ammonia (0.65 mL). Gaseous ammonia also was bubbled into the mixture until everything dissolved. A solution of carbon disulfide (0.72 g, 9.4 mmol) in 16 mL of ethanol was added, and the mixture was left to precipitate 7 for 3 h: yield 2.1 (97%), mp 246 °C dec. **7b** and **7c**: ^{1}H NMR (Me_2SO-d_6) (nondeuterated compound) δ 2.27 (3 H s, CH_3), 4.50 (2 H, s, CH_2), 6.20 (4 H, b, NH_4), 6.80 (3 H, b, NH_2 + NH), 7.82 (1 H, s, CH). **7b**: $C_7H_{12}DN_5S_2$ (232.3). **7c**: $C_7H_{11}D_2N_5S_2$ (233.4).

3-[(2-Methyl-4-amino-5-pyrimidinyl)methyl]-5-(2-hydroxyethyl)-2-thiothiazolone (8b,c).[5] A solution of **7b,c** (2.1 g, 9.1 mmol) in warm DMF/H_2O 1:1 (13 mL) was cooled to 20 °C, sodium iodide (0.8 g, 5.2 mmol) and 3-chloro-4-oxypentyl acetate (1.7 g, 9.5 mmol) was added, and the solution was stirred for 6 h. A precipitate was isolated from the cooled (4 °C) mixture, redissolved in HCl (13 mL, 10%), and heated on a steam bath for 15 min. The cold solution then was neutralized with NaOH (10%), and **8b,c** was isolated, heated with ethanol (20 mL), and isolated again, yield 1.4 g, 52%; mp 240 °C (lit.[8] 238–9 °C). ^{1}H NMR (DCl, TSS-standard), nondeuterated **8**: δ 2.27 (3 H, s, CH_3), 2.60 (3 H, s, CH_3), 2.90 (2 H, t, CH_2CH_2), 3.76 (2 H, t, CH_2OH), 5.33 (2 H, CH_2-bridge), 7.52 (1 H, s, CH).

Thiamin-*6′-d*$_1$ and *N*-CD_2 Hydrochloride (1b and 1c).[5] To an ice-cold suspension of thiothiazolone **8b,c** (1.4 g, 4.7 mmol) in water (4.5 mL) and concentrated hydrochloric acid (0.24 mL) was added slowly hydrogen peroxide (1.65 g, 30%, 14.5 mmol). The clear solution was heated to 60 °C, and sulfate was precipitated with a solution of barium chloride (1.14 g, 5.5 mmol) in water (5 mL). The filtrate was brought to dryness, taken up in hot ethanol (7.5 mL), and **1b,c** crystallized after cooling, yield 1.3 g (83%, over all 42%), melting point, of the raw material: **1b**, 238 °C, 90% D at C-6′; **1c**, 239 °C, 85% D at the methylene bridge and 35% D at 6′. Recrystallization raised the melting point to 250 °C. **1b**, $C_{12}H_{16}DN_4OSCl{\cdot}HCl$ (338.3); **1c**, $C_{12}H_{15}D_2N_4OSCl{\cdot}HCl$ (339.3).

1′-Methylthiaminium-*6′-d*$_1$ and *N*-CD_2 Perchlorate (1e and 1f). The procedure was essentialy the same as that[31] described for the nondeueterated material: 0.34 g (1 mmol) of **1b** yielded 250 mg (52%) of **1e**, mp 209 °C, $C_{13}H_{19}Cl_2DN_4O_9S$ (480.3); 1.2 g (3.5 mmol) of **1c** yielded 0.95 g (55%) of **1f**, mp 216–18 °C. ^{1}H NMR analysis revealed that **1e** was 90% deuterated at C-6′, **1f** 85% at the methylene bridge; 35% of C-6′ was still deuterated.

Kinetics. Pseudo-first-order kinetics were carried out spectrophotometrically as reported earlier.[18] However, for the more extensive study on the 6′-position of **1d** and **1e** a variation on the reported method was employed. A stock solution of phosphate buffer (0.0184 M Na_2HPO_4 and 0.0276 M KH_2PO_4) was made up with KCl to an ionic strength of 0.828 and kept under argon. To a 1-cm cell containing about 2 mg of **1d** or **1e** was added 3 mL (3.140 g) of buffer under argon. Following thermal equilibration of the cell in the thermostatted compartment for 15 min 100 ± 0.2 μL of 1.61 M stock Na_2SO_3 was added by a pipet dispenser with disposable tip. The change in the absorbance (about 0.250) was observed at 292 nm. Ten points were taken 10 min after mixing, covering a span of about 3 half-lives. Infinity values were measured but were corrected as needed by a least-squares computer program fitting the correlation coefficient to a value better than 0.9999. These infinity corrections in general were very small. The pH was measured immediately after a run with a PMX 2000 meter. The accuracy of the pH measurements is of the order 0.005. Ten pairs of kinetics runs were taken, but one pair was discarded because unaccountably the pH of the solution with the nondeuterated sample was 0.5 too high. The deuterated and nondeuterated substrates were measured alternately in order to minimize any temperature variation. The results are summarized as follows where the order of the data is run number and isotope identity/10^3k_{obs}, s^{-1}/pH/10^3k_2, $M^{-1}\,s^{-1}$. The fractional amount of free sulfite ion was calculated as earlier,[18] the second-order constant being given when k_{obs} is divided by the free sulfite ion concentration. 1H/1.53/6.94/42.6, 2D/1.56/6.93/43.7, 3D/1.56/6.94/43.5, 4H/1.51/6.94/42.0, 5H/1.45/6.93/40.6, 6D/1.56/6.93/43.6, 7H/1.54/6.93/43.1, 8D/1.52/6.92/42.9, 9D/1.52/6.91/43.3, 10H/1.44/6.92/40.6, 11H/1.45/6.94/40.3, 12D/1.53/6.93/42.8, 13H/1.42/6.93/39.8, 14D/1.53/6.93/42.9, 15D/1.54/6.91/43.9, 16H/1.49/6.93/41.7, 17D/1.56/6.93/43.7, 18H/1.46/6.93/40.8.

Acknowledgment. This work was supported by Grant P 5760 of the Austrian Fond zur Förderung der Wissenschaften; Hoffmann-LaRoche AG (Swizerland) kindy supplied 3-chloro-4-oxypentyl acetate. Dr. K. T. Leffek kindly called our attention to ref 20.

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Functionalization of Olefins by Alkoximidoylnitrenes

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Received November 1, 1988

(*N*-Cyano- and *N*-(methylsulfonyl)alkoxycarbimidoyl)nitrenes, generated in situ from the corresponding azides by 300-nm UV light, convert a variety of olefins cleanly and stereospecifically to the corresponding aziridines. These can readily be hydrolyzed to N-unsubstituted aziridines or ring-opened to allylic isoureas. The nitrenes can also be generated by thermolysis at 80 °C. The azides add to norbornene to give triazolines, which lose nitrogen to give the *exo*-aziridines.

Introduction

Additions of nitrenes to olefins have been studied since 1962.[1] Carbonylnitrenes, sulfonylnitrenes, alkoxynitrenes, phosphorylnitrenes, and certain (*N*-acylamino)nitrenes give aziridines.[2–4] Nevertheless, there are relatively few examples of intermolecular nitrene additions to olefins for actual use in synthesis. This might be due to a combination of circumstances. For example, (alkoxycarbonyl)nitrenes can be made conveniently and efficiently (below 0 °C if so desired) by α-elimination[5] or photolysis, and at 80 °C by thermolysis, from stable precursors which themselves do not react with olefins. Still, (alkoxycarbonyl)nitrenes are not very suitable for making aziridines. Being too reactive, they give appreciable quantities of various

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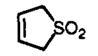
Table I. Yields and Solvent:Olefin Ratios for Reactions of Olefins with Imidoylnitrenes[a]

olefin	nitrene 1	nitrene 2	nitrene 3a	nitrene 3b
(*Z*)-2-butene				**4** 74% (81.5%)
(*Z*)-4-methyl-2-pentene	**5** 85% (92%) 2:1 78% (100%) 20:1 72% 195:1	**6** 57% 127:1 TH 27% 20:1 PH		**7** 93% (100%) 20:1 69% (91%) 1000:1 61% (69%) 2000:1
(*E*)-4-methyl-2-pentene	**8** 70% (78%) 3:1	**9** (az) + **10** (rr) 44% az + 8% rr TH 1.5:1 30% **9** 10:1 PH		**11** (100%) 9:1
but-3-enenitrile	**12** 100% 22:1			
methylenecyclohexane	**13** (67%) 23:1		**14** 70% (87%) 23:1	**15** 70% 23:1
ethylidenecyclohexane				**16** 73% 17:1
β-pinene	**17** 50% rr 11:1		**18** 58% rr 19:1	**19** 42% rr 13:1
cyclohexene	**20** 79% (91%) 0.5:1	**21** 62% 5:1 TH 27% 13:1 PH		**22** 75% 2.6:1
cycloheptene	**23** 59% 8:1	**24** (az) + **25** (rr) >21% az; 5% rr TH 8:1 21% **24** 10:1 PH	**26** 71% 23:1	**27** 81% 23:1
	**28** 57% 54:1			**29** 40% 105:1
methylcyclohexene	**30**[b]			**31** (100%) 23:1
α-pinene			**32** 70% 19:1	**33** 59% 38:1
norbornene	**34**[c]	**35**[c]	**36**[c]	**37**[c]

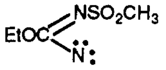
[a] Bold numbers are products. Yields of isolated products are given as "%"; yields determined by NMR are given as "(%)". The mole ratio of solvent to olefin is given as "*x*:1". All reactions are photolyses except in systems where both photolyses (PH) and thermolyses (TH) were done. The designation "rr" refers to rearranged product (the allylic isourea from ring-opening of the aziridine). [b] See text. [c] Norbornene reacted with all azides by the triazoline route to give derivatives of *exo*-3-azatricyclo[3.2.1.0^{2,4}]octane. Details are described in the discussion and the Experimental Section.

