Synthesis of Amino-β-lactams by the Photolytic Reaction of Imines with Pentacarbonyl[(dibenzylamino)carbene]chromium(0)

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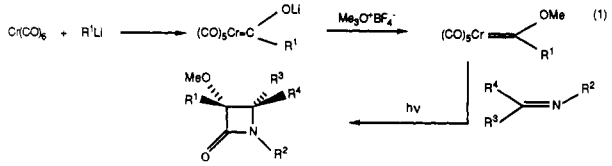
Abstract: Chromium–carbene complexes containing the [=C(H)NR_2] group were synthesized by the reaction of Vilsmeir's salts with $Cr(CO)_5^{2-}$. These carbenes were remarkably air stable and resistant to attack by nucleophiles. Photolytic reaction of these complexes with imines, oxazines, oxazolines, imidates, thiazines, and thiazolines produced β-lactams in fair to good yield. In most cases trans stereochemistry was observed. Representative dibenzylamino-β-lactams were debenzylated to produce β-lactams having a free NH_2 group α to the lactam carbonyl group.

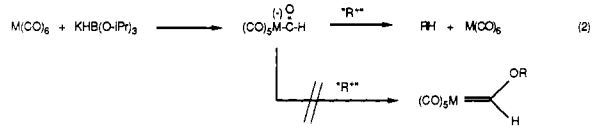
We recently reported a new synthetic approach to β-lactams which involves the photolytic reaction of heteroatom stabilized group VI (6)[22] (Cr, Mo) transition-metal–carbene complexes ("Fischer Carbenes") with imines (eq 1).[1] This reaction has a



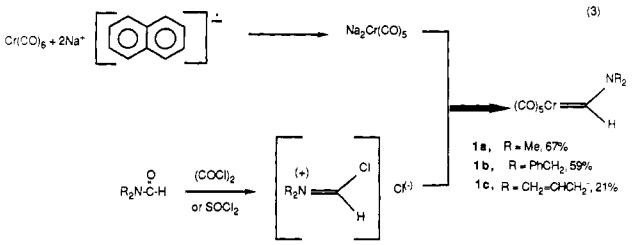
number of remarkable features. A wide variety of imines underwent facile reaction. These included acyclic imines of benzaldehyde, dihydroisoquinolines, quinoline itself, benzothiazines, thiazolines,[1] thiazines, and oxazines.[2] The reaction proceeded with high stereoselectivity. In most cases only a single diastereomer was formed. With optically pure methyl D-5,5-dimethyl-Δ^2-thiazoline-4-carboxylate as substrate, a single enantiomer of the bicyclic β-lactam penicillin derivative was produced.

In spite of this generality, several classes of imines were not efficiently converted to β-lactams in this process. The more basic imines of aliphatic aldehydes displaced the carbene moiety from the metal, producing metal carbonyl imine complexes and enol ethers from dimerization of the carbene moiety.[3] Oxazolines were converted to β-lactams only in very low yield, and oxazinone byproducts were formed as well, making oxapenam systems unavailable by this route.[2] Other –O—C=N– systems, such as imidates, were also unreactive toward the methoxyalkyl or -aryl carbenes studied.

Most limiting in regards to the use of this chemistry for this synthesis of β-lactams having biological activity is the constitution of the typical "Fischer" carbenes which are readily available. Virtually all biologically active β-lactams have a hydrogen and an amido group on the position α to the β-lactam carbonyl group.[4] However, the carbene complexes used above are produced by the reaction of an organolithium reagent with $M(CO)_6$, (eq 1) and hence ultimately place an *alkyl* group in the α position of the β-lactam. Formyl "ate" complexes of chromium and molybdenum are available by the reaction of the metal hexacarbonyl with trialkoxyborohydrides.[5] However, these formylate complexes are not only relatively unstable but are also strong *hydride* donors.[6] Thus, reaction with active alkylating agents produces the alkane and metal carbonyl rather than the desired hydridocarbene (eq 2). Aminocarbene complexes having hydrogen on the carbene



carbon have been made in modest yield by a different procedure, involving the addition of (chloromethylene)dialkylammonium chloride to metal carbonyl dianions (eq 3).[7] Herein we describe optimized procedures for the synthesis of several aminocarbene complexes of this type, as well as the results of the photolytic reactions of these complexes with a variety of imines to produce β-lactams.



Results and Discussion

Preparation of Aminocarbene Complexes $(CO)_5Cr{=}C(H)NR_2$ (1). The published procedure[7] for the preparation of the (dimethylamino)carbene complex **1a** (R = Me) involves the reduction of chromium hexacarbonyl with sodium amalgam in tetrahydrofuran at reflux to produce the chromium pentacarbonyl dianion. Addition of (chloromethylene)dimethylammonium chloride was reported to produce a 40% yield of the desired aminocarbene complex. In our hands this procedure provided variable, low yields of the desired complex, contaminated by an unidentified chromium complex difficult to separate from the desired carbene complex. Reduction of chromium hexacarbonyl by sodium amalgam has been shown to give varying amounts of $Cr_2(CO)_{10}^{2-}$ in addition to the desired $Cr(CO)_5^{2-}$,[8,9] leading to complicated reaction mixtures. In contrast, reduction of $Cr(CO)_6$ with sodium in liquid ammonia[9] cleanly produced the desired dianion, although the procedure was somewhat cumbersome. The best procedure, both for ease of operation and ultimate yield of carbene complex, proved to be that shown in eq 3. Reduction of $Cr(CO)_6$ by sodium naphthalenide,[10] followed by reaction of the resulting dianion with the appropriate Vilsmeir's salt produced

(1) (a) McGuire, M. A. Hegedus, L. S. *J. Am. Chem. Soc.* **1982**, *104*, 5538. (b) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun. C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

(2) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833.

(3) Bases such as pyridine cause a similar displacement of the carbene ligand. See: Fischer, E. O.; Plabst, W. *Chem. Ber.* **1974**, *107*, 3326.

(4) Durkheimer, W.; Blumbach, J.; Lattrell, R.; Scheunemann, K. H. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 180.

(5) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.

(6) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544. (b) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.

(7) Hartshorn, A. J.; Lappert, M. F.; Turner, K. *J. Chem. Soc., Dalton Trans.* **1978**, 348.

(8) Kaska, W. C. *J. Am. Chem. Soc.* **1968**, *90*, 6340.

(9) Ellis, J. E.; Hentges, S. G.; Kalina, D. G.; Hagen, G. P. *J. Organomet. Chem.* **1975**, *97*, 79.

(10) Darensbourg, M. Y.; Slater, S. *J. Am. Chem. Soc.* **1981**, *103*, 5914. Maher, J. M.; Beatty, R. P.; Cooper, N. J. *Organometallics* **1985**, *4*, 1354.

