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Chlorosulfonyl Isocyanate Reactions with *N*-(Alkoxycarbonyl)-2-azabicyclo[2.2.0]hex-5-enes. Regiospecific Two-Atom Insertion Pathways

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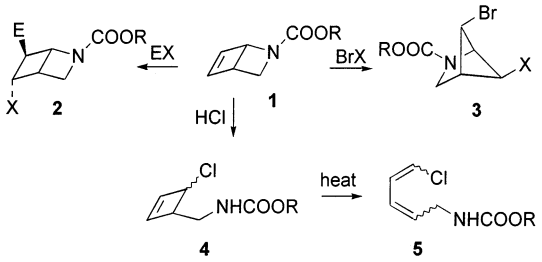
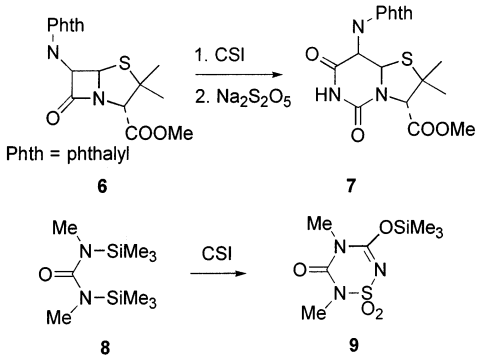
Abstract: Addition of the uniparticulate electrophile chlorosulfonyl isocyanate to the nitrogen atom of *N*-(alkoxycarbonyl)-2-azabicyclo[2.2.0]hex-5-enes **1** is followed by ring cleavage and recombination. The parent 4-methyl, 5-methyl, 5-bromo, and 5-phenyl azabicycles **1a**−**f** afforded novel 2,4-diaza-3-oxo-bicyclo[4.2.0]oct-7-enes **10a**−**f**. The 3-*endo*-phenyl azabicycle **1g** rearranged to a 6-styryl-1,3-diaza-2-oxocyclohex-4-ene **12**.

N-(Alkoxycarbonyl)-2-azabicyclo[2.2.0]hex-5-enes **1**, readily synthesized from pyridines via 1,2-dihydropyridines,[1,2] have now been shown to be useful substrates for a variety of novel monocyclic,[2−4] fused ring,[5−9] and bridged[7−9] nitrogen heterocycles. The reactions of azabicycles **1** at the olefin position have been found to show a large dependence on the folded nature of its structure and to be strongly influenced by the neighboring nitrogen. For example, additions of electrophiles to **1** show a preference for *exo* facial selectivity in the formation of cyclopropanes,[2] aziridines,[2,3] and epoxides.[2−4] The same *exo* selectivity is found for reductive Pd-catalyzed arylation[5] and catalytic hydrogenation.[5,6] The predominant mode of addition for *N*-sulfenyl chloride,[2] bromine,[7,8] and hypobromous acid[7,9] is to add the electrophile (E) at C_6-*exo* and the nucleophile (X) at C_5-*endo* to give structures **2**. With a bromonium ion as electrophile (BrX) a competitive nitrogen atom participation results in rearrangement to products **3** with the novel *N*-(alkoxycarbonyl)-2-azabicyclo[2.1.1]hexane ring system.[7−9]



It is also known that a proton adds not to the double bond of azabicycles **1**, but at nitrogen.[1,10] Fowler has reported that HCl affords a ring cleavage product **4**,[11] which can be thermally ring-opened to give diene **5**.[1]

Chlorosulfonyl isocyanate (CSI) is an extremely reactive heterocumulene known to undergo reaction with alkenes to form *β*-lactams.[12] CSI has also been reported to give products predicated upon interaction with nitrogen atoms. For example, the *β*-lactam **6** undergoes a two-atom-ring enlargement to give **7**,[13] and urea **8** affords the heterocycle **9**.[14]



It was not clear how CSI would react with azabicycles **1**, but the potential for generation of novel heterocyclic structures was apparent. We here report results for reaction of CSI with parent azabicycles **1a**,**b** and several C_3-, C_4-, and C_5-substituted analogues **1c**−**g**.

