of reflections near $\chi = 90°$, and the minimum relative transmission coefficient was 96.09%. Of 2477 unique data, 1842 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by direct methods and refined by full-matrix least squares based on F with $w = \sigma^{-2}(F_o)$. Non-hydrogen atoms were treated anisotropically, while hydrogen atoms were located in difference maps and refined isotropically. Final $R = 0.030$, $R_w = 0.052$ for 228 variables, and the maximum residual density was 0.21 eÅ^{-3}.

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Registry No. **3b**, 108345-06-8; **3c**, 108345-07-9; **3d**, 108345-08-0; **3e**, 108345-09-1; **3f**, 108365-56-6; **3g**, 6663-97-4; **3h**, 108345-11-5; **8**, 4628-94-8; **9c**, 31255-26-2; **10**, 108345-10-4; **11**, 108345-12-6; **12a**, 108365-57-7; **12b**, 108345-13-7; **12c**, 108345-14-8; **13**, 6264-40-0; bis(2-iodoethyl) ether, 34270-90-1; 1,2-bis(2-iodoethoxy)ethane, 36839-55-1; 2-chloroethyl methyl ether, 627-42-9.

Supplementary Material Available: Molecular structure of **10** with numbering scheme, tables of bond distances and angles, coordinates for heavy atoms, coordinates and thermal parameters for H atoms, anisotropic thermal parameters, and endocyclic torsion angles (6 pages). Ordering information is given on any current masthead page.

Synthesis and Carbodemetalation Reactions of 4-Methyl- and 5-Aryl-2-(trimethylsilyl)oxazoles. C–C Bond Formation at C_2 of the Oxazole Ring

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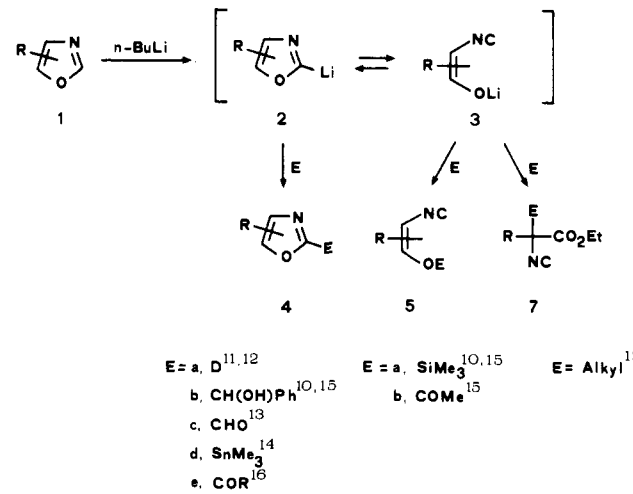
The title compounds **6a–d** have been prepared by sequential lithiation and silylation of the corresponding 2-H oxazoles and isomerization of the resulting α-isocyano silyl enol ethers. Silyloxazoles **6a–d** behave as stable 2-oxazolyl anion equivalents toward various carbon electrophiles (aldehydes, acyl chlorides, ketenes, azolium salts) to give 2-substituted oxazoles in good yields.

Oxazoles[1] continue to attract interest because of the presence of the oxazole ring in numerous biologically active compounds[2] and their use as auxiliaries in synthesis[3] in the form of latent carboxylic acid group equivalents[4] (triamide, ester, ω-cyano anhydride) and aza diene components in Diels–Alder reactions with acetylenes and alkenes[5] to give furans and pyridines as well as poly-

Scheme I



(1) Reviews: (a) Lakhan, R.; Ternai, B. *Adv. Heterocycl. Chem.* **1974**, *17*, 99. (b) Turchi, I. J.; Dewar, M. J. S. *Chem. Rev.* **1975**, *75*, 389. (c) Turchi, I. J. *Ind. Eng. Chem. Prod. Res. Dev.* **1981**, *20*, 32. (d) Turchi, I. J. *Oxazoles*; Wiley: New York, 1986.

(2) Virginiamycin family: Cocito, C. *Microbiol. Rev.* **1979**, *43*, 145. Kingston, D. G. I.; Kolpak, M. X.; LeFevre, J. W.; Borup-Grochtman, I. *J. Am. Chem. Soc.* **1983**, *105*, 5106. Meyers, A. I.; Amos, R. A. *J. Am. Chem. Soc.* **1980**, *102*, 870. Meyers, A. I.; Lawson, J. P.; Conver, D. R. *J. Org. Chem.* **1981**, *46*, 3119. Meyers, A. I.; Lawson, J. P.; Walker, D. G.; Linderman, R. J. *J. Org. Chem.* **1986**, *51*, 5111. Delpierre, G. R.; Eastwood, F. W.; Gream, G. E.; Kingston, D. G. I.; Sarin, P. S.; Lord Todd; Williams, D. H. *J. Chem. Soc. C* **1966**, 1653. Kingston, D. G. I.; Lord Todd; Williams, D. H. *Ibid.* **1966**, 1669. Berninamycin: Liesch, J. M.; Millington, D. S.; Pandey, R. C.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 8237. Liesch, J. M.; Rinehart, K. L., Jr. *Ibid.* **1977**, *99*, 1645. Conglobatin: Westley, J. W.; Lin, C.-M.; Evans, R. H.; Blount, J. F. *J. Antibiot.* **1979**, *32*, 874. Schregenberger, C.; Seebach, D. *Tetrahedron Lett.* **1984**, *25*, 5881. Calcimycin: Evans, D. A.; Sacks, C. E.; Kleschick, W. A.; Taber, T. R. *J. Am. Chem. Soc.* **1979**, *101*, 6789. Grieco, P. A.; Kanai, K.; Williams, E. *Heterocycles* **1979**, *12*, 1623. Antiinflammatories: Marchetti, E.; Mattalia, G.; Rosnati, V. *J. Med. Chem.* **1968** *11*, 1092. Marchetti, E. German Offen 2 108 437, 1971. Short, F. W.; Long, M. L. *J. Heterocycl. Chem.* **1969**, *6*, 707. Brown, K.; Cavalla, J. F.; Green, D.; Wilson, A. B. *Nature (London)* **1968**, *219*, 164. Antibiotics: (a) Neooxazolomycin: Takahashi, K.; Kawabata, M.; Uemura, D.; Iwadane, S.; Mitono, R.; Nakano, F.; Matsuzaki, A. *Tetrahedron Lett.* **1985**, *26*, 1077. (b) Oxazolomycin: Mori, T.; Takahashi, K.; Kashiwabara, M.; Uemura, D.; Katayama, C.; Iwadane, S.; Shizuri, Y.; Mitomo, R.; Nakano, F.; Matsuzaki, A. *Ibid.* **1985**, *26*, 1073. (c) Curromycin A: Ogura, M.; Nakayama, H.; Furihata, K.; Shimazu, A.; Seto, H.; Otake, N. *J. Antibiot.* **1985**, *38*, 669.