C–H insertion products together with the aziridines, and they also attack benzene rings, if present. Cyano- and sulfonylnitrenes also give C–H insertion, and they cannot be generated conveniently, or under mild conditions, respectively. Still others, such as (dialkylamino)nitrenes,[6] do not add to olefins at all.

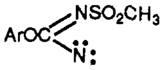
We have started developing a set of nitrene precursors, designed to yield, under mild conditions, an assortment of nitrenes of graded reactivities. Some of these are intended to attack only the most reactive functional groups (:S, :NR_3, HO, etc.), and others should also add to olefins (but not arenes), while still others should react with most functions, but not aliphatic C–H bonds. A preliminary communication[7] reported *N′*-sulfonyl- and *N′*-cyanocarbimidoylnitrenes. They do not react with aliphatic C–H bonds, and only the latter add to benzene. Four examples of addition to olefins are mentioned briefly in that communication.[7] For nitrenes in general, a literature[2-4] survey shows an approximate order of *substrate reactivity*: S: > N: > OH > C=C > benzene > CN > aliphatic CH. Examples for the first three substrates are sulfoxides, tertiary amines, and the oxygen atoms of alcohols. *Nitrene reactivity* depends strongly on the electronic effect of the group G attached to the electron-deficient nitrogen. More electron withdrawing G cause higher reactivity. The strongest electron-withdrawing groups G, such as SO_2, NC, or ROOC, make nitrenes capable of inserting into unactivated aliphatic C–H bonds and, thus, must be avoided if only aziridine formation is desired. The sensitivity of aziridines creates other limitations: heat, or UV of short wavelength (such as 254 nm from the mercury resonance line of common mercury lamps), often decomposes aziridines. Additional requirements for practical use are acceptable yields, applicability to a wide range of olefins, gentle reaction conditions, and stereospecificity. Certain alkoxycarbimidoylnitrenes do meet these requirements, as will be shown below.

Results and Discussion

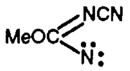
In this paper, we report additions to olefins of three types of imidoylnitrenes: *N′*-(methylsulfonyl)ethoxycarbimidoylnitrene (**1**), *N′*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoylnitrene (**2**), and *N′*-cyanoalkoxycarbimidoylnitrene **3a** (alkoxy = CH_3O) and **3b** (alkoxy = C_2H_5O), respectively. These nitrenes were made in situ



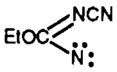
1



2



3a



3b

by photolysis (300 nm) or thermolysis (80 °C) of the corresponding azides. Olefins ranging from *cis*-2-butene to α-pinene gave aziridines in good yields, with complete cis stereospecificity. The 300-nm light does not affect most aziridines. Some strained aziridines, such as that from β-pinene, open spontaneously to the allylic isoureas; others do so upon heating or treatment with iodide ion. The allylic isoureas themselves can be valuable, as they can be hydrolyzed to the allylic amines or converted in other ways. Thermolysis, at 80–100 °C, is used to generate the nitrenes **1**, **2**, or **3** if the photochemistry of the system is encumbered by chromophores absorbing near 300 nm. However, some aziridines are unstable at 80 °C. Scheme I and Table I summarize our results.

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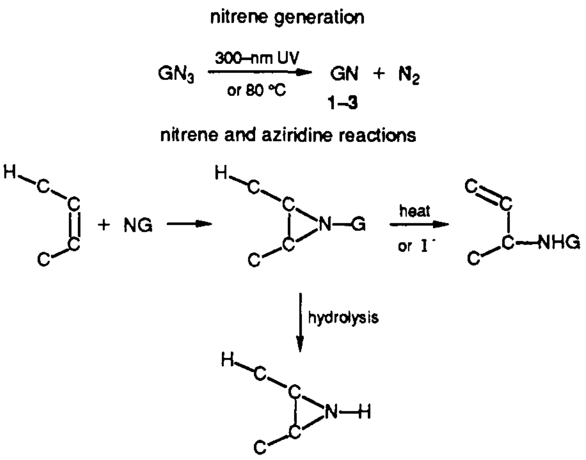
(7) Subba Rao, O.; Lwowski, W. *Tetrahedron Lett.* **1980**, *21*, 727.

Scheme I



Reactive nitrenes are very short lived, and the half-life of our singlet imidoylnitrenes is not known. They are generated in situ, in the singlet state, and then collide with solvent and with olefin molecules. In earlier studies[8] of alkoxy*carbonyl*nitrenes, we found a strong effect of the molar ratio of solvent to olefin on the stereospecificity of addition, due to intersystem crossing. This effect is absent with the new alkoxycarb*imidoyl*nitrenes. The mole ratio of solvent to olefin (see Table I) has no effect on the stereospecificity. Furthermore, high aziridine yields can be obtained even at low olefin concentrations (for examples, see compounds **5**, **7**, **28**, and **29**). Apparently, singlet alkoxycarbimidoylnitrenes persist much longer than do singlet alkoxycarbonylnitrenes. (The solvent to olefin ratio is only a crude measure for the chance for productive nitrene–olefin collisions, since it neglects solvation, known to exist with alkoxycarbonylnitrenes[9-12] and carbonylnitrenes.[13,14]) The data also show that acceptable yields can be obtained without using a large excess of olefin (see Experimental Section for **15**, **28**, and **29**).

Stereospecificity. The most sensitive test for the cis stereospecificity of the nitrene addition is provided by the reactions with the *cis*- and *trans*-4-methyl-2-pentenes. We find the ^{1}H NMR spectra of both the *cis*- and *trans*-aziridines to be sufficiently different to distinguish them in unpurified reaction mixtures. (See Experimental Section for **5–9**.) Moreover, the threshold of detection of any trans isomers is greatly improved by removing much of *cis*-aziridine. Cooling of the pentane solutions of the reaction mixtures from *cis*-4-methyl-2-pentene causes about 60% of the pure *cis*-aziridines **5** and **7** to crystallize, enriching any potential trans isomer in the mother liquors. Even small amounts of the nonstereospecifically formed aziridines would have been seen in the ^{1}H NMR spectra (see Experimental Section for the chemical shifts). Still, no trans isomers were found in reactions of the cis olefin. The liquid *trans*-2-isopropyl-3-methylaziridines **8** and **11** were isolated by chromatography. No cis isomer was detected in the crude reaction mixtures, the aziridine fractions, or in the other parts of the eluents. No nonstereospecific reaction was found in the thermolyses leading to **6** or **9**. In contrast to the additions of ethoxy*carbonyl*nitrene,[8] the imidoylnitrene reactions remained fully stereospecific even at low concentrations of olefin.

Aziridine Mass Spectra. All our aziridines show strong parent mass peaks (usually >10% of the base peak intensity) and straightforward fragmentation patterns. The base peaks correspond to the mass of the N-unsubstituted aziridines minus 1, perhaps the ring-opened imine radical cations. The parent olefin mass is always prominent, but for the parent nitrene mass, a strong peak is not seen. Instead, the N-substituent of the aziridine breaks up in a fashion depending on its structure. If the substituent Z on the imino function (C═NZ) is methylsulfonyl, masses 79 and 121 are observed, perhaps due to methylsulfonyl and methylsulfonyl isocyanate. Where Z is CN and RO is ethoxy, mass 70, corresponding to EtNHCN, is strong. Also observed are peaks of mass numbers corresponding to M$^+$ minus ethyl, ethylene, methyl, isopropyl (where applicable), and combinations of the latter losses and those mentioned before. The aziridines derived from cyclohexene also show strong peaks at 69, which might be due to cyclopentyl radical cation.

Photolysis vs Thermolysis. Photolysis using fluorescent lamps with a peak emission at 300 nm usually gave better yields than thermolysis. Some of our aziridines rearranged to allylic isoureas at the temperatures required for azide thermolysis (80–100 °C), but are stable to 300-nm light (but not to 254 nm). Photolysis may be encumbered by chromophores in any of the components of the system, such as the 2,6-dimethylphenoxy groups in **2**. Its cyclohexene adduct **21** was obtained in 27% yield by photolysis, but in 62% yield by thermolysis of the azide **36**. The nitrenes **3a** and **3b** gave the aziridines **26** and **27** in 71% and 81% yields, respectively, with cycloheptene. Its adduct with **2**, however, was obtained in the lowest yields encountered in this work. Thermolysis gave only a 21% yield of the aziridine **24**. Some of it rearranged to **25** (5% yield), and *N*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)-isourea (**10**) was formed in 21% yield, perhaps by a radical decomposition of **24**. Photolysis did no better, giving a 21% yield of **24**.

Hydrolysis to the N-unsubstitued aziridines is best done with 1.5 or 2 equiv of NaOH in methanol at room temperature (see Experimental Section for compounds **20**, **22**, and **34**). On a 200-mg scale, and without optimization, yields of 44–61% (the latter for *exo*-3-azatricyclo-[3.2.1.0^{2,4}]octane from **34**) were obtained.

Ring-opening by iodide converts the aziridines to allylic isoureas, which might be desired for further synthetic conversions. For example, 500 mg of 1-(*N'*-cyanoethoxycarbimidoyl)-1-azaspiro[2.5]octane (**15**) treated with sodium iodide in acetonitrile gave *N*-(1-cyclohexenylmethyl)-*N'*-cyano-*O*-ethylisourea in 60% yield.

Strained Olefins. Except for norbornene, the olefins in Table I do not react with the azides **1–3** in the dark at room temperature. It has long been known[15] that highly strained olefins, such as norbornene, do react with azides at room temperature in the dark, to form 1,2,3-triazolines. With electron-withdrawing substituents on the N-1 or N-3 of the triazoline, N_2 is lost spontaneously to give aziridines.[16] Our azides, too, behave this way, adding to norbornene at room temperature in the dark, to form N_2

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(16) For a review, see: Lwowski, W. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; J. Wiley and Sons: New York, 1984; Vol. I, pp 559–651.

and the *exo*-aziridines, **34**–**37**, respectively. Yields were good, and these 1,3-dipolar cycloaddition–elimination reactions could be synthetically useful.

