 1 H, HC*H*), 3.57–3.87 (m, 1 H, HC*H*), 4.43 (s, 1 H, 8-H); MS, m/e (relative intensity) 207 (17), 206 (M^+, 27), 205 (30), 191 (39), 178 (11), 177 (9), 164 (24), 163 (33), 150 (19), 136 (11), 135 (12), 123 (100), 108 (11), 95 (94), 82 (30), 67 (35), 57 (23), 55 (38), 41 (69), 39 (42).

(*Z*)- and (*E*)-3-[(Methoxycarbonyl)methylene]-1,6-dimethyl-2,6-diazabicyclo[2.2.0]hexan-5-one (4a). From 1.883 g (9.61 mmol) of **3a** in acetonitrile at −14 °C, a mixture of **4a** (26%) and **3a** (74%) was obtained after 4.5 h of irradiation. Column chromatography of the reaction mixture gave 0.317 g (17%) of (*Z*)-**4a** and 0.165 g (9%) of (*E*)-**4a**. The starting material **3a** (1.399 g, 74%) was recovered. Recrystallization of (*Z*)-**4a** from acetone–ether–pentane gave pale yellow plates: mp 150–153 °C; IR (KBr) 3350, 1760, 1680, 1630 cm^{-1}; UV (CH_3CN) λ_{max} 272 nm (ϵ 18000); ^1H NMR ($CDCl_3$) δ 1.76 (s, 3 H, 1-CH_3), 2.83 (s, 3 H, NCH_3), 3.70 (s, 3 H, OCH_3), 4.28 (s, 1 H, 4-H), 4.97 (s, 1 H, 3′-H), 7.20 (br, 1 H, NH); MS, m/e (relative intensity) 196 (M^+, 20), 168 (31), 165 (20), 164 (49), 139 (24), 109 (40), 98 (22), 82 (31), 68 (36), 58 (33), 56 (100), 42 (49). Recrystallization of (*E*)-**4a** from acetone–ether–pentane gave a white powder: mp 123–124 °C; IR (KBr) 3330, 1735, 1695, 1640 cm^{-1}; UV (CH_3CN) λ_{max} 269 nm (ϵ 17500); ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H, 1-CH_3), 2.83 (s, 3 H, NCH_3), 3.72 (s, 3 H, OCH_3), 4.68 (s, 1 H, 4-H), 4.99 (s, 1 H, 3′-H), 6.00 (br, 1 H, NH); MS, m/e (relative intensity), 196 (M^+, 8), 168 (11), 165 (9), 164 (19), 139 (10), 109 (15), 108 (10), 98 (14), 97 (13), 82 (17), 68 (19), 56 (100), 42 (22).

(*Z*)- and (*E*)-3-[(Ethoxycarbonyl)methylene]-1,6-dimethyl-2,6-diazabicyclo[2.2.0]hexan-5-one (4b). From 1.739 g (8.28 mmol) of **3b** in acetonitrile at −14 °C, a mixture of **4b** (26%) and **3b** (74%) was obtained after 4.5 h of irradiation. Column chromatography of the reaction mixture gave 0.338 g (19%) of (*Z*)-**4b** and 0.085 g (5%) of (*E*)-**4b**. The starting material **3b** (1.283 g, 73%) was recovered. Recrystallization of (*Z*)-**4b** from pentane–ether gave colorless needles: mp 86–88 °C; IR (KBr) 3300, 1750, 1690, 1620 cm^{-1}; UV (CH_3CN) λ_{max} 271 nm (ϵ 17600); ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7.5 Hz, 3 H, OCH_2CH_3), 1.76 (s, 3 H, 1-CH_3), 2.83 (s, 3 H, NCH_3), 4.14 (q, J = 7.5 Hz, 2 H, OCH_2CH_3), 4.27 (s, 1 H, 4-H), 4.95 (s, 1 H, 3′-H), 7.23 (br, 1 H, NH); MS, m/e (relative intensity) 210 (M^+, 4), 182 (11), 164 (16), 138 (10), 110 (10), 109 (15), 82 (11), 56 (100), 42 (18). Recrystallization of (*E*)-**4b** from pentane–ether gave colorless needles: mp 118.5–121 °C; IR (KBr) 3300, 1735, 1690, 1635 cm^{-1}; UV (CH_3CN) λ_{max} 270 nm (ϵ 14600); ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.5 Hz, 3 H, OCH_2CH_3), 1.71 (s, 3 H, 1-CH_3), 2.81 (s, 3 H, NCH_3), 4.15 (q, J = 7.5 Hz, 2 H, OCH_2CH_3), 4.63 (s, 1 H, 4-H), 4.98 (s, 1 H, 3′-H), 6.36 (br, 1 H, NH); MS, m/e (relative intensity) 211 (9), 210 (M^+, 60), 182 (9), 165 (40), 164 (21), 138 (68), 137 (17), 125 (10), 110 (23), 109 (42), 82 (11), 58 (14), 56 (100), 42 (26).