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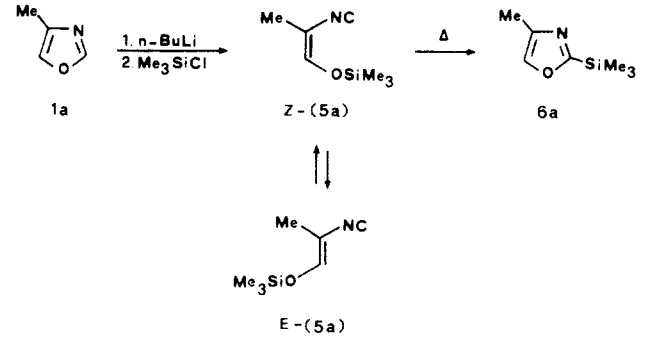
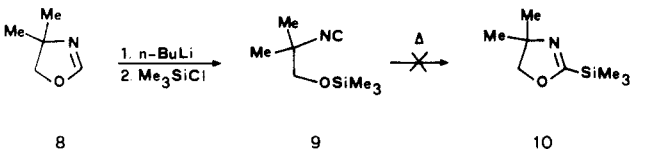
0022-3263/87/1952-3413$01.50/0

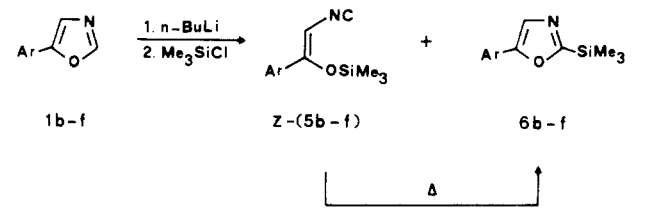
Scheme II



Scheme III



Scheme IV[a]



[a] Ar: **b**, Ph; **c**, 4-ClC_6H_4; **d**, 4-$MeOC_6H_4$; **e**, 2-thienyl; **f**, 2-pyridyl.

heterocyclic systems.[6] Recently, the dienophilic reactivity of the oxazole ring has also been reported.[7] Classical[1] and most of the recent[8a] synthetic methods to substituted oxazoles involve ring-forming reactions. Different approaches include the homologation of 2-methyloxazoles via alkyl metalated derivatives,[8b] the cross-coupling of Grignard reagents with 2-(methylthio)oxazoles,[8c] and the cycloadditions and Michael-type additions of ketenes to 2-H oxazoles and 2-dialkylamino derivatives.[8d] On the other hand, preparative methods via ring-metalated oxazoles are less common because of the substituent dependence of the site of metalation[9] and opening of the heterocycle. In fact, although most 2-H oxazoles **1** metalate at the 2-position,[10] the resulting 2-lithiooxazole **2** transforms into the open-chain tautomer lithio α-isocyano enolate **3**. Selective trappings of these species by appropriate electrophiles have been reported. For instance, sequential lithiation of various 4- and/or 5-substituted 2-H oxazoles **1** and treatment with D_2O[11,12] or benzaldehyde[10] lead to the corresponding 2-substituted oxazoles **4**, whereas quenching with chlorotrimethylsilane[10] or alkyl halides[12] affords the open-chain products **5** and **7**, respectively (Scheme I).

We extended the above observations to 4-methyloxazole (**1a**) and found that formylation[13] (DMF or *N*-formylmorpholine), stannylation[14] (trimethyltin chloride), and hydroxyalkylation (benzaldehyde)[15] occur via the heterocyclic anion **2** to give the corresponding 2-formyl-, 2-(trimethylstannyl)-, and 2-(hydroxyalkyl)oxazoles **4b–d** [E = CHO, $SnMe_3$, CH(OH)Ph], whereas silylation (Me_3SiCl)[15] and acylation (MeCOCl)[15] occur through the open-chain anion **3** to give the silyl enol ether **5a** (E = $SiMe_3$) and the acetyl enol ester **5b** (E = COMe), respectively. Particularly disturbing is the failure in acylating 2-lithiooxazoles in view of the numerous carbonyl-based elaborations of the resulting 2-acyloxazole derivatives. In the course of our research on alternative entries to 2-substituted oxazoles,[15] a report appeared[16] showing that carboxamides acylate the anion **2** to give 2-acyloxazoles **4** in moderate yields. Our approach, which stems from an extensive study on the functionalization of thiazoles and oxazoles[17a] and their use as auxiliaries in synthesis,[17b] exploits *stable* equivalents of the 2-oxazolyl anion **2** in the form of 2-trialkylsilyl or 2-trialkylstannyl derivatives. We give herein a full report of our previous observations[15] on the silyl derivatives, whereas the results on the stannyl compounds will be presented in a forthcoming paper.[14]