Conclusion. The experiments summarized in Table I show that aziridines can be made stereospecifically and in good yields, by generating (*N*-sulfonyl- or (*N*-cyanoalkoximidoyl)nitrenes from the corresponding azides in the presence of a variety of olefins. Open-chain and cyclic 1,2-substituted olefins gave the best yields, but 1,1,2-trisubstituted and 1,1-disubstituted (exocyclic) ones were not far behind. The fairly hindered α-pinene still gave a 70% isolated yield of **32**, without attempts to optimize the reaction conditions. Replacing ethoxy or methoxy in the nitrenes by 2,6-dimethylphenoxy produced a less effective nitrene, as far as aziridinations are concerned. However, as described in the accompanying paper,[17] *N'*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoylnitrene (**2**) was superior in aminating electron-rich aromatic rings.

Experimental Section

General. NMR spectra were taken on JEOL PS-100 (^{1}H) or Varian XL-200 spectrometers. Assignments of ^{13}C signals were confirmed by doing APT or off-resonance decoupled spectra. IR spectra were obtained by using Perkin-Elmer Model 621 and 283 instruments. Melting points are uncorrected. Mass spectra were taken on a Hitachi RMU-6 instrument, using 70-eV nominal ionization voltage. In discussing mass spectra, masses corresponding to that of a particular compound or ion are given by the compound's name or formula in parentheses. Elemental analyses were done by MicAnal, Tucson, AZ. Yields are those of isolated, pure material unless stated otherwise. The yields are not optimized; most experiments were done once or twice only.

Photolyses were performed in Rayonet photochemical reactors, using fluorescent UV lamps with a maximum emission at 300 nm. Silica photolysis tubes were suspended in the center of the reactor and contained axial cooling fingers, through which a glycol–water mixture at −10 °C was pumped. The length of the 16 UV lamps surrounding the photolysis tube was 26 cm, and the photolysis tubes were filled with peroxide-free mixtures of the azide, olefin, and dichloromethane to 26-cm height. Irradiation was stopped when the N_2 evolution became slow, after 5–9 h. Volatile materials were removed at 0.2 mmHg at room temperature and the residues analyzed by NMR and then chromatographed and/or crystallized. For **quantitative NMR analyses**, known fractions (250–350 mg) of the residues (above) were dissolved in $DCCl_3$ (to 1.0 mL). Trichloroethene (0.02–0.03 mL), weighed for greater accuracy, was added as standard, and molar concentrations and yields were computed from the proton signal integrals. Accuracy was about 5%.

Azides. The azide precursors to the nitrenes are readily made by acylating 5-alkoxytetrazoles.[18] These azides are quite stable and have been handled without any incident. Reasonable precautions should, of course be taken, since azides, and tetrazoles, are potentially explosive. Azides that are easily hydrolyzed to hydrazoic acid are, when ingested, strong, if short-acting, vasodilators.

***N'*-(Methylsulfonyl)ethoxycarbimidoyl azide (39)** (or ethyl 1-azido-*N*-(methylsulfonyl)formimidate), ***N'*-cyanomethoxycarbimidoyl azide (40)** (methyl 1-azido-*N*-cyanoformimidate), and ***N'*-cyanoethoxycarbimidoyl azide (41)** (ethyl 1-azido-*N*-cyanoformimidate) were prepared as described earlier.[18]

5-(2,6-Dimethylphenoxy)tetrazole (42). NaN_3 (14 g, 0.215 mol) in 50 mL of water and 20 mL of acetone and 2,6-dimethylphenyl cyanate[19] (14.7 g, 0.1 mol) in 30 mL of acetone were stirred for 1 h at 65 °C, the acetone was removed, and the solution was acidified with concentrated HCl. The tetrazole was filtered, washed with water, and recrystallized from methanol and water to give 13.25 g (70 %), mp 165–70. Four recrystallizations gave analytically pure material, mp 173–4 °C. IR (KBr): 3025 (w), 3000 (w), 2890 (m), 1600 (s), 1570 (s). ^{1}H NMR: 2.08 (s, 3 H), 7.12 (s, 3 H), 10.2–10.6 (br, 1 H). ^{13}C NMR: 16.01, 126.78, 129.35, 129.96, 150.75, 165.71. Anal. Calcd for $C_9H_{10}H_4O$: C, 56.83, H, 5.30; N, 29.46. Found: C, 56.46; H, 5.43; N, 29.49.

***N'*-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl Azide (43).** To 5-(2,6-dimethylphenoxy)tetrazole (5.7 g, 30 mmol) in 50 mL of THF was added methanesulfonyl chloride (3.44 g, 30 mmol) in 20 mL of THF with stirring at 0 °C. Triethylamine (3 g, 30 mmol) in 20 mL of THF was then added dropwise. After 2 h, triethylammonium hydrochloride was removed and washed with two 30-mL portions of THF. The residue from the combined THF solutions was chromatographed on a 60–100-mesh silica gel column. A 99:1 chloroform–ethyl acetate mixture eluted 6.5 g (80%) of **43**, mp 73–4 °C. IR ($CHCl_3$): 3025 (w), 2140 (vs), 1620 (vs), 1610 (vs), 1585 (s), 1320 (vs), 1300 (vs), 1155 (s), 1140 (vs). ^{1}H NMR: 2.24 (s, 6 H), 3.02 (s, 3 H), 7.08 (s, 3 H). ^{13}C NMR: 16.06, 42.49, 127.21, 128.97, 129.77, 149.16, 156.03. Anal. Calcd for $C_{10}H_{12}N_4SO_3$: C, 44.76; H, 4.51; N, 20.88. Found: C, 44.65; H, 4.76; N, 20.85.

***N'*-Cyano(2,6-dimethylphenoxy)carbimidoyl Azide (44).** To a cooled solution of 5-(2,6-dimethylphenoxy)tetrazole (9.5 g, 50 mmol) in 150 mL of peroxide-free anhydrous THF was added cyanogen bromide (5.3 g, 50 mmol) in 50 mL of THF, with cooling in an ice–salt bath. Triethylamine (5.05 g, 50 mmol) in 50 mL of THF was added over a period of 30 min. The mixture was stirred and allowed to come to room temperature over 2 h. Filtration, washing with THF, evaporation of the THF solutions, and chromatography on 100 g of silica gel, with chloroform, gave **44**. Recrystallization from a chloroform–petroleum ether mixture yielded 9.14 g (85%), mp 67–8 °C. IR (KBr): 3020 (w), 2220 (m), 2170 (s), 1630 (s), 1585 (s), 1335 (s), 1190 (s). ^{1}H NMR: 2.2 (s, 6 H), 7.05 (s, 3 H). ^{13}C NMR: 15.95, 110.66, 127.65, 129.25, 129.44, 129.51, 149.05. Anal. Calcd for $C_{10}H_{19}N_5O$: C, 55.80; H, 4.22; N, 32.54. Found: C, 55.73; H, 4.29; N, 32.29.

Reaction of 3b with *cis*-2-Butene. *cis*-2,3-Dimethyl-*N*-(ethoxy-*N'*-cyanocarbimidoyl)aziridine (4). **41** (1 g, 7.2 mmol), *cis*-2-butene (30 mL, 333 mmol, 8.8 M), and 38 mL of dichloromethane were irradiated at 20 °C for 13 h. NMR analysis indicated an 81.5% yield. Adsorbing of the crude **4** on 3 g of silica gel, eluting with 150 mL of benzene, and crystallizing from pentane at −25 °C gave 896 mg (74% yield) of pure aziridine, mp 48–9 °C. IR ($CHCl_3$): 3004 (m), 2990 (m), 2940 (w), 2203 (s), 2190 (m), 1570 (vs), 1555 (s), 1327 (s) cm^{-1}. ^{1}H NMR: 1.32 (t, 3 H), 1.37 (d, 6 H), 2.78 (m, 2 H), 4.24 (q, 2 H). Mass spectrum: M^+ = 167 (11); M − C_2H_5, 138 (6); aziridine − CN, 96 (34); aziridine − CONH, 113 (8); olefin + 14, 70 (100); olefin, 56 (32). Anal. Calcd for $C_8H_{13}N_3O$: C, 57.49; H, 7.78; N, 25.15. Found: C, 57.23; H, 7.91; N, 24.93.

Reactions with *cis*-4-Methyl-2-pentene. *cis*-2-Isopropyl-3-methyl-*N*-(*N'*-(methylsulfonyl)ethoxycarbimidoyl)aziridine (5). **39** (2 g, 10 mmol), *cis*-4-methyl-2-pentene (from Phillips Petroleum, containing <0.1% trans isomer) (5 mL, 38.8 mmol, 3.3 M), and 5 mL of dichloromethane irradiated for 13 h gave 2.539 g of crude **5**. NMR analysis indicated a 92% yield. Recrystallization from ethyl acetate–pentane at −25 °C gave 2.2 g (85% yield) of pure **5**, mp 65–6 °C. IR ($CHCl_3$): 3030 (w), 3010 (w), 2967 (w), 2935 (w), 1564 (vs), 1555 (vs), 1315 (s) cm^{-1}. ^{1}H NMR: 0.96 (d, 3 H), 1.1 (d, 3 H), 1.25 (t, 3 H), 1.43 (d, 3 H), 1.6 (m, 1 H), 2.31 (dd, 1 H), 3.03 (s, 3 H), 3.06 (m, 1 H), 4.16 (q, 2 H). ^{13}C NMR: 12.80, 13.86, 19.16, 20.89, 27.15, 42.41, 44.36, 49.05, 65.29, 164.66. Mass spectrum: M^+ = 248 (38); M − Me, 233 (10); M − Et, 219 (5); M − iPr, 205 (3); M − SO_2cH_3, 169 (37); olefin + N, 98 (100); EtOCN, 71 (40); olefin, 84 (60). Anal. Calcd for $C_{10}H_{20}N_2O_3S$: C, 48.39; H, 8.06; N, 11.29. Found: C, 48.19; H, 7.94; N, 11.17.

The mother liquor, after recovery of the 85% yield, was examined by NMR and found to contain rather pure *cis*-**5** and less than 1% trans isomer.

