(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.

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Functionalization of Phenyl Rings by Imidoylnitrenes

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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.

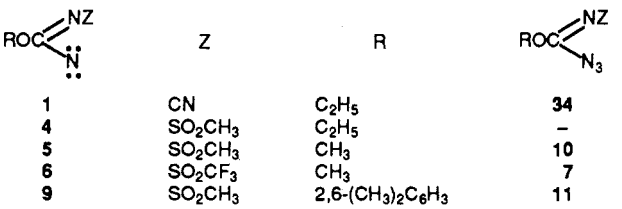
Introduction

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



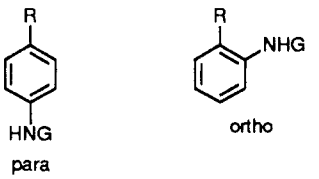
	Z	R	
1	CN	C_2H_5	**34**
4	SO_2CH_3	C_2H_5	–
5	SO_2CH_3	CH_3	**10**
6	SO_2CF_3	CH_3	**7**
9	SO_2CH_3	2,6-$(CH_3)_2C_6H_3$	**11**

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-

(1) Subbaraj, A.; Subba Rao, O.; Lwowski, W. *J. Org. Chem.*, preceding paper in this issue.
(2) Subba Rao, O.; Lwowski, W. *Tetrahedron Lett.* **1980**, *21*, 727.

0022-3263/89/1954-3952$01.50/0

Table I. Reactions of Imidoylnitrenes GN with Monosubstituted Benzenes[a]



benzene deriv	R′OC(=NSO$_2$CH$_3$)–N: R′	yield of N_2,[b] %	isoureas yield,[c] %	isoureas para:ortho ratio	yield[c] %	yield[c] *n*x
chlorobenzene	CH_3	90	0	–	100	**10x**
toluene	CH_3	95	92	**12:13** = 38:62	8	**10x**
toluene	Ar[d]	96	95	**14:15** = 33:67	5	**11x**
tert-butylbenzene	CH_3	96	55	**16:17** = 64:36	42	**10x**
tert-butylbenzene	Ar[d]	98	35	**18:19** = 75:25	65	**11x**
methoxybenzene	CH_3	98	83	**20:21** = 54:46	17	**10x**
methoxybenzene	Ar[d]	99	78	**22:23** = 63:37	0	**11x**

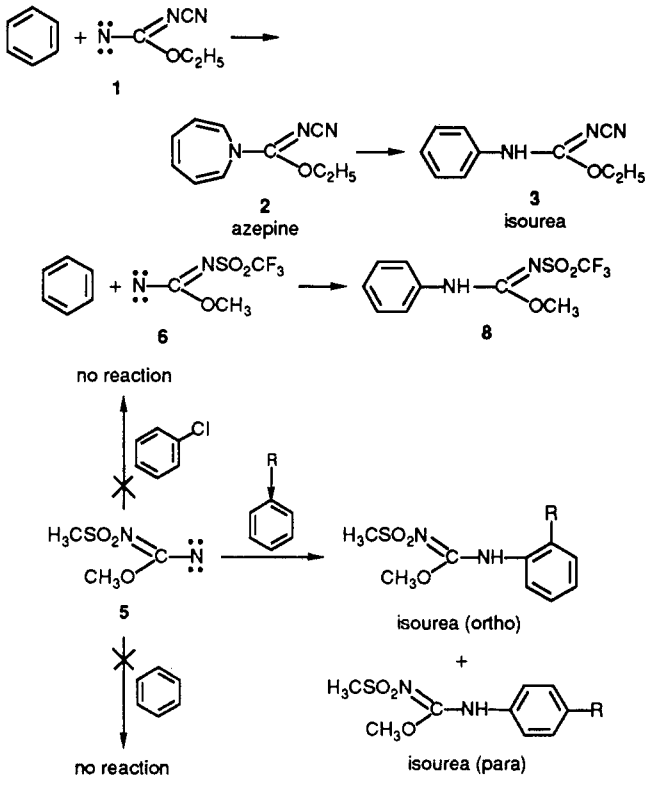
[a] Thermolyses at 80 °C; arene:azide ratio = 10:1 unless otherwise stated. [b] Yield based on total azide employed. [c] Yield based on azide decomposed (nitrogen evolved). [d] Ar = 2,6-dimethylphenyl.

thylsulfonyl)(2,6-dimethylphenoxy)carbimidoylnitrene (**9**), to probe for steric effects. We find that benzene derivatives with electron-donating substituents do react with both **5** and **9** to *N*-arylisoureas. (See Schemes I and II.)

Reactions with Benzene. *N*′-(Methylsulfonyl)methoxycarbimidoyl azide[3] (**10**) decomposed completely at 80 °C in the presence of benzene in 24 h, but did not give any products incorporating all or part of the benzene ring. Benzene is also inert toward *N*′-(methylsulfonyl)ethoxycarbimidoylnitrene (**4**), as are saturated hydrocarbons, acetonitrile, and THF. *N*′-(Methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl azide[1] (**11**) also decomposed quantitatively, under the same conditions, without attacking the benzene. When thermolyzed in such inert media, all the azides discussed here (and quite a few others[4]) give remarkably constant, but complex, product mixtures, not incorporating solvent or cosolute. Their composition does not depend on the nature of solvent and cosolute, as seen by VPC, IR, and NMR, and is characteristic for a given azide and different for different azides (see Experimental Section). We have not yet studied these mixtures, which are designated here by numbers ***n*x** for each azide ***n***, so that "**7x**" is the product mixture from the decomposition of the azide **7** in a medium with which **7** (or the nitrene **8** derived from it) does not react. In the absence of sufficient concentrations of reactive substrates, ***n*x** can be formed together with intermolecular nitrene products. In the presence of sufficiently reactive substrates, no ***n*x** is formed, and nitrene products are identified in up to quantitative yields.