Results and Discussion

The lithiation of 4-methyloxazole (**1a**) in diethyl ether with a *slight excess* (1.2–1.3 equiv) of *n*-BuLi and treatment with 1 equiv of chlorotrimethylsilane gave exclusively (NMR) the α-isocyano silyl enol ether (*Z*)-**5a** (Scheme II). Careful heating of crude (*Z*)-**5a** in a Fisher distillation apparatus induced isomerization into the cyclic tautomer 4-methyl-2-(trimethylsilyl)oxazole (**6a**), which was isolated in ca. 60% yield. When the lithiation of **1a** was carried out with 1 equiv or a deficiency of BuLi, distillation of the crude reaction mixture gave the unaltered isocyano silyl enol ether (*Z*)-**5a** and eventually the isomer (*E*)-**5a**.[18] In these cases, the isomerization of **5a** to **6a** could be achieved equally well by adding one or two pellets of potassium hydroxide to the distillation flask.[19] These results confirm

(5) For reviews of Diels–Alder reactions of oxazoles, see: Reference 1. Kompeiski, M. Y.; Florentev, V. L. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 540. Boger, D. L. *Tetrahedron* **1983**, *39*, 2869. Boger, D. L. *Chem. Rev.* **1986**, *86*, 781. Recent examples: Reddy, G. S.; Blatt, M. V. *Tetrahedron Lett.* **1980**, *21*, 3627. Liotta, D.; Saindane, M.; Ott, W. *Tetrahedron Lett.* **1983**, *24*, 2473. Levin, J. I.; Weinreb, S. M. *J. Org. Chem.* **1984**, *49*, 4325. Jacobi, P. A.; Walker, D. G.; Odeh, I. M. A. *J. Org. Chem.* **1981**, *46*, 2065. Kozikowski, A. P.; Hassan, N. M. *J. Org. Chem.* **1977**, *42*, 2039.

(6) Intramolecular Diels–Alder reactions of oxazoles: Jacobi, P. A.; Craig, J. *J. Am. Chem. Soc.* **1978**, *100*, 7748; Jacobi, P. A.; Walker, G. D.; Anick, B. A.; Frechette, R. F. *J. Am. Chem. Soc.* **1984**, *106*, 5585. Jacobi, P. A.; Selnick, H. G. *J. Am. Chem. Soc.* **1984**, *106*, 3041. Shimada, S.; Tojo, T. *Chem. Pharm. Bull.* **1983**, *31*, 4247. Levin, J. I.; Weinreb, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 1397.

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(8) For recent examples of oxazole synthesis, see: (a) Overman, L. E.; Tsuboi, S.; Angle, S. *J. Org. Chem.* **1979**, *44*, 2325. Lipshutz, B. H.; Hungate, R. W.; McCarthy, K. E. *J. Am. Chem. Soc.* **1983**, *105*, 7703. Meyers, A. I.; Lawson, J. P. *Tetrahedron Lett.* **1981**, *22*, 3163. (b) Nagao, Y.; Yamada, S.; Fujita, E. *Tetrahedron Lett.* **1983**, *24*, 2287, 2291. Wood, R. D.; Csanem, B. *Ibid.* **1983**, *24*, 4391. Lipshutz, B. H.; Hungate, R. W. *J. Org. Chem.* **1981**, *46*, 1410. Wasserman, H. H.; Gambale, R. J.; Pulwer, M. J. *Tetrahedron Lett.* **1981**, *22*, 1737. Baker, W. R. *J. Org. Chem.* **1985**, *50*, 3942. (c) Pridgen, L. N. *Synthesis* **1984**, 1047. (d) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Mastellari, A.; Medici, A.; Pedrini, P. *J. Org. Chem.* **1984**, *49*, 3478.

(9) Substituents strongly affect the kinetic and/or thermodynamic acidity of methyl group and/or ring protons. See: Reference 8. Meyers, A. I.; Walker, D. S. *J. Org. Chem.* **1982**, *47*, 2999.

(10) Schroeder, R.; Schollkopf, U.; Blume, E.; Hoppe, I. *Justus Liebigs Ann. Chem.* **1975**, 533.

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

(12) Jacobi, P. A.; Ueneg, S.; Coen, D. *J. Org. Chem.* **1979**, *44*, 2042.

(13) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A.; Pedrini, P. *Synthesis*, in press.

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(16) Pridgen, L. N.; Shilcrat, S. C. *Synthesis* **1984**, 1048.

(17) (a) Reviews: Dondoni, A. *Phosphorus and Sulfur* **1985**, *24*, 381. Dondoni, A. *Lect. Heterocycl. Chem.* **1985**, *8*, 3. For selected papers on oxazole chemistry, see ref 8d and 15. (b) Dondoni, A.; Fantin, G.; Fogagnolo, M.; Medici, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 835.

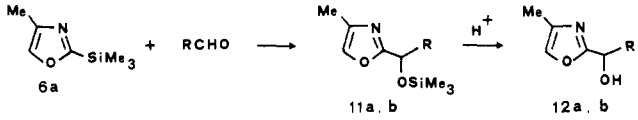
(18) The isomerization of (*Z*)-**5a** to (*E*)-**5a** (*Z*:*E* = 1.5) was carried out on treatment for former with an acid buffer (pH 4) and distillation.

Table I. Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Aldehydes

aldehyde	6a:RCHO	solvent	time, h/T, °C	yield, %	product distribn
PhCHO	1:2	neat	24/70	41	**12a**
i-C_3H_7CHO	1:2	neat	24/70	74	**12b**
D-glyceraldehyde acetonide (**13**)	1:2	neat	24/25	65	**15a** (79), **15b** (21)
(*R,S*)-2-phenylpropanal (**14**)[a]	1:2	neat	48/25	60	**16a**[a] (31), **16b**[a] (69)

[a] Onyl one enantiomer is shown in Scheme VI.