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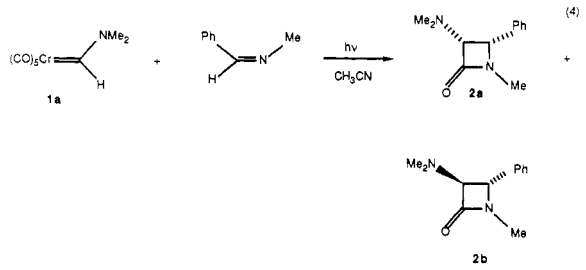
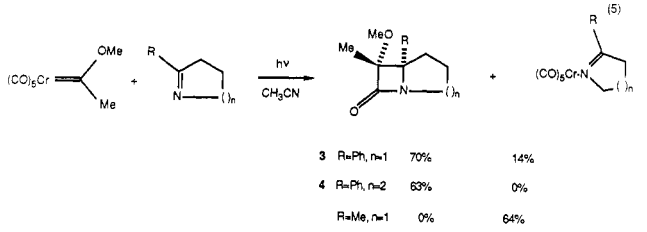
carbene complexes **1a–c** in fair to good yield. These aminocarbene complexes were considerably more stable toward air than the corresponding (alkyl) or (aryl)(alkoxy)carbenes. In the solid state they were easily handled and stored without precaution. In solution they were very slowly oxidized so that reactions and solution manipulations were carried out with minimal protection from prolonged exposure to air.

Photolytic Reactions of Aminocarbene 1a–c with Imines. Preliminary studies involved photolytic reactions between carbene complex **1** and the *N*-methylimine of benzaldehyde (eq 4). Under

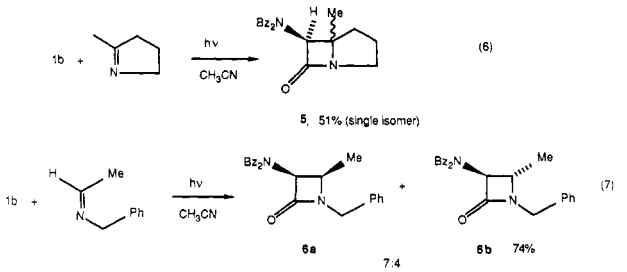


reaction conditions sufficient for facile reaction with (methoxy)(alkyl)carbene complexes (sunlight photolysis, Et_2O or THF solvent) virtually *no* reaction occurred. Use of the more polar (and coordinating) solvent acetonitrile resulted in slow (days) reaction in sunlight and fast (h) reaction by using 200–450-W Hanovia Lamp irradiation, to produce the *cis*-β-lactam **2a** in 30–44% as well as minor (0–12%) amounts of trans isomer **2b**.

β-Lactams having *free*-NH_2 groups were of most biological interest. Thus reactions of the (dibenzylamino)carbene complex **1b** were examined, since debenzylation of (*N*,*N*-dibenzylamino)-β-lactams (H_2, Pd/C) is a well-established procedure.[11] Carbene **1b** converted the *N*-methylimine of benzaldehyde into a 4.5/1 cis-to-trans mixture of the (*N*,*N*-dibenzylamino)-β-lactam in 50% yield. Although imines of aromatic aldehydes were readily converted to β-lactams upon photolytic reaction with (methoxy)(alkyl)chromium–carbene complexes,[1] the more basic imines of aliphatic aldehydes attacked the metal center displacing the carbene ligand (eq 5). In contrast the more stable aminocarbene



complex **1b** underwent efficient reaction with both cyclic (eq 6) and acyclic (eq 7) aliphatic imines, producing β-lactams in fair



to good yield. Note that a single isomer (stereochemistry unknown) was obtained with the cyclic imine while a mixture of cis and trans isomers resulted in the reaction of the acyclic imine.

Although (methoxy)(alkyl)carbene complexes converted oxazines to oxacepham derivatives in fair yield, oxazolines and imidates again reacted at the metal center, with loss of the carbene ligand.[2] In contrast aminocarbene complex **1b** appended the

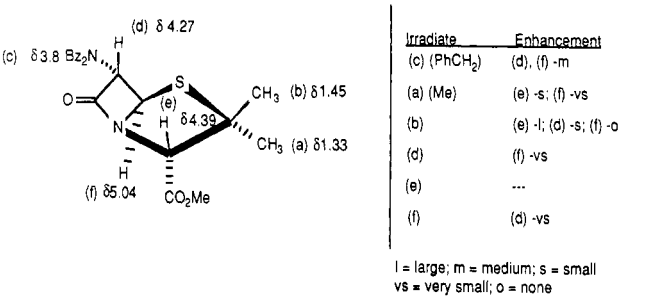
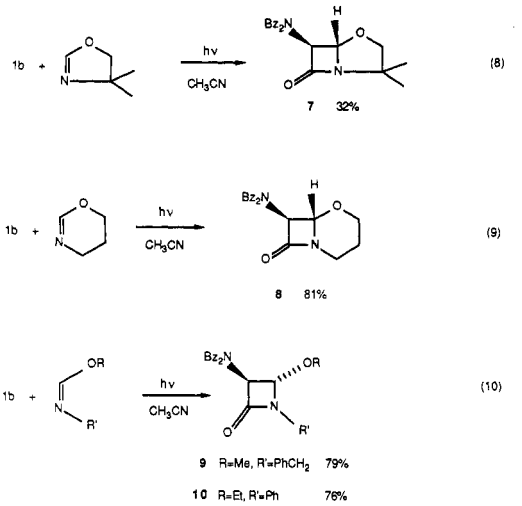
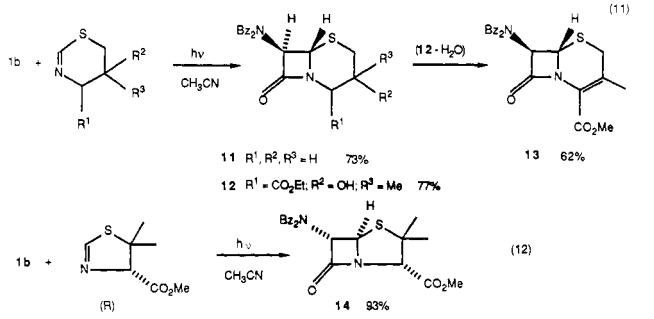


Figure 1.

β-lactam ring to oxazines (eq 8), oxazolines (eq 9), and imidates eq 10) in fair to excellent yield. In contrast to the acyclic imines, the acyclic imidates gave a single stereoisomer (trans) of the β-lactams.