Monosubstituted Benzenes. (See Table I.) Chlorobenzene did not react with methoxy-*N*′-(methylsulfonyl)carbimidoylnitrene (**5**), but alkylbenzenes and anisole did. Under our standard conditions (1:10 molar ratio of azide to aromatic reactant in acetonitrile at 78–80 °C for 24 h; N_2 yield near 100%), toluene and **5** gave the *N*-4- and *N*-2-tolylisoureas **12** and **13**, respectively, in the statistical ratio para:ortho = 1:2. Toluene and *N*′-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoylnitrene (**9**) also gave the statistical 1:2 ratio of *N*-4- and *N*-2-tolylisoureas **14** and **15**. This is reasonable, as the nitrene will initiate its interaction with the face of the phenyl ring and experience little steric hindrance in the case of toluene. With *tert*-butylbenzene and **5**, the para:ortho ratio reversed

Scheme II

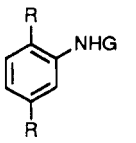
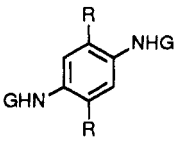


to about 2:1 (to give **16** and **17**, respectively) and to 3:1 with the bulkier nitrene **9** (to give **18** and **19**, respectively). Anisole and **5** produced in 83% yield a mixture of the *N*-(4-methoxyphenyl)- and *N*-(2-methoxyphenyl)-*N*′-(methylsulfonyl)-*O*-methylisoureas **20** and **21** in a 54:46 para:ortho ratio and a 17% yield of **10x** (see above). Anisole and **9** gave a 78% yield (by NMR) and a 63:37 ratio of the *N*-(4-methoxyphenyl) and *N*-(2-methoxyphenyl)-*N*′-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isoureas **22** and **23**, respectively.

Disubstituted Benzenes. (See Table II.) The nitrenes **5** and **9** reacted with 1,4-dialkylbenzenes about as expected on the basis of steric effects. The yields of isoureas **24–26** were lower, and those of **10x** and **11x** higher. The reaction of 1,4-dimethoxybenzene was studied only with the nitrene **5**. As azide:dimethoxybenzene ratio of 1:10 gave the monosubstitution product **27** quantitatively,

(3) Subba Rao, O.; Lwowski, W. *J. Heterocycl. Chem.* **1979**, *17*, 187.
(4) Dabbagh, H. Ph.D. Thesis, New Mexico State University, 1985.

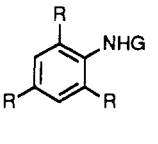
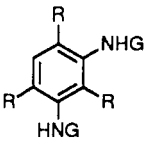
Table II. Reactions of Imidoylnitrenes GN with Disubstituted Benzenes[a]

benzene deriv	R′OC(=NSO$_2$CH$_3$)–N: R′	yield of N_2,[b] %	yields[c] (%) and products: monosubst	yields[c] (%) and products: disubst	yield[c]: %	yield[c]: nx
p-xylene	CH_3	79	40, **24**	0, –	51	**10x**
1,4-di-*tert*-butylbenzene,[e] 2:1	CH_3	100	10, **25**	0, –	90	**10x**
1,4-di-*tert*-butylbenzene	Ar[d]	95	33, **26**	0, –	67	**11x**
1,4-dimethoxybenzene	CH_3	94	94, **27**	0, **28**	0	**10x**
1,4-dimethoxybenzene,[f] 1:1	CH_3	79	50, **27**	20, **28**	30	**10x**

[a] Thermolysis at 80 °C; arene:azide ratio = 10:1 unless otherwise stated. [b] Yield based on total azide employed. [c] Yield based on azide decomposed (nitrogen evolved). [d] Ar = 2,6-dimethylphenyl. [e] Arene:azide ratio = 2:1. [f] Arene:azide ratio = 1:1.

Table III. Reactions of Imidoylnitrenes GN with Trisubstituted Benzenes[a]

benzene deriv	R′OC(=NSO$_2$CH$_3$)–N: R′	yield of N_2,[b] %	yields[c] (%) and products: monosubst	yields[c] (%) and products: disubst	yield[c]: %	yield[c]: nx
mesitylene	CH_3	98	80, **29**	0, –	20	**10x**
1,3,5-tri-*tert*-butylbenzene	CH_3	99	0, –	0, –	100	**10x**
1,3,5-tri-*tert*-butylbenzene	Ar[d]	na[g]	0, –	0, –	100	**11x**
1,3,5-trimethoxybenzene	CH_3	100	95, **30**	0, **31**	5	**10x**
1,3,5-trimethoxybenzene,[f] 1:1	CH_3	79	64, **30**	16, **31**	20	**10x**
1,3,5-trimethoxybenzene,[e] 2:1	Ar[d]	100	83, **32**	5, **33**	12	**11x**

[a] Thermolyses at 80 °C; arene:azide ratio = 10:1 unless otherwise stated. [b] Yield based on total azide employed. [c] Yields based on azide decomposed (nitrogen evolved). [d] Ar = 2,6-dimethylphenyl. [e] Arene:azide ratio = 2:1. [f] Arene:azide ratio = 1:1. [g] Not applicable.

indicating strong activation and little steric hindrance. With a 1:1 ratio, the yield (based on decomposed azide and corrected for the stoichiometry) was 70%, consisting of a 50% yield of monosubstituted (**27**) and a 20% yield of 1,4-disubstituted product (**28**), which was also obtained by thermolyzing **10** in the presence of **27**.