(*Z*)- and (*E*)-3-[(Methoxycarbonyl)methylene]-6-methyl-2,6-diazabicyclo[2.2.0]hexan-5-one (4c). From 1.293 g (7.10 mmol) of **3c** in acetonitrile at −20 °C, a mixture of **4c** and **3c** was obtained after 4 h of irradiation. Column chromatography gave 0.193 g (15%) of (*Z*)-**4c** and 0.113 g (9%) of (*E*)-**4c**. The starting material **3c** (0.939 g, 73%) was recovered. Recrystallization of (*Z*)-**4c** from acetone–ether gave colorless needles: mp 156–162 °C; IR (KBr) 3370, 1750, 1685, 1655 cm^{-1}; UV (CH_3CN) λ_{max} 270 nm (ϵ 17700); ^1H NMR ($CDCl_3$) δ 2.92 (s, 3 H, NCH_3), 3.70 (s, 3 H, OCH_3), 4.50 (m, 1 H, 4-H), 5.01 (d, $J_{3'\text{-}4}$ = 1.0 Hz, 1 H, 3′-H), 5.42 (dd, $J_{1\text{-}4}$ = 2.0 Hz, $J_{1\text{-}2}$ = 1.2 Hz, 1 H, 1-H), 7.07 (br, 1 H, NH); MS, m/e (relative intensity) 182 (M^+, 4), 154 (39), 152 (27), 122 (15), 113 (13), 110 (17), 98 (14), 95 (41), 84 (42), 68 (26), 66 (15), 59 (13), 55 (15), 42 (100), 39 (15). Recrystallization of (*E*)-**4c** from acetone–ether–pentane gave white powder: mp 144–147 °C; IR (KBr) 3340, 1740, 1700, 1630 cm^{-1}; UV (CH_3CN)

λ_{max} 268 nm (ϵ 17 500); ^{1}H NMR ($CDCl_3$) δ 2.93 (s, 3 H, NCH_3), 3.73 (s, 3 H, OCH_3), 4.93 (m, 1 H, 4-H), 5.03 (d, $J_{3'-4}$ = 1.4 Hz, 1 H, 3'-H), 5.37 (dd, J_{1-4} = 2.0 Hz, J_{1-2} = 1.2 Hz, 1 H, 1-H), 6.03 (br, 1 H, NH); MS, m/e (relative intensity) 182 (M^+, 19), 154 (29), 151 (22), 122 (20), 113 (15), 110 (12), 98 (13), 95 (33), 84 (36), 83 (21), 69 (33), 68 (24), 59 (11), 55 (21), 42 (100). The analytical data of **2a–d** and **4a–c** are shown in Table IV (supplementary material).

Quantum Yield Determination. A solution containing **1b** or **2b** (20–26 mM) in acetonitrile was irradiated with a low-pressure mercury lamp (60 W) under an argon atmosphere through a Corning 9-54 color filter at 20–21 °C. After irradiation, the solvent was evaporated under vacuum and methanol was added to the oily residue. The formed or unreacted Dewar 4-pyrimidinone **2b** was converted to the β-lactam **5**.[5a] Analyses of **1b** and **5** were performed by HPLC with hexane–CH_2Cl_2–CH_3CN (92:5:3) as the mobile phase and benzyl cyanide was used as an internal standard. The original Dewar **2b** was estimated by the measured amount of **5** and the correction factor (1.06) based on the yield (94%) determined by HPLC for the conversion of **2b** to **5**.

The light intensity of the low-pressure mercury lamp was measured by cyclopentanone–4-pentenal actinometry (Φ = 0.38 at 254 nm).[15] The measured intensity was (1.41 ± 0.07) × 10^{17} quanta/s.

The quantum yields of **1b** to **2b** and **2b** to **1b** were 0.043 at 5.1% conversion and 0.94 at 3.6% conversion, respectively.

***N*-Methyl-3-(1-amino-2,2-dimethylpropylidene)-4-methoxy-4-methyl-2-azetidinone (5).** From 1.761 g (9.78 mmol) of **1b** in liquid NH_3–ether at −40 °C, a mixture of **2b** (31%) and **1b** (69%) was obtained after 9 h of irradiation. The reaction mixture was dissolved in 200 mL of methanol. The solution was allowed to stand for 44 h at 0 °C. After removal of the solvent, ether was added to the oily residue. On cooling, crude crystals of **5** (0.462 g, 22%) were separated and collected by filtration. The starting material **1b** (1.172 g, 67%) was recovered by column chromatography of the filtrate on alumina. Recrystallization of **5** from methanol–ether–pentane gave colorless needles: mp 152–153 °C; UV (MeOH) λ_{max} 277 nm (ϵ 20500); MS, m/e 212 (M^+). Anal. Calcd for $C_{11}H_{20}N_2O_2$: C, 62.23; H, 9.50; N, 13.20. Found: C, 61.94; H, 9.42; N, 13.12.

