Urea as the Most Reactive and Versatile Nitrogen Nucleophile for the Palladium(2+)-Catalyzed Cyclization of Unsaturated Amines

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Abstract: Urea (known as an ambident nucleophile) serves as a specific nitrogen nucleophile for the palladium(2+)-catalyzed aminocarbonylation of unsaturated amines. *N*-2-Propenyl-, *N*-3-butenyl, *N*-4-pentenyl-, and *N*-5-hexenylureas undergo an aminocarbonylation (0.1–0.01 equiv of $PdCl_2$, 3.0 equiv of $CuCl_2$, 1 atm of CO in methanol at 0 °C to room temperature) to provide 4-[(methoxycarbonyl)methyl]-2-imidazolidinones, 4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinones, 1,3-diazabicyclo[4.3.0]nonane-2,4-diones, and 1,3-diazabicyclo[4.4.0]decane-2,4-diones, respectively, in high yields. The effects of solvents and the R^1 and R^2 substituents of *N*-2-propenylureas [R^1(2-propenyl)NCONHR^2] and *N*-3-butenylureas [R^1(3-butenyl)NCONHR^2] on the ease of cyclization and the relative reactivity of amino nucleophiles (urea > carbamate > tosylamide > benzamide) toward the cyclization are also discussed.

Much work has been done on the palladium(2+)-promoted amination of alkenes.[1] However, most of these reactions are stoichiometric with respect to Pd(2+).[2] The main reason for this is the strong coordination of amine to Pd(2+). Alkenes to be activated for nucleophilic attack by the coordination with Pd(2+) are prone to be displaced by the strong coordination of amine to Pd(2+). Another reason is high susceptibility of the starting amine and/or its product to an oxidizing agent, which is used to oxidize the Pd(0), formed in situ after one cycle of oxidative amination of olefins, to Pd(2+) in order to maintain a catalytic cycle. This problem has been partly overcome by protection of amine with electron-withdrawing groups, as observed in the catalytic cyclization of *o*-allylanilines[3] and carbamates and sulfonamides of unsaturated amines, developed by Hegedus et al.[4] According to this method, a variety of important classes of nitrogen heterocycles have been synthesized. Aminocyclization of N-protected unsaturated amines, however, suffers from its limited structural flexibility. Usually substitution on the olefin either results in no reaction or alters the course of the reaction.[3a] Cyclization forming five-membered nitrogen heterocycles is abundant, while cyclization to form six-membered nitrogen heterocycles is very rare.[4a,f]

In this paper we describe the first palladium(2+)-catalyzed ureidocyclization of *N*-2-propenylurea **7**, *N*-3-butenylurea **1**, *N*-4-pentenylurea **11**, and *N*-5-hexenylurea **16** to give rise to five-membered (**9**), six-membered (**3**), bicyclic[4.3.0] (**12**), and bicyclic[4.4.0]nitrogen heterocycles (**17**), respectively. The second and the fourth examples are especially noteworthy, as these reactions constitute some very rare examples that form the six-membered nitrogen heterocycles. Very importantly, these reactions tolerate substitution on olefins. The versatile reactivity of urea as compared with the hitherto commonly used benzamides, tosylamides, and carbamates and also the solvent effects on the amino cyclization are discussed.

Table I. Optimization of Conditions for Aminocarbonylation of *N*-Benzyl-*N*-3-butenyl-*N'*-methylurea (**1d**: $R^1 = CH_2Ph$, $R^2 = Me$)

entry	conditions[a]	% isolated yield of product 3d	5d	6d
1	$PdCl_2$ (0.1), $CuCl_2$ (3), CO in MeOH, room temp, 2 h	82		14
2	$PdCl_2$ (0.1), $CuCl_2$ (3), in MeOH under argon, room temp, 1 day			43
3	$PdCl_2$ (0.1), $CuCl_2$ (3), CO in MeOH, 0 °C, 12 h; room temp, 3 h	82		
4	$PdCl_2$ (0.01), $CuCl_2$ (3), CO in MeOH, 0 °C, 12 h; room temp, 2 days	78		
5	$PdCl_2$ (0.1), $CuCl_2$ (3), NaOAc (3), 47 CO in MeOH, 0 °C, 12 h; room temp, 2 days	47	33[b]	

[a] Figures in parentheses refer to the equivalents of reagents to **1d**. CO (1 atm). [b] Based on 65% conversion.

Results and Discussion

In pursuit of a convenient and general method for the synthesis of physiologically important β,γ- and β,δ-diamino- and aminohydroxy acids,[5] we examined aminocyclization of ureas **1** and **7** and carbamates **2** and **8** (eq 1 and 4). Because of many precedents, we had no doubt about the success in the palladium(2+)-catalyzed aminocyclization of carbamates **2** and **8**. However, unfortunately, carbamates **2** and **8** did not undergo the expected cyclization despite our extensive study on the reaction conditions. These carbamates either were unreactive or gave intractable mixtures of products. On the other hand, the corresponding ureas **1** and **7**, very fortunately, did undergo the cyclization. For example, *N*-3-butenylurea **1** gave 4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (**3**) in high yield (eq 1). Under certain conditions, either aminochlorination product **6**, noncyclized methoxycarbonylation product **4**, or dimethoxycarbonylation product **5** was obtained as a byproduct (eq 1).

In Table I are summarized the results of experiments undertaken for the optimization of conditions, using *N*-benzyl-*N*-3-butenyl-*N'*-methylurea (**1d**) as a probe. The reaction is usually

(1) (a) Bäckvall, J.-E. *Acc. Chem. Res.* **1983**, *16*, 335. (b) Hegedus, L. S. *Tetrahedron* **1984**, *40*, 2415. (c) Parker, K. A.; O'Fee, R. P. *J. Org. Chem.* **1983**, *48*, 1547. (d) Hegedus, L. S.; Åkermark, B.; Zetterberg, K.; Olsson, L. F. *J. Am. Chem. Soc.* **1984**, *106*, 7122. (e) Åkermark, B.; Zetterberg, K. *Ibid.* **1984**, *106*, 5560. (f) Hegedus, L. S.; Mulhern, T. A.; Asada, H. *Ibid.* 1986, *108*, 6224.

(2) Palladium(2+)-catalyzed nonoxidative pyrrole synthesis from 1-amino-3-alkyn-2-ol: (a) Utimoto, K.; Miwa, H.; Nozaki, H. *Tetrahedron Lett.* **1981**, *22*, 4277. Apparent Pd(2+)-catalyzed oxidative cyclization of unsaturated amines to cyclic imines: (b) Pugin, B.; Venanzi, L. M. *J. Am. Chem. Soc.* **1983**, *105*, 6877.

(3) (a) Hegedus, L. S.; Allen, G. F.; Bozell, J. J.; Waterman, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 5800. (b) Hegedus, L. S.; Allen, G. F.; Olsen, D. J. *Ibid.* **1980**, *102*, 3583.

(4) (a) Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 2444. (b) Danishefsky, S.; Taniyama, E. *Tetrahedron Lett.* **1983**, *24*, 15. (c) Larock, R. C.; Liu, C.-L.; Lau, H. H.; Varaprath, S. *Ibid.* **1984**, *25*, 4459. (d) Tamaru, Y.; Kobayashi, T.; Kawamura, S.; Ochiai, H.; Yoshida, Z. *Ibid.* **1985**, *26*, 4479. (e) Tamaru, Y.; Hojo, M.; Kawamura, S.; Yoshida, Z. *J. Org. Chem.* **1986**, *51*, 4089. (f) Lathbury, D.; Vernon, P.; Gallagher, T. *Tetrahedron Lett.* **1986**, *27*, 6009.

(5) (a) Hirama, M.; Shigemoto, T.; Yamazaki, Y.; Itô, S. *J. Am. Chem. Soc.* **1985**, *107*, 1797; (b) *Tetrahedron Lett.* **1985**, *26*, 4133. (c) Arrowsmith, R. J.; Carter, K.; Dann, J. G.; Davies, D. E.; Harris, C. J.; Morton, J. A.; Lister, P.; Robinson, J. A.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1986**, 755.

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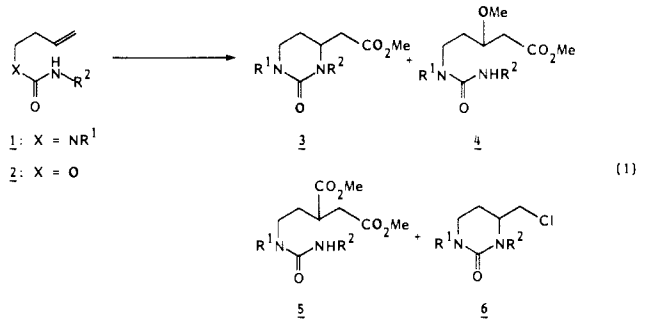
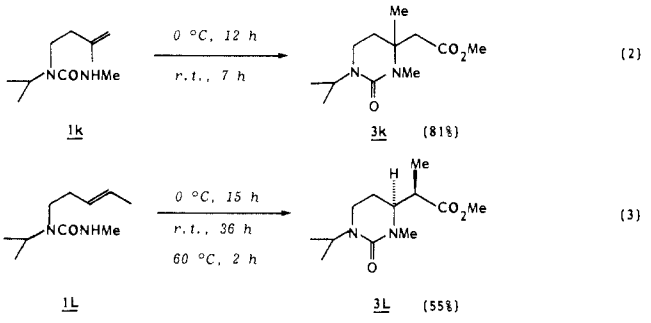


performed under 1 atm of carbon monoxide (a balloon) in methanol in the presence of $PdCl_2$ (0.1 equiv) and $CuCl_2$ (3.0 equiv). The reaction proceeds smoothly at ambient temperature and provides the expected product **3d** (82%) together with a considerable amount of aminochlorination product **6d** (14%) (entry 1 in Table I). Only **6d** was obtained in the absence of carbon monoxide (entry 2).[6] Under basic conditions (entry 5), the formation of **6d** was completely eliminated; however, in this case a new type of product, noncyclized dimethoxycarbonylation product **5d**,[7] was formed in an amount almost equal to **3d**. For the selective formation of **3d**, a temperature control was found to be most effective (entry 3); when the reaction was carried out at 0 °C for 12 h and then at ambient temperature for several hours, **3d** could be obtained selectively. Monitoring the reaction by TLC revealed that when the reaction was conducted at an ambient temperature (entry 1), **6d** was first formed and then **3d** began to accumulate without an appreciable increase in the amount of **6d**. This observation suggests some changes of catalytic species during the course of the reaction. At 0 °C, a catalytic species responsible for aminocarbonylation may be formed without yielding aminochlorination product **6d**. The reaction using $PdCl_2$ in as small an amount as 0.01 equiv selectively provides **3d** in respectable yield by conducting the reaction at 0 °C for the same period of time as the reaction using 0.1 equiv of $PdCl_2$ and then for a longer period of time at room temperature for the completion of the reaction (entries 3 and 4). Although, for the reactive substrates, it may be possible to bring the reaction to completion by the use of 0.01 equiv of $PdCl_2$ as a catalyst, we applied the conditions shown in entry 3 as the optimized one in order to keep the uniformity.

The ease of the cyclization reaction (1) is highly dependent on the steric and electronic effects of the substituents on the nitrogen atoms of urea. Results are summarized in Table II. With substituent R^2 = Me (invariable), the yields gradually increase as the steric bulk of the R^1 substituents (entries 1–4) increase and drops when R^1 becomes a group as large as *tert*-butyl (entry 5). When R^1 = H, no cyclization product was obtained. Instead, methoxycarbonylation product **4a** was obtained as the sole identified product. A similar trend, but to a lesser extent, can be seen with respect to the variation of steric bulk of R^2 (entries 3 vs 7).