Trisubstituted Benzenes. (See Table III.) 1,3,5-Trimethylbenzene and **5** gave an 80% yield of the monosubstituted product, *N*-(2,4,6-trimethylphenyl)-*N*′-(methylsulfonyl)-*O*-methoxyisourea (**29**), and 20% of **10x**. 1,3,5-Tri-*tert*-butylbenzene did not react with either **5** or **9**; only **10x** and **11x** were formed, respectively. In contrast, 1,3,5-trimethoxybenzene did react with both nitrenes in high yields, to give **30** and **32**, respectively. Moreover, some disubstituted products, **31** and **33**, were formed even when a 1:10 azide: substrate ratio was used.

Discussion

Our results show the attack of benzenes by imidoylnitrenes to be quite sensitive to the electron availability in the benzene. Attaching just one methyl group to benzene changes the yields from 0% to 92% with **5**, and to 95% with **9**. Strong steric hindrance is observed only with *tert*-butyl-substituted benzenes. 1,3,5-Trimethoxybenzene adds both **5** and **9** in high yields, and even forms disubstitution products, 1,2,3,4,5-pentasubstituted benzenes. Mono- and di-*tert*-butylbenzenes react with diminished yields, but 1,3,5-tri-*tert*-butylbenzene does not react with either nitrene. Even **9** can attack the position between two methyl or methoxy groups, but neither nitrene could access the carbon between two *tert*-butyl groups. The results agree with a facial, rather than radial, approach vector of the nitrene.

In all reactions, we obtained isoureas, formally products of insertion into an aromatic C–H bond. In many other reactions of nitrenes with phenyl rings, the primary products are N-substituted azepines. Azepines could have been formed initially and then rearranged in the isoureas. This indeed might be the mode of reaction of **1** with benzene. Alternatively, the initial adduct of the benzene π-electron system with **5**, **6**, or **9** could have rearranged directly to the apparent C–H insertion product, without first forming an azepine, or spending much time in the system of azanorcaradiene–azepine isomerizations. We cannot rule out intermediate *N*-imidoylazepines: The rearrangement of *N*-acylazepines to aminoaryl derivatives takes place readily in other systems.[5] Abramovitch,[6] for example, obtained apparent nitrene insertion into aromatic C–H bonds when he generated (methylsulfonyl)nitrene in benzene. At 120 °C, he could not detect azepines, but was able to trap intermediate *N*-(methylsulfonyl)azepine with TCNE, and he did isolate azepine when working at a lower temperature. A single attempt on our part, using TCNE, did not trap azepine (see Experimental Section, **34**).

The nitrene **9** should be particularly useful in synthesis. Its precursor **11** is easily prepared, is indefinitely stable in the refrigerator, and decomposes to the nitrene completely at 80 °C in 24 h. It produced the best yields in our experiments, giving isoureas that can be readily hydrolyzed

(5) Lwowski, W.; Maricich, T. J. *J. Am. Chem. Soc.* **1985**, *87*, 3630.
(6) Abramovitch, R. A.; Bailey, T. D.; Takaya, T.; Uma, V. *J. Org. Chem.* **1974**, *39*, 340.

to their parent aromatic amines. Aliphatic C–H bonds are not attacked,[1] nor are phenyls lacking electron-donating substituents. In its other reactions, **9** is similar to **5**. The reactions of **9** with olefins[1] and alcohols are described in the preceding paper. The new nitrene $CH_3OC(=NSO_2CF_3)N$ (**6**) is somewhat more reactive than **9**. Like **1**, it does attack unsubstituted benzene, but its azide precursor $CH_3OC(=NSO_2CF_3)N_3$ (**7**) is quite susceptible to hydrolysis, thus less practical than $C_2H_5OC(=NCN)N_3$, the precursor to **1**.

Experimental Section

General. The products obtained were characterized spectroscopically and by elemental analysis as described in the preceding paper.[1]

Azide Thermolyses. General. Unless stated otherwise, azides were thermolyzed in 50 mL of acetonitrile at 78–80 °C for 24 h, using a 1:10 molar ratio of azide to the intended reactant. Acetonitrile and excess reactant were removed at 2 mmHg and 40 °C. The residue was analyzed by ^1H NNR, using tetrachloroethylene or dichloromethane as an internal standard, with an accuracy of about 5%. The residue was chromatographed on basic alumina, using chloroform–hexane (95:5) as the eluent. Often, part or all of the product arose from the azide alone, not incorporating solvent or intended reactant. The properties of these "azide-only" product mixtures did not depend on the nature of the other components in the system and were remarkably constant for each azide, as seen by their spectra and their chromatographic behavior (they usually eluted last). They are named by the number of the azide, with an **x** appended, e.g., **7x**.

Azides. *N'*-(Methylsulfonyl)methoxycarbimidoyl azide (or methyl 1-azido-*N*-(methylsulfonyl)formimidate) (**10**) and ***N'*-cyanoethoxycarbimidoyl azide** (ethyl 1-azido-*N*-cyanoformimidate) (**34**) were reported earlier.[3] The preparation of ***N'*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl azide** (**11**) from 5-(2,6-dimethylphenoxy)tetrazole (**35**) is described in the accompanying paper.[1]

***N'*-((Trifluoromethyl)sulfonyl)methoxycarbimidoyl Azide (7).** To a stirred solution of 5 g (50 mmol) of 5-methoxytetrazole in 500 mL of anhydrous, peroxide-free THF was added dropwise at 0 °C under argon 5.54 g (52 mmol) of trifluoromethanesulfonyl chloride in 25 mL of THF over 30 min. After another 30 min, 5.37 mL (52 mmol) of triethylamine was added during 1 h. Two hours later the $Et_3N{\cdot}HCl$ was filtered and washed with THF, and the concentrated THF solutions were passed twice through short silica gel columns (20 g each). Elution with chloroform–ethyl acetate (95:5) gave 5.2 g (50% yield, considering recovered tetrazole). **7** is stable at room temperature and decomposes above 100 °C. It hydrolyzes very easily to 5-methoxytetrazole. Recrystallization from ether–hexane (1:1) gave pure **7**, mp 51–2 °C. ^1H NMR: 4.08 (s). ^{13}C NMR ($CDCl_3$) (^1H decoupled): 59.6, 118.8 (q, J = 319 Hz), 160.1. IR ($CHCl_3$): 3080 (w), 2900 (w), 2160 (s), 2200 (s). Anal. Calcd for $C_3H_3N_4O_3F_3S$: C, 15.52; H, 1.30; N, 24.13. Found: C, 15.81; H, 1.23; N, 24.16.