The requisite 2-azabicyclo[2.2.0]hex-5-enes **1a**,**b**,[1] **1c**,**d**,[7] and **1g**[2] were prepared as previously described. The 5-bromo derivative **1e** was prepared from 4-bromopyridine in two steps: sodium borohydride reduction in methanol in the presence of benzyl chloroformate af-

(1) (a) Fowler, F. W. *J. Org. Chem.* **1972**, *37*, 1321. (b) Beeken, P.; Bonfiglio, J. N.; Hasan, I.; Piwinski, J. J.; Weinstein, B.; Zollo, I. A.; Fowler, F. W. *J. Am. Chem. Soc.* **1979**, *101*, 6677.

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(9) (a) Krow, G. R.; Lester, W. S.; Liu, N.; Yuan, J.; Hiller, A.; Duo, J.; Herzon, S. B.; Nguyen, Y.; Cannon, K. *J. Org. Chem.* **2001**, *66*, 1811. (b) Krow, G. R.; Yuan, J.; Lin, G.; Sonnet, P. E. *Org. Lett.* **2002**, *4*, 1259.

(10) (a) Michels, G.; Fink, J.; Maas, G.; Regitz, M. *Tetrahedron Lett.* **1985**, *26*, 3315. (b) Michels, G.; Hermesdorf, M.; Schneider, J.; Regitz, M. *Chem. Ber.* **1988**, *121*, 1775.

(11) We have also observed ring cleavage between the *N*-(alkoxycarbonyl) group and C_3 with HBr or Me_3SiI when the 5,6-alkene was not present. See ref 5.

(12) For recent reviews, see: (a) Miller, M. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; J. Wiley & Sons: New York, 1995; Vol. 2, p 1213. (b) Dhar, D. N.; Murthy, K. S. K. *Synthesis* **1986**, 437. (c) Kamai, A.; Sattur, P. B. *Heterocycles* **1987**, *26*, 1051.

(13) Campbell, M. M.; Harcus, R. G.; Nelson, K. H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 817.

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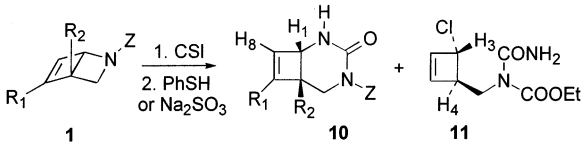
TABLE 1. Products Formed in the Reaction of CSI with 2-Azabicyclo[2.2.0]hex-5-enes 1

entry	substrate	substituents R_1	R_2	R_3	Z	conditions[a]	product(s) (ratio)	yield (%)
1	**1a**	H	H	H	COOEt	A	**10a** + **11** 45:55)	45
2	**1b**	H	H	H	COOBn	B	**10b**	62
3	**1c**	H	Me	H	COOEt	A	**10c**	32
4	**1d**	Me	H	H	COOEt	A	**10d**	82
5	**1e**	Br	H	H	COOBn	B	**10e**	75
6	**1f**	Ph	H	H	COOBn	B	**10f**	70
7	**1g**	H	H	Ph	COOBn	B	**12**	70[b]

[a] A: −30 °C, thiophenol/pyridine workup. B: rt, sodium sulfite workup. [b] Yield of 85% prior to the reductive workup step.

forded a sensitive 5-bromo-1,2-dihydropyridine, which upon irradiation in acetone gave azabicycle **1e**. The 5-phenyl isomer **1f** was prepared by treating the bromo derivative **1e** with phenyl boronic acid in the presence of $Pd(PPh_3)_4$ in ethanol/aqueous sodium carbonate.[15]