The effect of substituents on the ease of cyclization may be rationalized as follows. Owing to a strong conjugation of the lone-pair electrons on the nitrogen atom with the carbonyl, the rotational barrier around C_{sp^2}–N bonds of urea is rather high and urea generally favors a conformation with a planar structure.[8] Hence, for unsymmetrically substituted ureas like **1**, four kinds of stable rotational conformers are possible. The substituents R^1 and R^2 with moderate steric bulk may cooperate to increase the population of the conformer shown after **1**, relative to the other three conformers. The cyclization is only possible through this conformer. Phenyl group seriously retards the reaction, probably owing to its electron-withdrawing nature (entries 6 and 8). When ureas are unreactive, methoxycarbonylation occurs over cyclization (entries 1 and 8).

Reaction 1 is noteworthy in the following three points: The first is the behavior of urea as a specific nitrogen nucleophile. This is quite important, as urea is known as a typical ambident nucleophile and generally serves as the oxygen nucleophile toward alkylating agents.[8] The specific reaction at the nitrogen atom may be rationalized by assuming that the olefin activated by the coordination with Pd(2+) acts as a soft electrophile.[9] The second is the ring size formed in this cyclization. As compared with other nucleophiles (e.g., hydroxyl[10] and carboxyl),[11] the reactivity of amides is such that we sometimes experience difficulties in the cyclization reactions forming six-membered nitrogen heterocycles.[4a,12] This difficulty may partly be ascribed to the larger loss of entropy in the cyclization, as compared with the cyclization forming five-membered rings. The examples listed in Table II (and eq 2, 3, and 6 (n = 2), vide infra) clearly indicate the utility of the present ureidocarbonylation for the synthesis of six-membered nitrogen heterocycles. Finally and most importantly, the present ureidocarbonylation tolerates substitution on olefins. Two examples are shown in eq 2 and 3. It is frequently pointed out



that substitution on olefin seriously deteriorates the palladium(2+)-assisted cyclization. Two main factors seems to contribute to this: One is the decrease of stability of an olefin–palladium complex as the substitution on the olefin increases.[14] Another factor is an inhibition of an approach of a nucleophile to the sterically crowded electrophilic center. As compared with entry 3 (Table II), reaction 2 clearly indicates that the 3-methyl group of **1k** has nothing to do with the reactivity. On the other hand, the 4-methyl group of **1L** appreciably retards the reaction (reaction 3). The product **3l** was isolated as a single stereoisomer, and the structure was tentatively assigned as 4*S*′,1′*R*′ on the basis of trans aminocarbonylation to the olefin (vide infra).

The last two examples in Table II were examined to clarify the possibility of a chiral induction on the cyclization using chiral ureas (**1i** and **1j**). Unfortunately, however, the diastereoselectivity was only moderate (diastereomeric excess ca. 50%). Owing to the importance of developing new synthetic methods of chiral amino acids, the strategy along this line is the subject of further study.

(6) (a) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5538. (b) Tamaru, Y.; Hojo, M.; Higashimura, H.; Yoshida, Z. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 735.

(7) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810.

(8) (a) Hegarty, A. F. "Derivative of Carbon Dioxide". In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon: New York, 1979; Vol. 2. The N vs O ambident reactivity of amide derivatives is very controversial owing to its synthetic importance: (b) Hirama, M.; Iwashita, M.; Yamazaki, Y.; Itô, S. *Tetrahedron Lett.* **1984**, *25*, 4963. (c) Knapp, S.; Rodriques, K. E.; Levorse, A. T.; Ornaf, R. M. *Ibid.* **1985**, *26*, 1803. (d) Krook, M. A.; Miller, M. J. *J. Org. Chem.* **1985**, *50*, 1126. (e) Toshimitsu, A.; Terao, K.; Uemura, S. *Ibid.* **1987**, *52*, 2018.

(9) Ho, T.-L. *Hard and Soft Acids and Bases Principle in Organic Chemistry*; Academic: New York, 1977.

(10) (a) Semmelhack, M. F.; Bodurow, C. *J. Am. Chem. Soc.* **1984**, *106*, 1496. (b) Semmelhack, M. F.; Bodurow, C.; Baum, M. *Tetrahedron Lett.* **1984**, *25*, 3171. (c) Tamaru, Y.; Kobayashi, T.; Kawamura, S.; Ochiai, H.; Hojo, M.; Yoshida, Z. *Ibid.* **1985**, *26*, 3207. (d) Walkup, R. D.; Park, G. *Ibid.* **1987**, *28*, 1023.

(11) (a) Kasahara, A.; Izumi, T.; Sato, K.; Maemura, M.; Hayasaka, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1899. (b) Korte, D. E.; Hegedus, L. S.; Wirth, R. K. *J. Org. Chem.* **1977**, *42*, 1329.

(12) For example, N-protected (tosylamide, carbamate) 3-hydroxy-4-pentenylamines undergo an iodoamination by treatment with I_2 (ether–H_2O–$NaHCO_3$) to provide *cis*-2-(iodomethyl)-3-hydroxypyrrolidines in high yields,[13] while N-protected 4-hydroxy-5-hexenylamines would not undergo the similar cyclization under the similar of enforcing conditions.

(13) Tamaru, Y.; Kawamura, S.; Tanaka, K.; Yoshida, Z. *Tetrahedron Lett.* **1984**, *25*, 1063.

(14) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Wiley: New York, 1973; p 377.

Table II. Palladium(2+)-Catalyzed Intramolecular Aminocarbonylation of *N*-3-Butenylurea **1**

entry	urea **1** no.	R^1	R^2	conditions[a]	% isolated yield (% conversion)[b]	diastereomer ratio of **3**
1	**1a**	H	Me	A	**3a**: 0. **4a**: 21	
2	**1b**	Me	Me	A	**3b**: 58	
3	**1c**	*i*-Pr	Me	A	**3c**: 82	
4	**1d**	CH_2Ph	Me	A	**3d**: 82	
5	**1e**	*t*-Bu	Me	A	**3e**: 47	
6	**1f**	Ph	Me	A	**3f**: 58 (87)	
7	**1g**	*i*-Pr	*i*-Pr	A	**3g**: 84	
8	**1h**	Ph	Ph	A	**3h**: 35. **4h**: 6 (44)	
9	**1i**	*i*-Pr	CH(Me)Ph	B	**3i**: 75 (83)	78:22
10	**1j**	*i*-Pr	CH(Me)-α-naphthyl	B	**3j**: 50 (91)	75:25

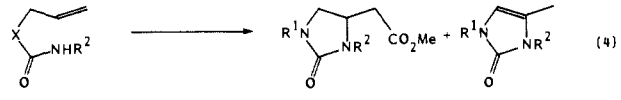
[a] **1** (1.0 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3.0 mmol), under 1 atm of CO in 5 mL of methanol. Key: A, 0 °C for 12 h and then room temperature for 2 h; B, 0 °C for 3 days and then room temperature for 2 h. [b] Yields are for the purified products, based on conversions. Unless otherwise specified, conversion is 100%.

Table III. Palladium(2+)-Catalyzed Intramolecular Aminocarbonylation of *N*-2-Propenylurea **7**

entry	urea **7** no.	R^1	R^2	conditions[a]	% isolated yield
1	**7a**	CH_2Ph	Me	C	**9a**: 61. **10a**: 18
2	**7a**	CH_2Ph	Me	D	**9a**: 92
3	**7b**	*i*-Pr	*i*-Pr	C	**9b**: 61. **10b**: 18
4	**7b**	*i*-Pr	*i*-Pr	D	**9b**: 85
5	**7c**	Me	Me	D	**9c**: 66
6	**7d**	*i*-Pr	CH(Me)Ph	E	**9d**: 56 [67:33][b]

[a] **7** (1.0 mmol), $PdCl_2$ (0.1 mmol), $CuCl_2$ (3.0 mmol) under 1 atm of CO in 5 mL of methanol. Key: C, 0 °C for 12 h and then room temperature for 3 h; D, 0 °C for 24 h and then room temperature for 3 h; E, 0 °C for 4 days and then room temperature for 3 h. [b] Diastereomeric ratio.

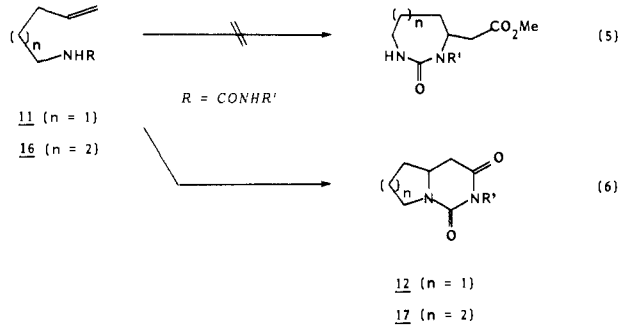
In Table III are summarized the results of ureidocyclization of four kinds of *N*-2-propenylureas **7**. The reaction behavior of **7** is quite similar to that of **1**, except that a presumable intermediate, 4-(palladomethyl)-2-imidazolidinone, is prone to undergo a dehydropalladation (conditions C, entries 1 and 3, Table III). Dehydro-3*H*-imidazol-2-one **10** may be produced after a further isomerization of double bonds (eq 4). This side reaction can be



(4)

completely suppressed by doing the reaction at 0 °C for a long period of time (conditions **D**, entries 2 and 4), and the yield of 4-[(methoxycarbonyl)methyl]-2-imidazolidinone **9** was greatly improved. Again in this case, the diastereoselectivity was only moderate (entry 6, de ≈ 30%).

Next, we examined *N*-4-pentenylurea (**11**, R = CONHR′) and *N*-5-hexenylurea (**16**, R = CONHR′) in the expectation that these ureas might cyclize to form seven- and eight-membered nitrogen heterocycles, respectively (eq 5). However, this was not the case,



(5)

(6)

and bicyclic 5,6-dihydrouracil derivatives **12** and **17** were obtained from **11** and **16**, respectively, in high yields (eq 6). These results indicate that the both nitrogen atoms of urea served as specific nitrogen nucleophiles. The products **12** and **17** may be derived by a sequential aminopalladation of the olefin with the internal nitrogen atom and an insertion of CO into the Pd–C bond, followed by an acylation of the terminal nitrogen atom. A similar acylation of urea at the nitrogen atom with a presumable acylpalladium intermediate was reported by Fuchikami et al.[15]

The present aminopalladation is reminiscent of the palladium-mediated or -catalyzed amination of *o*-allylanilines and N-protected unsaturated amines developed by Hegedus et al.[3,4] Successful application of this method seems to be generally confined to the formation of five-membered nitrogen heterocycles from the terminal nonsubstituted olefins. In this context, the ready formation of **17**, containing a six-membered bicyclic [4.4.0] system is quite surprising and suggests the high versatility of urea toward aminopalladation reaction. Accordingly, we extensively studied the reactivity of urea in comparison with the other common amino nucleophiles (carbamate, tosylamide, benzamide), varying the ring sizes of products and substitution patterns on the olefins. We also examined the solvent effects on this cyclization. Results are summarized in Table IV.