Reactions with Benzene. Thermolysis of 10 in Benzene. A solution of 2 g (11.2 mmol) of $MeOC(=NSO_2Me)N_3$ (**10**) and 10 mL (112 mmol) of benzene in 50 mL of acetonitrile, heated in an oil bath at 80 °C for 24 h, evolved 100% of the calculated volume of N_2. Concentration of the solution at 2 mmHg at room temperature left a yellow viscous residue (**10x**). Its ^1H NMR spectrum showed many overlapping singlets: 10–15 between 2.7 and 3.62 ppm (integral 40) and 10–15 between 3.7 and 4.5 ppm (integral 40), as well as a broad signal at 5.6 ppm (area 1.5). No signals were found in the aromatic region.

Thermolysis of 11 in Benzene. **11** (1 g, 37 mmol) and 3.33 g of benzene (373 mmol) gave the expected volume of N_2 and a residue **11x**, whose ^1H NMR spectrum showed unresolved signals around 2.2 ppm (area 30) overlapping singlets between 2.5 and 3.2 ppm (area 14), a broad signal at 4.4 ppm (area 1), and unresolved signals between 6.7 and 7.1 ppm (area 15). The ratio 30:15 for the upfield and the downfield signals is that expected for material having only the 2,6-dimethylphenyl moiety as its aromatic constituent. The material resisted separation by VPC or column chromatography and has not yet been investigated further.

***N*-(*N'*-Cyanoethoxycarbimidoyl)azepine (2) and *N*-Phenyl-*N'*-cyano-*O*-ethoxyisourea[7] (3).** Benzene (32.5 mL), **34** (0.3 g, 2.2 mmol), and dichloromethane (27.5 mL), divided into three equal portions, were irradiated with 300-nm light for 90 min each. Sixty percent of the expected N_2 was evolved, leaving a dark brown mixture. Separation on 1-mm silica gel plates, using chloroform–ethyl acetate (85:15), gave a mixture rich in azepine and low in isourea (R_f 0.67–0.76) and, at higher R_f values, mixtures containing less azepine and more isourea. Complete separation was not achieved. By NMR, the azepine: isourea ratio was 1.17:1, and the total yield, 58%. Crystallization from ethyl acetate–pentane at −25 °C gave crystals of a 1:3 azepine–isourea mixture.

Thermolysis of 7 in Benzene. **7** (8.6 mmol) in benzene (50 mL) at 80 °C did not produce nitrogen, but 2 g (8.6 mmol) of **7** and 10 mL of benzene in 50 mL of peroxide-free diglyme in an oil bath at 115 °C for 24 h gave 92% of the expected N_2. The residue did not show the ^1H NMR signals of **7x** (obtained by thermolysis in diglyme alone), but those of *N*-phenyl-*N'*-((trifluoromethyl)sulfonyl)-*O*-methylisourea (**8**). Chromatography produced 1.95 g (80%) of pure **8**, mp 40–1 °C. ^1H NMR: 4.0 (s, 3 H), 7.09–7.55 (m, 5 H), 9.25 (br, 1 H). ^{13}C NMR: 57.14, 119.72 (q, J = 320 Hz), 123.7, 127.3, 129.4, 134.1, 159.2. Anal. Calcd for $C_9H_9N_2O_3F_3S$: C, 38.80; H, 3.21; N, 9.93. Found: C, 38.31; H, 3.21; N, 9.92.

Reactions with Monosubstituted Benzenes. Chlorobenzene. Thermolysis of **10** in chlorobenzene, under the conditions described above for thermolysis with benzene, gave only **10x** and no products derived from chlorobenzene.

Thermolysis of 10 with Toluene. **10** (0.309 g, 1.74 mmol) with toluene (1.8 mL, 17.4 mmol) gave 95% of the expected N_2. ^1H NMR analysis of the residue indicated the presence of a 36% yield of *N*-(*p*-tolyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**12**) and a 62% yield of the corresponding *o*-tolyl isomer **13**. The reaction was not investigated further.

Thermolysis of 11 with Toluene. **11** (2.52 g, 9.4 mmol) with toluene (10 mL, 94 mmol) gave 95% of the expected N_2 volume. NMR analysis of the brown residue indicated near quantitative formation of a 1:2 mixture of the *p*- and *o*-tolyl isoureas **14** and **15**. Filtration of a chloroform solution through 4 g of basic alumina gave a white mixture of the ortho and para compounds. Soxhlet extraction with 150 mL of ether gave 1.2 g (35%) of *N*-(*o*-tolyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**15**), mp 113–4 °C (from dichloromethane–hexane). ^1H NMR: 2.20 (s, 6 H), 2.41 (s, 3 H), 3.45 (s, 3 H), 7.05 (s, 3 H), 7.19–7.50 (m, 4 H), 9.08 (br, 1 H). ^{13}C NMR: 16.33, 18.02, 42.49, 126.16, 126.32, 126.77, 127.43, 128.64, 129.95, 130.89, 133.08, 134.04, 148.38, 155.42. Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.12; H, 6.22; N, 8.39.