At Low Olefin Concentrations. Use of 4.8 mol % olefin in dichloromethane (2.6 mmol of azide, 24 mmol of olefin, and 30 mL of dichloromethane) gave a *cis*-aziridine yield of nominal 100% by NMR and a 78% yield of pure, solid **5**. A 0.5 mol % olefin concentration (1.3 mmol of azide, 7.9 mmol of olefin, 100 mL of CH_2Cl_2) gave a 72% yield of the isolated *cis*-aziridine. The mother liquor did contain *cis*- but no *trans*-aziridine, of which a 1% yield could have been readily detected by our NMR technique.

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Light Stability. Irradiation of 0.4 g of **5** in 10 mL of dichloromethane at 0 °C with 300-nm light for 30 h did not show decomposition or isomerization (by ^{1}H NMR). A similar experiment, in dibromomethane solution, resulted in complete decomposition after 17 h.

***cis*-2-Isopropyl-3-methyl-*N*-(*N'*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)aziridine (6). (a) Thermolysis.** A solution of **43** (1.132 g, 4.2 mmol) and *cis*-4-methyl-2-pentene (2.36 g, 28 mmol, 0.82 M) in 30 mL of dioxane was heated to reflux for 16 h. Recrystallization from petroleum ether and pentane at −25 °C gave **6** (775 mg, 56.6% yield), mp 65–7 °C. No *trans*-aziridine was found. IR ($HCCl_3$): 3030 (w), 3010 (w), 2970 (w), 1600 (s), 1585 (s), 1570 (m), 1330 (s), 1300 (s), 1140 (s), and 1130 (s) cm^{-1}. ^{1}H NMR: 0.98 (d, J = 6 Hz, 3 H), 1.16 (d, J = 6 Hz, 3 H), 1.25 (d, J = 6 Hz, 3 H), 1.4–1.8 (m, 1 H), 2.14 (d, 3 H), 2.22 (s, 3 H), 2.56 (q, 1 H), 2.84 (s, 3 H), 2.96–3.2 (m, 1 H), 7.04 (s, 3 H). ^{13}C NMR: 12.66, 16.18, 19.15, 21.05, 27.10, 42.51, 44.77, 50.00, 126.01, 128.64, 128.70, 129.78, 130.03, 149.01, 163.24. Mass spectrum: M^+ = 324 (15); M − SO_2CH_3, 245 (45); M − ArOCN, 147 (65); ArOH, 122 (100); mass of ArO and of $MeSO_2NCO$, 121 (100); olefin + 14, 98 (98); olefin, 84 (100). Anal. Calcd for $C_{16}H_{24}N_2O_3S$: C, 59.23; H, 7.46; N, 8.63. Found: C, 59.22; H, 7.44; N, 8.70.

(b) Photolysis. *cis*-4-Methyl-2-pentene (2 g, 23.8 mmol, 0.75 M) and *N'*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl azide (**43**) (0.67 g, 2.5 mmol) in 30 mL of dichloromethane were irradiated for 22 h. Chromatography on silica gel with chloroform and ethyl acetate (95:5) gave 220 mg of **6** (27% yield), mp 65–7 °C.

***cis*-2-Isopropyl-3-methyl-*N*-(*N'*-cyanoethoxycarbimidoyl)aziridine (7). (a) Photolysis at 5 mol % Olefin Concentration.** **41** (1 g, 7.2 mmol) and *cis*-4-methyl-2-pentene (9 mL, 70 mmol, 0.18 M) in 88 mL of dichloromethane (5 mol % olefin solution) irradiated for 10.5 h gave 1.439 g of residue. Nominal yield by NMR: 100%. Cooling of a pentane solution of the residue to −25 °C for 14 h gave 1.3 g of **7**, a 92.5% yield, mp 63–4 °C. The NMR spectrum of the mother liquor showed the presence of much *cis*-aziridine, while no (<1%) trans isomer could be detected. IR ($CHCl_3$): 3003 (m), 2968 (m), 2200 (s), 1569 (vs), 1555 (s), and 1328 (s) cm^{-1}. ^{1}H NMR: 0.98 (d, 3 H), 1.13 (d, 3 H), 1.32 (t, 3 H), 1.49 (d, 3 H), 1.6 (m, 1 H), 2.32 (dd, 1 H), 2.86 (m, 1 H), 4.24 (q, 2 H). Mass spectrum: M^+ = 195 (15); M − Me, 180 (13); M − C_2H_4, 167 (25); M − Et, 166 (30); M − $iPrCH_2$, 138 (20); olefin + NH, 99 (30); olefin + 14, 98 (100); olefin, 84 (69); EtOCN, 71 (20); EtNHCN, 70 (75). Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.51; H, 8.78; N, 21.52. Found: C, 61.40; H, 8.60; N, 21.38.

(b) Photolysis at 0.1 mol % Olefin Concentration. Azide **41** (0.25 g, 1.8 mmol), *cis*-4-methyl-2-pentene (2.26 mL, 18 mmol, 0.016 M), and dichloromethane (1144 mL) were irradiated for 10.5 h to give 0.44 g of a viscous residue. Quantitative NMR analysis indicated a 91% yield of **7**. Crystallization from 20 mL of pentane at −25 °C gave 239 mg of mp 62–62.5°, a 69% isolated yield. The pentane mother liquor contained mostly **7**, by NMR. No trans isomer could be detected.

(c) Photolysis at 0.05 mol % Olefin Concentration. The photolysis was repeated using 164 mg (1.2 mmol) of the azide **41**, 1.48 mL (12 mmol) of the olefin, and 1500 mL of dichloromethane. NMR analysis indicated a 68.7% aziridine yield, and 140 mg (60.8% yield) could be isolated by crystallization. By NMR, about 70% of the material in the mother liquor was different from the *cis*- or *trans*-aziridines.

Reactions with *trans*-4-Methyl-2-pentene. *trans*-2-Isopropyl-3-methyl-*N*-(*N'*-(methylsulfonyl)ethoxycarbimidoyl)aziridine (8). **39** (2 g, 10 mmol), *trans*-4-methyl-2-pentene (15 mL, 120 mmol, 4 M), and 15 mL of dichloromethane irradiated for 13 h gave a 77.7% yield (by NMR) of **8**. Chromatography on silica gel gave 1.8 g of **8**, a 70% yield. TLC on 1-mm silica gel plates, using an 85:15 mixture of chloroform and ethyl acetate, gave pure aziridine (R_f = 0.7–0.9), liquid at room temperature. IR ($CHCl_3$): 3004 (w), 2966 (m), 2940 (w), 1560 (vs), 1316 (s), 1136 (s), 1116 (s) cm^{-1}. ^{1}H NMR: 0.95 (d, 3 H), 1.03 (d, 3 H), 1.32 (t, 3 H), 1.38 (d, 3 H), 1.7 (m, 1 H), 2.36 (m, 1 H), 2.79 (m, 1 H), 3.04 (s, 3 H), 4.24 (q, 2 H). Anal. Calcd for $C_{10}H_{20}N_2O_3S$: C, 48.39; H, 8.06; N, 11.29. Found: C, 48.17; H, 7.93; N, 11.07.

***trans*-2-Isopropyl-3-methyl-*N*-(*N'*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)aziridine (9). (a) Thermolysis.** **43** (1.132 g, 4.2 mmol) and *trans*-4-methyl-2-pentene (20 mL, 155 mmol, 3.9 M) in 20 mL of dioxane, for 8 h at reflux, and chromatography on 70 g of silica gel, eluting with 95:5 chloroform–ethyl acetate, gave (in the fractions between 100 and 400 mL) 610 mg of **9**, a 44% yield, mp 94–97.5 °C (from petroleum ether). The next 200 mL of eluate contained 85 mg (8.3% yield) of *O*-(2,6-dimethylphenyl)-*N*-(methylsulfonyl)isourea (**10**), mp 184–5 °C. The following data are for aziridine **9**. IR (KBr): 2970 (m), 2930 (w), 1590 (s), 1575 (s), 1330 (s), 1300 (s), 1135 (s) cm^{-1}. ^{1}H NMR: 1.01 (d, 3 H), 1.11 (d, 3 H), 1.53 (d, 3 H), 1.76 (m, 1 H), 2.2 (s, 6 H), 2.5 (q, J = 3 Hz, 1 H), 2.82 (s, 3 H), 2.92 (q, 1 H), 7.04 (s, 3 H). ^{13}C NMR: 16.38, 16.76, 18.97, 20.05, 30.14, 42.39, 53.06, 126.06, 128.48, 128.66, 129.79, 149.21, 160.95. The mass spectrum is quite similar to that of the cis isomer **6**: M^+ = 324 (25); M − Me, 309 (3); M − iPr, 281 (15); M − SO_2Me, 245 (38); M − ArOCN, 147 (42); ArOH, 122 (100); ArO$^•$, $MeSO_2NCO$, 121 (85); olefin + 14, 98 (100); olefin − 1, 83 (80). Anal. Calcd for $C_{16}H_{24}N_2O_3S$: C, 59.23; H, 7.46; N, 8.63. Found: C, 59.28; H, 7.57; N, 8.61. IR spectrum of **10** (KBr): 3440 (s), 3220 (s), 1610 (s), 1560 (s), 1280 (s), 1270 (s), and 1195 (s) cm^{-1}. ^{1}H NMR: 2.16 (s, 6 H), 2.89 (s, 3 H), 7.08 (s, 3 H), 6.84–7.36 (br).

(b) Photolysis. **43** (1.132 g, 4.2 mmol), *trans*-4-methyl-2-pentene (4 g, 46 mmol, 1.4 M), and 30 mL of dichloromethane were irradiated for 22 h. Chromatography on 100 g of silica gel, as above, gave some undecomposed azide and 414 mp (a 30% yield) of **9**, mp 95.0–.5 °C.