As for the solvent effects on conversions and yields, aprotic solvents, such as tetrahydrofuran and dichloromethane, are inferior to protic solvents (cf. entries 1–4 and 7 vs 8). In almost all cases, acetic acid containing 3 equiv of sodium acetate gave the most satisfactory results (entries 15 vs 16, 19 vs 20, 31 vs 32, and 33 vs 34). For example, the cyclization of **11a** takes 3 days for completion of the reaction in tetrahydrofuran or in dichloromethane, while only 1 day is required when conducted in methanol or acetic acid–NaOAc (entries 1–4). The yield of **12a** increases in the order dichloromethane (33%), tetrahydrofuran (72%), and methanol (79%) and finally becomes quantitative (acetic acid–NaOAc, 95%). Very contrasting results were observed for the cyclization of **11d** (R = CONHMe, entries 19 and 20). In methanol, no reaction took place and the starting material was completely recovered. In acetic acid–NaOAc, on the other hand, the cyclization product **12d** (R^1 = Me) was produced in 69% isolated yield based on 77% conversion.

It is premature to discuss the reason for the superiority of protic solvents to aprotic solvents for the present cyclization. However, we feel that protic solvents work in at least two ways to accelerate the reaction. One is a solvation of chloride ion of $PdCl_2$ by hydrogen bonding, which results in exposure of Pd(2+) for the coordination to the olefin. Another is a protonation of the amino nucleophiles, which might render the coordination of the amino nucleophiles to Pd(2+) weak.

As for the reactivity of amino nucleophiles toward the intramolecular aminopalladation reaction, urea was found to be most reactive, and carbamate was more reactive than tosylamide. Benzamide was by far the least reactive. Interestingly, the relative reactivity of carbamate to tosylamide seems to be the reverse of

(15) Pd(0)-catalyzed synthesis of uracils: (a) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1982**, *23*, 4099. (b) Kasahara, A.; Fukuda, N. *Chem. Ind. (London)* **1976**, 485.

the previously reported reactivity order.[4f,13] This trend may be clearly seen in the comparisons of entries 11–16 and entries 25–27. In both series of experiments (entries 11–16 and 25–27), the ratios of the aminocarbonylation products to the protioamination products (**12** or **13** to **14**) or to the methoxycarbonylation products (**17** or **18** to **19**) systematically decrease in the order urea > carbamate > tosylamide > benzamide. Urea **11c** (R = CONHMe) provides the aminocarbonylation product **12c** (R′ = Me) exclusively (entry 15), while the corresponding benzamide **11c** (R = COPh) only yielded a noncyclization product, *N*-benzoyl-2,2,4-trimethyl-4-methoxypentylamine (100% based on 44% conversion, entry 11). Tosylamide **11c** (R = SO_2Tol) and carbamate **11c** (CO_2Me) are the intermediates of these two extremes and provide mixtures of the aminocarbonylation products **13c** and the protioamination products **14c** (entries 12 and 13).

The mechanism for the formation of the protioamination product **14c** is not clear at present. However, the reaction course involving aminopalladation followed by the protonolysis of the Pd–C bond of the thus formed 2-(palladomethyl)pyrrolidine intermediate may be eliminated on the basis of the following observations: As compared with the results in entry 13, when the aminocarbonylation of **11c** (R = CO_2Me) was carried out under 45 atm of CO, **14c** (R = CO_2Me) was formed in an increased amount at the expense of **13c** (R = CO_2Me).

The results in entries 8–10 clearly indicate that the ease of the first cyclization forming the pyrrolidine ring is independent of the electronic nature of the substituents on the terminal nitrogen atom, while the second cyclization forming the dihydrouracil ring is subject to suppression by the electron-withdrawing substituents (see also entries 20 and 21).

The aminocarbonylation forming five-membered rings proceeds much more smoothly than that forming six-membered rings. To our surprise, under our reaction conditions not only urea but also carbamate and tosylamide undergo cyclization to give six-membered nitrogen heterocycles, the latter two being in marginal success (entries 25 and 26). In light of the previously reported failure of cyclization of similar substrates (mostly undertaken in tetrahydrofuran),[4a] these reactions may partly owe their success to the change of solvents (vide supra). The results in entries 31–34 indicate that the cyclization forming six-membered nitrogen heterocycles is general for a wide structural variety of substrates.

In Table IV are also listed the results for the cyclization of the unsaturated amines with methyl substituents on the double bonds (**11c–e**, **16b**). Among these, especially rewarding is the cyclization of terminally methyl substituted **11d** and **11e**. The cyclization is stereospecific. From the trans isomers **11d** (R = CONHMe, CONHPh) were obtained the 5*R*′,6*S*′ isomers **12d**, and from the cis isomers **11e** (R = CONHMe, CONHPh) were obtained the 5*S*′,6*S*′ isomers **12e**, specifically. The structures of **12d** and **12e** were determined on the basis of the coupling constants in their ^1H NMR spectra [**12d** (R′ = Me), $^3J_{H(5)H(6)}$ = 3.7 Hz; **12e** (R′ = Me), $^3J_{H(5)H(6)}$ = 12.2 Hz] and the complete isomerization of **12d** to **12e** under a base-catalyzed equilibration (catalyst KO-*t*-Bu in THF at room temperature for 3 days). This stereochemical outcome clearly indicates that the aminopalladation and hence the aminocarbonylation specifically take place in a fashion trans to the double bonds, as an insertion of carbon monoxide into a Pd–C bond proceeds with retention of configuration.[16] The stereochemical integrity of the starting materials (**11d** and **11e**, R = CONHMe) was found to be intact, when these ureas were recovered at 77% and 80% conversions, respectively. The structures of both diastereomers (**13d**, **13e**), obtained from **11d** and **11e** (R = CO_2Me), respectively, were tentatively assigned on the basis of the trans aminocarbonylation. The 2*S*′,1′*R*′ structure of **15e** (R = CONHMe, CONHPh), obtained as a single diastereomer, was based on the trans aminopalladation followed by an inversion of configuration of an oxidative cleavage of the Pd–C bond with $CuCl_2$.[17]

The limitation of the present aminocarbonylation may be seen in the results of entries 28–30. In these reactions, the starting materials were quantitatively recovered.

Experimental Section

Melting points were determined in capillary tubes with a Büchi apparatus and were not corrected. Unless otherwise specified, short-path (bulb-to-bulb) distillations were carried out in a Kugelrohr apparatus. Microanalyses were performed by the Microanalysis Center of Kyoto University. Analyses agreed with the calculated values within 0.3%. Infrared spectra were measured with a Hitachi Model EPI-63 grating spectrophotometer. Proton magnetic resonance spectra were determined either at 60 MHz on a JEOL JNM-PMX60 instrument, at 90 MHz on a JEOL FX90Q instrument, or at 400 MHz on a JEOL GX400 instrument with tetramethylsilane as an internal standard. ^{13}C NMR spectra were determined at 22.4 MHz on a JEOL FX90Q instrument with tetramethylsilane as an internal standard. Mass spectra were measured on a JEOL D-300 instrument (high-resolution mass spectrophotometer).

Solvents and Reagents. Unless otherwise specified, the following solvents and reagents (reagent grade) were used without further purification: acetic acid, methanol, diethyl ether, sodium acetate, palladium chloride, cupric chloride, carbon monoxide, methyl isocyanate, phenyl isocyanate, benzyl isocyanate, (*R*)-(+)-α-methylbenzyl isocyanate (Aldrich), 1-(1-naphthyl)ethyl isocyanate (Aldrich), allyl bromide, 3-butenyl bromide, primary amines. Tetrahydrofuran and diethyl ether were dried and distilled from benzophenone and sodium immediately prior to use under a nitrogen atmosphere. Dichloromethane, acetonitrile, and isobutyronitrile were distilled over CaH_2 under nitrogen.

General Procedure for the Preparation of *N*-2-Propenylurea 7 and *N*-3-Butenylurea 1. 2-Propenyl bromide, 3-butenyl bromide, 3-methyl-3-butenyl iodide (prepared from commercially available 3-methyl-3-buten-1-ol via tosylation (TsCl–pyridine at 0 °C in dichloromethane)[18] and an iodide–tosylate exchange (2 equiv of NaI in acetone at 56 °C), or *trans*-3-pentenyl bromide[19] was added in large excess of an appropriate primary amine (20 equiv) at 0 °C. After completion of addition, an ice bath was removed, and the mixture was stirred at room temperature for 1 day. After distillation of an excess of primary amine through a Vigreux column, aqueous 50% NaOH was added. The mixture was extracted with ether (3×). After the ether extracts were dried over $MgSO_4$ and the solvent was evaporated, the residue was distilled to provide a secondary amine (80–90% yields). Into the thus obtained secondary amine dissolved in dry ether (0.5 M) was added an equal amount of isocyanate with stirring at 0 °C. After the mixture was stirred for 3 h at 0 °C, the solvent was evaporated and the residue was purified either by distillation under reduced pressure or by column chromatography over silica gel (benzene–EtOAc, EtOAc, EtOAc–acetone, or EtOAc–EtOH); 95–100% yields.

***N*-3-Butenyl-*N*′-methylurea (1a).** Into an argon-purged solution of 3-buten-1-ol (720 mg, 10 mmol) and triphenylphosphine (2.88 g, 11 mmol) in 15 mL of dry THF containing a suspension of phthalimide (1.62 g, 11 mmol) was slowly added diethyl azodicarboxylate (DEAD; 1.91 g, 11 mmol) with stirring in an ice bath. The reaction mixture becomes homogeneous after completion of DEAD addition. After being stirred for 3 h at 0 °C, the mixture was diluted with *n*-hexane and filtered. The filtrate was washed with 1 N HCl and then was saturated $NaHCO_3$. The crude *N*-3-butenylphthalimide, obtained by evaporation of the solvents after drying over $MgSO_4$, was converted to 3-butenylamine hydrochloride according to the procedure reported by L. I. Smith.[20] Crude yield is 98%. Into a solution of the thus formed crude 3-butenylamine hydrochloride (ca. 10 mmol) and triethylamine (20 mmol) in dry THF (20 mL) was added methyl isocyanate (10 mmol) at 0 °C, and the mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was dissolved in ether and washed with 1 N HCl (15 mL + 2 mL) and then with saturated $NaHCO_3$. After being dried over $MgSO_4$ and the solvent evaporated, the residue was purified by column chromatography over silica gel (EtOAc–acetone gradient) to provide **1a** in 83% overall yield: IR (neat film) 3350 (s), 1630 (s), 1590 (s), 1280 (m), 1250 (m), 905 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (br q, *J* = 6.6 Hz, 2 H), 4.4 (br s, 1 H), 5.1–5.3 (m, 2 H), 5.7–6.1 (m, 1 H).

General Procedure for the Preparation of *N*-4-Pentenylurea 11 and *N*-5-Hexenylurea 16. α-Lithioacetonitrile, generated by addition of *n*-BuLi (21 mmol, 1.6 M hexane solution) into a solution of acetonitrile (20 mmol) in 30 mL of dry THF at −78 °C followed by stirring at −78

(16) Stille, J. K.; Divakaruni, R. *J. Am. Chem. Soc.* **1978**, *100*, 1303.
(17) (a) Bäckvall, J.-E. *Tetrahedron Lett.* **1977**, 467. (b) Bäckvall, J.-E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393.
(18) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967; Vol. 1, p 1180.
(19) Crombie, L.; Harper, S. H. *J. Chem. Soc.* **1950**, 1714.
(20) Smith, L. I.; Emerson, O. H. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 151.