Repeated recrystallization from chloroform–ether of the material remaining unextracted in the thimble gave pure *N*-(*p*-tolyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**14**), mp 173–4 °C. ^1H NMR: 2.20 (s, 6 H), 2.38 (s, 6 H), 2.38 (s, 3 H), 2.90 (s, 3 H), 7.05 (s, 3 He, 7.09–7.30 (m, 4 H), 9.19 (br, 1 H). ^{13}C NMR: 16.33, 20.94, 42.53, 123.63, 126.17, 128.64, 129.85, 130.12, 132.12, 136.37, 148.35, 154.88. Anal. Calcd for $C_{17}H_{20}N_2O_3S$: C, 61.42; H, 6.06; N, 8.43. Found: C, 61.21; H, 6.18; N, 8.29.

Thermolysis of 10 with *tert*-Butylbenzene. **10** (1.0 g, 5.6 mmol) with *tert*-butylbenzene (8.7 mL, 56 mmol) gave a 96% yield of N_2 and (by NMR analysis of the residue) a 55% yield of a 64:36 mixture of *N*-(2-*tert*-butylphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**17**). ^1H NMR para compound **16**: 1.32 (s, 9 H), 3.09 (s, 3 H), 3.78 (s, 3 H), 7.15 (d, J = 2 Hz, 2 H), 7.35 (d, J = 2 Hz), 8.90 (br, 1 H). ^1H NMR, ortho compound **17**: 1.20 (s, 9 H), 3.04 (s, 3 H), 3.90 (s, 3 H), 7.05–7.50 (m, 4 H), 9.03 (br, 1 H). We did not succeed in separating the isomers.

Thermolysis of 11 with *tert*-Butylbenzene. **11** (2.86 g, 10 mmol) with *tert*-butylbenzene (13.4 g, 100 mmol) produced 98% of the expected N_2. NMR analysis of the black residue indicated the presence of a 48% yield of **11x** and a 52% yield of a 3:1 mixture of *N*-(*p*-*tert*-butylphenyl)- and *N*-(*o*-*tert*-butylphenyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isoureas (**18** and **19**, respectively). Chromatography eluted first a mixture of the isomeric isoureas (48% yield) and later the viscous, yellow,

(7) Subba Rao, O.; Lwowski, W., unpublished results.

"azide thermolysate" **11x** (see above) not incorporating solvent or substrate. Soxhlet extraction in the isourea mixture, using a 1:1 ether/hexane mixture, gave a small quantity of the product **18** of nitrene attack in the para position of the *tert*-butylbenzene, mp 156–7 °C (from ether/hexane). ^{1}H NMR: 1.51 (s, 9 H), 2.22 (s, 6 H), 2.95 (s, 3 H), 7.02 (s, 3 H), 7.2–7.56 (m, 4 H), 9.2 (br, 1 H). ^{13}C NMR: 16.89, 30.67, 34.99, 42.78, 126.11, 126.64, 127.14, 127.86, 128.73, 129.61, 129.97, 132.29, 145.24, 148.54, 155.18. Anal. Calcd for $C_{20}H_{26}N_2O_3S$: C, 64.14; H, 6.99; N, 7.48. Found: C, 63.85; H, 7.10; N, 7.45. After 2 h of extraction, left in the thimble of the Soxhlet apparatus was a small amount of the ortho isomer **19**, mp 189–90 °C (from chloroform–ether). ^{1}H NMR: 1.50 (s, 9 H), 2.16 (s, 6 H), 2.83 (s, 3 H), 6.95 (s, 3 H), 6.97–7.075 (m, 4 H), 9.25 (br, 1 H).

Thermolysis of 10 with Anisole. **10** (2 g, 11 mmol) with anisole (12 mL, 110 mmol) gave 98% of the expected N_2. NMR analysis indicated an 83% yield of a 54:46 mixture of *N*-(4-methoxyphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**20**) and *N*-(2-methoxyphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**21**) and a 17% yield of **10x**. Chromatography did not separate the isomers, but did separate them from **10x**. Soxhlet extraction with benzene for 5 min dissolved the para-substituted anisole adduct **20**, mp 111–2 °C (from chloroform–hexane). ^{1}H NMR: 3.09 (s, 3 H), 3.80 (s, 3 H), 3.89 (s, 3 H, 6.97 (q, 4 H J = 10 Hz), 8.88 (br, 1 H). ^{13}C NMR: 42.68, 55.66, 114.28, 125.34, 128.22, 1546.85, 157.90. Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.50; H, 5.56; N, 10.85. Found: C, 46.52; H, 5.46; N, 10.82. Continued Soxhlet extraction with benzene, for 90 min, left in the thimble a small amount of the ortho isomer **18**, which was recrystallized from chloroform–ether, to give **21**, mp 93–4 °C. ^{1}H NMR: 3.06 (s, 3 H), 3.86 (s, 3 H), 3.91 (s, 3 H), 6.80–7.53 (m, 4 H), 9.45 (br, 1 H). Anal. Calcd for $C_{10}H_{14}N_2O_4S$: C, 46.50; H, 5.56; N, 10.85. Found: C, 46.24; H, 5.41; N, 10.80.