In a similar manner, thiazines (eq 11) and thiazolines (eq 12) were converted to the corresponding bicyclic β-lactams by photolytic reaction with aminocarbene complex **1b**. As was previously observed with the (methoxy)(alkyl)carbene complex,[1,2] the chiral cyclic thiazoline ($[\alpha]_D^{25}$ +51.9°, eq 12) produced a *single* dia-



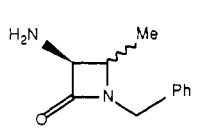
stereoisomer by high field NMR spectroscopic examination of the crude reaction mixture. Recrystallization gave a 93% yield of pure material, assigned the trans stereochemistry from the magnitude of the coupling constants of H_5 and H_6 (J = 1.3 Hz vs. ~4 Hz for the cis isomer). (In the case of biologically active penams and cephams this is the unnatural stereoisomer. Methods to invert the stereochemistry of the position α to the carbonyl group have been developed.)[12] The purified material had a rotation of $[\alpha]_D^{25}$ +109.7 (*c*, 1, $CHCl_3$). Thus the β-lactam forming reaction appears to have occurred to give >99% diastereoisomeric excess. Provided partial epimerization of the starting thiazoline

(11) Guanti, G.; Banfi, L.; Narisano, E.; Scolastico, C.; Bosone, E. *Synthesis* **1985**, 609.

(12) (a) Jen, T.; Frazee, J.; Hoover, J. R. E. *J. Org. Chem.* **1973**, *38*, 2857. (b) Yoshioka, M.; Tsuji, T.; Uyeo, S.; Yamamoto, S.; Aoki, T.; Nishitani, Y.; Mori, S.; Satoh, H.; Hamada, Y.; Ishitobi, H.; Nagata, W. *Tetrahedron Lett.* **1980**, *21*, 351. (c) Hashimoto, T.; Watanabe, T.; Kawano, Y.; Tanaka, T.; Miyadera, T. *Heterocycles* **1978**, *11*, 207.

did not occur during the reaction, the product **14** should be optically pure. The *absolute* stereochemistry of **14** was shown by NOE experiments to be as depicted in eq 12 and Figure 1 (Experimental Section). Most significantly, the stereochemistry at the critical C-5 position is that found in penicillin itself.

(Dibenzylamino)-β-lactams **6**, **8**, and **9** were cleanly debenzylated by hydrogenolysis (1 atm H_2 Pd/C catalyst, EtOH, 2–4 h) to give amino-β-lactams **15–17** in 88%, 94%, and 86% yield, respectively. Note that the *N*-benzyl*amide* group was not cleaved



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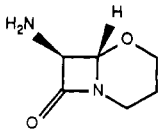

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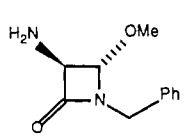

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under these conditions. The sulfur-containing β-lactams **11–14** resisted debenzylation even in the presence of more than 1 equiv of catalyst. Under forcing conditions decomposition of the β-lactam occurred rather than clean debenzylation. Solutions to this problem as well as chromium–carbene based *direct* syntheses of NH_2-containing β-lactams are currently being developed.

Experimental Section

General Procedures. Melting points were taken on a Mel-Temp apparatus and are uncorrected. The 60-MHz ^1H NMR spectra were obtained with a Varian T-60 NMR spectrometer. IBM-200 and 270 NMR spectrometers were used for the 200- and 270-MHz ^1H NMR spectra, respectively. IR spectra were recorded either on a Beckman 4240 or a Beckman Acculab 3 spectrophotometer. Ultraviolet irradiation of the reaction mixtures was carried out with a Conrad-Hanovia 7825 medium-pressure mercury lamp operating at 450 W, by using a Conrad-Hanovia 7830-C power supply. A Brinkman 12M20-type constant-temperature bath was used to keep the reaction temperature at 0 °C.

Radial layer chromatographic technique was used for the purifications in most cases, by using Chromatotron Model 7924 with either Merck silica gel 60 PF or Merck aluminum oxide 60 GF as the stationary phase, unless otherwise noted. Merck silica gel 60 was used for column chromatography.

Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. Tetrahydrofuran (Fisher, reagent grade) was distilled from benzophenone ketyl under a nitrogen atmosphere just prior to use. Hexane was distilled at atmospheric pressure and stored over molecular sieve 4Å. Methylene chloride (Fisher) and acetonitrile (Matheson) were distilled over CaH_2 and stored over molecular sieve 4Å.

Chromium hexacarbonyl (Pressure Chemicals), naphthalene (Baker), oxalyl chloride (Aldrich), 10% palladium on charcoal (Aldrich), ethanol (Midwest Solvents, absolute), and methanol (Fisher) were obtained from commercial suppliers and used without further purifications.

The following chemicals were prepared according to the literature procedures: 3,4-dihydro-5-methyl-2*H*-pyrrole,[13] methyl 5,5-dimethyl-4*H*-1,3-thiazoline-4-carboxylate,[14] 4,4-dimethyl-1,3-oxazoline,[15] 5,6-dihydro-4*H*-1,3-oxazine,[16] 5,6-dihydro-4*H*-1,3-thiazine,[16,17] 5-hydroxy-5-methyl-5,6-dihydro-4*H*-1,3-thiazine-4-carboxylate,[12c] benzylethylideneamine,[18] methyl *N*-benzylformimidate,[19] ethyl *N*-phenylformimidate,[20] 2-phenyl-4,5-dihydro-3*H*-pyrrole,[21] and 2-phenyl-3,4,5,6-tetrahydropyridine.[21]

***N*,*N*-Dibenzylformamide.** Dibenzylamine (19.7 g, 0.1 mol) was heated under reflux for 72 h in 50 mL of ethyl formate. The excess ethyl formate was removed under reduced pressure, and the white solid was recrystallized from hexane/ether to yield 20.7 g of white crystals (92%): mp 53–53.5 °C; ^1H NMR (60 MHz, $CDCl_3$, Me_4Si) δ 4.25 (s, 2, $PhCH_2$), 4.33 (s, 2, $PhCH_2$), 7.05–7.45 (m, 10, ArH), 8.45 (s, 1, C*H*O); IR (KBr pellet) 1680 (C=O). Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.81; H, 6.52; N, 6.16.

Preparation of *N*,*N*-Diallylformamide. The above procedure was followed by using 27.6 g (0.28 mol) of diallylamine and 100 mL of ethyl formate, heating at reflux for 22 h. Distillation of the crude formamide (bp 48 °C/1 mmHg) gave 34 g (97%) of a colorless liquid: ^1H NMR (270 MHz, $CDCl_3$) δ 3.70 (m, 2, $-CH_2-$), 3.90 (m, 2, $-CH_2-$), 4.9–5.3 (m, 4, C=C*H*$_2$), 5.5–5.8 (m, 2, C*H*=C), 8.05 (s, 1, C*H*O); IR (film) 1670 cm^{-1} (C=O). Anal. Calcd for $C_7H_{11}NO$: C, 67.20; H, 8.80; N, 11.20. Found: C, 67.36; H, 8.67; N, 11.35.