Table IV. Palladium(2+)-Catalyzed Aminocarbonylation of N-Protected 4-Pentenylamines and 5-Hexenylamines

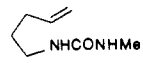
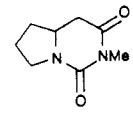
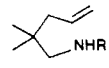
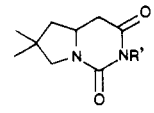
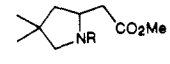
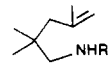
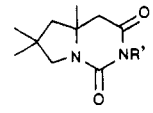
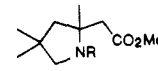
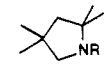
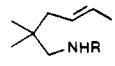
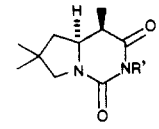
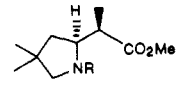
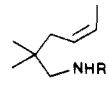
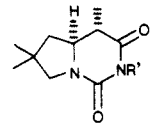
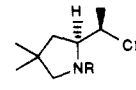
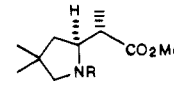
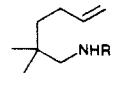
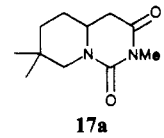
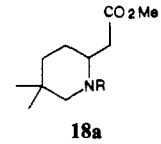
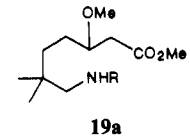
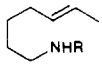
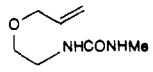
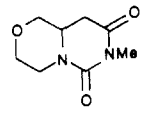
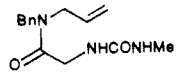
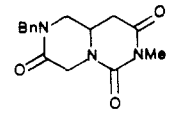
entry	substrate	conditions:[a] solvent (day)	% isolated yields of products[b]		
	 **11a**		 **12a**		
1		CH_2Cl_2 (3)	33		
2		THF (3)	72		
3		MeOH (1)	79		
4		AcOH (1)	95		
	 **11b**		 **12b**	 **13b**	
5	R = SO_2Tol	MeOH (1)		97	
6	R = CO_2Me	MeOH (1)		92	
7	R = CONHMe	CH_2Cl_2 (1)	66		
8	R = CONHMe	MeOH (1)	95		
9	R = $CONHCH_2Ph$	MeOH (1)	69	28	
10	R = CONHPh	MeOH (1)	29	51	
	 **11c**		 **12c**	 **13c**	 **14c**
11	R = COPh	MeOH (2)		e	
12	R = SO_2Tol	MeOH (2)		60	38
13	R = CO_2Me	MeOH (2)		59	25
14	R = CO_2Me	MeOH (2)[c]		32	49
15	R = CONHMe	MeOH (2)	77 (84)		
16	R = CONHMe	AcOH (2)	99		
	 **11d**		 **12d**	 **13d**	
17	R = SO_2Tol	MeOH (2)		79 (43)	
18	R = CO_2Me	MeOH (1)		63	
19	R = CONHMe	MeOH (2)	no reaction		
20	R = CONHMe	AcOH (2)	69 (77)		
21	R = CONHPh	AcOH (2)	61 (57)		
	 **11e**		 **12e**	 **15e**	 **13e**
22	R = CO_2Me	MeOH (2)[d]			73 (55)
23	R = CONHMe	AcOH (2)[d]	34	43	
24	R = CONHPh	AcOH (2)[d]	48	29	
	 **16a**		 **17a**	 **18a**	 **19a**
25	R = SO_2Tol	MeOH (3)		58	30
26	R = CO_2Me	MeOH (3)		77	16
27	R = CONHMe	MeOH (2)	81		
	 **16b**				
28	R = SO_2Tol	MeOH (2)	no reaction		
29	R = CO_2Me	MeOH (2)	no reaction		
30	R = CONHMe	AcOH (2)	no reaction		

Table IV (Continued)

entry	substrate	conditions:[a] solvent (day)	% isolated yields of products[b]
	 **16c**		 **17c**
31		MeOH (2)	26
32		AcOH (2)	95 (70)
	 **16d**		 **17d**
33		MeOH (2)	48
34		AcOH (2)	71

[a] $PdCl_2$ (0.1 mmol), $CuCl_2$ (3.0 mmol), and CO (1 atm, a rubber balloon) in 5 mL of the solvent indicated for 1.0 mmol of substrate at room temperature for the period of time shown in parentheses. The reaction in AcOH contains NaOAc (3.0 mmol). [b] Yields are for the purified products. The figures in parentheses refer to conversions. Unless otherwise noted, the conversion is 100%. [c] This reaction was done under 45 atm of CO. [d] A mixture of **11e** and **11d** (80:20) was used. The yields and the structures were indicated for the products derived from **11e**. [e] An addition product of methanol (*N*-benzoyl-2,2,4-trimethyl-4-methoxyamine) was isolated in 100% yield (44% conversion).

°C for 2 h, was alkylated by treatment with allyl bromide (21 mmol at −78 °C for 2 h) or *trans*-3-pentenyl bromide[19] (21 mmol at −78 °C for 2 h and then at room temperature overnight). α-Lithioisobutyronitrile, generated by addition of isobutyronitrile (20 mmol) into a solution of lithium diisopropylamide (21 mmol) in THF–benzene (30–13 mL) at 0 °C followed by stirring at 0 °C for 2 h, was alkylated by treatment with allyl bromide (21 mmol at 0 °C for 3 h), 2-methyl-2-propenyl bromide (21 mmol at 0 °C for 3 h), 3-butenyl bromide (21 mmol at 0 °C for 3 h and then at room temperature overnight), *trans*-2-butenyl tosylate (at 0 °C for 3 h and then at room temperature overnight), or 2-butynyl tosylate (21 mmol at −78 °C for 3 h and then at room temperature overnight). *trans*-2-Butenyl tosylate and 2-butynyl tosylate were prepared in situ by treatment of these alcohols (0.5 M THF solution) with an equal amount of *n*-BuLi (1.6 M hexane solution) and then with an equal amount of tosyl chloride under argon all through at −78 °C. Generally a bromide was added to a solution of an lithiated nitrile, and a solution of lithiated nitrile was added to a solution of a tosylate-containing suspension of LiCl. 5-Cyano-5-methyl-2-hexyne (10 mmol, 1.21 g) was hydrogenated to give a mixture of *cis*- and *trans*-5-cyano-5-methyl-2-hexene (8:2, 97% yield) in 5 mL of dry methanol in the presence of Lindler catalyst (90 mg)[21] under 1 atm of H_2 at room temperature (240-mL uptake of H_2). The thus prepared unsaturated nitriles were purified by distillation under reduced pressure (80–90% yields). An unsaturated nitrile (10 mmol) was added under nitrogen to a suspension of $LiAlH_4$ (0.76 g, 20 mmol) in 40 mL of ether at room temperature with stirring. The mixture was stirred, refluxed for 2 h, and then cooled in an ice bath. A mixture of THF–water (5:1, v/v, 4.6 mL) and then 15% aqueous NaOH was added dropwise into the reaction mixture with vigorous stirring and cooling. After filtration of a dry granular precipitate and washing with THF, the filtrate was condensed to leave a colorless oil, which was purified by distillation; 85–90% yields. Into a solution of an amine in dry ether (0.5 M) was added an equal amount of isocyanate with stirring at 0 °C. After the mixture was stirred for 3 h at 0 °C, ether was evaporated and the residue was purified by means of column chromatography over silica gel (benzene–EtOAc, EtOAc, EtOAc–acetone, or EtOAc–EtOH); 95–100% yields.

***N*-(*trans*-2,2-Dimethyl-4-hexenyl)-*N'*-methylurea 11d**: oil; IR (neat film) 3350 (s), 1635 (s), 1575 (s), 1260 (m), 965 (m), 755 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 60 °C) δ 0.85 (s, 6 H), 1.66 (br d, J = 5.0 Hz, 3 H), 1.77–1.95 (m, 2 H), 2.76 (d, J = 5.2 Hz, 3 H), 2.79 (d, J = 6.1 Hz, 2 H), 4.68 (br s, 2 H), 5.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 17.5, 24.7, 26.8, 34.7, 43.1, 50.3, 127.3, 127.4, 159.9.

***N*-(*cis*-2,2-Dimethyl-4-hexenyl)-*N'*-methylurea 11e**: oil; IR (neat film) 3350 (s), 1640 (s), 1580 (s), 1260 (s), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$ at 60 °C) δ 0.88 (s, 6 H), 1.59 (d, J = 5.1 Hz, 3 H), 1.96 (d, J = 6.6 Hz, 2 H), 2.75 (d, J = 4.9 Hz, 3 H), 3.01 (d, J = 6.1 Hz, 2 H), 4.8 (br s, 1 H), 5.3–5.7 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.6, 24.6, 26.7, 36.7, 43.0, 50.2, 125.6, 126.4, 159.9.

***N*-[2-(Allyloxy)ethyl]-*N'*-methylurea (16c)**. 2-(Allyloxy)ethylamine, prepared according to the method reported by A. I. Meyers et al.,[22] was treated with methyl isocyanate according to the procedure described above to give **16c** in quantitative yield after column chromatography over silica gel (EtOAc–acetone gradient): IR (neat film) 3320 (s), 1630 (s), 1570 (s), 1260 (s), 1100 (s), 925 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.75 (d, J = 4.9 Hz, 1 H), 3.3–3.6 (m, 4 H), 3.99 (dt, J = 5.4, 1.2 Hz, 2 H), 4.09–5.37 (m, 2 H), 5.91 (ddt, J = 14.7, 10.0, 5.4 Hz, 1 H).

***N*-[2-(*N*-Benzyl-*N*-allylamino)-2-oxoethyl]-*N'*-methylurea (16d)**. A mixture of benzylallylamine (2.94 g, 20 mmol) and triethylamine (4.04 g, 40 mmol) was added into a solution of chloroacetyl chloride (4.52 g, 40 mmol) in 20 mL of benzene at 0 °C under nitrogen. After the mixture was stirred at room temperature, benzene and the excess chloroacetyl chloride were removed by distillation at room temperature under reduced pressure, and the residue was washed with ether. After evaporation of ether, the residue was dissolved in dry methanol (50 mL) containing an excess of ammonia and kept for 2 days at room temperature. After evaporation of methanol, the residue was dissolved in ether and washed with 2 mL of saturated Na_2CO_3. The ether extract was dried over $MgSO_4$ and condensed to 50 mL. Into this mixture was added methyl isocyanate (20 mmol) at 0 °C, and the mixture was stirred overnight at room temperature. Evaporation of the solvent gave a sticky oil, which was subjected to column chromatography over silica gel (EtOAc–acetone gradient) to give **16d** in 56% overall yield: IR (neat film) 3350 (s), 1630 (s), 1570 (s), 1220 (s), 925 (m), 735 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.71 (br s, 3 H), 3.84, 4.01 (br d, J = 5.4 Hz, 2 H, $CH_2CH{=}CH_2$), 4.17 (br s, 2 H), 4.50, 4.60 (s, 2 H, CH_2Ph), 4.9–5.2 (m, 3 H, including NH), 5.45–5.9 (m, 2 H, including NH), 7.27 (m, 5 H).