Thermolysis of 11 with Anisole. **11** (1.5 g, 5.5 mmol) with anisole (6 g, 55 mmol) gave nitrogen in 99% yield. NMR analysis of the residue indicated a mixture of para and ortho products in 78% yields, in a ratio of *N*-(4-methoxyphenyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**22**) to *N*-(2-methoxyphenyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**23**) of 63:37. Soxhlet extraction with ether gave the para compound **22**, mp 177–9 °C. ^{1}H NMR: 2.19 (s, 6 H), 2.91 (s, 3 H), 3.80 (s, 3 H), 7.04 (s, 3 H), 7.15 (q, 4 H), 9.08 (br, 1 H). ^{13}C NMR: 16.30, 42.54, 55.48, 114.44, 125.76, 126.15, 128.19, 130.02, 148.39, 155.15, 258.21. Anal. Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.79; N, 8.04. Found: C, 58.28; H, 5.81; N, 7.93. Crystallization from chloroform–petroleum ether of the material remaining in the thimble gave pure ortho compound **23**, mp 128–9 °C. ^{1}H NMR: 2.21 (s, 6 H), 2.93 (s, 3 H), 3.94 (s, 3 H), 6.82–7.79 (m, 4 H), 7.08 (s, 3 H), 6.95 (br, 1 H). ^{13}C NMR: 16.30, 42.53, 55.95, 110.87, 120.78, 122.68, 125.19, 126.22, 128.69, 130.12, 148.37, 150.48, 154.71. Anal. Calcd for $C_{17}H_{20}N_2O_4S$: C, 58.60; H, 5.79; N, 8.04. Found: C, 58.30; H, 5.75; N, 7.99.

Reactions with Disubstituted Benzenes. Thermolysis of 10 with *p*-Xylene. **10** (2 g, 11.9 mmol) with *p*-xylene (15 mL, 119 mmol) gave a 78% yield of N_2. NMR analysis indicated the formation of a 49% yield of *N*-(2,5-dimethylphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**24**) and 51% of **10x**. Elution with chloroform from basic alumina and recrystallization from dichloromethane gave 1.22 g (40%) of **21**, mp 173–4 °C. ^{1}H NMR: 2.20 (s, 3 H), 2.28 (s, 3 H), 3.03 (s, 3 H), 3.80 (s, 3 H), 6.88–7.13 (m, 3 H), 8.41 (br, 1 H). ^{13}C NMR: 17.43, 20.93, 42.58, 55.68, 126.24, 127.81, 129.58, 130.55, 133.76, 136.40, 157.16. Anal. Calcd for $C_{11}H_{16}N_2O_3S$: C, 51.54; H, 6.30; N, 10.90. Found: C, 51.49; H, 6.49; N, 10.89.

Photolysis of 10, with 300-nm light in a Rayonet reactor, was exceedingly slow in the presence of a 10-fold molar ratio of *p*-xylene. When a 1:2 ratio was used, it was still slow. A solution of 0.712 g (4 mmol) of the azide with 8 mmol of *p*-xylene in 30 mL of dichloromethane and 20 mL of acetonitrile for 3 days at 0 °C produced a quantitative yield of N_2, 0.34 g (35%) of **24**, and a 65% yield of **10x**.

Thermolysis of 10 with 1,4-Di-*tert*-butylbenzene. **10** (1.96 g, 11 mmol) with 1,4-di-*tert*-butylbenzene (4.2 g, 22 mmol) gave a 100% yield of N_2. After removal of excess substrate by extraction with petroleum ether, NMR analysis of the residue indicated a 90% yield of **10x** and 10% of monoadduct. Crystallization from chloroform gave slightly impure *N*-(2,5-di-*tert*-butylphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**25**), mp 124–9 °C. ^{1}H NMR: 1.30 (s, 9 H), 1.38 (s, 9 H), 2.95 (s, 3 H), 3.78 (s, 3 H), 7.08–7.30 (m, 3 H), 8.80 (br, 1 H). Mass spectrum: 340 (M^+).

Thermolysis of 11 with 1,4-Di-*tert*-butylbenzene. **11** (1.5 g, 5.6 mmol) with 1,4-di-*tert*-butylbenzene (10.1 g, 56 mmol) gave a 95% yield of N_2, a 33% yield of *N*-(2,5-di-*tert*-butylphenyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea) (**26**) and 67% of **11x** (by NMR). Chromatography gave **26**, mp 175–6 °C (chloroform–petroleum ether). ^{1}H NMR: 1.30 (s, 9 H), 1.50 (s, 9 H), 2.25 (s, 6 H), 2.95 (s, 3 H), 7.02 (s, 3 H), 7.35–7.44 (m, 3 H), 9.25 (br, 1 H). ^{13}C NMR: 16.89, 30.78, 31.20, 34.25, 34.64, 42.79, 124.93, 126.06, 126.85, 127.07, 128.72, 128.81, 129.98, 132.93, 142,39, 148.65, 149.69, 155.37. Anal. Calcd for $C_{24}H_{34}N_2O_3S$: C, 66.94; H, 7.96; N, 6.91. Found: C, 66.84; H, 8.16; N, 6.41.

Thermolysis of 10 with *p*-Dimethoxybenzene. 1:10 Molar Ratio. **10** (1.86 g, 10.5 mmol) with *p*-dimethoxybenzene (14.5 g, 105 mmol), gave 94% yields (based on decomposed azide) of N_2 and *N*-(2,5-dimethoxyphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**27**), mp 80–1 °C from dichloromethane–hexane). ^{1}H NMR: 3.12 (s, 3 H), 3.73 (s, 3 H), 3.81 (s, 3 H), 3.91 (s, 3 H), 6.61 (dd, J = 10 Hz, 1 H), 6.85 (d, J = 4 Hz, 1 H), 7.15 (d, J = 0.5 Hz 1 H), 9.56 (br, 1 H). ^{13}C NMR: 42.45, 55.77, 56.48, 108.76, 109.36, 111.34, 126.02, 144.18, 153.36, 156.25. Anal. Calcd for $C_{11}H_{16}N_2O_3S$: C, 45.82; H, 5.56; N, 9.72. Found: C, 45.61; H, 5.63; N, 9.76.