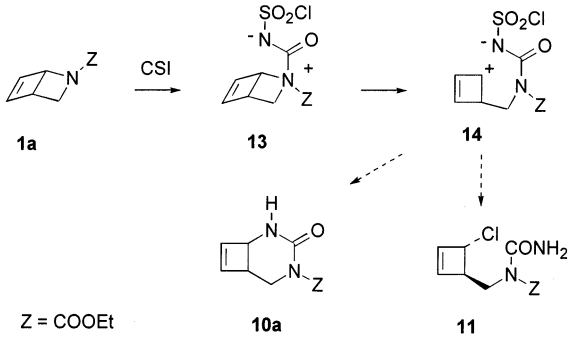


	R_1	R_2	Z
a	H	H	COOEt
b	H	H	COOBn
c	H	Me	COOEt
d	Me	H	COOEt
e	Br	H	COOBn
f	Ph	H	COOBn

Chlorosulfonyl isocyanate was reacted with azabicycles **1a**−**f** in methylene chloride either at −30 °C or ambient temperature and the initial products were reacted with thiophenol or sodium sulfite to remove the chlorosulfonyl group. Insertion products **10** were isolated; a product **11** also was afforded in a reaction of **1a**. The results are shown in Table 1.

Reaction of the parent **1a** (entry 1) gave a mixture of two major products **10a** and **11** when a thiophenol workup was used. Structure **10a** could be provisionally assigned from its ^{1}H NMR spectrum. The olefinic protons $R_1 = H_7$ (d, $J = 2.7$ Hz) and H_8 (d), at δ 6.15 and δ 6.11, were mutually coupled with a small coupling constant expected for olefinic protons in a cyclobutene. The bridgehead proton H_1 (t, $J = 4.5$ Hz) at δ 4.25 was coupled to NH and bridgehead proton H_6, confirming the regiochemistry of the insertion reaction. The remaining bridgehead proton H_6 (dd, $J = 4.5$, 3.9 Hz) at δ 3.54 was also coupled to H_{5x} (dd, $J = 13.5$, 3.9 Hz), the top face methylene proton, at δ 3.23.[16] The major product **11** was shown to be a chlorocyclobutene. Two olefinic protons at δ 6.31 (d, $J = 2.7$ Hz) and δ 6.16 (d) were mutually coupled. Proton H_3 at δ 5.04 (d, $J = 3.9$ Hz) on the chlorine-bearing carbon has been assigned a trans orientation with H_4 at δ 3.43 (ddd, $J = 10.5$, 4.5, 3.9 Hz) based on the small vicinal coupling constant. The reaction

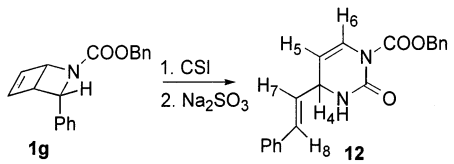
SCHEME 1



of CSI with the *N*-COOBn parent structure **1b** using a sodium sulfite workup (entry 2) afforded the insertion product **10b** in improved yield without ring cleavage.

Although the C_4 methyl group in azabicycle **1c** at the bridgehead (entry 3) introduces steric hindrance on the top face of the molecule, insertion product **10c** was still obtained. The ^{1}H NMR spectrum of **10c** was similar to that of **10a**, but with the bridgehead proton H_6 and its associated couplings removed. A C_5 methyl group in azabicycle **1d** (entry 4) introduces a group expected to increase the electron density of the olefinic bond and also stabilize a positive charge at the adjacent position. The result, however, did not change and azabicycle **10d**, which has a single olefinic proton at δ 5.73 (s), was obtained in excellent yield. Introduction of a bromine at C_5 in **1e** (entry 5) or even the C_5 phenyl in **1f** (entry 6) also failed to direct CSI addition to the olefinic bond. Azabicycles **10e** and **10f** again showed the single olefinic resonance in their ^{1}H NMR spectrum in addition to the expected couplings for the remaining protons.