Scheme V[a]

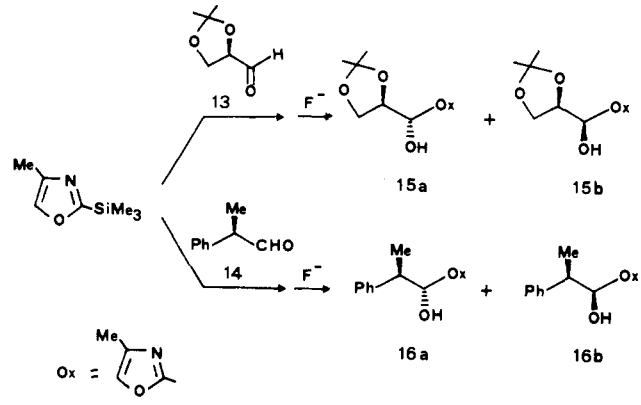


[a] R: **a**, Ph; **b**, i-C_3H_7.

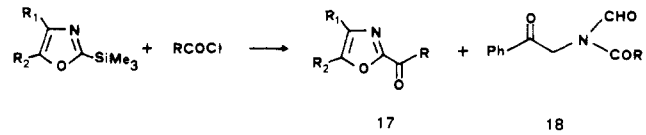
Schollkopf's observations[10] on the lithio isocyano enolate quenching by chlorotrimethylsilane and, in addition, show the heretofore unreported cyclization of the resulting silyl enol ether into a silyloxazole. This isomerization, which is a 1,5-migration of the silyl group from oxygen to carbon in an electroneutral system, was unexpected on the basis of relative bond strengths (O–Si is stronger than C–Si).[20] Thermodynamic compensation is very likely provided by the concomitant formation of the aromatic oxazole ring. Accordingly, the β-*O*-trimethylsilyl ethyl isocyanide **9** resulting from sequential lithiation and silylation of the oxazoline **8**, *did not* cyclize[14] to the 2-(trimethylsilyl)oxazoline **10** (Scheme III). It is worth mentioning that silyl migrations from oxygen to carbon have been observed[21] in neutral and anionic systems wherein the unfavorable replacement of a stronger O–Si bond by a weaker C–Si bond is outweighed by the formation of a more conjugated system. Mechanistically, the isomerization of (*Z*)-**5a** to **6a** can be viewed as an intramolecular insertion reaction of the nucleophilic isonitrile group[22] into the oxygen–silicon bond. The process appears to require the presence of a nucleophile, such as OH^-, which probably assists by interaction with silicon in the cleavage of the strong oxygen–silicon bond.

Under conditions similar to those described above, 5-aryl-2-(trimethylsilyl)oxazoles **6b–d** were prepared from the corresponding 5-aryloxazoles **1b–d** (Scheme IV). In these cases, unlike that of **1a**, chlorotrimethylsilane appeared to silylate both the cyclic and the open-chain anions **2** and **3** (See Scheme I) to give the 2-silyloxazole **6** and the silyl enol ether **5** in comparable amounts. Distillation of the reaction mixture induced isomerization of the latter into the former as observed above. Unfortunately, several attempts to apply the method to the synthesis of the 5-thienyl and 5-pyridyl derivatives **6e** and **6f** have failed because of the decomposition on distillation of the thienyl silyl enol ether (*Z*)-**5e** and the lack of formation of the pyridyl derivative (*Z*)-**5f** due to competing metalation of the pyridine rather than the oxazole ring.

Scheme VI



Scheme VII



With a ready source of 2-(trimethylsilyl)oxazoles **6a–d** at hand, their reactivity toward carbon electrophiles was explored in order to assess their synthetic utility as precursors to 2-substituted oxazoles. Treatment of **6a** with benzaldehyde and isobutyraldehyde (70 °C, 24 h) gave the corresponding *O*-(trimethylsilyl)carbinols **11a** and **11b**, viz., products from 1,2-addition of the C–Si bond of **6a** to the aldehyde carbonyl group. Adducts **11a** and **11b** were desilylated under mild acid conditions into alcohols **12a** and **12b** (Scheme V; Table I). The scope of this approach to oxazolylcarbinols from 2-silyloxazoles was not extensively investigated, since these compounds are directly accessible from 2-lithiooxazoles,[10] although in lower yields.

It is, however, worth noting that the addition of 4-methyl-2-(trimethylsilyl)oxazole (**6a**) to two α-chiral aldehydes (Scheme VI), namely (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**13**) and (*R,S*)-2-phenylpropanal (**14**), showed some diastereoselectivity (ca. 4:1), which favored the anti isomer **15a** with the former and the syn isomer **16b** with the latter (Table I). Our previous identification of isomers **15a** and **15b** from their ^1H NMR spectra was uncertain.[23] Transformation of oxazolylglycerols **15a** and **15b** into their 3-*O*-acetyl derivatives and comparison of their NMR spectra with those of the corresponding furylglycerols[24] allowed us to make a more confident assignment, and in contrast to our previous report,[23] we conclude that the major isomer is the anti diastereomer **15a**. The stereochemistry of the major syn diastereomer

(19) The isolation of the silyl enol ether (*Z*)-**5a** or its conversion to the silyloxazole **6a** appeared to be strongly dependent on the "basicity" of the resulting reaction mixture *before* distillation. A deficiency of BuLi produced an acidic reaction mixture, which ensured the isolation of (*Z*)-**5a**, whereas an excess of BuLi produced a basic reaction mixture and caused the conversion of (*Z*)-**5a** into **6a**.

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(25) (a) D-Glyceraldehyde acetonide (**13**): References 17b and 24. McGarvey, G. J.; Kimura, M.; Oh, T.; Williams, J. M. *J. Carbohydr. Chem.* **1984**, *3*, 125. Jurczak, J.; Pikul, S.; Bauer, T. *Tetrahedron* **1986**, *42*, 447. (b) (*R,S*)-2-Phenylpropanal (**14**): Heathcock, C. H.; Kiyooka, S.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214. Fujita, M.; Hiyama, T. *J. Am. Chem. Soc.* **1985**, *107*, 4085.