1:1 Molar Ratio. Thermolysis of 10.4 mmol of **10** in the presence of 10.4 mmol of *p*-dimethoxybenzene gave 97% of the expected N_2, 30% of **10x**, 50% of the monoadduct **27**, and 19% of the diadduct *N,N'*-bis(*N''*-(methylsulfonyl)methoxycarbimidoyl)-1,4-diamino-2,5-dimethoxybenzene (**28**). Chromatography gave pure **28**, mp 214–5 °C (from chloroform). ^{1}H NMR: 3.08 (s, 6 H), 3.80 (s, 6 H), 3.91 (s, 6 H), 7.09 (s, 2 H), 9.41 (br, 2 H). ^{13}C NMR: 42.51, 55.85, 56.71, 106.71, 122.36, 144.09, 156.21. Anal. Calcd for $C_{14}H_{22}N_4O_8S_2$: C, 38.35; H, 5.06; N, 12.79. Found: C, 38.48; H, 5.17; N, 13.15.

The diadduct **28** was also obtained in 80% yield from monoadduct **27** (0.5 g, 1.7 mmol) and **10** (0.31 g, 17.3 mmol), by using the standard thermolysis conditions.

Reactions with Trisubstituted Benzenes. Thermolysis of 10 with Mesitylene. **10** (1.5 g, 8.4 mmol) with mesitylene (12 mL, 8.4 mmol) gave yields of 98% of N_2, 80% (by NMR) of *N*-(2,4,6-trimethylphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**29**), and 20% of **10x**. Chromatography and recrystallization gave 1.5 g (66%) of **29**, mp 131–2 °C. ^{1}H NMR: 2.20 (s, 6 H), 2.28 (s, 3 H), 3.08 (s, 3 H), 3.79 (s, 3 H), 6.90 (s, 2 H), 8.46 (br, 1 H). ^{13}C NMR: 18.10, 20.96, 42.54, 55.68, 128.98, 130.19, 135.28, 137.75, 157.90. Anal. Calcd for $C_{12}H_{18}N_2O_3S$: C, 53.31; H, 6.71; N, 10.36. Found: C, 53.39; H, 6.74; N, 10.43.

Thermolyses of 10 and 11 with 1,3,5-tri-*tert*-butylbenzene gave only N_2 in almost quantitative yields, no products containing the substrate molecule, and the azide thermolysates **10x** and **11x**, respectively.

Thermolysis of 10 and 1,3,5-Trimethoxybenzene. 1:1 Molar Ratio. **10** (3.0 g, 16.9 mmol) and 1,3,5-trimethoxybenzene (2.8 g, 16.9 mmol) gave a 79% yield of N_2. NMR analysis of the residue showed a 20% yield of **10x**. Chromatography gave a 4:1 mixture of mono and diadducts (by NMR), separable by chromatography on silica with chloroform–ethyl acetate (95:5) elution. *N*-(2,4,6-trimethoxyphenyl)-*N'*-(methylsulfonyl)-*O*-methylisourea (**30**) has mp 150–1 °C (from chloroform–ether). ^{1}H NMR: 3.05 (s, 3 H), 3.70 (s, 3 H), 3.72 (s, 6 H), 3.74 (s, 3 H), 6.15 (s, 2 H), 8.19 (br, 1 H). ^{13}C NMR: 41.88, 55.48, 55.55, 55.95, 90.66, 105.49, 156.24, 158.86, 160.37. Anal. Calcd for $C_{12}H_{18}N_2O_6S$: C, 44.28; H, 5.70; N, 8.80. Found: C, 44.22; H, 5.51; N, 8.77. The minor product, *N,N'*-bis(*N''*-(methylsulfonyl)methoxycarbimidoyl)-1,3-diamino-2,4,6-trimethoxybenzene (**31**) has mp 224–6 °C (from chloroform). ^{1}H NMR: 3.05 (s, 6 H), 3.76 (s, 9 H), 3.80 (s, 6 H), 6.27 (s, 1 H), 8.30 (br, 1 H). ^{13}C NMR: 42.27, 55.76, 56.10, 61.20, 91.81, 110.48, 153.48, 155.31, 158.39. Anal. Calcd for $C_{15}H_{24}N_4O_9S$: C, 38.40; H, 5.16; N, 11.96. Found: C. 38.07; H, 5.17; N, 11.89.

1:10 Molar Ratio. **10** (1 g, 5.6 mmol) and trimethoxybenzene (9.5 g, 56 mmol) gave yields of 100% of N_2, 95% of the monoadduct **30**, 5% of the diadduct **31**, and no detectable amount of **10x**.

Thermolysis of 11 with 1,3,5-Trimethoxybenzene. 1:2

Molar Ratio. 11 (2.0 g, 7.5 mmol) with 1,3,5-trimethoxybenzene (2.5 g, 15 mmol) produced a 100% yield of N_2 and, nearly quantitatively, a mixture of mono- and diadducts, in an 87:13 ratio. Chromatography gave *N*-(2,4,6-trimethoxyphenyl)-*N'*-(methylsulfonyl)-*O*-(2,6-dimethylphenyl)isourea (**32**), mp 209–10 °C. ^{1}H NMR: 2.15 (s, 6 H), 2.96 (s, 3 H), 3.80 (s, 3 H), 3.85 (s, 6 H), 6.19 (s, 2 H), 7.00 (s, 3 H), 8.39 (br, 1 H). ^{13}C NMR: 15.76, 41.86, 55.48, 55.74, 90.39, 125.84, 128.40, 130.10, 130.24, 148.43, 156.89, 157.25, 160.85. Anal. Calcd for $C_{19}H_{24}N_2O_6S$: C, 55.87; H, 59.92; N, 6.86. Found: C, 55.19; H, 6.00; N, 6.97. The diadduct *N,N'*-bis(*N''*-(methylsulfonyl)(2,6-dimethylphenoxy)carbimidoyl)-1,3-diamino-2,4,6-trimethoxybenzene (**33**) has mp 285 ° dec. ^{1}H NMR (DMSO-d_6): 2.18 (s, 12 H), 2.95 (s, 8 H), 3.96 (s, 6 H), 4.04 (s, 3 H), 6.60 (s, 1 H), 7.00 (s, 6 H), 8.80 (br, 2 H). Anal. Calcd for $C_{29}H_{36}N_4O_9S$: C, 53.69; H, 5.59; N, 8.64. Found: C, 53.69; H, 5.60; N, 8.54.