***trans*-2-Isopropyl-3-methyl-*N*-(*N'*-cyanoethoxycarbimidoyl)aziridine (11).** **41** (1 g, 7.2 mmol) and *trans*-4-methyl-2-pentene (9 mL, 72 mmol, 1.47 M) in 41 mL of dichloromethane irradiated for 10.5 h gave **11** quantitatively (by NMR). The residue, in benzene, was filtered through 2 g of silica gel and then purified by thick-layer chromatography on silica gel. We did not obtain **11** crystalline. IR ($CHCl_3$): 3007 (m), 2973 (m), 2878 (m), 2201 (s), 1570 (v), 1332 (s) cm^{-1}. ^{1}H NMR: 0.96 (d, 3 H), 1.04 (d, 3 H), 1.33 (t, 3 H), 1.41 (d, 3 H), 1.7 (m, 1 H), 2.26 (m, 1 H), 2.80 (m, 1 H), 4.27 (q, 2 H). Anal. Calcd for $C_{10}H_{17}N_3O$: C, 61.54; H, 8.72; N, 21.54. Found: C, 61.54; H, 8.68; N, 21.78.

Reaction with 3-Butenenitrile. 1-(*N'*-(Methylsulfonyl)ethoxycarbimidoyl)-2-(cyanomethyl)aziridine (12). Irradiation of 0.48 g (0.005 mol) of **39** and 1-cyano-2-propene (2 mL, 0.025 mol, 0.71 M) in 35 mL of dichloromethane gave 0.58 g (100% yield) of crude, solid **12**. Three recrystallizations from chloroform–petroleum ether gave analytically pure material, mp 114.5–115 °C. The IR spectrum showed bands at 2260 and 1589 cm^{-1}. ^{1}H NMR: 1.33 (t, 3 H), 2.48 (d, 1 H), 2.75 (d, 1 H), 3.06 (s, 3 H), 2.85–3.19 (m, 3 H), 4.24 (q, 2 H). ^{13}C NMR: 13.80, 20.66, 31.68, 36.53, 42.50, 66.47, 115.61, 163.14. Mass spectrum: p^+ = 231 (4), loss p − 44 (C_2H_4), p − 79 ($MeSO_2$), p − 124 ($MeSO_2OEt$), m = 122 (50) $(MeSO_2NEt)^+$, 121 (20) ($MeCH{=}NSO_2Me$), 82 (68) (NCC_3H_6N), 81 (38) (NCC_3H_5N), 79 (70) (SO_2Me), 68 (60) (NCC_3H_5), etc. Anal. Calcd for $C_8H_{13}N_3SO_3$: C, 41.54; H, 5.66; N, 18.17. Found: C, 41.60; H, 5.89; N, 18.15.

Reactions with Methylenecyclohexane. 1-(*N'*-(Methylsulfonyl)ethoxycarbimidoyl)-1-azaspiro[2.5]octane (13). Methylenecyclohexane (2 g, 21 mmol, 0.69 M), **39** (489 mg, 2.5 mmol), and dichloromethane (30 mL) irradiated for 7.15 h gave a liquid containing (by NMR) a 67% yield of **13**. M^+ = 260 (17). ^{1}H NMR: 1.3 (t, J = 7 Hz) embedded in 1.06–2.3 (m, 13 H), 2.44 (d, 2 H), 3.03 (s, 3 H), 4.22 (q, 2 H). IR ($CHCl_3$): 2990, 1615 (s), 1575 (s).

***N*-(Methylsulfonyl)-*N'*-(1-cyclohexenylmethyl)-*O*-ethylisourea (45).** Crude **13** (above) corresponding to 220 mg (0.8 mmol) was treated with 700 mg of NaI in 10 mL of acetonitrile, heated to 60–75 °C for 5 h, the acetonitrile removed, and 2 mL of water added. Extraction with chloroform and then recrystallization from petroleum ether gave crystals at −25 °C, liquid at room temperature. IR ($CHCl_3$): 3330 (w), 2925 (w), 1620 (s), 1220 (vs). ^{1}H NMR: 1.28 (t, 3 H), 1.4–1.8 (complex, 4 H), 1.8–2.16 (br, 4 H), 2.96 (s, 3 H), 3.67 (d, 2 H), 4.14 (q, 2 H), 5.6 (br, 1 H), 7.0–7.4 (br, 1 H). Anal. Calcd for $C_{11}H_{20}N_2O_3S$: C, 50.74; H, 7.74; N, 10.79. Found: C, 50.71; H, 7.95; N, 10.90.

1-(*N'*-Cyanomethoxycarbimidoyl)-1-azaspiro[2.5]octane (14). Methylenecyclohexane (2 g, 21 mmol, 0.7 M), **40** (410 mg, 3.3 mmol), and 30 mL of dichloromethane irradiated for 5.15 h gave an 87% yield of **14** (by NMR). Crystallization from petroleum ether gave 335 mg (70%), mp 49–49.5 °C. M^+ = 193 (45). IR ($CHCl_3$): 2950, 2195 (m), 1585 (s). ^1H NMR: 1.2–2.3 (m, 10 H), 2.38 (s, 1 H), 2.39 (s, 1 H), 3.85 (s, 3 H). ^{13}C NMR: 24.82, 25.19, 33.21, 39.64, 50.87, 57.00, 114.62, 171.37. Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.74. Found: C, 62.17; H, 8.04; N, 21.97.

***N*-Cyano-*N'*-(1-cyclohexenylmethyl)-*O*-methylisourea (46).** Spiro aziridine **14** (280 mg, 1.5 mmol) and sodium iodide (500 mg, 3.3 mmol) in acetonitrile (25 mL) at 70 °C for 5 h, followed by workup as above, gave **46** (100 mg, 53.7%), mp 84–84.5 °C. IR (KBr): 3240 (m), 2930 (m), 2190 (s), 1635 (s), 1620 (s). M^+ = 193 (45). ^1H NMR: 1.52–1.73 (m, 4 H), 1.86–1.98 (br, 2 H), 1.98–2.09 (br, 2 H), 3.68–3.79 (d, 2 H), 3.85 (s, 3 H), 5.60–5.68 (br, 1 H), 5.71–5.83 (br, 1 H). ^{13}C NMR: 22.06, 22.40, 24.72, 26.34, 48.19, 56.10, 116.01, 125.28, 132.78, 164.60. Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.74. Found: C, 62.25; H, 7.71; N, 21.68.

1-(*N'*-Cyanoethoxycarbimidoyl)-1-azaspiro[2.5]octane (15). Methylenecyclohexane (2 g, 21 mmol, 0.69 M), **41** (0.40 g, 2.9 mmol), and dichloromethane (30 mL) were irradiated for 8 h. Crystallization from petroleum ether gave 415 mg (70%) of **15**, mp 47.5–48 °C. M^+ = 207 (35). IR 2940 (m), 2200 (s), 1580 (s). ^1H NMR: 1.32 (3 H), 1.2–2.3 (m, excl the triplet at 1.32, 10 H), 2.36 (s, 1 H), 2.37 (s, 1 H), 4.27 (q, 2 H). ^{13}C NMR: 14.19, 22.07, 22.42, 26.34, 48.19, 65.53, 116.23, 125.38, 132.98, 164.11. Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.97; H, 7.99; N, 19.98.

***N*-Cyano-*N'*-(1-cyclohexenylmethyl)-*O*-ethylisourea (47).** Spiro aziridine **15** (300 mg, 1.5 mmol), sodium iodide (500 mg, 3.3 mmol), and acetonitrile (10 mL) were heated to 60–75 °C for 5 h and worked up as was **45**, to give **47** (180 mg, 60%), mp 103–4 °C. IR (KBr): 3240 (m), 3180 (m), 3170 (m), 2180 (s), 1635 (s), 1630 (s), 1625 (s). M^+ = 207 (100). ^1H NMR: 1.32 (t, 3 H), 1.49–1.76 (m, 4 H), 1.86–2.1 (complex, 4 H), 3.72 (d, 2 H), 4.28 (q, 2 H), 5.59–5.69 (br, 1 H), 5.77–5.82 (br, 1 H). Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.80; H, 8.22; N, 20.27.

Reaction with Ethylidenecyclohexane. 1-(*N'*-Cyanoethoxycarbimidoyl)-2-methyl-1-azaspiro[2.5]octane (16). Ethylidenecyclohexane (3 g, 27 mmol, 0.91 M), **41** (690 mg, 5 mmol), and 30 mL of dichloromethane were irradiated for 9 h. Crystallization from petroleum ether gave **16** (806 mg, 73%), mp 56.5–7 °C. IR ($CHCl_3$): 3010 (w), 2950 (m), 2870 (w), 2210 (s), 1575 (s). ^1H NMR: 0.92–2.24 (m, contg d and t, 16 H), 2.6 (q, *J* = 6 Hz, 1 H), 4.24 (q, *J* = 7 Hz, 2 H). ^{13}C NMR: 13.04, 14.03, 25.05, 25.12, 25.69, 29.30, 34.66, 45.90, 53.47, 66.24, 114.94, 171.16. Anal. Calcd for $C_{12}H_{19}N_3O$: C, 65.13; H, 8.65; N, 18.99. Found: C, 65.31; H, 8.79; N, 19.20.

Reactions with (–)-*β*-Pinene. *N*-((6,6-Dimethylbicyclo[3.1.1]-2-heptenyl)methyl)-*N'*-(methylsulfonyl)-*O*-ethylisourea (17). (–)-*β*-Pinene (6 g, 44 mmol, 1.47 M), **39** (1.93 g, 10 mmol), and dichloromethane (30 mL) irradiated for 22.45 h gave 300 mg of **17** (from ethyl acetate and petroleum ether). Cooling of the petroleum ether extract of the mother liquor gave another 1.19 g, for a 50% yield; mp 81–2 °C (from petroleum ether). M^+ = 300 (80). IR (KBr): 3350 (m), 3000 (m), 2980 (m), 1625 (s), 1615 (s). ^1H NMR: 0.83 (s, 3 H), 1–1.4 (m, contg t and d, 7 H), 1.9–2.52 (m, 5 H), 2.98 (s, 3 H), 3.62–3.8 (m, 2 H), 4.25 (q, 2 H), 5.34–5.48 (m, 1 H), 7.04–7.28 (br, 1 H). ^{13}C NMR: 14.31, 20.88, 26.03, 31.05, 31.41, 38.05, 40.70, 42.20, 43.99, 45.98, 64.44, 118.89, 143.11, 158.00. Anal. Calcd for $C_{14}H_{24}N_2SO_3$: C, 55.97; H, 8.05; N, 9.32. Found: C, 56.19; H, 8.15; N, 9.41.