Preparation of Disodium Pentacarbonylchromium. In a thoroughly dried, 300-mL, round-bottomed flask equipped with a magnetic stirring bar, a septum inlet, and an argon supply tube were placed 6.4 g (50 mmol) of naphthalene and 1.26 g (52 mmol) of sodium under argon. THF (100 mL) was added to the mixture through a double-tipped needle. The mixture turned dark green almost instantaneously as the solids dissolved. In a separate 500-mL, round-bottomed flask fitted with a pressure-equalizing dropping funnel, a magnetic stirring bar, and an argon-filled balloon was added 5.50 g of chromium hexacarbonyl (25 mmol) and 300 mL of THF. The aforementioned THF solution of sodium naphthalenide was transferred to the dropping funnel by means of a double-ended needle. The flask was cooled to −78 °C, and the contents of the dropping funnel were added to the suspension of $Cr(CO)_6$ over the period of 1 h. The dark suspension thus formed was allowed to reach room temperature and stirred overnight to give a dark orange, clear solution of disodium pentacarbonylchromium which was ready for further syntheses.

[(*N*,*N*-Dibenzylamino)methylene]chromium(0) Pentacarbonyl (1b). Dibenzylformamide (6.20 g, 27.5 mmol) was dissolved in 30 mL of THF in a 1000-mL, three-necked, round-bottomed vessel equipped with a gas inlet tube, a septum cap, a magnetic stirring bar, and a 500-mL pressure-equalizing dropping funnel under an argon atmosphere. The gas inlet was connected to an argon-filled balloon, and 4.80 mL of oxalyl chloride (55 mmol) was added via a syringe with stirring. After 30 min, the volatile materials were removed thoroughly in vacuo, and the remaining yellow Vilsmeir's salt was redissolved in 120 mL of THF. The solution was chilled to −78 °C and treated, through the dropping funnel, with the THF solution of disodium pentacarbonylchromium, over a 2-h period. The cooling bath was then removed, and stirring was continued for 2 h at room temperature. The solvents were removed under a reduced pressure, and the residue was purified by passage through 30 g of silica gel. Elution with hexane gave all naphthalene. Further elution with 5% CH_2Cl_2/hexane gave 5.94 g of the pure chromium–carbene complex (59%) as yellow needles: mp 130–131 °C; ^1H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 4.57 (s, 2, $PhCH_2$), 5.14 (s, 2, $PhCH_2$), 6.95–7.40 (m, 10 ArH), 11.32 (s, 1, =CH); IR ($CHCl_3$) 3000, 2040, 1975, 1925, cm^{-1}; UV (hexane) λ_{max} 373 nm (ε 7716). Anal. Calcd for $C_{20}H_{15}CrNO_5$: C, 59.85; H, 3.77; N, 3.49. Found: C, 59.66; H, 3.82; N, 3.33.

[(*N*,*N*-Dimethylamino)methylene]chromium(0) Pentacarbonyl (1a). The above procedure was used to produce 4.17 g (67%) of carbene from 2.00 g (27.5 mmol) of dimethylformamide, as yellow crystals: mp 69–70 °C (lit.[7] 64–66 °C); ^1H NMR (60 MHz, $CDCl_3$) δ 3.50 (s, 3, NCH_3), 3.70 (s, 3, NCH_3), 10.80 (s, 1 =C*H*); IR (CH_2Cl_2) 2050 (s), 1980 (s) cm^{-1}; UV (hexane) λ_{max} 365 nm (ε 2100).

[(*N*,*N*-Diallylamino)methylene]chromium(0) Pentacarbonyl (1c). The above procedure using 10 mmol of $Na_2Cr(CO)_5$ in 100 mL of THF gave 0.67 g (21%) of the carbene complex **1c** as yellow crystals: mp 37.5–38.5 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 4.10 (m, 2, CH_2-C=), 4.60 (m, 2, CH_2C=), 5.05–5.50 (m, 4, =C*H*$_2$), 5.90 (m, 2, CH=C), 10.90 (s, 1, =CH); IR ($CHCl_3$) γ 2060 (s), 1985 (m), 1930 (s) cm^{-1}; UV (hexane) λ_{max} 389 (ε 10140). Anal. Calcd for $C_{12}H_{11}NO_5Cr$: C, 47.85; H, 3.68; N, 4.65. Found: C, 47.67; H, 3.80; N, 4.53.

(13) Bielawski, J.; Brandange, S.; Lindblom, L. *J. Heterocyclic Chem.* **1978**, *15*, 97.

(14) Bell, M. R.; Carlson, J. A.; Oesterlin, R. *J. Org. Chem.* **1972**, *37*, 2733.

(15) Meyers, A. I.; Collington, E. W. *J. Am. Chem. Soc.* **1970**, *92*, 6676.

(16) Wenker, H. *J. Am. Chem. Soc.* **1935**, *57*, 1079.

(17) Ito, Y.; Inubushi, Y.; Zenbayashi, M.; Tomita, S.; Saegusa, T. *J. Am. Chem. Soc.* **1973**, *95*, 4448.

(18) Campbell, K. N.; Sommers, A. H.; Campbell, B. K. *J. Am. Chem. Soc.* **1944**, *66*, 82. Direct distillation of the *N*-benzylimine from KOH, as implicated in the literature, gave a rearranged imine, ethylbenzylideneamine, as the only isolable product. Thus, the workup method was modified as follows: After KOH treatment of the reaction mixture obtained from benzylamine and acetaldehyde, the mixture was extracted with ether. The ether layer was washed twice with water, dried (Na_2SO_4), and evaporated. Further distillation gave the imine without undesirable rearrangement: bp 72 °C/2 mmHg. Although this aliphatic imine is fairly stable when stored at −20 °C, it turns yellow and viscous at room temperature in a matter of hours.

(19) Guzman, A.; Muchowski, J. M.; Naal, N. T. *J. Org. Chem.* **1981**, *46*, 1224. The method for the preparation of methyl *N*-2-(phenylethyl)formimidate was used for this *N*-benzyl derivative: bp 66 °C/1 mmHg.

(20) Roberts, R. M.; Vogt, P. J. *Org. Synth.* **1955**, *35*, 65.

(21) Salathiel, R.; Burch, J. M.; Hixon, R. M. *J. Am. Chem. Soc.* **1937**, *59*, 984.