In azabicycle **1g** an endo phenyl group has been introduced at the C_3 position (entry 7). There is now the reasonable possibility of CSI insertion involving C_3, since positive charge might be stabilized at this position as well as C_1. Indeed, the unusual product **12** is now observed. The major couplings in the ^{1}H NMR spectrum of **12** were for the doubly allylic proton H_4 at δ 4.67 (ddd, $J = 10.3$, 7.7, 1.3 Hz), which allowed assignment of olefinic protons H_5 at δ 5.08 (dd, $J = 10.3$, 8.3 Hz) and H_7 at δ 6.11 (dd, $J = 15.7$, 7.7 Hz). The proton H_5 has a smaller 8.3 Hz olefinic coupling with proton H_6 at δ 6.98 (dd, $J = 8.3$, 1.3 Hz), as expected for a cis double bond; the proton H_7 has a larger coupling with proton H_8 at δ 6.49 (d, $J = 15.7$ Hz), as expected for a trans substituted double bond.

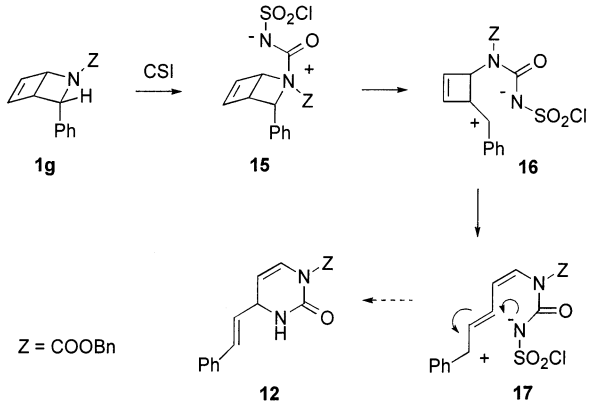


An explanation for the molecular rearrangements leading to the cyclobutenes **10a**−**f** and **11** is shown in Scheme 1, using the parent azabicycle **1a** as an example. Addition of CSI to the nitrogen atom on the exo face affords a zwitterionic species **13**, which might ring open to give the cyclobutenyl allylic cation **14**. Intramolecular ring closure of **14** provides the observed azabicycle **10a** upon reductive workup. Alternatively, if chloride ion is

(15) (a) Sharp, M. J.; Cheng, W.; Snieckus, V. *Tetrahedron Lett.* **1987**, *28*, 5093. (b) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(16) The structure of **10a** was confirmed by X-ray structure analysis.

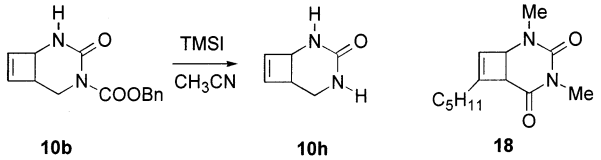
SCHEME 2



present, intermediate **14** might be trapped to afford the chlorocyclobutene **11** upon reductive workup.

A mechanism for formation of the monocyclic heterocycle **12** from reaction of CSI with azabicycle **1g** is shown in Scheme 2. Addition of CSI to the nitrogen atom affords a zwitterion **15**, which ring opens not at the cyclobutene carbon, but at the benzylic position to give the cyclobutenyl cation **16**. Ring opening of this cation affords an extended pentadienyl cationic system **17**.[17] If the vinylic nitrogen atom is cis oriented, ring closure can occur to give the heterocycle **12** after reductive workup.[20]

We note that the *N*-COOBn group of azabicycle **1b** can be removed using TMSiI/acetonitrile to give structure **10h**.[21] Thus, the structures **10a**−**f** discussed in this paper are selectively *N*-protected 5-deoxy analogues of structures such as **18**, formed by photoaddition of 1,3-dimethyluracil with 1-heptyne,[22] and should have potential for incorporation into nucleotides.