Attempt To Trap Azepine. Thermolysis of *N'*-Cyanomethoxycarbimidoyl Azide[2] in the Presence of *p*-Xylene and Tetracyanoethylene. The azide (1.5 g, 12 mmol), *p*-xylene (120 mmol), and tetracyanoethylene (5 mmol) produced a 99% yield of N_2. Chromatography produced 1.46 g (61%) of *N*-(2,5-dimethylphenyl)-*N'*-cyano-*O*-methylisourea (**35**), but no TCNE adduct. Recrystallization from dichloromethane–hexane gave **35**, mp 172–3 °C. ^{1}H NMR: 2.21 (s, 3 H), 2.31 (s, 3 H), 3.81 (s, 3 H), 7.00–7.20 (m, 3 H), 7.80 (br, 1 H). ^{13}C NMR: 17.31, 20.85, 58.41, 115.55, 127.17, 128.69, 130.68, 130.89, 133.17, 136.54, 163.48. M^+ = 203. Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.45; N, 20.67. Found: C, 64.94; H, 6.44; N, 20.81.

Strong Participation of Selenium Substituents in Decomposition of Pyrazolines Formed by 1,3-Dipolar Cycloaddition of Appropriate Vinyl Selenides with Diazoalkanes

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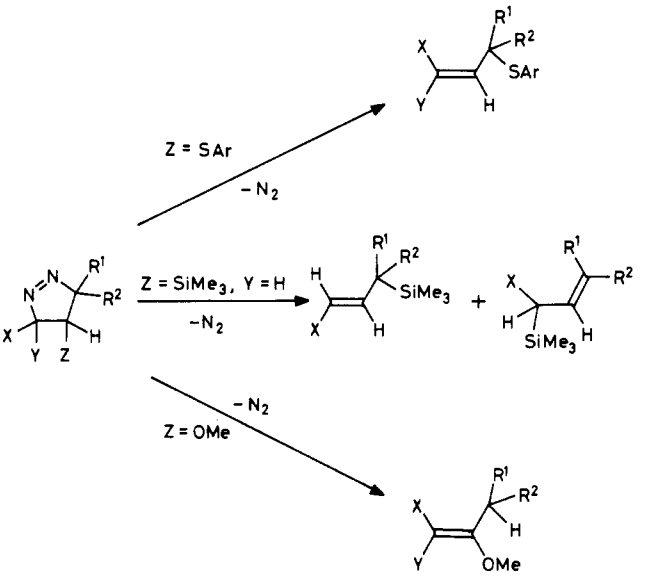
Decomposition of 4-(arylseleno)pyrazolines (**3**) bearing two electron-withdrawing groups such as COOMe, COMe, and CN at C-3, which were prepared in situ by reaction of the corresponding aryl vinyl selenides (**2**) with diazoalkanes, are reported. The pyrazolines decompose below 0 °C to give allyl aryl selenide derivatives (**4**) by migration of 4-arylseleno group to C-5 concerted with extrusion of nitrogen. Facile decomposition of the pyrazolines with migration of the selenium substituent is explained by strong contribution of intramolecular diazonium salt resonance structure, within which arylseleno groups strongly participate in the decomposition. Most reactions of **2** with 2 mol of diazoalkanes gave the pyrazolines **5**, whereas reaction of **2c** with 2 mol of 2-diazopropane gave a reverse orientation adduct, the pyrazoline **9**.

There is continuing interest in the decomposition of pyrazolines from synthetic, mechanistic, and theoretical points of view.[1] We have been interested in effects of heteroatoms on decomposition of 4-heteroatom-substituted pyrazolines bearing two geminal electron-withdrawing groups at C-3. Three types of the effects of heteroatom substituents on the decomposition of pyrazolines have been reported. We have found that 4-(arylthio)pyrazolines, geminally substituted with two electron-withdrawing groups at C-3, decompose quantitatively to allyl sulfide derivatives by concerted migration of 4-arylthio group to C-5 with loss of nitrogen under mild conditions.[2] However, decomposition of a 4-trimethylsilyl group substituted pyrazoline bearing an electron-withdrawing group at C-3 leads to migration of the 4-trimethylsilyl group to C-3 or to C-5, depending on the bulkiness of the substituent at C-5;[3] the mechanism seems to be different from the case of 4-(arylthio)pyrazolines in the sense that the trimethylsilyl group has positive character opposing the nucleophilic sulfur group (Scheme I). On the other hand, analogous 4-alkoxypyrazolines generally cause predominant 4-hydride migration to C-5 with elimination of nitrogen.[4] This observation prompted us to investigate the

Scheme I



effect of the 4-arylseleno group on decomposition of the 4-(arylseleno)pyrazolines: how the 4-arylseleno group behaves on decomposition (like arylthio or trimethylsilyl group) because a seleno group is also able to eliminate reductively.[5] We have found that 4-(arylseleno)-substi-

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