(22) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 and 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

General Procedure for the Synthesis of β-Lactams through the Photolytic Reaction of Imines with [(*N*,*N*-Dialkylamino)methylene]chromium(0) Pentacarbonyl. The chromium carbene complex was placed in a Pyrex test tube and dissolved in acetonitrile (5–10 mL per 1 mmol of the carbene complex). The tube was sealed with a rubber septum. The vessel was evacuated and purged with argon (three cycles) to replace the air with argon. The appropriate imine was then introduced via a syringe as stated in the individual synthesis, and the tube was irradiated either under direct sunlight or by a 450-W UV lamp. When the scale exceeded 2 mmol, it was advisable to divide the reaction mixture into several smaller tubes for efficiency of the irradiation. The progress of the reaction was periodically monitored by analytical TLC (silica gel). The reaction mixture turned from bright yellow to green or brown as the reaction proceeded. After complete consumption of the carbene complex, the solvent was evaporated, and the dark green residue was taken in 1:1 hexane/ether. The mixture was then placed in a light box, equipped with six 20-W Vitalite fluorescent lamps or on the roof top under sunlight to air-oxidize the chromium-containing byproduct(s). It took 1–2 days in the lamp box and 1 sunny day on the roof top. The precipitate, which developed during the air oxidation, was removed by filtration through Celite, and the filtrate was evaporated to give crude β-lactam, which was purified by extraction and/or chromatography. Further details for purifications will be found in each synthesis.

Synthesis of 1-Methyl-3-(*N*,*N*-dimethylamino)-4-phenyl-β-azetidinone (2a, 2b). The reaction of carbene complex **1a** (0.25 g, 1.00 mmol) with the *N*-methylimine of benzaldehyde (0.24 g, 2.00 mmol) in 10 mL of acetonitrile was complete after 20 h of 450-W irradiation. After oxidation and purification by Chromatotron chromatography (silica gel 1:1 hexane/ether) 30–40% of the cis isomer **2a** was obtained, along with 12–0% of the trans isomer **2b**.

***cis*-2a**: mp 82 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.04 (s, 6, N-(CH_3)$_2$), 2.74 (s, 3, NCH_3), 3.72 (1, d, J = 4.5 Hz, C*H*Ph), 4.53 (brd, J = 4.5 Hz, C*H*(NMe_2)), 7.34 (5, s, ArH); IR (CH_2Cl_2) γ 1730 (s, C=O) cm^{-1}; mass spectrum (EI) 204 (M^+). Anal. Calcd for $C_{12}H_{16}N_2O$: C, 70.56; H, 7.89; N, 13.71. Found: C, 70.36; H, 7.80; N, 13.60.

***trans*-2a**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.35 (s, 6, N(CH_3)$_2$), 2.75 (s, 3, NCH_3), 3.60 (s, 1, C*H*Ph), 4.50 (s, 1 C*H*NMe_2), 7.2–7.4 (m, 5 ArH).

Synthesis of 1-Methyl-3-(*N*,*N*-dibenzylamino)-4-phenyl-β-azetidinone. Following the procedure above using complex **1b** (0.40 g, 1.00 mmol), the reaction was complete in 7 h. Purification of Chromatotron as above gave 0.146 g (41%) of the cis isomer and 0.034 g (9%) of the trans isomer. Cis isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.90 (s, 3, NCH_3); 3.5–3.8 (m, 4, PhCH_2N), 4.45 (d, 1, J = 4.5 Hz, PhC*H*), 4.63 (d, 1, J = 4.5 Hz, C*H*NBz_2), 6.9–7.6 (m, 15, ArH); IR (CH_2Cl_2) γ 1745 (C=O) cm^{-1}; mass spectrum (CI-NH_3) 357 (M + 1). Anal. Calcd for $C_{23}H_{24}N_2O$: C, 77.53; H, 6.74; N, 7.86. Found: C, 77.36; H, 6.78; N, 7.70.

Trans isomer: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.70 (s, 3 NCH_3), 3.6–3.9 (m, 4, PhCH_2N), 4.05 (s, 1, PhC*H*), 4.45 (s, 1, C*H*NBz_2), 7.0–7.7 (m, 15, ArH).

Synthesis of 3. In a 100-mL Airlessware flask was placed 0.125 g (0.5 mmol) of pentacarbonyl(methoxymethyl)carbenechromium(0). The system was flushed with argon, and 2-phenyl-4,5-dihydro-3*H*-pyrrole (0.073 g, 0.50 mmol) in 40 mL of argon-saturated acetonitrile was added by syringe. Sunlight irradiation (8 h) followed by air oxidation gave the crude product, which was purified by Chromatotron (silica gel, hexane/ethyl acetate, 2:3) producing 0.081 g (70%) of the product as white crystals: mp 79–80 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.53 (s, 3, CH_3), 2.0–2.2 (m, 4, $-CH_2-$), 3.01 (s, 3, OCH_3), 3.10 (m, 1) 3.76 (m, 1, $-NCH_2-$), 7.2–7.4 (m, 5, ArH); IR (CH_2Cl_2) γ 1760 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.67; H, 7.50, N, 6.05.

Synthesis of 4. Following the exact procedure above 0.077 g (63%) of **4**, mp 70–71 °C, was obtained: ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.25, 1.40 (m, 2, $-CH_2-$), 1.55 (s, 3, CH_3), 1.65 (m, 2, $-CH_2-$), 1.85 (dt, 1, J's = 2.8, 13.0 Hz, C*H*CH_2N), 2.30 (d, 1, J = 13.0 Hz, C*H*CH_2N), 2.95 (s, 3, CH_3O), 3.05 (dt, 1, J's = 2.8, 13.0 Hz, $-CH_2N$), 4.00 (dd, 1, J's = 5.7, 13.0 Hz), 7.1–7.3 (m, 5, ArH); IR (CH_2Cl_2) γ 1750 (C=O) cm^{-1}. Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.80; N, 5.71. Found: C, 73.44; H, 7.83; N, 5.69.

Synthesis of 5. The carbene complex **1b** (0.80 g, 2.00 mmol) and 3,4-dihydro-5-methyl-2*H*-pyrrole (0.18 g, 2.20 mmol) were combined in 40 mL of acetonitrile as described in the General Procedure. The mixture was divided in four 20-mL Pyrex test tubes and placed under direct sunlight for 1 day, after which no carbene complex was found in the reaction mixture. Standard isolation followed by Chromatotron purification (silica gel, 1:1 hexane/ether) yielded 0.324 g (51%) of white crystals: mp 63–64 °C; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.26–1.42 (m, 1, CH), 1.34 (s, 3, CH_3), 1.59 (m, 1, CH), 1.92 (m, 2), 2.86 (m, 1, CH_2N), 3.52 (m, 1, CH_2N), 3.76 (s, 1, C*H*NBz_2), 3.82 (d, J = 14 Hz, 2, $-CH$Ph), 3.93 (d, J = 14 Hz, 2, $-CH$Ph), 7.19–7.41 (m, 10, ArH); IR ($CHCl_3$) γ 1734 (C=O) cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_2O$: C, 78.72; H, 7.55; N, 8.74. Found: C, 78.81; H, 7.44; N, 8.91.