General Procedure for the Palladium(2+)-Catalyzed Aminocarbonylation of Unsaturated Urea, Carbamate, and Tosylamide (1, 7, 11, 16). A 10-mL two-necked round-bottom flask, containing a magnetic stirring bar, $PdCl_2$ (17.6 mg, 0.1 mmol), and $CuCl_2$ (400 mg, 3 mmol), was fitted with a serum cap and a reflux condenser equipped at the top with a three-way stopcock connected to a balloon filled with carbon monoxide. For the reaction in acetic acid, sodium acetate (249 mg, 3 mmol) was also placed in the flask. The apparatus was purged with carbon monoxide by repeating a pumping–filling several times via a three-way stopcock. An unsaturated amide (**1**, **7**, **11**, **16**; 1 mmol) dissolved in a given solvent (5 mL) was introduced to the flask via syringe, and the mixture was stirred at the temperature and for the period of time indicated in Tables I–IV. After evaporation of the solvent to dryness, ethyl acetate was added and the mixture was filtered with suction through a Celite pad on a medium fritted funnel. The filter cake was washed several times with ethyl acetate, and the filtrate was washed with saturated $NaHCO_3$. After being dried over $MgSO_4$ and the solvent evaporated, the residue was subjected to purification by column chromatography over silica gel [e.g., **3k**; ethyl acetate, **5d**, **6d**; hexane–ethyl acetate, 1:2 v/v, **9a**, **10a**; hexane–ethyl acetate, 1:2 v/v, **12b**, **13b**; hexane–ethyl acetate, 2:1 v/v **13c**, **14c** (carbamate); hexane–ethyl acetate, 7:1 v/v, **13c**, **14c** (tosylate); hexane–ethyl acetate, 10:1–5:1 v/v, **17a**; ethyl acetate, **18a**, **19a**; hexane–ethyl acetate, 3:1 v/v]. The physical and spectral data of the products are as follows.

(21) Freifelder, M. *Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary*; Wiley: New York, 1978.

(22) Meyers, A. I.; Poindexter, G. S.; Brich, Z. *J. Org. Chem.* **1978**, *43*, 892.

The products listed in Tables I and II and eq 2 and 3 follow:

***N*-[3-Methoxy-4-(methoxycarbonyl)butyl]-*N'*-methylurea (4a: R^1 = H, R^2 = Me)**: IR (neat film) 3360 (s), 1730 (s), 1640 (s), 1570 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.75 (q, J = 6.3 Hz, 2 H), 2.54 (m, 2 H), 2.74 (d, J = 2.9 Hz, 3 H), 3.25 (m, 2 H), 3.29 (s, 3 H), 3.69 (s, 3 H), 3.69 (m, 1 H), 5.12 (br s, 1 H), 5.30 (br s, 1 H); mass spectrum, m/z (relative intensity) 218 (M, 8), 203 (15), 101 (100).

1,3-Dimethyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3b: R^1 = R^2 = Me): IR (neat film) 1730 (s), 1630 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.07 (m, 2 H), 2.48 (dd, J = 8.4, 14.0 Hz, 1 H), 2.64 (dd, J = 5.1, 14.0 Hz, 1 H), 2.93 (s, 6 H), 3.30 (m, 2 H), 3.70 (s, 3 H), 3.77 (m, 1 H); high-resolution mass spectrum for $C_9H_{16}N_2O_3$, calcd 200.11600, found m/z (relative intensity) 200.11380 (M, 25), 127 (100).

1-Isopropyl-3-methyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3c: R^1 = *i*-Pr, R^2 = Me): IR (neat film) 1730 (s), 1620 (s), 1500 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 5.9 Hz, 6 H,), 1.90 (m, 2 H), 2.47 (dd, J = 8.4, 14.3 Hz, 1 H), 2.65 (dd, J = 4.1, 14.3 Hz, 1 H), 2.93 (s, 3 H), 3.12 (m, 2 H), 3.70 (s, 3 H), 3.70 (m, 1 H), 4.71 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.3, 25.6, 34.1, 34.3, 36.8, 44.6, 51.5, 53.0, 154.9, 171.1; high-resolution mass spectrum for $C_{11}H_{20}N_2O_3$, calcd 228.14744, found m/z (relative intensity) 228.14844 (M, 50), 213 (100), 155 (35).

1-Benzyl-3-methyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3d: R^1 = benzyl, R^2 = Me): IR (neat film) 1732 (s), 1630 (s), 1210 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (m, 2 H), 2.48 (dd, J = 9.0, 14.3 Hz, 1 H), 2.66 (dd, J = 4.6, 14.3 Hz, 1 H), 3.00 (s, 3 H), 3.14 (m, 2 H), 3.68 (s, 3 H), 3.78 (m, 1 H), 4.48 (d, J = 14.9 Hz, 1 H), 4.65 (d, J = 14.9 Hz, 1 H), 7.28 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 25.8, 34.1, 37.0, 41.2, 51.2, 53.8, 126.7, 127.6, 128.2, 138.2, 155.5, 170.8; high-resolution mass spectrum for $C_{15}H_{20}N_2O_3$, calcd 276.14732, found m/z (relative intensity) 276.14612 (M, 45), 203 (67), 91 (100).

***N*-[3,4-Bis(methoxycarbonyl)butyl]-*N*-benzyl-*N'*-methylurea (5d: R^1 = benzyl, R^2 = Me)**: IR (neat film) 3350 (s), 1725 (s), 1623 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.82 (m, 2 H), 2.62 (m, 3 H), 2.80 (d, J = 3.5 Hz, 3 H), 3.26 (t, J = 7.9 Hz, 2 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 4.47 (s, 2 H), 4.95 (q, J = 3.5 Hz, 1 H), 7.27 (s, 5 H); high-resolution mass spectrum for $C_{17}H_{24}N_2O_5$, calcd 336.16844, found m/z (relative intensity) 336.16614 (M, 3), 278 (40), 120 (35), 91 (100).

1-Benzyl-3-methyl-4-(chloromethyl)-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (6d: R^1 = benzyl, R^2 = Me): IR (neat film) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.04 (m, 2 H), 3.04 (s, 3 H), 2.97–3.73 (m, 5 H), 4.50 (d, J = 7.0 Hz, 1 H), 4.63 (d, J = 7.0 Hz, 1 H), 7.27 (s, 5 H); high-resolution mass spectrum for $C_{13}H_{17}N_2OCl$, calcd 252.10301, found m/z (relative intensity) 252.10321 (M, 30), 203 (65), 91 (100).

1-*tert*-Butyl-3-methyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3e: R^1 = *t*-Bu, R^2 = Me): IR (neat film) 1730 (s), 1625 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (s, 9 H), 1.88 (m, 2 H), 2.41 (dd, J = 9.0, 15.2 Hz, 1 H), 2.70 (dd, J = 4.9, 15.2 Hz, 1 H), 2.90 (s, 3 H), 3.28 (m, 2 H), 3.69 (s, 3 H), 3.69 (m, 1 H); high-resolution mass spectrum for $C_{12}H_{22}N_2O_3$, calcd 242.16298, found m/z (relative intensity) 242.16218 (M, 5), 228 (10), 227 (100), 113 (25).

1-Phenyl-3-methyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3f: R^1 = Ph, R^2 = Me): IR (neat film) 1730 (s), 1640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.03 (m, 2 H), 2.63 (dd, J = 10.0, 15.7 Hz, 1 H), 2.78 (dd, J = 5.1, 15.7 Hz, 1 H), 3.00 (s, 3 H), 3.72 (s, 3 H), 3.72 (m, 3 H), 7.28 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 26.0, 34.1, 37.1, 44.7, 51.5, 53.6, 125.0, 125.3, 128.3, 143.6, 154.5, 170.9; high-resolution mass spectrum for $C_{14}H_{18}N_2O_3$, calcd 262.1316, found m/z (relative intensity) 262.1289 (M, 55), 189 (100).

1,3-Diisopropyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3g: R^1 = R^2 = *i*-Pr): IR (neat film) 1730 (s), 1620 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (d, J = 6.8 Hz, 6 H), 1.12 (d, J = 6.8 Hz, 3 H), 1.14 (d, J = 6.8 Hz, 3 H), 1.91 (m, 2 H), 2.55 (d, J = 7.6 Hz, 2 H), 3.15 (m, 2 H), 3.70 (s, 3 H), 3.81 (m, 1 H), 4.60 (m, 2 H); high-resolution mass spectrum for $C_{13}H_{24}N_2O_3$, calcd 256.17866, found m/z (relative intensity) 256.17856 (M, 35), 241 (100), 186 (50), 141 (85).

1,3-Diphenyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3h: R^1 = R^2 = Ph): mp 134.5–135.5 (benzene–hexane); IR (KBr disk) 1735 (s), 1630 (s), 1480 (s), 1420 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (m, 2 H), 2.53 (dd, J = 8.4, 14.9 Hz, 1 H), 2.71 (dd, 5.4, 14.9 Hz, 1 H), 3.58 (s, 3 H), 3.80 (m, 2 H), 4.45 (m, 1 H), 7.16–7.51 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 26.8, 37.8, 45.1, 51.6, 54.9, 125.3, 126.5, 128.0, 128.4, 128.8, 141.6, 143.5, 153.9, 170.8; mass spectrum, m/z (relative intensity) 324 (M, 95), 265 (50), 251 (100).

1-Isopropyl-3(*R*)-(α-methylbenzyl)-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3l: R^1 = *i*-Pr, R^2 = (*R*)-α-methylbenzyl, a mixture of 4*R* and 4*S*): mp 80.0–81.5 °C (benzene–hexane); IR (KBr disk) 1730 (s), 1620 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ (major diastereomer) 1.12 (d, J = 9.7 Hz, 6 H), 1.56 (d, J = 6.8 Hz, 3 H), 1.80 (m, 2 H), 2.55 (d, J = 7.8 Hz, 2 H), 3.10 (m, 2 H), 3.53 (m, 1 H), 3.62 (s, 3 H), 4.71 (hept, J = 9.7 Hz, 1 H), 5.90 (q, J = 6.8 Hz, 1 H), 7.26 (s, 5 H); ^1H NMR ($CDCl_3$) δ (minor diastereomer) 1.10 (d, J = 9.7 Hz, 6 H), 1.50 (d, J = 6.8 Hz, 3 H), 1.80 (m, 3 H), 2.03 (dd, J = 10.8, 15.9 Hz, 1 H), 3.10 (m, 2 H), 3.48 (s, 3 H), 3.66 (m, 1 H), 4.71 (hept, J = 9.7 Hz, 1 H), 5.90 (q, J = 6.8 Hz, 1 H), 7.26 (s, 5 H). Anal. Calcd for $C_{18}H_{26}N_2O_3$: C, 67.89; H, 8.23; N, 8.80. Found: C, 67.59; H, 8.40; N, 8.50.

1-Isopropyl-3-[1-(1-naphthyl)ethyl]-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3j: R^1 = *i*-Pr, R^2 = CH(Me)-1-Naph, a mixture of diastereomers): mp 129.0–131.0 °C (benzene–hexane); IR (KBr disk) 1725, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ (major diastereomer) 1.15 (d, J = 6.8 Hz, 6 H), 1.65 (m, 2 H), 1.73 (d, J = 6.2 Hz, 3 H), 2.58 (m, 2 H), 3.07 (m, 2 H), 3.38 (m, 1 H), 3.63 (s, 3 H), 4.85 (m, J = 6.8 Hz, 1 H), 6.55 (q, J = 6.2 Hz, 1 H), 7.32–8.53 (m, 7 H). Anal. Calcd for $C_{22}H_{28}N_2O_3$: C, 71.70; H, 7.67; N, 7.60. Found: C, 71.92; H, 7.76; N, 7.54.

1-Isopropyl-3,4-dimethyl-4-[(methoxycarbonyl)methyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (3k): 155 °C (0.1 mmHg); IR (neat film) 1735 (s), 1625 (s), 1500 (s), 1460 (s), 1350 (s), 755 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 7.0 Hz, 3 H), 1.35 (s, 3 H), 1.67–2.43 (m, 2 H; coalescing to a pair of d, J = 13.7 Hz, by irradiation at 3.12), 2.47 (d, J = 13.8 Hz, 1 H), 2.67 (d, J = 13.8 Hz, 1 H), 2.87 (s, 3 H), 3.02–3.24 (m, 2 H), 3.67 (s, 3 H), 4.72 (hept, J = 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 19.0, 19.1, 25.1, 27.8, 33.1, 33.8, 41.7, 44.7, 51.0, 54.5, 155.3 (br), 170.2. Anal. Calcd for $C_{12}H_{22}N_2O_3$: C, 59.48; H, 9.15; N, 11.56. Found: C, 59.32; H, 9.37; N, 11.65.