(17) There is an issue as to how cation **17** has a cis enamine structure. One possibility is that the stereochemistry is derived during ring opening of cyclobutene **16**. Cyclobutene ring opening would be expected to be disrotatory. It is known that powerful π electron acceptor substituents are likely to show little stereochemical preference in cyclobutene ring openings. For cation **16** interaction of the fragmenting σ bond with the acceptor cation should favor inward opening, but insofar as the filled orbitals of the attached phenyl substituent are involved they should promote outward opening. The nitrogen substituent would be expected to rotate outward;[18] the strongly electron withdrawing groups on nitrogen might alter this preference in competition with the benzyl cation group. A second more likely possibility is that the rotational barrier for the dienyl cation, lowered by the stabilizing nitrogen and phenyl substituents, allows for the requisite geometry of **17** needed for ring closure to be accessed.[19]

(18) (a) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (b) For a review of cyclobutene ring openings, see: Dolbier, W. R., Jr.; Koroniak, H.; Houk, K. N.; Sheu, C. *Acc. Chem. Res.* **1996**, *29*, 471.

(19) For an analogy to the rotational barrier with allyl cations, see: Bollinger, J. M.; Brinich, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4025.

(20) Kallel, E. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 6006. Torquoselectivity in pentadienyl cation ring closures has been discussed. Products of electrocyclic closure of pentadienyl cation **17** were not observed.

(21) Ihara, M.; Taniguchi, N.; Noguchi, K.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1277.

Experimental Section

General Methods.[8] *N*-(Ethoxycarbonyl)-2-azabicyclo[2.2.0]-hex-5-enes **1a**[1] and **1c**,**d**[7] and *N*-(benzyloxycarbonyl)-2-azabicyclo-[2.2.0]hex-5-enes **1b**[1] and **1g**[2] were prepared as previously described; for syntheses of 5-bromo (**1e**) and 5-phenyl (**1f**) analogues see the Supporting Information. ^{1}H NMR spectra were recorded at 300 or 400 MHz and ^{13}C NMR spectra were recorded at 75.5 or 100 MHz in $CDCl_3$ solvent. Flash column chromatography was performed with use of Fisher Davisil Grade 633 silica gel Type 60A (200−425 mesh).

General Procedure for Reaction of Chlorosulfonylisocyanate (CSI) with *N*-(Alkoxycarbonyl)-2-azabicyclo[2.2.0]-hex-5-enes 1. (A) The alkene **1** (7 mmol) in CH_2Cl_2 (20 mL) under argon was cooled to −20 °C and CSI (1.1 g, 8 mmol) in CH_2Cl_2 (6 mL) was added over 10 min. The solution was allowed to stir between −20 and −30 °C for 2 h. The mixture was slowly diluted with cold acetone (5 mL) at −70 °C. The solution was then treated with thiophenol (1.4 mL, 1.5 g, 14 mmol), followed by pyridine (849 mL, 830 mg, 11 mmol) in acetone (5 mL).[23] The solution was brought to room temperature, water (5 mL) was added, and the reaction was stirred for 30 min. The aqueous layer was separated and extracted with CH_2Cl_2 (3 × 5 mL). The combined organic extracts were combined, washed with water (5 mL), and dried over $MgSO_4$. The solvent was removed and the residue was chromatographed. (B) Method A was altered to carry out the reaction at room temperature. The removal of the chlorosulfonyl group was carried out by addition of anhydrous sodium sulfite (300 mg) in water (4 mL)/mmol of alkene **1**.[23]