1-Benzyl-3-(*N*,*N*-dibenzylamino)-4-methyl-β-azetidinone (6a and 6b). A mixture of the carbene complex **1b** (0.82 g, 2.04 mmol) and benzylethylideneamine (0.27 g, 2.04 mmol) dissolved in 20 mL of acetonitrile was irradiated under direct sunlight in two Pyrex test tubes for 2 days. After usual oxidative workup, the ether solution of the crude β-lactam was extracted 6 times with 20-mL portions of aqueous 4 N HCl. The aqueous extracts were combined and carefully brought to pH 9 by slow addition of solid Na_2CO_3. The mixture was then extracted with CH_2Cl_2 (3 × 40 mL), and the organic phase was dried over anhydrous sodium sulfate. Evaporation of the solvent gave almost pure β-lactam, which was further purified by Chromatotron (silica gel, 7:3 hexane/ether) to afford 0.56 g (74%) of a colorless oil. This specimen consisted of a 6:4 mixture of *cis*-(**6a**) and *trans*-(**6b**) β-lactams. **6a**: ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si) δ 1.22 (d, J = 7 Hz, 3, CH_3), 3.51 (dq, J = 5 and 7 Hz, 1, N-C*H*(CH_3)), 3.89 (s, 4, NCH_2Ph), 4.14 (d, J = 15 Hz, 1, NC*H*Ph), 4.17 (d, J = 5 Hz, 1 C*H*NBz_2), 4.58 (d, J = 15 Hz, 1, NC*H*Ph), 7.1–7.4 (m, 15, ArH); IR ($CHCl_3$) γ 1750 (C=O) cm^{-1}. **6b**: ^{1}H NMR (200 MHz, $CDCl_3$, Me_4Si) δ 1.07 (d, J = 6 Hz, 3, CH_3), 3.52 (dq, J = 2 and 6 Hz, 1, NC*H*(CH_3)), 3.62 (d, J = 14 Hz, 2, NCH_2Ph), 3.76 (d, J = 2 Hz, 1, C*H*NBz_2), 3.84 (d, J = 14 Hz, 2, PhCH_2), 3.99 (d, J = 15 Hz, 1), 4.69 (d, J = 15 Hz, 1, NCH_2Ph), 7.1–7.4 (m, 15, ArH); IR ($CHCl_3$) γ 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{25}H_{26}N_2O$: C, 81.05; H, 7.07; N, 7.56. Found: C, 80.88; H, 7.33; N, 7.39.

Synthesis of 7. The mixture of the carbene complex **1b** (0.80 g, 2.00 mmol) and 4,4-dimethyl-2-oxazoline (0.22 g, 2.20 mmol) dissolved in 20 mL of CH_3CN was irradiated under sunlight for 1^1/$_2$ days at 24 °C in two 20-mL Pyrex test tubes. Standard isolation and subsequent chromatography with Chromatotron (aluminum oxide, 3:1 hexane/ether) yielded 0.22 g (32%) of a white solid: mp 120–121 °C; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.15 (s, 3, CH_3), 1.54 (s, 3, CH_3), 3.56 (d, J = 8 Hz, 1, OC*H*), 3.74 (d, J = 14 Hz, 2, $-CH_2$Ph), 3.78 (d, J = 8 Hz, 1, OC*H*), 3.83 (d, J = 14 Hz, 2, -CH_2Ph), 3.97 (s, 1, C*H*NBz_2), 5.16 (s, 1, HCNO), 7.20–7.40 (m, 10, ArH); IR ($CHCl_3$) γ 1765 (C=O) cm^{-1}. Anal. Calcd for $C_{21}H_{24}N_2O_2$: C, 74.97; H, 7.19; N, 8.33. Found: C, 75.15; H, 7.19; N, 8.55.

Synthesis of 8. The reaction of the chromium complex **1b** (0.81 g, 2.02 mmol) with the 1,3-oxazine (0.17 g, 2.02 mmol) under the irradiation with a 450-W Hanovia lamp was complete after 40 h at 0 °C. After usual air oxidation, the ether solution of the crude mixture was extracted with 6 portions of aqueous 4 N HCl (20 mL each). The aqueous phase was brought to pH 9 by careful addition of Na_2CO_3 and was extracted 3 times with 40-mL portions of CH_2Cl_2. The organic layer was evaporated to give a yellow oil, which was purified by Chromatotron (silica gel, 1:1 hexane/ether) to give 0.53 g (81%) of the oxacepham as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.41 (dd, J = 3 and 14 Hz, 1), 1.75 (m, 1, CH_2), 2.99 (dt, J = 5 and 12 Hz, 1, NCH) 3.55 (dt, J = 13 Hz, 1, OCH), 3.67 (d, J = 14 Hz, 2, $PhCH_2$), 3.82 (d, J = 14 Hz, 2, $PhCH_2$), 3.87 (dd, J = 5 and 12 Hz, 1, NCH), 4.02 (br d, J = 13 Hz, 1, OCH), 4.07 (s, 1, C*H*NBz_2), 4.84 (s, 1, HCNO), 7.2–7.5 (m, 10, ArH); IR (film) γ 1760 (C=O) cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2O_2$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.55; H, 6.70, N, 8.70.

***trans*-1-Benzyl-3-(*N*,*N*-dibenzylamino)-4-methoxy-β-azetidinone (9).** Sunlight irradiation of the carbene complex **1b** (0.82 g, 2.04 mmol) and methyl *N*-benzylformimidate (0.29 g, 2.04 mmol) in 20 mL of acetonitrile for 2^1/$_2$ days left no starting carbene complex, as evidenced by analytical TLC. This mixture was oxidatively treated to remove chromium byproduct(s) and then taken up in ether. Extraction of the ether solution by aqueous 4 N HCl (6 × 20 mL) was carried out, followed by addition of sodium carbonate to the combined aqueous layer until the solution became weakly basic (pH ~ 9). The mixture thus obtained was extracted back with 3 40-mL portions of methylene chloride, and the organic extracts were dried over sodium sulfate and evaporated. Purification of the remaining oil by Chromatotron (silica gel, 1:1 hexane/ether) gave pure β-lactam as colorless plates (0.55 g, 79%): mp 64 °C, ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 3.11 (s, 3, OCH_3), 3.66 (d, J = 14 Hz, 2, $PhCH_2$), 3.81 (d, J = 14 Hz, 2, $PhCH_2$), 4.02 (s, 1, C*H*NBz_2), 4.09 (d, J = 15 Hz, 1, PhCH), 4.59 (s, 1, C*H*NO), 4.64 (d, J = 15 Hz, 1, PhCH), 7.1–7.5 (m, 15, ArH); IR (KBr pellet) γ 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.70; H, 6.55; N, 7.38.