1-Isopropyl-3-methyl-4(*S'*)-[(1'*R'*)-(methoxycarbonyl)ethyl]-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (31): bp 160 °C (0.1 mmHg); IR (neat film) 1735 (s), 1630 (s), 1505 (s), 1460 (s), 1205 (s), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 6.8 Hz, 6 H), 1.25 (d, J = 7.1 Hz, 3 H), 1.53–2.09 (m, 2 H), 2.50–3.29 (m, 3 H), 3.44 (dt, J = 2.8, 6.9 Hz, 1 H; coalescing to d, J = 6.9 Hz, by irradiation at 1.86), 3.69 (s, 3 H), 4.66 (m, 1 H); high-resolution mass spectrum for $C_{12}H_{22}N_2O_3$, calcd 242.3174, found m/z (relative intensity) 242.1615 (M, 6), 227 (7), 155 (100).

Products listed in Table III follow:

1-Benzyl-3-methyl-4-[(methoxycarbonyl)methyl]-2-imidazolidinone (9a: R^1 = benzyl, R^2 = Me): IR (neat film) 1730 (s), 1690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.48 (dd, J = 8.4, 15.9 Hz, 1 H), 2.69 (dd, J = 7.0, 15.9 Hz, 1 H), 2.80 (s, 3 H), 2.94 (dd, J = 6.2, 8.1 Hz, 1 H), 2.43 (t, J = 8.1 Hz, 1 H), 3.66 (s, 3 H), 3.70 (m, 1 H), 4.36 (s, 2 H), 7.28 (s, 5 H); ^{13}C NMR ($CDCl_3$) δ 29.2, 37.3, 48.0, 48.2, 51.6, 52.3, 127.2, 127.9, 128.4, 140.0, 160.4, 170.7; high-resolution mass spectrum for $C_{14}H_{18}N_2O_3$, calcd 262.13177, found m/z (relative intensity) 262.13327 (M, 40), 189 (55), 188 (35), 91 (100).

1,5-Dihydro-1-benzyl-3,4-dimethyl-2*H*-imidazolone (10a: R' = benzyl, R^2 = Me): IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.98 (d, J = 1.3 Hz, 3 H), 3.17 (s, 3 H), 4.72 (s, 2 H), 5.83 (q, J = 1.3 Hz, 1 H), 7.26 (s, 5 H); mass spectrum, m/z (relative intensity) 202 (M, 100), 111 (65), 91 (70).

1,3-Diisopropyl-4-[(methoxycarbonyl)methyl]-2-imidazolidinone (9b: R^1 = R^2 = *i*-Pr): IR (neat film) 1735 (s), 1690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.09 (d, J = 6.6 Hz, 6 H), 1.21 (d, J = 6.8 Hz, 3 H), 1.22 (d, J = 6.8 Hz, 3 H), 2.46 (dd, J = 9.0, 16.1 Hz, 1 H), 2.79 (dd, J = 3.7, 16.1 Hz, 1 H), 2.95 (dd, J = 5.4, 8.5 Hz, 1 H), 3.47 (t, J = 8.5 Hz, 1 H), 3.71 (s, 3 H), 3.65–4.39 (m, 3 H); mass spectrum, m/z (relative intensity) 242 (M, 15), 228 (15), 227 (100), 169 (40), 127 (35).

1,3-Dimethyl-4-[(methoxycarbonyl)methyl]-2-imidazolidinone (9c: R^1 = R^2 = Me): IR (neat film) 1730 (s), 1700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (dd, J = 8.3, 16.0 Hz, 1 H), 2.75 (dd, J = 4.6, 16.0 Hz, 1 H), 2.75 (s, 3 H), 2.77 (s, 3 H), 3.01 (dd, J = 6.3, 8.5 Hz, 1 H), 3.53 (t, J = 8.5 Hz, 1 H), 3.71 (s, 3 H), 3.80 (m, 1 H); mass spectrum, m/z (relative intensity) 186 (M, 10), 113 (100), 112 (50).

1-Isopropyl-3-((*R*)-α-methylbenzyl)-4-[(methoxycarbonyl)methyl]-2-imidazolidinone (9d: R^1 = *i*-Pr, R^2 = (*R*)-CH(Me)Ph; a mixture of two diastereomers): IR (neat film) 1735 (s), 1690 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ (major isomer) 1.12 (d, J = 6.8 Hz, 6 H), 1.60 (d, J = 6.8 Hz, 3 H), 2.42 (dd, J = 11.3, 16.2 Hz, 1 H), 2.70 (dd, J = 3.8, 16.2 Hz, 1 H), 2.94 (m, 1 H), 3.46 (m, 1 H), 3.57 (m, 1 H), 3.63 (s, 3 H), 4.18 (hept, J = 6.8 Hz, 1 H), 5.24 (q, J = 6.8 Hz, 1 H), 7.31 (s, 5 H); ^1H NMR ($CDCl_3$) δ (minor isomer) 1.13 (d, J = 6.8 Hz, 6 H), 1.69 (d, J = 6.8 Hz, 3 H), 1.94 (dd, J = 6.8, 13.5 Hz, 1 H), 2.10 (dd, J = 2.4, 13.5 Hz, 1 H); mass spectrum, m/z (relative intensity) 304 (M, 55)8 289 (70), 199 (30), 185 (30), 127 (100), 105 (80).

Products listed in Table IV follow:

3-Methyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12a): mp 63.0–64.0 °C (benzene–hexane); IR (KBr disk) 1708 (s), 1655 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.43–2.37 (m, 4 H), 2.37 (dd, J = 15.9, 13.1 Hz, 1 H), 2.83

(dd, J = 15.9, 3.9 Hz, 1 H), 3.16 (s, 3 H), 3.60 (m, 3 H). Anal. Calcd for $C_8H_{12}N_2O_2$: C, 57.12; H, 7.20; N, 16.66. Found: C, 56.99; H, 7.31; N, 16.51.

3,8,8-Trimethyl-1,3-diazaobicyclo[4.3.0]nonane-2,4-dione (12b: R′ = Me): mp 61.8–62.1 °C (benzene–hexane); IR (KBr disk) 1720 (s), 1660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.19 (s, 3 H), 1.53 (dd, J = 10.0, 12.0 Hz, 1 H), 1.96 (dd, J = 5.9, 12.0 Hz, 1 H), 2.40 (dd, J = 13.2, 15.9 Hz, 1 H), 2.78 (dd, J = 4.2, 15.9 Hz, 1 H), 3.14 (s, 3 H), 3.29 (d, J = 11.0 Hz, 1 H), 3.38 (d, J = 11.0 Hz, 1 H), 3.88 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 27.0, 36.6, 38.2, 47.1, 50.8, 58.2, 151.7, 169.0; mass spectrum, m/z (relative intensity) 196 (M, 95), 181 (35), 141 (30), 140 (100), 113 (30). Anal. Calcd for $C_{10}H_{16}N_2O_2$: C, 61.19; H, 8.23; N, 14.28. Found: C, 61.46; H, 8.38; N, 14.26.

3-Benzyl-8,8-dimethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12b: R′ = benzyl): mp 87.0–88.0 °C (benzene–hexane); IR (KBr disk) 1715 (s), 1670 (s), 1460 (s), 1355 (m), 1165 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.15 (s, 3 H), 1.51 (dd, J = 9.0, 12.5 Hz, 1 H), 1.96 (dd, J = 5.6, 12.5 Hz, 1 H), 2.39 (dd, J = 13.2, 15.6 Hz, 1 H), 2.81 (dd, J = 4.0, 15.6 Hz, 1 H), 3.28 (d, J = 11.2 Hz, 1 H), 3.40 (d, J = 11.2 Hz, 1 H), 3.89 (m, 1 H), 4.39 (s, 2 H), 7.30 (m, 5 H). Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.55; H, 7.42; N, 10.29. Found: C, 70.25; H, 7.45; N, 10.33.

3-Phenyl-8,8-dimethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12b: R′ = Ph): mp 173.0–174.0 °C (benzene–hexane); IR (KBr disk) 1710 (s), 1670 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (s, 3 H), 1.22 (s, 3 H), 1.58 (dd, J = 10.3, 12.4 Hz, 1 H), 2.04 (dd, J = 5.9, 12.4 Hz, 1 H), 2.59 (dd, J = 12.9, 15.9 Hz, 1 H), 2.93 (dd, J = 4.1, 15.9 Hz, 1 H), 3.36 (d, J = 11.7 Hz, 1 H), 3.41 (d, J = 11.7 Hz, 1 H), 4.09 (m, 1 H), 7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 27.1, 27.2, 36.8, 39.0, 47.3, 51.2, 58.6, 127.9, 128.6, 128.8, 135.7, 151.4, 168.9. Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.73; H, 7.04; N, 10.85. Found: C, 69.50; H, 7.02; N, 10.87.

***N*-(Tolylsulfonyl)-2-[(methoxycarbonyl)methyl]-4,4-dimethylpyrrolidine (13b: R = SO_2Tol)**: mp 59.5–60.5 °C (benzene–hexane); IR (KBr disk) 1730 (s), 1345 (s), 1305 (s), 1160 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.51 (s, 3 H), 1.04 (s, 3 H), 1.50 (dd, J = 8.1, 12.5 Hz, 1 H), 1.88 (dd, J = 7.1, 12.5 Hz, 1 H), 2.43 (s, 3 H), 2.58 (dd, J = 9.0, 16.4 Hz, 1 H), 3.04 (d, J = 10.3 Hz, 1 H), 3.17 (d, J = 10.3 Hz, 1 H), 3.32 (dd, J = 3.9, 16.4 Hz, 1 H), 3.68 (s, 3 H), 3.93 (m, 1 H), 7.32 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{16}H_{23}NO_4S$: C, 59.04; H, 7.14; N, 4.30; S, 9.85. Found: C, 59.10; H, 7.27; N, 4.23; S, 9.96.

***N*-(Methoxycarbonyl)-2-[(methoxycarbonyl)methyl]-4,4-dimethylpyrrolidine (13b: R = CO_2Me)**: IR (neat film) 1730 (s), 1700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3 H), 1.09 (s, 3 H), 1.50 (dd, J = 8.5, 12.7 Hz, 1 H), 2.02 (dd, J = 7.1, 12.7, Hz, 1 H), 2.40 (dd, J = 8.8, 15.4 Hz, 1 H), 2.90–3.67 (m, 3 H), 3.66 (s, 3 H), 3.67 (s, 3 H), 4.19 (m, 1 H); high-resolution mass spectrum for $C_{11}H_{19}NO_4$, calcd 229.13129, found m/z (relative intensity) 229.13019 (M, 10), 170 (45), 156 (75), 43 (100).