Table II. Reactions of 2-(Trimethylsilyl)oxazoles 6a,b with Acyl Chlorides (RCOCl)

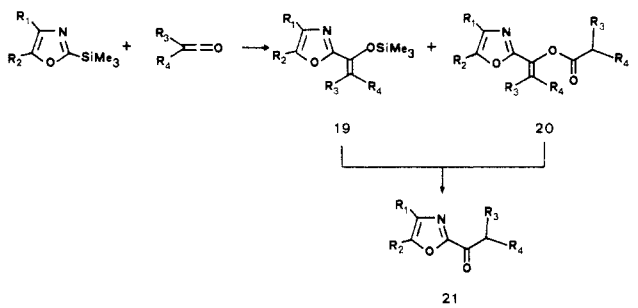
entry	oxazole R_1	oxazole R_2	RCOCl, R	6:RCOCl	solvent	time, h/T, °C	product (yield, %)
1	Me	H	Me	1:2	CH_2Cl_2	19/25	**17a** (80)
2	Me	H	Ph	1:2	C_6H_6	12/80	**17b** (40)
3	Me	H	EtO	1:2	C_6H_6	4/80	**17c** (84)
4	Me	H	MeO_2C	1:2	C_6H_6	2/80	**17d** (30)
5	H	Ph	Me	1:10	neat	4/25	**17e** (32)
6	H	Ph	Ph	1:10	neat	18/80	**17f** (29)
7	H	Ph	EtOH	1:4	C_6H_6	5/80	**17g** (13), **18g** (17)
8	H	Ph	MeO_2C	1:4	C_6H_6	3/80	**17h** (23)
9	H	Ph	$MeO_2C(CH_2)_2$	1:10	neat	4/25	**17i** (30)
10	H	Ph	$Me(CH_2)_4$	1:10	neat	24/25	**17l** (25), **18l** (37)
11	H	Ph	9-octadecene	1:10	neat	24/25	**17m** (60)

Table III. Reactions of 2-(Trimethylsilyl)oxazoles 6a,b with Ketenes

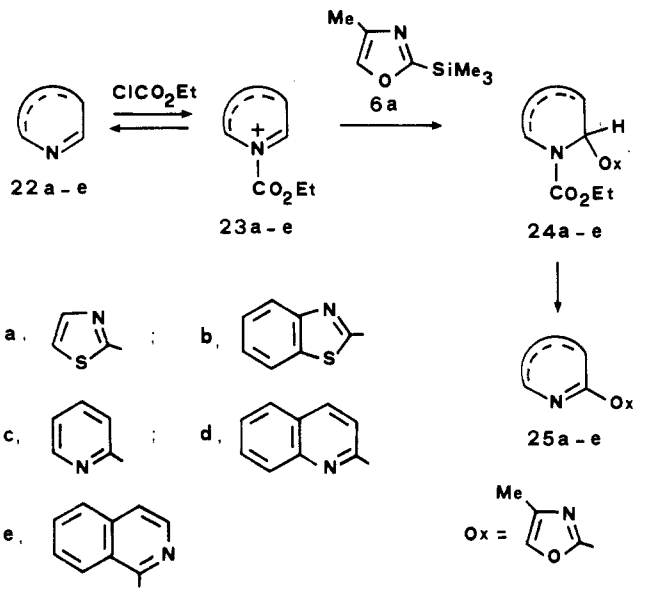
oxazole R_1	oxazole R_2	ketene R_3	ketene R_4	oxazole:ketene	time, h/T, °C	solvent	product (yield, %)
Me	H	Cl	Cl	1:1	1/25	*n*-hexane	**21a** (32)
Me	H	CN	CMe_3	1:2	0.25/25	benzene	**21b** (64), **20b** (25)[a]
H	Ph	Cl	Cl	1:2	2/25	*n*-hexane	**21c** (80)
H	Ph	CN	CMe_3	1:2	2/25	benzene	**21d** (80)

[a] Obtained only by crystallization of the reaction mixture (see the Experimental Section).

Scheme VIII



Scheme IX



16b was established by X-ray crystallography.[26] Thus, the observed diastereofacial selectivities of the carbonyl addition of D-glyceraldehyde acetonide (**13**) and 2-phenylpropanal (**14**) by the silyloxazole **6a** are in agreement with those reported for reactions of other organometallic compounds to these aldehydes.[25] It is worth commenting, however, that the stereochemical control of the addition of **6a** to **13** is much less efficient than that observed with 2-(trimethylsilyl)thiazole (≥95%).[17b]

Treatment of silyloxazoles **6a** and **6b** with acyl chlorides gave the corresponding 2-acyloxazoles **17** in moderate to good yields (Scheme VII, Table II). This overcomes the aforementioned failure in acylating 2-H oxazoles via lithiation and quenching with acyl chlorides. A byproduct observed in some cases (Table II, entries 7 and 10) was the *N*-formylamide **18**, which is formulated to arise the hydrolytic cleavage of the *N*-acyloxazolium salt. Successful reactions were observed with various aliphatic acyl chlorides, whereas among aromatic derivatives only benzoyl chloride showed a satisfactory reactivity.[27] Interestingly enough, the reaction can be applied to acyl chloride esters of dicarboxylic acids (Table II, entries 4, 8, and 9), thus allowing the direct introduction of a difunctional moiety.