***trans*-1-Phenyl-3-(*N*,*N*-dibenzylamino)-4-ethoxy-β-azetidinone (10).** The carbene complex **1b** (0.20 g, 0.5 mmol) and ethyl *N*-phenylformimidate (0.082 g, 0.55 mmol) were placed in a Pyrex tube in 10 mL of acetonitrile. The solution was then irradiated for 1 day by sunlight.

Standard isolation and purification of the β-lactam by Chromatotron (silica gel 7747, 1:1 hexane/ether) gave a colorless oil, which upon crystallization (hexane/ether 1:1) yielded 0.146 g (76%) of white crystals: mp 67 °C; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.12 (t, J = 7 Hz, 3, CH_3), 3.44 (q, J = 7 Hz, 2, OCH_2), 3.79 (d, J = 14 Hz, 2, $PhCH_2$), 3.90 (d, J = 14 Hz, 2, $PhCH_2$), 4.20 (d, J = 1 Hz, 1 $CHNBz_2$), 5.20 (d, J = 1 Hz, 1, CHNO), 7.06–7.59 (m, 15, ArH); IR ($CHCl_3$) γ 1755 (C=O) cm^{-1}. Anal. Calcd for $C_{25}H_{26}N_2O_2$: C, 77.69; H, 6.78; N, 7.25. Found: C, 77.82; H, 6.82; N, 7.30.

Synthesis of the Cepham 11. The reaction, which took 15 h with the 450-W lamp, was carried out by using 0.81 g (2.05 mmol) of the chromium-aminocarbene complex **1b** and 0.23 g (2.26 mmol, 1.1 equiv) of the 1,3-thiazine in 20 mL of acetonitrile at 0 °C. After usual isolation, the crude materials were taken up in ether, and 6 extractions with aqueous 4 N HCl were carried out (20 mL each). The combined aqueous layers were adjusted at pH 9 by careful addition of solid Na_2CO_3, and extracted 3 times with methylene chloride (40 mL each). The organic phase was dried over sodium sulfate and evaporated, and the residual yellow oil was purified by Chromatotron (silica gel, 1:1 hexane/ether) to yield 0.58 g (73%) of the title compound as colorless needles: mp 114.5–115.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.60 (m, 1, CH), 1.76 (br d, J = 14 Hz, 1, CH), 2.6–2.9 (m, 3, CH), 3.56 (d, J = 14 Hz, 2, $PhCH_2$), 3.85 (d, J = 14 Hz, 2, $PhCH_2$), 3.97 (dd, J = 4 and 14 Hz, 1, C*H*S), 4.17 (s, 1, C*H*NBz_2), 4.64 (s, 1, C*H*NS), 7.2–7.5 (m, 10, ArH); IR (KBr pellet) γ 1730 (C=O) cm^{-1}. Anal. Calcd for $C_{22}H_{20}N_2OS$: C, 70.97; H, 6.55; N, 8.28. Found: C, 70.84; H, 6.65; N, 8.05.

Synthesis of 12. Under irradiation of sunlight, the mixture of the chromium carbene complex **1b** (0.16 g, 0.40 mmol) and the 1,3-thiazine (0.11 g, 0.48 mmol) in 5 mL of acetonitrile was allowed to react for 2 days. After oxidation of the chromium-containing materials, the mixture was purified by Chromatotron (silica gel, 1:2 hexane/ether) to give the cepham **12** (0.11 g, 64%) as a mixture of two diastereomers. **12a** (less polar isomer): ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.29 (s, 3, CH_3), 1.30 (t, J = 7 Hz, 3 CH_3), 2.45 (d, J = 14 Hz, 1, CH_2S), 3.46 (d, J = 14 Hz, 1 CH_2S), 3.58 (d, J = 14 Hz, 2, $PhCH_2$), 3.81 (s, 1, –OH), 3.85 (d, J = 14 Hz, 2, $PhCH_2$), 4.18 (m, 2, OCH_2), 4.25 (d, J = 1.5 Hz, 1, NC*H*(CO_2R)), 4.40 (s, 1 $CHNBz_2$) 5.11 (s, 1, CHNS), 7.2–7.4 (m, 10, ArH); IR ($CHCl_3$) γ 1765 (C=O), 1730 (COOEt) cm^{-1}. **12b** (more polar isomer): ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.28 (t, J = 7 Hz, 3, CH_3), 1.52 (s, 3, CH_3), 2.51 (d, J = 14 Hz, 1 CH_2S), 3.08 (d, J = 14 Hz, 1, CH_2S), 3.58 (d, J = 14 Hz, 2, $PhCH_2$), 3.80 (s, 1, –OH), 3.85 (d, J = 14 Hz, 2, $PhCH_2$), 4.22 (q, J = 7 Hz, 2, OCH_2), 4.26 (s, 1, NC*H*(CO_2R)), 4.42 (s, 1, C*H*NBz_2), 4.95 (s, 1, CHNS), 7.2–7.4 (m, 10, ArH); IR ($CHCl_3$) γ 1760 (C=O), 1730 (COOEt) cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_4S$: C, 65.43; H, 6.41; N, 6.39; S, 7.28. Found: C, 65.50; H, 6.46; N, 6.35; S, 7.10.

Synthesis of 13. The β-lactam **12** (0.044 g, 0.1 mmol) was placed in a 25-mL, round-bottom flask fitted with an argon-filled balloon, a magnetic stirring bar, and a septum cap. THF (1 mL) was added, and the flask was cooled to 0 °C. To this was added 0.042 mL of *n*-butyllithium (2.38 M in hexanes, 0.1 mmol) through a syringe. After 10 min, the mixture was treated with methanesulfonyl chloride (16 mg, 0.15 mmol), and stirring was continued for further 30 min at 0 °C. Volatile materials were then removed in vacuo, and the residue was purified by TLC (silica gel, 2:8 hexane/ether) to yield 0.026 g (62%) of the desired unsaturated ester: ^{1}H NMR (270 MHz, $CDCl_3$, Me_2Si) δ 1.24 (t, J = 6 Hz, 3, –OCH_2—CH_3), 1.97 (s, 3, CH_3), 3.03 (d, J = 18 Hz, 1, –S—CH_2–), 3.36 (d, J = 18 Hz, 1, –S—CH_2), 3.62 (d, J = 13 Hz, 2, –CH_2Ph) 3.87 (d, J = 13 Hz, 2, –CH_2Ph), 4.12 (s, 1, Bz_2N—CH–), 4.26 (m, 2, –OCH_2CH_3), 4.55 (s, 1, C*H*NS), 7.1–7.5 (m, 10, ArH); IR ($CHCl_3$) γ 1730 (C=O), 1780 (C=O) cm^{-1}. Anal. Calcd for $C_{24}H_{26}N_2O_3S$: C, 68.22; H, 6.20; N, 6.63. Found: C, 68.19; H, 6.33; N, 6.44.