***N*-[(Benzylamino)carbonyl]-2-[(methoxycarbonyl)methyl]-4,4-dimethylpyrrolidine (13b: R = CONHCH$_2$Ph)**: IR (neat film) 3300 (s), 1740 (s), 1640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 1.08 (s, 3 H), 1.53 (dd, J = 8.5, 12.9 Hz, 1 H), 2.02 (dd, J = 8.3, 12.9 Hz, 1 H), 2.48 (dd, J = 8.1, 15.6 Hz, 1 H), 3.10 (m, 3 H), 3.63 (s, 3 H), 4.25 (m, 1 H), 4.41 (d, J = 2.7 Hz, 2 H), 4.62 (br s, 1 H), 7.29 (s, 5 H); mass spectrum, m/z (relative intensity) 304 (M, 25), 170 (80), 98 (100).

***N*-[(Phenylamino)carbonyl]-2-[(methoxycarbonyl)methyl]-4,4-dimethylpyrrolidine (13b: R = CONHPh)**: mp 116.5–117.5 °C (benzene–hexane); IR (KBr disk) 1740 (s), 1640 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 3 H), 1.14 (s, 3 H), 1.54 (dd, J = 8.1, 12.7 Hz, 1 H), 2.07 (dd, J = 7.6, 12.7 Hz, 1 H), 2.53 (dd, J = 7.1, 16.0 Hz, 1 H), 3.05 (dd, J = 4.6, 16.0 Hz, 1 H), 3.13 (d, J = 9.5 Hz, 1 H), 3.38 (d, J = 9.5 Hz, 1 H), 3.67 (s, 3 H), 4.38 (m, 1 H), 6.68 (br s, 1 H), 7.35 (m, 5 H).

3,6,8,8-Tetramethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12c: R′ = Me): bp 140 °C (0.1 mmHg); IR (neat film) 1710 (s), 1670 (s), 1470 (s), 1445 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 3 H), 1.20 (s, 3 H), 1.28 (s, 3 H), 1.81 (s, 2 H), 2.67 (s, 2 H), 3.17 (s, 3 H), 3.22 (d, J = 11.5 Hz, 1 H), 3.65 (d, J = 11.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 25.4, 26.6, 27.3, 28.6, 36.9, 44.9, 53.4, 56.9, 57.5, 150.7, 168.5. Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.40; H, 9.25; N, 13.23. Found: C, 62.69; H, 8.79; N, 13.43.

***N*-(Tolylsulfonyl)-2-[(methoxycarbonyl)methyl]-2,4,4-trimethylpyrrolidine (13c: R = SO_2Tol)**: IR (neat film) 1745 (s), 1340 (s), 1165 (s), 670 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.99 (s, 3 H), 1.04 (s, 3 H), 1.60 (s, 3 H), 1.70 (d, J = 13.4 Hz, 1 H), 2.20 (d, J = 13.4 Hz, 1 H), 2.42 (s, 3 H), 2.86 (d, J = 15.4 Hz, 1 H), 3.09 (s, 2 H), 3.18 (d, J = 15.4 Hz, 1 H), 3.63 (s, 3 H), 7.29 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 27.1, 27.2, 35.9, 45.7, 51.0, 53.3, 61.0, 65.8, 127.0, 129.1, 137.9, 142.6, 171.0; high-resolution mass spectrum for $C_{17}H_{25}NO_4S$ – Me, calcd 324.4141, found m/z (relative intensity) 324.1294 (M – Me, 9), 266 (100), 184 (66).

***N*-(Methoxycarbonyl)-2-[(methoxycarbonyl)methyl]-2,4,4-trimethylpyrrolidine (13c: R = CO_2Me)**: bp 125 °C (0.1 mmHg); IR (neat film) 1740 (s), 1705 (s), 1445 (s), 1375 (s), 775 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.13 (s, 3 H), 1.54 (s, 3 H), 1.71 (d, J = 12.9 Hz, 1 H), 2.15 (br d, J = 12.9 Hz, 1 H), 2.89 (br s, 2 H), 3.16 (d, J = 11.0 Hz, 1 H), 3.31 (br d, J = 11.0 Hz, 1 H), 3.63 (s, 3 H), 3.66 (br s, 3 H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 26.6, 27.6, 28.2, 35.2, 43.5, 50.8, 51.4, 52.6, 60.8, 61.8, 154.7, 171.3. Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.02; H, 9.04; N, 5.74. Found: C, 59.18; H, 9.05; N, 5.65.

***N*-Benzoyl-4-methoxy-2,2,4-trimethylpentylamine**: bp 200 °C (0.1 mmHg); IR (neat film) 3350 (s), 1650 (s), 1535 (s), 1300 (m), 1075 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 1.26 (s, 6 H), 1.56 (s, 2 H), 3.26 (s, 3 H), 3.40 (d, J = 6.3 Hz, 2 H), 7.33–7.88 (m, 5 H); high-resolution mass spectrum for $C_{16}H_{25}NO_3$, calcd 263.3790, found m/z (relative intensity) 263.1888 (5), 175 (35), 135 (21), 105 (100), 73 (100).

***N*-(Tolylsulfonyl)-2,2,4,4-tetramethylpyrrolidine (14c: R = SO_2Tol)**: bp 190 °C/0.1 mmHg; IR (neat film) 1335 (s), 1155 (s), 1095 (m), 815 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.03 (s, 6 H), 1.49 (s, 6 H), 1.70 (s, 2 H), 2.41 (s, 3 H), 3.07 (s, 2 H), 7.26 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.1, 27.2, 29.5, 35.8, 56.8, 61.1, 65.2, 127.1, 129.0, 138.2, 142.3. Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 63.61; H, 8.83; N, 4.95; S, 11.32. Found: C, 64.29; H, 8.44; N, 5.05; S, 11.36.

(5*R*′,6*S*′)-3,5,8,8-Tetramethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12d: R′ = Me): IR (neat film) 1710 (s), 1675 (s), 1470 (s), 1320 (s), 1025 (s), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (d, J = 7.3 Hz, 3 H), 1.13 (s, 3 H), 1.20 (s, 3 H), 1.66 (m, 2 H), 2.75 (dq, J = 3.7, 7.3 Hz, 1 H), 3.14 (s, 3 H), 3.16 (d, J = 11.0 Hz, 1 H), 3.47 (d, J = 11.0 Hz, 1 H), 4.02 (dt, J = 3.7, 8.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 10.5, 26.9, 27.0, 36.6, 39.3, 41.2, 54.1, 59.0, 151.7, 173.7; high-resolution mass spectrum for $C_{11}H_{18}N_2O_2$, calcd 210.1369, found m/z (relative intensity) 210.1382 (M, 89), 195 (42), 154 (75), 98 (74), 69 (100).

(5*R*′,6*S*′)-3-Pbenyl-5,8,8-trimethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12d: R′ = Ph): mp 75.9–76.2 °C ($CHCl_3$–hexane); IR (KBr disk) 1720 (s), 1670 (s), 1460 (s), 1430 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (s, 3 H), 1.20 (s, 3 H), 1.23 (d, J = 7.1 Hz, 3 H), 1.69 (m, 2 H), 2.84 (dq, J = 3.7, 7.1 Hz, 1 H), 3.20 (d, J = 11.0 Hz, 1 H), 3.46 (d, J = 11.0 Hz, 1 H), 4.22 (dt, J = 3.7, 8.5 Hz, 1 H; coalescing to d, J = 3.7 Hz, by irradiation at 1.69), 6.99–7.53 (m, 5 H).

***N*-(Tolylsulfonyl)-2(*S*′)-[1′(*R*′)-(methoxycarbonyl)ethyl]-4,4-dimethylpyrrolidine (13d: R = SO_2Tol)**: IR (neat film) 1745 (s), 1600 (m), 1340 (s), 1155 (s), 820 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.53 (s, 3 H), 1.01 (s, 3 H), 1.16 (d, J = 7.3 Hz, 3 H), 1.44–2.11 (m, 2 H; coalescing to a pair of br d, J = 11.5 Hz at 1.67 and 1.93, by irradiation at 4.06), 2.41 (s, 3 H), 3.05 (d, J = 10.7 Hz, 1 H), 3.18 (m, 1 H), 3.22 (d, J = 10.7 Hz, 1 H), 3.64 (s, 3 H), 4.06 (ddd, J = 4.2, 6.1, 9.1 Hz, 1 H; coalescing to d, J = 4.2 Hz, by irradiation at 1.75), 7.28 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 13.2, 21.2, 25.9, 26.0, 37.6, 42.6, 51.1, 61.3, 62.0, 127.3, 129.2, 137.1, 142.9, 174.4; high-resolution mass spectrum for $C_{17}H_{25}NO_4S$ – Me, calcd 324.4141, found m/z (relative intensity) 324.1254 (1, M – Me), 252 (100), 184 (23), 155 (19).

***N*-(Methoxycarbonyl)-2(*S*′)-[1′(*R*′)-(methoxycarbonyl)ethyl]-4,4-dimethylpyrrolidine (13d: R′ = CO_2Me)**: bp 125 °C (0.1 mmHg); IR (neat film) 1735 (s), 1705 (s), 1450 (s), 1390 (s), 1200 (s), 770 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (s, 3 H), 1.08 (s, 3 H), 1.09 (d, J = 7.1 Hz, 3 H), 1.75 (m, 2 H), 2.89 (d, J = 10.5 Hz, 1 H), 3.03–3.51 (m, 2 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 4.08 (dt, J = 4.4, 8.5 Hz, 1 H; coalescing to d, J = 4.4 Hz, by irradiation at 1.75); ^{13}C NMR ($CDCl_3$, 60 °C) δ 12.5, 25.4, 26.1, 36.8, 41.1 (br), 51.1, 51.8, 59.4, 155.6, 174.4. Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.02; H, 9.04; N, 5.74. Found: C, 58.90; H, 8.98; N, 5.76.

(5*S*′,6*S*′)-3,5,8,8-Tetramethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12e: R′ = Me): mp 171.6–172.0 °C (hexane); IR (KBr disk) 1710 (s), 1670 (s), 1470 (s), 1285 (s), 740 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.19 (s, 3 H), 1.21 (d, J = 6.8 Hz, 3 H), 1.55 (dd, J = 12.2, 9.3 Hz, 1 H), 2.01 (dd, J = 12.2, 6.3 Hz, 1 H), 2.30 (dq, J = 12.2, 6.8 Hz, 1 H), 3.15 (s, 3 H), 3.32 (d, J = 11.0 Hz, 1 H), 3.41 (d, J = 11.0 Hz, 1 H), 3.53 (ddd, J = 6.3, 9.3, 12.2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 11.5, 27.1, 27.5, 36.6, 42.2, 46.8, 57.1, 58.7, 151.9, 172.1. Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.40; H, 9.25; N, 13.23. Found: C, 62.27; H, 9.00; N, 13.20.

(5*S*′,6*S*′)-3-Phenyl-5,8,8-trimethyl-1,3-diazabicyclo[4.3.0]nonane-2,4-dione (12e: R′ = Ph): mp 157.7–158.4 °C (EtOAc–hexane); IR (KBr disk) 1720 (s), 1675 (s), 1440 (s), 1200 (s), 1175 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 3 H), 1.22 (s, 3 H), 1.28 (d, J = 6.8 Hz, 3 H), 1.61 (dd, J = 11.7, 10.3 Hz, 1 H), 2.07 (dd, J = 11.7, 5.9 Hz, 1 H), 2.51 (dq, J = 12.9, 6.8 Hz, 1 H), 3.35 (d, J = 11.0, 1 H), 3.46 (d, J = 11.0 Hz, 1 H), 3.72 (ddd, J = 12.9, 10.3, 5.9 Hz, 1 H), 7.01–7.57 (m, 5 H); ^{13}C

NMR ($CDCl_3$) δ 11.1, 26.8, 36.3, 42.4, 46.5, 57.0, 58.6, 127.5, 128.6, 135.9, 151.1, 171.7. Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.56; H, 7.40; N, 10.29. Found: C, 70.36; H, 7.44; N, 10.23.