Attempts were made to extend the scope of the carbodemetalation of silyloxazoles **6** to other activated carboxylic acid derivatives. While anhydrides failed to react under forcing conditions and/or in the presence of fluoride ion as a catalyst, activated ketenes such as dichloro- and *tert*-butylcyanoketene reacted with either **6a** and **6b** to give the corresponding silyl enol ether **19** and the silyl enol ester **20**. Both products were transformed under very mild acid conditions into the corresponding 2-acyloxazoles **21** (Scheme VIII Table II). While the formation of the silyl

Table IV. Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Azaryls 22a–e via Their Ethoxycarbonyl Salts 23a–e

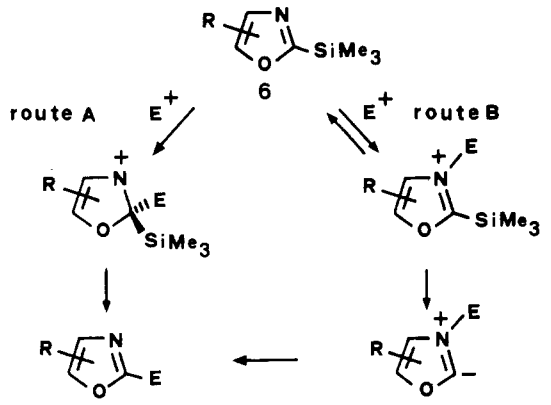
reagent[a]	time,[b] h	adducts **24**[c] (yield, %)	time,[d] h	azadiaryls **25** (yield, %)
23a	3	**24a** (35)	5	**25a** (77)
23b	24	**24b** (35)	3	**25b** (66)[e]
23c	5	**24c** (18)	1	**25c** (72)
23d	5	**24d** (43)	0.5	**25d** (44)
23e	1	**24e** (57)	1	**25e** (98)

[a] Solvent, CH_2Cl_2. [b] Reaction time to adduct **24**. [c] Solvent, benzene. [d] Reaction time to azadiaryl **25**. [e] Reaction carried out at room temperature.

(26) We thank Prof. G. Valle (Centro Studi Biopolimeri, CNR, Padova) for the X-ray structure determination of **16b**. Full details of the crystallographic analysis will be published in a forthcoming report.

(27) This problem can be overcome by the use of a 2-(trialkylstannyl)oxazole. The reaction of 4-methyl-2-(trimethylstannyl)oxazole with benzoyl chloride (benzene, room temperature, 1 h) gives the corresponding 2-benzoyloxazole in 90–95% yield.

Scheme X



enol ether **19** can be simply viewed as a 1,2-addition of the silyloxazole **6** to the ketene carbonyl, the formation of the enol ester **20** is probably due to the reaction of **6** with the dimer of the ketene.

Successful carbodesilylation reactions of silyloxazoles **6a** were achieved by heteroaryl cations **23a–e** generated in situ from heterocycles **22** (thiazole, pyridine, and their benzo derivatives) and ethyl chloroformate (Scheme IX).[28] In each case, the reaction gave exclusively the corresponding 2-substituted oxazole **24** in modest to good yields (Table IV), thus proving to be a highly regioselective carbon–carbon bond forming process at C_2 of the selected heteroaryl cation **23**. Products **24a–e** were readily transformed by oxidative deacylation with *o*-chloroanil into 2-azaryl-substituted oxazoles **25**. Hence, the overall sequence provides an entry to various unsymmetrical azadiaryls, which should be useful as building blocks toward biologically active compounds.[29]

Information on the mechanism of the above carbodesilylation reactions is minimal. In addition to a direct ipso substitution process on the silyloxazole **6** (route A), a more complex scheme (route B) involving a C_2 oxazolium ylide as a key intermediate[30] appears conceivable (Scheme X). In the latter case, as discussed for the reactions of 2-(trimethylsilyl)thiazole with the same electrophiles,[17,31] the driving force for the very facile C–Si bond cleavage should be provided by the thermodynamic stability of the azolium ylide. Indirect evidence for nitrogen quaternization[32] of **6**, an essential step in formation of the ylide, is provided by the formation of the open-chain byproduct **18**.

In conclusion, 2-(trimethylsilyl)oxazoles **6** are storable compounds that behave as stable 2-oxazolyl anion equivalents toward carbon electrophiles to give the corresponding C_2-substituted oxazoles in modest to good yields. Of special relevance is the reaction of **6** with acyl chlorides, since this is a straightforward method for the introduction of a carbonyl group at C_2 of the oxazole ring. This reaction is amenable to large-scale preparations of 2-acyloxazoles and oxazolyl keto esters.

Experimental Section

General Procedures. All melting points are uncorrected. ^1H and ^{13}C NMR spectra (in $CDCl_3$) were obtained on a 80-MHz Bruker WP 80 spectrometer. Chemical shifts are given in δ downfield from Me_4Si. Mass spectra were recorded at 70 eV on a Varian MAT CH7 high-resolution mass spectrometer. IR spectra were obtained on a Perkin-Elmer Model 297 grating spectrometer. Elemental analyses were performed on a Carlo Erba elemental analyzer Model 1106. All experiments were carried out under N_2 and with freshly distilled and dried solvents.

4-Methyloxazole (**1a**) was commercially available (Janssen Chimica). 5-Phenyloxazole (**1b**; mp 36–38 °C), 5-(4-chlorophenyl)oxazole (**1c**; mp 66–67 °C), 5-(4-methoxyphenyl)oxazole [**1d**; mp 66–68 °C (lit.[33] mp 65 °C)], 5-(2-thienyl)oxazole [**1e**; bp 108–110 °C (16 mmHg)], and 5-(2-pyridyl)oxazole [**1f**; 120–121 °C (16 mmHg)] were prepared as described.[34] Trimethylchlorosilane (Me_3SiCl), acetyl chloride, ethyl chloroformate, benzoyl chloride, methyl oxalyl chloride, benzaldehyde and isobutyraldehyde were commercially available. (*R*)-2,3-*O*-isopropylideneglyceraldehyde (**13**) was prepared according to the literature procedure.[25a] The commercially available (*R,S*)-2-phenylpropanal (**14**) (Aldrich Chemical Co.) was purified before use.[25b] *tert*-Butylcyanoketene (TBCK) was generated in situ before each experiment by thermal decomposition of the proper azidoquinone.[35] Dichloroketene (DCK) was generated in situ by dehydrochlorination of dichloroacetyl chloride with triethylamine.[36]