***N*-((6,6-Dimethylbicyclo[3.1.1]-2-heptenyl)methyl)-*N'*-cyano-*O*-methylisourea (18).** (–)-*β*-Pinene (3.4 g, 25 mmol, 0.83 M), **40** (625 mg, 5 mmol), and 30 mL of dichloromethane were irradiated for 11.45 h. Crystallization from methanol gave **18** (680 mg, 58%), mp 121–2 °C. M^+ = 233 (20). IR (KBr): 3250 (w), 3215 (w), 3190 (w), 2915 (w), 2195 (m), 1635 (s). ^1H NMR: 0.88 (s, 3 H), 1.26 (s, 3 H), 1.72 (d, 1 H), 1.96–2.48 (m, 5 H), 3.60–3.76 (m, 2 H), 3.8 (s, 3 H), 5.32–5.48 (m, 1 H), 6.08–6.40 (br, 1 H). ^{13}C NMR: 21.02, 26.08, 31.16, 31.55, 38.14, 40.70, 44.01, 46.59, 56.08, 115.94, 119.86, 142.94. Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.20; N, 18.01. Found: C, 66.85; H, 8.35; N, 17.92.

***N*-((6,6-Dimethylbicyclo[3.1.1]-2-heptenyl)methyl)-*N'*-cyano-*O*-ethylisourea (19).** (–)-*β*-Pinene (10 g, 73.5 mmol, 1.2 M), **41** (1.39 g, 10 mmol), and dichloromethane (60 mL) irradiated for 20 h and crystallized from petroleum ether gave 1.04 g, 42%, of the isourea corresponding to the ring-opened spiro aziridine, mp 111–2 °C (from petroleum ether). M^+ = 247 (50). IR (KBr): 3240 (m), 2930 (m), 2200 (s), 1625 (s). ^1H NMR: 0.8 (s, 3 H), 1.1–1.36 (m, incl s and t, 7 H), 1.74–2.5 (m, 4 H), 3.67 (q, *J* = 2 Hz, 1 H), 3.73 (q, *J* = 2 Hz, 1 H), 4.25 (q, *J* = 7 Hz, 2 H), 5.3–5.48 (m, 1 H), 7.16–7.38 (br, 1 H). ^{13}C NMR: 14.16, 21.00, 26.05, 31.13, 31.53, 38.12, 40.69, 44.02, 46.52, 65.55, 106.12, 119.76, 119.76, 142.95. Anal. Calcd for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56; N, 16.99. Found: C, 68.14; H, 8.70; N, 16.78.

Reactions with Cyclohexene. 7-(*N'*-(Methylsulfonyl)ethoxycarbimidoyl)-7-azabicyclo[4.1.0]heptane (20). Azide **39** (2 g, 10 mmol), cyclohexene (15 mL, 148 mmol, 7.4 M), and 5 mL of dichloromethane irradiated for 14.5 h gave 2.59 g of crude **20**. NMR analysis indicated a 91% yield. A saturated ethyl acetate solution of the residue, kept at –25 °C for 48 h, gave crystalline **20** (2.024 g, 79%), mp 57–58.5 °C. IR ($CHCl_3$): 1561 (vs), 1555 (vs). Mass spectrum: M^+ = 240. ^1H NMR: 1.0–2.40 (m, incl t at 1.3, 11 H), 3.0 (m, 2 H), 3.02 (s, 3 H), 4.18 (q, 2 H). ^{13}C NMR: 13.95, 19.73, 23.34, 40.59, 42.18, 65.47, 164.88. Anal. Calcd for $C_{10}H_{18}N_2O_3S$: C, 48.78; H, 7.32; N, 11.38. Found: C, 48.53; H, 7.07; N, 11.30.

Hydrolysis of 20. To 246 mg (1 mmol) of 7-(*N'*-(methylsulfonyl)ethoxycarbimidoyl)-7-azabicyclo[4.1.0]heptane (**20**) was added a solution of NaOH (50 mg, 1.25 mmol) in 30 mL of methanol. One drop of water was added, and the mixture was kept at room temperature for 24 h. The methanol was removed in vacuo after 2 h at room temperature, 1 mL of saturated sodium chloride solution was added, and the mixture was extracted with 3 × 30 mL of chloroform, which was removed after drying over sodium sulfate. The N-unsubstituted aziridine, 7-azabicyclo[4.1.0]heptane, was converted to a solid for quantitation. Heating to reflux for 2 h with phenyl isocyanate (140 mg, 1.15 mmol) in 10 mL of petroleum ether (bp 35–65 °C) gave the phenyl isocyanate adduct, 7-(*N*-phenylcarbamoyl)-7-azabicyclo[4.1.0]heptane (**48**), 120 mg (corresponding to a 55% yield of the unsubstituted aziridine, assuming quantitative recovery), mp 155–6 °C (lit.[20] mp 158–9 °C). IR: 3330, 1660, 1600, 1540 cm^{-1}. ^1H NMR spectrum: 1.0–1.6 (br, 4 H), 1.6–2.0 (br, 4 H), 2.75 (s, 2 H), 6.98–7.52 (m, 5 H).

7-(*N'*-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)-7-azabicyclo[4.1.0]heptane (21). (a) Photolysis. *N'*-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl azide (**43**) (1.32 g, 4.22 mmol) and cyclohexene (3 g, 36.6 mmol, 1.36 M) in 30 mL of dichloromethane were irradiated for 26.5 h. Elution from silica gel by 95:5 chloroform and ethyl acetate and then recrystallization from petroleum ether gave 370 mg (27%) of **21**.

(b) Thermolysis. The azide (536 mg, 2 mmol) and 2 g (24 mmol, 1.4 M) of cyclohexene in 15 mL of dioxane were heated to reflux for 21 h to give 400 mg (62% yield) of **21**, mp 93–4 °C (from petroleum ether). IR (KBr): 2940 (m), 1605 (vs), 1585 (s), 1320 (s), 1295 (vs), 1145 (s) cm^{-1}. ^1H NMR: 1.04–1.4 (m, 4 H), 1.52–1.8 (m, 4 H), 2.2 (s, 6 H), 2.92 (s, 3 H), 2.98 (m, 2 H), 7.04 (s, 3 H). ^{13}C NMR: 16.30, 19.58, 22.95, 41.09, 42.34, 126.23, 128.48, 128.79, 129.96, 149.16, 163.48. Mass spectrum: M^+ = 322 (4); loss of SO_2CH_3, 243 (18); M – dimethylphenoxy, 201 (79); M – dimethylphenol, 200 (34); dimethylphenol and/or $C_6H_{10}N$–CN, 122 (100); dimethylphenoxy, 121 (79); SO_2CH_3, 79 (36); and other expected peaks. Anal. Calcd for $C_{16}H_{22}N_2O_3S$: C, 59.60; H, 6.88; N, 8.69. Found: C, 59.22; H, 7.18; N, 8.74. Aziridine **21** decomposes slowly at room temperature.

7-(*N'*-Cyanoethoxycarbimidoyl)-7-azabicyclo[4.1.0]heptane (22). Cyclohexene (12 mL, 118 mmol, 5.9 M), **41** (1.39 g, 10 mmol), and 20 mL of dichloromethane irradiated for 13 gave **22**, 1.66 g (75%), mp 62.5–3 °C. IR (KBr): 2950 (m), 2190 (m), 1565 (s), 1560 (s), and 1555 (s) cm^{-1}. Mass spectrum: M^+ = 195 (15); loss of ethylene and ethyl, 165 (7), 164 (10); M – EtO and CN, 122 (90); cyclohexene, 82 (30); M – NCNCOEt, 96 (50), 97 (20); EtNCN, 69 (100); HNCN, 41 (100). ^1H NMR: 1.2–2.28 (m, 11 H incl t at 1.32), 2.89 (t, 2 H), 4.24 (q, 2 H). Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.74. Found: C, 62.80; H, 7.88; N, 21.57.

Hydrolysis of 22. 22 (193 mg, 1 mmol) and 130 mg (3 mmol) of NaOH in 30 mL of methanol were used as above with **20**, and the N-unsubstituted aziridine was quantitated with phenyl isocyanate (140 mg, 1.15 mmol) as above, to give 86 mg of 7-(*N*-phenylcarbamoyl)-7-azabicyclo[4.1.0]heptane (**48**), mp 152–4 °C. Assuming no loss in the last reaction, the aziridine yield was 44%.

Reactions with Cycloheptene. 8-(*N*′-(Methylsulfonyl)ethoxycarbimidoyl)-8-azabicyclo[5.1.0]octane (23). Cycloheptene (3 g, 31 mmol, 0.69 M), **39** (0.96 g, 5 mmol), and 45 mL of dichloromethane irradiated for 8.45 h gave 766 mg (59%) of **23**, mp 54.5–55 °C. IR (CCl_4): 2940 (w), 2930 (w), 1585 (s), 1580 (s), 1315 (s), 1210 (s), 1195 (s). ^1H NMR: 1.14–1.68 (m, 9 H, incl t at 1.30), 1.8–2.16 (m, 4 H), 2.96 (t, 2 H), 3.03 (s, 3 H), 4.18 (q, 2 H). ^{13}C NMR: 13.96, 25.07, 28.73, 31.25, 42.55, 45.10, 63.31, 165.06. Anal. Calcd for $C_{11}H_{20}N_2O_3S$: C, 50.74; H, 7.74; N, 10.76. Found: C, 50.96; H, 7.64; N, 10.89.

8-(*N*′-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)-8-azabicyclo[5.1.0]octane (24). (a) Thermolysis. Cycloheptene (3 g, 31 mmol, 1.57 M), **43** (1.072 g, 4 mmol), and 20 mL of dioxane, heated to 90 °C for 9 h, precipitated 250 mg (20.7% yield) of *N*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**10**), mp 182–4 °C. ^{13}C NMR of **10**: 16.10, 42.19, 126.32, 128.70, 130.39, 148.07, 157.83. Chromatography of the residue (silica gel, chloroform–ethyl acetate) gave 70 mg (5.2% yield) of *N*-(*N*′-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)-3-amino-1-cycloheptene (**25**), mp 103–5 °C, identified by its ^{13}C NMR: 16.33, 25.83, 26.57, 26.76, 31.58, 34.56, 126.06, 126.41, 128.61, 130.15, 137.66, 148.51, 155.36. Later fractions gave a mixture of **25** and **24** (0.3 g, 22%) and finally the aziridine **24** (0.32 g, 24%), mp 83–5 °C (from petroleum ether).