Synthesis of 14. The carbene complex **1b** (0.20 g, 0.5 mmol) and methyl 5,5-dimethyl-4*H*-1,3-thidazoline-4-carboxylate (0.096 g, 0.55 mmol, $[\alpha]_D^{25}$ +51.9°) together with 10 mL of CH_3CN were placed in a Pyrex tube and irradiated with a 450-W lamp at 0 °C for 9 h. Standard isolation followed by direct crystallization (1:1 hexane/ether) yielded 0.19 g of white solid (93%): mp 120–121 °C, $[\alpha]_D^{25}$ +109.7°; ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.33 (s, 3, CH_3), 1.45 (s, 3, CH_3), 3.66 (s, 3, CH_3O), 3.77 (d, J = 14 Hz, 2, $PhCH_2$), 3.86 (d, J = 14 Hz, 2, $PhCH_2$), 4.27 (d, J = 1.3 Hz, 1, $CHNBz_2$), 4.39 (s, 1, $CH(CO_2Me)$), 5.04 (d, J = 1.3 Hz, 1, CHNS), 7.1–7.3 (m, 10, ArH); IR (CH_2Cl_2) γ 1760 (C=O), 1740 ($COOCH_3$) cm^{-1}; mass spectrum (NH_3-CI) 411 (M + 1). Anal. Calcd for $C_{23}H_{26}N_2O_3S$: C, 67.29; H, 6.38; N, 6.84. Found: C, 67.47; H, 6.53, N, 6.74.

Nuclear Overhauser Effects in 14. Complete NOE correlations were measured on a Nicolet NT-360 instrument in $CDCl_3$. The results are summarized in Figure 1. Irradiation of the benzyl methylenes c resulted in a modest enchancement of d and f, confirming the chemical shift assignments of these protons. The absolute stereochemistry of e was known from that of the chiral starting material. Irradiation of the upfield methyl group a resulted in a small enhancement of f. Irradiation of the downfield methyl b led to a large enhancement of e, indicating a cis relationship, a small enhancement of d indicating a distant cis relationship, and *no* enhancement of f, indicating a trans relationship. Irradiation of d led to a small enhancement of f, corroborating its assigned trans disposition. Irradition of e led to *no* enhancement again indicating its trans relationship to f.

1-Benzyl-3-amino-4-methyl-β-azetidinone (15). General Method for the Debenzylation of the 3-(Dibenzylamino)-β-lactams. The dibenzylamino–monobactam (a 6:4 mixture of **6a** and **6b** (0.085 g, 0.23 mmol) was dissolved in 5 mL of ethanol in a 50-mL, round-bottomed flask equipped with a magnetic stirring bar and a gas inlet tube. To this solution was added 0.24 g of 10% palladium on C (0.25 mmol) under argon. The mixture was placed under an atmospheric pressure of hydrogen by the use of a hydrogen-filled balloon. After 3 h, no (dibenzylamino)-β-lactam was found by analytical TLC. The mixture was filtered through a pad of Celite, washed with CH_2Cl_2, and purified by Chromatotron (silica gel, 1:9 CH_3OH/CH_2Cl_2) to give 0.066 g (88%) of the free amino-β-lactam as a 6:4 mixture of diastereomers. *cis*-**15**: ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.12 (d, J = 6 Hz, 3, CH_3), 1.67 (br, 2, NH_2), 3.68 (dq, J = 5 and 6 Hz, 1, NC*H*CH_3), 4.11 (d, J = 15 Hz, 1, PhCH), 4.21 (d, J = 5 Hz, 1, C*H*NH_2), 4.52 (d, J = 15 Hz, 1, $PhCH_2$), 7.2–7.4 (m, 5, ArH); IR γ 3400 (NH_2), 1740 (C=O) cm^{-1}. *trans*-**15**: ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.23 (d, J = 6 Hz, 3, CH_3), 1.67 (br, 2, NH_2), 3.28 (q, J = 6 Hz, 1, C*H*CH_3), 3.70 (s, 1, C*H*NH_2), 4.10 (d, J = 15 Hz, 1, PhCH), 4.59 (d, J = 15 Hz, 1, PhCH), 7.2–7.4 (m, 5, ArH); IR ($CHCl_3$) γ 3400 (NH_2), 1740 (C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_2O$: C, 69.45; H, 7.42; N, 14.73. Found: C, 69.65; H, 7.19; N, 14.85.

Synthesis of Aminooxacepham (16). (Dibenzylamino)oxacepham (**8**, 0.092 g, 0.29 mmol) was treated with 0.30 g of 10% Pd/C (0.32 mmol) under an atmospheric pressure of hydrogen. Filtration followed by chromatography by Chromatotron (silica gel, 5% $MeOH/CH_2Cl_2$) gave 0.050 g (94%) of the pure free amino β-lactam as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.52 (br d, J = 6 Hz, 1, CH), 1.70 (br m, 2, NH_2), 1.72 (m, 1, CH), 3.06 (dt, J = 5 and 12 Hz, 1, NCH), 3.65 (dt, J = 2 and 12 Hz, 1, OCH), 3.99 (dd, J = 5 and 12 Hz, 1, NCH), 4.03 (s, 1, C*H*NH_2), 4.10 (dd, J = 2 and 12 Hz, 1, OC*H*), 4.68 (s, 1, CHNO); IR ($CHCl_3$) γ 3400 (NH_2), 1750 (C=O) cm^{-1}. Anal. Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found: C, 50.53; H, 7.24; N, 19.63.

***trans*-1-Benzyl-3-amino-4-methoxy-β-azetidinone (17).** This compound was obtained by hydrogenolysis of 0.18 g (0.46 mmol) of the parent dibenzylamino derivative in the presence of 0.54 g of 10% Pd on C (0.51 mmol) under H_2 for 3 h. Chromatographic (Chromatotron, silica gel, 5% $MeOH/CH_2Cl_2$) separation gave 0.07 g (75%) of the title β-lactam as a colorless oil: ^{1}H NMR (270 MHz, $CDCl_3$, Me_4Si) δ 1.64 (br m, 2, NH_2), 3.31 (s, 3, OCH_3), 4.01 (s, 1, C*H*NH_2), 4.18 (d, J = 15 Hz, 1, PhCH), 4.46 (s, 1, C*H*OMe), 4.62 (d, J = 15 Hz, 1, PhCH), 7.2–7.5 (m, 5, ArH); IR ($CDCl_3$) 3400 (NH_2), 1725 (C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{14}N_2O$: C, 64.06; H, 6.84; N, 13.58. Found: C, 63.86; H, 6.67; N, 13.47.

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