4-*N*-(Ethoxycarbonyl)-2,4-diaza-3-oxo[4.2.0]oct-7-ene (10a) and 4-[*N*-(Aminocarbonyl)-*N*-(ethoxycarbonyl)]aminomethyl-3-chlorocyclobutene (11). According to general Method A there was obtained from olefin **1a** (1 g, 7 mmol) and CSI (1.1 g, 8 mmol) after chromatography (1:1 hexane:ether) 273 mg (20%) of insertion product **10a** at R_f 0.47 (12:1 ethyl acetate:2-propanol), mp 134−136 °C (pet ether/2-propanol): ^{1}H NMR δ 6.57 (br, 1 H), 6.15 (d, J = 2.7 Hz, 1 H), 6.11 (d, J = 2.7 Hz, 1 H), 4.38 (d, J = 13.5 Hz, 1 H), 4.29 (q, J = 7.2 Hz, 2 H), 4.25 (t, J = 4.5 Hz, 1 H), 3.54 (dd, J = 4.5, 3.9 Hz, 1 H), 3.23 (dd, J = 13.5, 3.9 Hz, 1 H), 1.34 (t, J = 7.2 Hz, 3 H); ^{13}C NMR δ 155.7, 154.4, 139.3, 137.8, 62.8, 52.8, 46.0, 43.9, 14.3; HRMS *m*/*z* 197.0926, calcd for $C_9H_{13}N_2O_3$ (M + H) 197.0925. Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.16; N, 14.28. Found: C, 55.07; H, 6.37; N, 13.88. See Supporting Information for the X-ray analysis. Also obtained was 349 mg (25%) of a white crystalline cyclobutene **11** at R_f 0.22 (1:1 hexane:ether), mp 124−125 °C (pet ether/2-propanol): ^{1}H NMR δ 8.43 (s, 1 H), 6.31 (d, J = 2.7 Hz, 1 H), 6.16 (d, J = 2.7 Hz, 1 H), 5.44 (s, 1 H), 5.04 (d, J = 3.9 Hz, 1 H), 4.31 (q, J = 7.2 Hz, 2 H), 4.16 (dd, J = 14.1, 4.5 Hz, 1 H), 4.02 (dd, J = 14.1, 10.5 Hz, 1 H), 3.43 (ddd, J = 10.5, 4.5, 3.9 Hz, 1 H), 1.39 (t, J = 7.2 Hz, 3 H); HRMS *m*/*z* 235.0060 and 233.0694, calcd for $C_9H_{13}N_2O_3{}^{37,35}Cl$ 235.0060 and 233.0695. Anal. Calcd for $C_9H_{13}N_2O_3Cl$: C, 46.46; H, 5.63; N, 12.04. Found: C, 46.26; H, 5.81; N, 11.75.

4-*N*-(Benzyloxycarbonyl)-2,4-diaza-3-oxo[4.2.0]oct-7-ene (10b). Olefin **1b** (430 mg, 2 mmol) and CSI (180 μL, 2.1 mmol) were stirred at ambient temperature for 1 h, solvent was removed, and the residue after chromatography (4:1 hexane:ethyl acetate) afforded 606 mg (85%) of a CSI insertion product at R_f 0.74 (2:3 hexane:ethyl acetate). Immediate reduction of this product (356 mg, 1 mmol) according to general Method B afforded 201 mg (73%) of **10b** at R_f 0.30 (2:3 hexane:ethyl acetate): ^{1}H NMR δ 7.26 (br, 5 H), 6.60 (br, 1 H), 6.06 (d, J = 2.7 Hz, 1 H), 6.00 (d, J = 2.7 Hz, 1 H), 5.25 (s, 2 H), 4.36 (d, J = 13.6 Hz, 1 H), 4.17 (t, J = 9.0, 4.6 Hz, 1 H), 3.46 (br, 1 H), 3.18 (dd, J = 13.6, 3.8 Hz, 1 H); ^{13}C NMR δ 155.9, 154.7, 139.8, 138.2, 130.3, 128.9, 128.4, 128.1, 68.5, 53.2, 46.4, 44.5; HRMS *m*/*z* 281.0902, calcd for $C_{14}H_{14}N_2O_3Na$ (M + Na) 281.0903.

4-*N*-(Ethoxycarbonyl)-6-methyl-2,4-diaza-3-oxo[4.2.0]oct-7-ene (10c). According to general Method A after 2 h there was

(22) Yang, D.-Y.; Begley, T. P. *Tetrahedron Lett.* **1993**, *34*, 1709.