(b) Photolysis. Cycloheptene (4.5 g, 47 mmol, 1.34 M), **43** (1.34 g, 5 mmol), and 30 mL of dichloromethane irradiated for 26 h gave, by chromatography, 350 mg (20.8%) of **24**, mp 85–7 °C. IR ($CHCl_3$): 2930 (m), 1600 (s), 1580 (s), 1330 (s), 1305 (s), 1180 (s). ^1H NMR: 0.8–2 (complex, 10 H), 2.24 (s, 6 H), 2.84–3.08 (complex, incl s at 2.92, 5 H), 7.04 (s, 3 H). ^{13}C NMR: 16.30, 25.03, 28.34, 30.99, 42.49, 45.83, 126.19, 128.74, 130.06, 149.13, 163.80. Anal. Calcd for $C_{17}H_{24}N_2O_3S$: C, 60.68; H, 7.19; N, 8.33. Found: C, 60.69; H, 7.42; N, 8.25.

8-(*N*′-Cyanomethoxycarbimidoyl)-8-azabicyclo[5.1.0]octane (26). Cycloheptene (2 g, 21 mmol, 0.66 M) and **40** (315 mg, 2.5 mmol) in dichloromethane (30 mL) irradiated for 7.4 h gave **26**, 362 mg (71%), mp 77–8 °C (from petroleum ether). IR (CCl_4): 2940 (m), 2215 (m), 1590 (s), 1455 (s), 1345 (m). ^1H NMR: 1.01–1.24 (m, 1 H), 1.35–1.78 (m, 5 H), 1.81–1.99 (m, 2 H), 2.08–2.29 (m, 2 H), 2.90 (m, 2 H), 3.84 (s, 3 H). ^{13}C NMR: 25.08, 28.41, 31.03, 44.86, 56.97, 105.13, 173.79. M^+ = 193 (7). Anal. Calcd for $C_{10}H_{15}N_3O$: C, 62.15; H, 7.82; N, 21.74. Found: C, 62.16; H, 7.81; N, 21.57.

8-(*N*′-Cyanoethoxycarbimidoyl)-8-azabicyclo[5.1.0]octane (27). Cycloheptene (2 g, 21 mmol, 0.66 M), **41** (0.34 g, 2.5 mmol), and 30 mL of dichloromethane irradiated for 8.36 h gave 429 mg (81%) of **27**, mp 71.5–72 °C (from petroleum ether). IR (CCl_4): 2940 (m), 2210 (m), 1585 (s), 1325 (s), 1200 (s), 1185 (s). ^1H NMR: 1.1–1.25 (m, 1 H), 1.3 (t, *J* = 8 Hz, 3 H), 1.36–1.8 (m, 5 H), 1.82–2.0 (m, 2 H), 2.07–2.26 (m, 2 H), 2.87 (2 t, 2 H), 4.23 (q, *J* = 8 Hz, 2 H). ^{13}C NMR: 13.97, 25.10, 28.43, 31.06, 44.77, 66.46, 114.23, 173.21. M^+ = 207 (10). Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.82; H, 8.02; N, 20.10.

Reactions with 2,5-Dihydrothiophene 1,1-Dioxide. 4-(*N*′-(Methylsulfonyl)ethoxycarbimidoyl)-1-thia-4-azabicyclo[3.1.0^{3,5}]hexane 1,1-Dioxide (28). 2,5-Dihydrothiophene 1,1-dioxide (butadienesulfone, Sulfolene) (1.2 g, 10 mmol, 0.29 M), **39** (0.96 g, 5 mmol), and 35 mL of dichloromethane irradiated for 8 h gave 800 mg (56.8%) of **28**, mp 168–9 °C. IR ($CHCl_3$): 3015 (w), 1595 (s), 1420 (s), 1335 (s), 1140 (s). ^1H NMR: 1.33 (t, 3 H), 3.27 (s, 3 H), 3.48 (d, *J* = 2 Hz, 4 H), 3.8 (t, *J* = 2 Hz, 2 H), 4.25 (q, 2 H). ^{13}C NMR: 13.79, 40.03, 42.32, 53.48, 66.63, 161.12. M^+ = 282 (1). Anal. Calcd for $C_8H_{14}N_2O_5S$: C, 34.03; H, 5.00; N, 9.92. Found: C, 33.87; H, 4.92; N, 9.96.

4-(*N*′-Cyanoethoxycarbimidoyl)-1-thia-4-azabicyclo[3.1.0^{3,5}]hexane 1,1-Dioxide (29). 2,5-Dihydrothiophene 1,1-dioxide (0.62 g, 5.2 mmol, 0.15 M), **41** (347 mg, 2.5 mmol), and 35 mL of dichloromethane irradiated for 9.20 h gave a residue containing some butadienesulfone. Recrystallization from chloroform and petroleum ether afforded **29** (232 mg, 40%), mp 153–4 °C. IR ($CHCl_3$): 2210 (m), 1600 (s), 1335 (s). ^1H NMR: 1.36 (t, *J* = 7 Hz, 3 H), 3.51 (d, *J* = 2 Hz, 4 H), 3.72 (t, *J* = 2 Hz, 2 H), 4.34 (q, *J* = 7 Hz, 2 H). M^+ = 229 (4). Anal. Calcd for $C_8H_{11}N_3O_3S$: C, 41.91; H, 4.84; N, 18.32. Found: C, 41.75; H, 5.01; N, 18.25.

Reaction with 1-Methylcyclohexene. 1-Methyl-7-(*N*′-(methylsulfonyl)ethoxycarbimidoyl)-7-azabicyclo[4.1.0]heptane (30). 1-Methylcyclohexene (2.49 g, 25 mmol, 0.77 M), **39** (0.48 g, 2.5 mmol), and 30 mL of dichloromethane irradiated for 7 h gave crude **30** (by NMR). It could not be crystallized, decomposed on silica gel, and ring-opened on neutral alumina, adding H_2O, presumably to give *N*-(methylsulfonyl)-*N*′-(2-hydroxy-2-methylcyclohexyl)isourea (**49**). The following spectral data are for aziridine **30**. IR ($CHCl_3$): 3010 (w), 2950 (m), 1620 (w), 1570 (s), 1380 (m), 1315 (s), 1295 (s). ^1H NMR: 1.2–2.3 (overlapping, t at 1.3 and s at 1.34, 14 H), 2.9 (dd, 1 H), 3.02 (s, 3 H), 4.22 (q, 2 H). M^+ = 260 (12). The following spectral data are for **49**. M^+ = 278 (24). IR (CCl_4): 3500–3400 (br), 3230 (w), 2945 (m), 1620 (s), 1490 (s), 1105 (s). ^1H NMR: 1.0–2.04 (complex, incl s at 1.2 and t at 1.3, 14 H), 2.4 (br, s, 1 H), 2.98 (s, 3 H), 4.26 (q, 2 H), 3.64 (m, 1 H), 7.2–7.4 (br, 1 H).

1-Methyl-7-(*N*′-cyanoethoxycarbimidoyl)-7-azabicyclo[4.1.0]heptane (31). 1-Methylcyclohexene (2 g, 21 mmol, 0.65 M), **41** (0.35 g, 2.5 mmol), and 30 mL of dichloromethane irradiated for 5 h gave a 100% yield (by NMR) of **31**. Recrystallization from petroleum ether at −25 °C gave crystals, melting below room temperature. IR ($CHCl_3$): 3015 (w), 2950 (w), 1575 (s), 1330 (s). ^1H NMR: 1–2.4 (overlapping, incl t at 1.3 and s at 1.38, 14 H), 2.72 (t, 1 H), 4.24 (q, 2 H). M^+ = 207 (45). Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.62; H, 8.17; N, 20.29.

Reactions with α-Pinene. 2,8,8-Trimethyl-3-(*N*′-cyanomethoxycarbimidoyl)-3-azatricyclo[4.1.1.0^{2,4}]octane (32). *dl*-α-Pinene (3.4 g, 25 mmol, 0.76 M), **40** (625 mg, 5 mmol), and 30 mL of dichloromethane irradiated for 12.1 h gave 1.289 g of solid **32**. Recrystallization from petroleum ether afforded 814 mg (70% yield), mp 79–80 °C. IR (CCl_4): 2930 (w), 2200 (w), 1580 (s), 1190 (s). ^{13}C NMR: 20.54, 20.94, 26.30, 26.70, 26.85, 39.96, 40.06, 42.82, 44.76, 56.83, 113.23, 114.28, 170.52. M^+ = 233 (10). ^1H NMR: 0.96 (s, 3 H), 1.31 (s, 3 H), 1.41 (s, 3 H), 1.61–1.9 (m, 2 H), 1.98–2.26 (m, 4 H), 2.84 (br, 1 H), 3.85 (s, 3 H). Anal. Calcd for $C_{13}H_{19}N_3O$: C, 66.92; H, 8.20; N, 18.01. Found: C, 66.85; H, 8.35; N, 18.14.

2,8,8-Trimethyl-3-(*N*′-cyanoethoxycarbimidoyl)-3-azatricyclo[4.1.1.0^{2,4}]octane (33). *dl*-α-Pinene (3.4 g, 25 mmol, 0.38 M), **41** (695 mg, 5 mmol), and 60 mL of dichloromethane irradiated for 11.4 h gave 726 mg (59%) of **33**, mp 79.5–80 °C. IR (CCl_4): 2985 (m), 2940 (m), 2205 (m), 1580 (s), 1340 (s), 1190 (s). ^1H NMR: 0.96 (s, 3 H), 1.32 (t, *J* = 7 Hz, and s, 6 H), 1.4 (s, 3 H), 1.48–1.9 (m, 2 H), 1.96–2.24 (m, 4 H), 2.84 (br, 1 H), 4.27 (q, *J* = 7 Hz, 2 H). ^{13}C NMR: 14.08, 20.53, 20.87, 26.30, 26.60, 26.70, 39.95, 40.06, 42.75, 44.78, 52.53, 66.27, 114.98, 170.05. M^+ = 247 (45). Anal. Calcd for $C_{14}H_{21}N_3O$: C, 67.98; H, 8.56; N, 16.99. Found: C, 67.99; H, 8.60; N, 16.85.