***N*-(Methoxycarbonyl)-2(*S*')-[1'(*S*')-(methoxycarbonyl)ethyl]-4,4-dimethylpyrrolidine (13e: R = CO_2Me)**: bp 120 °C (0.1 mmHg); IR (neat film) 1740 (s), 1705 (s), 1455 (s), 1395 (s), 1200 (s), 775 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 3 H), 1.03 (d, J = 7.1 Hz, 3 H), 1.07 (s, 3 H), 1.42-1.83 (m, 2 H), 2.90 (d, J = 10.7 Hz, 1 H), 3.17-3.76 (m, 2 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 4.32 (ddd, J = 5.5, 8.0, 9.4 Hz; coalescing to d, J = 5.5 Hz, by irradiation at 1.60); ^{13}C NMR ($CDCl_3$) δ 9.3, 25.5, 26.2, 36.8, 40.6, 51.2, 52.0, 58.1, 60.2, 155.6, 174.3. Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.02; H, 9.04; N, 5.74. Found: C, 59.02; H, 8.93; N, 5.80.

***N*-[(Methylamino)carbonyl]-2(*S*')-[1'(*R*')-chloroethyl]-4,4-dimethylpyrrolidine (15e: R = CONHMe)**: mp 137.0-137.5 °C (benzene-hexane); IR (KBr disk) 3370 (s), 1625 (s), 1540 (s), 1380 (s), 1345 (m), 865 (m), 655 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 3 H), 1.13 (s, 3 H), 1.83 (d, J = 6.8 Hz, 3 H), 1.64 (m, 1 H; coalescing to d, J = 11.7 Hz, by irradiation at 4.18), 1.85 (m, 1 H; coalescing to d, J = 11.7 Hz, by irradiation at 4.18), 2.80 (d, J = 4.6 Hz, 3 H), 3.02 (d, J = 9.3 Hz, 1 H), 3.08 (d, J = 9.3 Hz, 1 H), 4.15 (br s, 1 H), 4.18 (dt, J = 2.9, 7.8 Hz, 1 H), 5.00 (dq, J = 2.9, 6.8 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 21.0, 25.4, 27.1, 37.7, 38.5, 59.7, 60.3, 61.8, 157.7. Anal. Calcd for $C_{10}H_{19}N_2OCl$: C, 54.91; H, 8.76; N, 12.81; Cl, 16.21. Found: C, 54.97; H, 9.00; N, 12.74; Cl, 16.02.

***N*-[(Phenylamino)carbonyl]-2(*S*')-[1'(*R*')-chloroethyl]-4,4-dimethylpyrrolidine (15e: R = CONHPh)**: mp 170.5-171.2 °C (THF-hexane); IR (KBr disk) 1635 (s), 1450 (m), 1390 (m), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (s, 3 H), 1.17 (s, 3 H), 1.38 (d, J = 6.8 Hz, 3 H), 1.72 (dd, J = 12.5, 7.8 Hz, 1 H), 1.93 (dd, J = 12.5, 9.3 Hz, 1 H), 3.20 (s, 2 H), 4.27 (ddd, J = 9.3, 7.8, 2.7 Hz, 1 H), 5.02 (dq, J = 2.7, 6.8 Hz, 1 H), 6.21 (br s, 1 H). Anal. Calcd for $C_{15}H_{21}N_2OCl$: C, 64.16; H, 7.54; N, 9.98; Cl, 12.63. Found: C, 63.97; H, 7.73; N, 9.84; Cl, 12.52.

3,9,9-Trimethyl-1,3-diazabicyclo[4.4.0]decane-2,4-dione (17a): mp 79.0-80.0 °C (benzene-hexane); IR (KBr disk) 1705 (s), 1650 (s), 1440 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.98 (s, 6 H), 1.50 (m, 4 H), 2.31 (d, J = 12.9 Hz, 1 H), 2.51 (dd, J = 10.3, 16.8 Hz, 1 H), 2.83 (dd, J = 5.3, 16.8 Hz, 1 H), 3.19 (m, 1 H), 3.19 (s, 3 H), 4.02 (dd, J = 2.0, 12.9 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.1, 27.4, 28.8, 29.2, 30.1, 36.6, 37.6, 49.7, 55.4, 154.4, 167.8; mass spectrum, m/z (relative intensity) 210 (M, 20), 195 (20), 141 (100). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.82; H, 8.64; N, 13.32. Found: C, 63.00; H, 8.73; N, 13.20.

***N*-(Tolylsulfonyl)-2-[(methoxycarbonyl)methyl]-5,5-dimethylpiperidine (18a: R = SO_2Tol)**: mp 64.5-65.5 °C (benzene-hexane); IR (KBr disk) 1735 (s), 1340 (s), 1160 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3 H), 0.90 (s, 3 H), 1.05-2.05 (m, 4 H), 2.25 (dd, J = 4.2, 15.0 Hz, 1 H), 2.41 (s, 3 H), 2.60 (dd, J = 10.0, 15.0 Hz, 1 H), 2.60 (d, J = 12.9 Hz, 1 H), 3.36 (d, J = 12.9 Hz, 1 H), 3.62 (s, 3 H), 4.47 (m, 1 H), 7.26 (d, J = 8.3 Hz, 2 H), 7.66 (d, J = 8.3 Hz, 2 H). Anal. Calcd for $C_{17}H_{25}NO_4S$: C, 60.14; H, 7.44; N, 4.13; S, 9.44. Found: C, 60.11; H, 7.54; N, 4.12; S, 9.50.

***N*-(Methoxycarbonyl)-2-[(methoxycarbonyl)methyl]-5,5-dimethylpiperidine (18a: R = CO_2Me)**: IR (neat film) 1740 (s), 1700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (s, 3 H), 0.93 (s, 3 H), 1.20-2.21 (m, 4 H), 2.52 (d, J = 7.1 Hz, 2 H), 2.59 (d, J = 13.7 Hz, 1 H), 3.57 (d, J = 13.7 Hz, 1 H), 3.66 (s, 3 H), 3.68 (s, 3 H), 4.73 (q, J = 7.1 Hz, 1 H); high-resolution mass spectrum for $C_{12}H_{21}NO_4$, calcd 243.14700, found m/z (relative intensity) 243.14928 (M, 5), 184 (30), 170 (100).

***N*-(Tolylsulfonyl)-2,2-dimethyl-5-methoxy-6-(methoxycarbonyl)-hexylamine (19a: R = SO_2Tol)**: IR (neat film) 3280 (s), 1740 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (s, 6 H), 1.31 (m, 4 H), 2.42 (s, 3 H), 2.45 (m, 2 H), 2.65 (d, J = 6.8 Hz, 2 H), 3.33 (s, 3 H), 3.60 (m, 1 H), 3.68 (s, 3 H), 4.70 (t, J = 6.8 Hz, 1 H), 7.30 (d, J = 8.3 Hz, 2 H), 7.74 (d, J = 8.3 Hz, 2 H); mass spectrum, m/z (relative intensity) 371 (M, 1), 266 (20), 216 (65), 184 (95), 155 (100).

***N*-(Methoxycarbonyl)-2,2-dimethyl-5-methoxy-6-(methoxycarbonyl)-hexylamine (19a: R = CO_2Me)**: IR (neat film) 3350 (s), 1740-1700 (br s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (s, 6 H), 1.10-1.67 (m, 4 H), 2.42 (dd, J = 15.0, 5.9 Hz, 1 H), 2.57 (dd, J = 15.0, 6.3 Hz, 1 H), 3.01 (d, J = 6.6 Hz, 2 H), 3.34 (s, 3 H), 3.60 (m, 1 H), 3.66 (s, 3 H), 3.69 (s, 3 H), 4.80 (br s, 1 H); mass spectrum, m/z (relative intensity) 275 (M, 1), 242 (10), 212 (12), 187 (15), 170 (20), 155 (100).

3-Methyl-1,3-diaza-8-oxabicyclo[4.4.0]decane-2,4-dione (17c): mp 75.5-76.5 °C (benzene-hexane); IR (KBr disk) 1710 (s), 1660 (s), 1450 (s) cm^{-1}; ^1H NMR (benzene-d_6, 400 MHz) δ 1.49 (dd, J = 16.4, 12.8 Hz, H_{5a}), 1.91 (dd, J = 16.4, 4.4 Hz, H_{5e}), 2.41 (dd, J = 11.2, 10.1 Hz, H_{7a}), 2.56 (dddd, J = 12.8, 10.1, 4.4, 3.4 Hz, H_6), 2.59 (ddd, J = 13.3, 12.2, 3.8 Hz, H_{10a}), 3.02 (td, J = 12.2, 2.8 Hz, H_{9a}), 3.17 (ddd, J = 11.2, 3.4, 1.0 Hz, H_{7e}), 3.28 (s, 3 H), 3.50 (ddt, J = 12.2, 3.8, 1.0 Hz, H_{9e}), 3.86 (ddd, J = 13.3, 2.8, 1.0 Hz, H_{10e}). Anal. Calcd for $C_8H_{12}N_2O_3$: C, 52.16; H, 6.58; N, 15.21. Found: C, 52.31; H, 6.53; N, 15.15.

3-Methyl-8-benzyl-1,3,8-triazabicyclo[4.4.0]decane-2,4,9-trione (17d): mp 152.0-153.0 °C (benzene-hexane); IR (KBr disk) 1715 (s), 1655 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.43 (dd, J = 9.3, 16.8 Hz, 1 H), 2.76 (dd, J = 5.6, 16.8 Hz, 1 H), 3.18 (s, 3 H), 3.28 (m, 2 H), 3.79 (m, 1 H), 4.17 (d, J = 18.4 Hz, 1 H), 4.51 (d, J = 14.4 Hz, 1 H), 4.57 (d, J = 18.4 Hz, 1 H), 4.76 (d, J = 14.4 Hz, 1 H), 7.10-7.45 (m, 5 H). Anal. Calcd for $C_{15}H_{17}N_3O_3$: C, 62.69; H, 5.98; N, 14.62. Found: C, 62.76; H, 5.95, N, 14.62.

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Oxygen Donation by an Intermediate in the Reaction of $^3CF_2$ with O_2

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Abstract: Reaction of $^3CF_2$, produced by reaction of arc-generated carbon atoms with CF_3, with oxygen in the presence of alkenes oxygenates alkenes to epoxides, which are formed stereospecifically, and carbonyl compounds. The reaction is postulated to involve the intermediacy of difluorodioxirane, which transfers oxygen stereospecifically to the alkene. Ab initio calculations demonstrate that the difluorodioxirane is more stable than the corresponding carbonyl oxide and that closure of the carbonyl oxide to the dioxirane should be rapid. The results of these calculations are compared to those on the parent CH_2O_2 system. Reaction of carbon atoms with oxygen and alkenes in the absence of CF_3 gives nonstereospecific epoxidation presumably through the intermediacy of O atoms.

Ever since carbonyl oxides, **1**, were first proposed by Criegee as intermediates in the ozonolysis reaction,[1] there has been growing interest in these species and in their isomers, the dioxiranes **2** and the dioxymethylenes **3**.[2-5] Compounds **1** and **2** appear to have rather different chemistry with **1** reacting predominately by cycloaddition pathways[2-5] and **2** functioning mainly as an oxygen

(1) Criegee, R. *Rec. Chem. Prog.* **1957**, *18*, 111.

(2) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745.

(3) Kuczkowski, R. L. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 2, pp 197-276.

0002-7863/88/1510-4002$01.50/0