Lithiation of 4-Methyloxazole (1a) and Quenching with Acetyl Chloride and Benzaldehyde. A solution of *n*-BuLi (36 mmol) in *n*-hexane was added dropwise to a cooled (−78 °C) and stirred solution of 4-methyloxazole (**1a**, 3 g, 36 mmol) in diethyl ether (40 mL). After being stirred for 1 h, half of the solution was quenched with acetyl chloride (1.47 g, 18 mmol) in diethyl ether (25 mL). Workup of the reaction mixture (aqueous solution of $NaHCO_3$, anhydrous Na_2SO_4) gave after distillation at reduced pressure 1.4 g (62%) of (*Z*)-2-isocyano-*O*-acetyl-1-propen-1-ol [(*Z*)-**5g**]: bp 93–94 °C (15 mmHg); IR (film) 3100 (CH), 2100 (N≡C), 1765 (C=O), 1685 (C=C) cm^{-1}; ^1H NMR δ 1.95 (d, 3 H, =CMe, J = 1.6 Hz), 2.26 (s, 3 H, COMe), 7.27 (q, 1 H, =CH, J = 1.6 Hz); ^{13}C NMR δ 15.59 (q), 19.32 (q), 108.18 (s), 133.96 (d), 166.9 (s), 170.01 (s); mass spectrum, m/e (relative intensity) 125 (M^+, 9), 110 (6), 73 (21), 43 (100). Anal. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.55; H, 5.66; N, 11.21.

The other half of the mixture from the metalation of **1a** was quenched with benzaldehyde (2.91 g, 18 mmol) in the same solvent (20 mL). Workup of the reaction mixture (after, anhydrous Na_2SO_4) and chromatography of the residue on silica gel (1:1 *n*-hexane–diethyl ether) gave 1.35 g of unreacted benzaldehyde and 1.08 g (34%) of carbinol **4b**: mp 79–81 °C (from diethyl ether–*n*-hexane); IR (KBr) 1615, 1575 cm^{-1}; ^1H NMR δ 2.12 (d, 3 H, =CMe, J = 1.4 Hz), 4.65 (br, 1 H, OH), 5.9 (br, 1 H, aliphatic CH), 7.42 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 189 (M^+, 82) 161 (20), 107 (96), 79 (100), 77 (74). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.85; H, 5.88; N, 7.37.

4-Methyl-2-(trimethylsilyl)oxazole (6a). A solution of *n*-BuLi in *n*-hexane (132 mmol) was added dropwise to a cooled (−78 °C) and stirred solution of 4-methyloxazole (**1a**; 10 g, 120 mmol) in dry ethyl ether (150 mL). After 1 h, the reaction mixture was quenched with a solution of Me_3SiCl (8.37 mL, 120 mmol) in diethyl ether (100 mL) and allowed to stand at −78 °C for 1 h. After the temperature was raised to 25 °C, the reaction mixture was filtered through Celite, and the solvent was removed under vacuum to give 16.7 g (90%) of essentially pure (NMR) (*Z*)-2-

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isocyano-*O*-(trimethylsilyl)-1-propen-1-ol [(*Z*)-**5a**]. Distillation of the crude material in a Fischer apparatus (Mikro-SPALTROHR-Kolonne MMS 202) [oil bath, 100 °C (15 mmHg)] gave 11.16 g (60%) of 4-methyl-2-(trimethylsilyl)oxazole (**6a**) and 2.79 g (15%) of (*Z*)-**5a**.

(*Z*)-**5a**: bp 70–72 °C (15 mmHg); IR (film) 2100 (N=C), 1665 (C=C) cm^{-1}; ^1H NMR δ 0.27 (s, 9 H, $OSiMe_3$), 1.82 (br, 3 H, =CMe), 6.27 (br, 1 H, =CH); ^{13}C NMR δ −1.81 (q, $OSiMe_3$), 15.28 (q, =CMe), 106 (s, =CMe), 139.56 (d, =CH), 166.59 (s, N=C); mass spectrum, *m/e* (relative intensity) 155 (M^+, 24) 140 (35), 73 (100). Anal. Calcd for $C_7H_{13}NOSi$: C, 54.14; H, 8.44; N, 9.02. Found: C, 54.20; H, 8.47; N, 9.00.

4-Methyl-2-(trimethylsilyl)oxazole (**6a**): bp 50–52 °C (15 mmHg); IR (film) 1660 (C=C), 1590 (C=N) cm^{-1}; ^1H NMR δ 0.36 (s, 9 H, $SiMe_3$) 2.21 (d, 3 H, =CMe, J = 1.2 Hz), 7.47 (q, 1 H, =CH, J = 1.2 Hz); ^{13}C NMR δ −2.0 (q, $SiMe_3$), 11.12 (q, =CMe), 136.2 (s, C_4), 136.6 (d, =CH), 170.4 (s, C_2); mass spectrum, *m/e* (relative intensity) 155 (M^+, 20), 140 (24), 73 (100). Anal. Calcd for $C_7H_{13}NOSi$: C, 54.14; H, 8.44; N, 9.02. Found: C, 54.18; H, 8.46; N, 9.01.

The same reaction was carried out with 120 mmol of **1a** and 120 mmol of *n*-BuLi. After being quenched with Me_3SiCl (120 mmol) and workup as above, the reaction mixture was distilled giving 13 g (70%) of (*Z*)-**5a**. Distillation of (*Z*)-**5a** over one to two pellets of KOH gave 5.5 g (42%) of the silyloxazole **6a** and 2.3 g (18%) of unaltered material.