Azide Reactions with Norbornene. *exo*-3-(*N*′-(Methylsulfonyl)ethoxycarbimidoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (34). Norbornene (2.38 g, 25 mmol, 0.78 M) and **39** (0.46 g, 24 mmol) in 30 mL of benzene at room temperature evolved 75% of the expected N_2 in 2 h and, after 20 h, gave 680 mg (98%) of crude **34**. Recrystallization from ethyl acetate and petroleum ether gave mp 87–8 °C. IR (CCl_4): 2960 (w), 1580 (s), 1415 (s), 1330 (m), 1310 (s), 1195 (s). ^1H NMR: 0.87 (d, 1 H), 1.16–1.59 (complex, t at 1.30, 8 H), 2.62 (s, 2 H), 3.02 (s and d, 5 H), 4.18 (q, 2 H). ^{13}C NMR: 13.99, 25.39, 28.21, 36.31, 42.16, 42.64, 65.26, 162.50. Anal. Calcd for $C_{11}H_{18}N_2O_3S$: C, 51.14; H, 7.02; N, 10.84. Found: C, 51.40; H, 6.83; N, 10.83.

Hydrolysis of 34. 34 (258 mg, 1 mmol), sodium hydroxide (50 mg, 1.25 mmol), and 20 mL of methanol were kept at room temperature for 1 h. The methanol was evaporated, 2 mL of saturated aqueous NaCl solution added, and the aziridine extracted with chloroform, to give 130 mg of a solid. Phenyl isothiocyanate (1.5 mmol) in petroleum ether produced 150 mg (61%) of 3-(*N*-phenylthiocarbamoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (**50**), mp 117–9 °C (lit. mp[21] 119–120 °C). IR ($CHCl_3$): 3410 (s), 1195

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(20) Hassner, A.; Heathcock, C. *Tetrahedron* **1964**, *20*, 1037.

(s). ^{1}H NMR: 0.76–1.52 (m, 6 H), 2.38 (s, 2 H), 2.7 (s, 2 H), 7.12–7.44 (m, 5 H), 9.04–2.28 (br, 1 H).

***exo*-3-(N'-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (35).** Norbornene (1 g, 10.6 mmol, 0.35 M) and **43** (536 mg, 2 mmol) in 30 mL of dichloromethane reacted at room temperature without irradiation. After 3 h, 92% of the expected amount of N_2 had evolved. Crystallization of the residue from petroleum ether gave 379 mg (57%) of **35**, mp 94–5 °C. IR ($CHCl_3$): 2970 (w), 1600 (s), 1585 (s), 1390 (s), 1335 (s), 1190 (s), 1135 (s). ^{1}H NMR: 0.84 (d, J = 8 Hz, 1 H), 1.04 (m, 5 H), 2.2 (s, 6 H), 2.5 (s, 2 H), 2.85 (s, 3 H), 3.04 (s, 2 H), 7.02 (s, 3 H). ^{13}C NMR: 16.27, 25.28, 28.28, 36.22, 42.42, 42.90, 125.85, 126.06, 128.67, 129.99, 148.95. M^+ = 334 (10). Anal. Calcd for $C_{17}H_{22}N_2O_3S$: C, 61.07; H, 6.63; N, 8.38. Found: C, 61.14; H, 6.65; N, 8.67.

***exo*-3-(N'-Cyanomethoxycarbimidoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (36).** Norbornene (0.6 g, 6.4 mmol, 0.58 M) and **40** (625 mg, 5 mmol) in 10 mL of dichloromethane evolved N_2 briskly for 3 h at room temperature; crude **36** (780 mg, 82%), mp 88–9 °C (from chloroform–petroleum ether). IR (CCl_4): 2960 (w), 2880 (w), 2200 (m), 2210 (m), 1590 (vs), 1450 (s), 1385 (s), 1345 (s), 1210 (s), 1190 (s). ^{1}H NMR: 0.92 (d, 1 H), 1.1–1.7 (m, 5 H), 2.66 (s, 2 H), 2.94 (s, 2 H), 3.84 (s, 3 H). ^{13}C NMR: 25.46, 28.21, 36.23, 41.43, 56.84, 113.97, 170.63. M^+ = 191 (100). Anal. Calcd for $C_{10}H_{13}N_3O$: C, 62.80; H, 6.85; N, 21.97. Found: C, 62.89; H, 6.74; N, 21.84.

***exo*-3-(N'-Cyanoethoxycarbimidoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (37).** Norbornene (1.58 g, 16.8 mmol, 0.53 M) and **41** (0.35 g, 2.5 mmol) in 30 mL of dioxane reacted at room temperature in the dark for 12 h. Crystallization from petroleum ether gave 400 mg (77%) of **37**, mp 51–2 °C. IR ($CHCl_3$): 2205 (m), 1580 (s), 1345 (s), 1200 (s). ^{1}H NMR: 0.8–1.0 (br d, 1 H), 1.0–1.7 (complex, t at 1.3, 8 H), 2.66 (s, 2 H), 2.8 (s, 2 H), 4.25 (q, 2 H). ^{13}C NMR: 13.91, 25.42, 28.16, 36.18, 41.32, 66.26, 114.01, 170.11. M^+ = 205 (30). Anal. Calcd for $C_{11}H_{15}N_3O$: C, 64.37; H, 7.36; N, 20.47. Found: C, 64.37; H, 7.49; N, 20.31.

***exo*-3-(N'-Cyano(2,6-dimethylphenoxy)carbimidoyl)-3-azatricyclo[3.2.1.0^{2,4}]octane (51).** Norbornene (2.84 g, 30 mmol, 0.94 M) and **44** (1 g, 4.7 mmol) in 30 mL of dichloromethane evolved N_2 briskly for 15 min and were kept in the dark for 2 h. Recrystallization from petroleum ether gave 1.078 g (82.5%) of **51**, mp 105–6 °C. IR ($CHCl_3$): 3000 (m), 2980 (w), 2200 (m), 1595 (s), 1580 (s), 1390 (s), 1345 (s). ^{1}H NMR: 0.8–1.04 (br d, 1 H), 1.12–1.8 (m, 5 H), 2.16 (s, 6 H), 2.48–2.8 (br, 2 H), 3.04 (s, 2 H), 7.04 (s, 3 H). M^+ = 281 (90). Anal. Calcd for $C_{17}H_{19}N_3O$: C, 72.56; H, 6.81; N, 14.93. Found: C, 72.56; H, 6.91; N, 14.90.

Acknowledgment. Part of this work was supported by the National Science Foundation (CHE 76-00949).

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Functionalization of Phenyl Rings by Imidoylnitrenes

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Received November 1, 1988

The electrophilic reactivity of imidoylnitrenes ROC(=NZ)N can be controlled by the choice of Z. With Z = SO_2CH_3, benzenes react only if they bear electron-donating substituents. The resulting N-arylisoureas, ROC(=NZ)NHAr, can be obtained conveniently and in high yields, without competing insertion of the nitrenes into aliphatic C–H bonds.

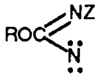
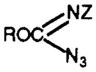
Introduction

Nitrene reactivity spans a very wide range, as discussed in the preceding paper.[1] In a program to provide a set of nitrenes, GN, of graded reactivities, we have constructed so far part of a set with G = ROC(=NZ), alkoximidoylnitrenes.[1,2] With the "control substituent" Z = CN, N'-cyanoethoxycarbimidoylnitrene (**1**) converted benzene to a mixture of N-(N'-cyanoethoxycarbimidoyl)azepine (**2**) and N-phenyl-N'-cyano-O-ethoxyisourea (**3**), while N'-(methylsulfonyl)ethoxycarbimidoylnitrene (**4**) (Z = SO_2CH_3) did not attack benzene.[2] We expected that increasing the electron availability in aryl moieties would increase the aryl reactivity over that of unsubstituted benzene. We therefore studied reactions of imidoylnitrenes with substituted benzenes.

Results and Discussion

As a sensitive probe for the effect of electron availability in aromatics, we desired a singlet nitrene almost, but not quite, reactive enough to attack unsubstituted benzene, i.e., one that would "decompose" (rearrange, fragment, dimerize, etc.) at a rate at least 200 times faster than that for attacking benzene under normal reaction conditions.

Scheme I. Azides and Nitrenes

	Z	R	
1	CN	C_2H_5	**34**
4	SO_2CH_3	C_2H_5	–
5	SO_2CH_3	CH_3	**10**
6	SO_2CF_3	CH_3	**7**
9	SO_2CH_3	2,6-$(CH_3)_2C_6H_3$	**11**

Such a rate factor would make the reaction with benzene go undetected in normal synthetic work. This submarginal nitrene should require only a small increase of the electron-withdrawing effect of G in GN to make its reaction with benzene observable. To learn whether N'-(methylsulfonyl)methoxycarbimidoylnitrene (**5**) might be at the desired reactivity level, we changed G from SO_2CH_3 to SO_2CF_3. Since the effect of the CF_3 group must be transmitted through the $SO_2N{=}C$ moiety, this is only a modest change in electron availability at the nitrene nitrogen. N'-((Trifluoromethyl)sulfonyl)methoxycarbimidoylnitrene (**6**) was generated from the corresponding azide **7**, thermolysis of which in benzene did indeed produce N-phenyl-N'-((trifluoromethyl)sulfonyl]-O-methylisourea (**8**) in 80% yield, confirming our hope that **6** is just above, and **5** just below, the reactivity needed for attacking benzene. Consequently, we used **5** for the studies described below. In addition, we used the more hindered N'-(me-

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