Registry No. **1a**, 32363-51-2; **1b**, 93715-36-7; **1c**, 93715-37-8; **1d**, 93715-38-9; **1e**, 17758-19-9; **2a**, 76599-91-2; **2b**, 93715-39-0; **2c**, 93715-40-3; **2d**, 93715-41-4; **3a**, 93715-42-5; **3b**, 93715-43-6; **3c**, 93715-44-7; (*Z*)-**4a**, 93715-45-8; (*E*)-**4a**, 93715-46-9; (*Z*)-**4b**, 93715-47-0; (*E*)-**4b**, 93715-48-1; (*Z*)-**4c**, 93715-49-2; (*E*)-**4c**, 93715-50-5; **5**, 93715-51-6; 2,6-dimethyl-4(3*H*)-pyrimidinone, 6622-92-0; 6-*tert*-butyl-2-methyl-4(3*H*)-pyrimidinone, 66700-33-2; 2-benzyl-6-*tert*-butyl-4(3*H*)-pyrimidinone, 93715-52-7; 6-methyl-4(3*H*)-pyrimidinone, 3524-87-6; 6-[(methoxycarbonyl)methyl]-2-methyl-4(3*H*)-pyrimidinone, 93715-53-8; 6-[(ethoxycarbonyl)methyl]-2-methyl-4(3*H*)-pyrimidinone, 54554-50-6; 6-[(methoxycarbonyl)methyl]-4(3*H*)-pyrimidinone, 93715-54-9; 2-amino-3,4,5,6-tetrahydropyridine hydrochloride, 16011-96-4; ethyl trimethylacetoacetate, 17094-34-7.

Supplementary Material Available: Chemical name, melting points, molecular ion, and analytical data for 4(3*H*)-pyrimidinones and analytical data for the 4-pyrimidinones **1b–d**, **2a–d**, **3a–c**, and **4a–c** (Tables III and IV) (2 pages). Ordering information is given on any current masthead page.

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Acyl and Sulfonyl Isocyanates in β-Lactam Synthesis

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The preparation of β-lactams from the reactions of several acyl and sulfonyl activated isocyanates with alkenes was studied. Three compounds, (2,2,2-trichloroethoxy)sulfonyl, 2,2,2-trichloroethanesulfonyl, and trifluoroacetyl isocyanates, were shown to be preparatively useful. After the alkene–isocyanate cycloaddition reaction the N-substituent was removed either reductively or via selective hydrolysis. The reaction was applied to styrene, methylenecyclohexane, 4-methylene-1-phenylcyclohexane, and 5-benzyl- and 5-methyl-3,4-dihydro-2*H*-pyrans.

The β-lactam ring system occurs widely in several structurally diverse classes of clinically important antibacterial agents. These include the penicillins, the cephalosporins, the nocardicins, the carbapenems, and the monobactams.[1] Since these antibiotics are widely applied in human medicine, a plethora of structural variations has been prepared by partial and total synthesis. These chemical studies have, in turn, led to detailed structure–activity profiling and the development of novel more active antibiotics.

In the total synthesis of these substances it is necessary to decide how to construct the β-lactam ring. Of the many existing strategies, the condensation reaction of an alkene with an activated isocyanate is especially useful. In order for this reaction to be practical, the isocyanate must be carefully chosen. Firstly, the nitrogen must be substituted by an electron-withdrawing group. This is essential to permit the cycloaddition to take place with a sufficiently high rate constant. Secondly, the N-substituent must be easily removable, after the cycloaddition, under mild conditions that do not disrupt the strained and activated

(1) For examples, see: "Cephalosporins and Penicillins Chemistry and Biology"; Flynn, E. H., Ed.; Academic Press: New York, 1972. "Topics in Antibiotic Chemistry"; Sammes, P. G., Ed.; Ellis Horwood Ltd.: Chichester, 1980; Volumes 3 and 4. Asai, M.; Haibara, K.; Muroi, M.; Kintaka, K.; Kishi, T. *J. Antibiot.* **1981**, *34*, 621. Parker, W. L.; Koster, W. H.; Cimarusti, C. M.; Floyd, D. M.; Lui, W.-C.; Rathnum, M. L. *Ibid.* **1982**, *35*, 189.

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