(23) Malpass, J. R.; Tweddle, N. J. *J. Chem. Soc., Perkin Trans. 1* **1977**, 874.

obtained from olefin **1c** (312 mg, 1.87 mmol) and CSI (200 μL, 265 mg, 1.87 mmol) after chromatography (1:1 hexane:ether) 127 mg (32%) of insertion product **10c** at R_f 0.56 (12:1 ethyl acetate: 2-propanol), mp 127−129 °C (pet ether/2-propanol): ^{1}H NMR δ 7.0 (br, 1 H), 6.03 (d, J = 2.7 Hz, 1 H), 6.00 (d, J = 2.7 Hz, 1 H), 4.20 (q, J = 6.9 Hz, 2 H), 4.14 (d, J = 13.5 Hz, 1 H), 3.67 (d, J = 4.5 Hz, 1 H), 2.94 (d, J = 13.5 Hz, 1 H), 1.25 (t, J = 6.9 Hz, 3 H), 1.20 (s, 3H); ^{13}C NMR δ 155.1, 154.1, 141.7, 135.6, 62.7, 58.2, 52.4, 49.3, 19.3, 14.3; HRMS *m*/*z* 211.1083, calcd for $C_{10}H_{15}N_2O_3$ (M + H) 211.1084.

4-*N*-(Ethoxycarbonyl)-7-methyl-2,4-diaza-3-oxo[4.2.0]oct-7-ene (10d). According to general Method A after 1 h there was obtained from olefin **1c** (500 mg, 3 mmol) and CSI (297 μL, 483 mg, 3.4 mmol) after crystallization from ether 515 mg (82%) of white crystalline insertion product **10d** at R_f 0.14 (10:1 ether: hexane), mp 131−132 °C (pet ether/2-propanol): ^{1}H NMR δ 6.03 (br, 1 H), 5.73 (s, 1 H), 4.35 (dd, J = 13.5, 1.5 Hz, 1 H), 4.20 (q, J = 7.2 Hz, 2 H), 3.27 (br, 1 H), 3.12 (dd, J = 13.5, 3.6 Hz, 1 H), 1.64 (s, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.20 (s, 3H); ^{13}C NMR δ 156.0, 155.0, 148.6, 131.7, 63.4, 50.6, 47.8, 43.3, 15.0, 14.7; HRMS *m*/*z* 211.1090, calcd for $C_{10}H_{15}N_2O_3$ (M + H) 211.1084.

4-*N*-(Benzyloxycarbonyl)-7-bromo-2,4-diaza-3-oxo[4.2.0]-oct-7-ene (10e). According to general Method B after 1 h there was obtained from olefin **1e** (150 mg, 0.5 mmol) and CSI (43 μL, 0.5 mmol) after chromatography (2:1 hexane:ethyl acetate) 136 mg (81%) of insertion product **10e** at R_f 0.2 (1:1 hexane: ethyl acetate): ^{1}H NMR δ 7.36−7.2 (br, 5 H), 6.19 (s, 1 H), 6.05 (br, 1 H), 5.24 (s, 2 H), 4.41 (dd, J = 13.9, 1.4 Hz, 1 H), 4.23 (t, J = 4.3 Hz, 1 H), 3.61 (br, 1 H), 3.20 (dd, J = 13.5, 3.6 Hz, 1 H); ^{13}C NMR δ 154.5, 153.7, 138.5, 135.5, 128.5, 128.2, 128.0, 122.2, 68.5, 52.1, 51.9, 42.4; HRMS *m*/*z* 358.9996 and 360.9991, calcd for $C_{14}H_{13}N_2O_3{}^{79,81}BrNa$ (M + Na) 359.0007 and 360.9987.

4-*N*-(Benzyloxycarbonyl)-7-phenyl-2,4-diaza-3-oxo[4.2.0]-oct-7-ene (10f). According to general Method B after 1 h there was obtained from olefin **1f** (146 mg, 0.5 mmol) and CSI (43 μL, 0.5 mmol) 130 mg (75%) of insertion product **10f** at R_f 0.17 (1:1 hexane:ethyl acetate): ^{1}H NMR δ 7.29−7.04 (br, 10 H), 6.30 (s, 1 H), 5.92 (br, 1 H), 5.18 (d, J = 12.4 Hz, 1 H), 4.96 (d, J = 12.4 Hz, 1 H), 4.64 (dd, J = 13.5, 1.5 Hz, 1 H), 4.23 (t, J = 4.4 Hz,1 H), 3.84 (br, 1 H), 3.42 (dd, J = 13.6, 3.8 Hz, 1 H); ^{13}C NMR δ 155.2, 153.7, 146.8, 135.6, 132.0, 127.9, 125.5, 125.8, 68.1, 49.3, 44.4, 43.7; HRMS *m*/*z* 335.1393, calcd for $C_{20}H_{19}N_2O_3$ (M + H) 335.1396.

1-*N*-(Benzyloxycarbonyl)-4-(*trans*-2-phenylethenyl)-1,3-diaza-2-oxo-cyclohex-5-ene (12). According to general Method B after 1 h there was obtained from olefin **1g** (146 mg, 0.5 mmol) and CSI (43 μL, 0.5 mmol) after chromatography (3:1 hexane: ethyl acetate) 120 mg (70%) of rearrangement product **12** at R_f 0.26 (1:2 hexane:ethyl acetate): ^{1}H NMR δ 7.35 (br, 10 H), 6.98 (dd, J = 8.3, 1.3 Hz, 1 H), 6.49 (d, J = 15.7 Hz, 1 H), 6.11 (dd, J = 15.7, 7.7 Hz, 1 H), 5.47 (br, 1 H), 5.33 (s, 2 H), 5.08 (dd, 10.3, 8.3 Hz, 1 H), 4.67 (ddd, 10.3, 7.7, 1.3 Hz, 1 H); ^{13}C NMR δ 151.4, 149.2, 135.6, 135.1, 128.5, 128.3, 128.1, 127.3, 131.5, 126.6, 124.1, 106.1, 68.9, 54.6; HRMS *m*/*z* 357.1226, calcd for $C_{20}H_{18}N_2O_3Na$ (M + Na) 357.1215.

2,4-Diaza-3-oxo[4.2.0]oct-7-ene (10h). Trimethylsilyl iodide (240 μL, 1.63 mmol) was slowly added to a solution of *N*-(benzyloxycarbonyl) substituted alkene **10b** (140 mg, 0.54 mmol) in dry acetonitrile (10 mL) with ice cooling and the mixture was stirred for 30 min. After concentration of the solution under reduced pressure the residue was combined with 10% HCl (5 mL) with ice cooling and extracted with CH_2Cl_2 (3 × 10 mL). The extracts were washed with water (5 mL) and brine (5 mL) and dried over sodium sulfate and solvent was removed in vacuo to give a residue, which was chromatographed (1:1 hexane:ethyl acetate) to give 54 mg (80%) of parent heterocycle **10h**, R_f 0.40 (1:5 hexane:ethyl acetate): ^{1}H NMR δ 6.13 (d, J = 2.7 Hz, 1 H), 5.99 (d, J = 2.7 Hz, 1 H), 5.57 (br, 1 H), 4.20 (d, J = 3.2 Hz, 1 H), 3.30 (m, 1 H), 3.19 (dd, J = 12.3, 4.4 Hz, 1 H), 3.11 (dd, J = 12.3, 2.7 Hz, 1 H); ^{13}C NMR δ 160.8, 138.6, 138.2, 53.4, 44.1, 41.1; HRMS *m*/*z* 125.0713, calcd for $C_6H_9N_2O$ 125.0715.

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Supporting Information Available: Tables of crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters accompany the ORTEP drawing for structure **10a**, experimental details for **1e** and **1f**, and ^{1}H and ^{13}C NMR spectra for other new structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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