The reaction was also carried out with 120 mmol of **1a** and 114 mmol of *n*-BuLi. After being quenched with Me_3SiCl (120 mmol) and workup as above, the reaction mixture was distilled to give 5.2 g (28%) of (*Z*)-**5a** and 3.5 g (19%) of (*E*)-2-isocyano-*O*-(trimethylsilyl)-1-propen-1-ol [(*E*)-**5a**]: bp 83–86 °C (15 mmHg); ^1H NMR δ 0.22 (s, 9 H, $SiMe_3$), 1.85 (br, 3 H, =CMe), 6.8 (br, 1 H, =CH).

5-Aryl-2-(trimethylsilyl)oxazoles 6b–d. General Procedure. A solution of *n*-BuLi in *n*-hexane (33 mmol) was added dropwise to a cooled (−78 °C) and stirred solution of an oxazole **1b–d** (30 mmol) in dry THF (100 mL). After 1 h, the reaction mixture was quenched with a solution of Me_3SiCl (30 mmol) in dry diethyl ether (50 mL) and allowed to stand at −78 °C for 1 h. After the temperature was raised to 25 °C, the reaction mixture was filtered through Celite and the solvent was removed under vacuum. The products were isolated by distillation in a Fischer apparatus (Mikro-SPALTROHR-Kolonne MMS 202) (oil bath 150–160 °C).

The crude product from the reaction of oxazole **1b** was found (NMR) to be a 1:1 mixture of the isocyano silyl enol ether (*Z*)-**5b** and 2-(trimethylsilyl)oxazole **6b**. Compound (*Z*)-**5b** showed the following spectroscopic data: IR (film) 2110 (N=C), 1630 (C=C) cm^{-1}; ^1H NMR δ 0.27 (s, 9 H, $OSiMe_3$), 5.77 (s, 1 H, =CH), 7.2–7.7 (m, 5 H, ArH). Distillation of the mixture gave 3.2 g (50%) of 5-phenyl-2-(trimethylsilyl)oxazole (**6b**): bp 110–112 °C (1.5 mmHg); IR (film) 1460, 1250 cm^{-1}; ^1H NMR δ 0.42 (s, 9 H, $SiMe_3$), 7.2–7.7 (m, 6 H, ArH, =CH); mass spectrum, *m/e* (relative intensity) 217 (M^+, 74), 202 (57), 73 (100). Anal. Calcd for $C_{12}H_{15}NOSi$: C, 66.31; H, 6.95; N, 6.44. Found: C, 66.35; H, 6.92; N, 6.47.

The crude product from the reaction of oxazole **1c** was a 2:1 mixture of isocyano silyl enol ether (*Z*)-**5c** and the 2-(trimethylsilyl)oxazole **6c**. Compound (*Z*)-**5c** showed the following: IR (film) 2105 (N=C), 1625, 1600 cm^{-1}; ^1H NMR δ 0.28 (s, 9 H, $OSiMe_3$), 5.72 (s, 1 H, =CH), 7.3 (s, 4 H, ArH). Distillation of the crude mixture gave 3.76 g (50%) of 5-(*p*-chlorophenyl)-2-(trimethylsilyl)oxazole (**6c**): bp 94–96 °C (0.1 mmHg); IR (film) 1580, 1565 cm^{-1}; ^1H NMR δ 0.42 (s, 9 H, $SiMe_3$), 7.2–7.62 (m, 5 H, ArH, =CH); mass spectrum, *m/e* (relative intensity) 251 (M^+, 44), 236 (29), 179 (25), 73 (100). Anal. Calcd for $C_{12}H_{14}ClNOSi$: C, 57.24; H, 5.60; N, 5.56. Found: C, 57.22; H, 5.58; N, 5.59.

The crude product from the reaction of oxazole **1d** was a 4:1 mixture of the isocyano silyl enol ether (*Z*)-**5d** and 2-(trimethylsilyl)oxazole **6d**. Compound (*Z*)-**5d** showed the following spectroscopic data: IR (film) 2105 (N=C) cm^{-1}; ^1H NMR δ 0.28 (s, 9 H, $OSiMe_3$), 3.54 (s, 3 H, OMe), 5.68 (s, 1 H, =CH), 6.95 (d, 2 H, ArH), 7.37 (d, 2 H, ArH). Distillation of the crude mixture gave 2.59 g (35%) of 5-(*p*-methoxyphenyl)-2-(trimethylsilyl)oxazole (**6d**): bp 128–130 °C (0.7 mmHg); IR (film) 1625 cm^{-1}; ^1H NMR δ 0.41 (s, 9 H, $SiMe_3$), 3.81 (s, 3 H, OMe), 6.9 (d, 2 H, ArH), 7.2 (s, 1 H, =CH), 7.55 (d, 2 H, ArH); mass spectrum, *m/e* (relative intensity) 247 (M^+, 63), 232 (23), 217 (20), 202 (15), 175 (42), 132 (30), 73 (100). Anal. Calcd for $C_{13}H_{17}NO_2Si$: C, 63.12; H, 6.93; N, 5.66. Found: C, 63.17; H, 6.90; N, 5.64.

The ^1H NMR spectrum of the crude mixture obtained from the oxazole **1e** showed the presence of the isocyano silyl enol ether (*Z*)-**5e**: IR (film) 2100, 1615 cm^{-1}; ^1H NMR δ 0.35 (s, 9 H), 5.75 (s, 1 H), 7.1–7.3 (m, 3 H). Distillation of the crude reaction mixture caused decomposition of the product.

The reaction carried out with the oxazole **1f** did not give the silyl enol ether (*Z*)-**5f** and/or the silyloxazole **6f** but only an unidentified solid material.

Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Benzaldehyde and Isobutyraldehyde. General Procedure. The oxazole **6a** (0.5 g, 3.2 mmol) and the aldehyde (6.4 mmol) were heated at 70 °C for 24 h (Table I). The ^1H NMR spectrum of the crude reaction mixture showed the presence of the (trimethylsilyl)carbinols **11**. The crude product was dissolved in THF (10 mL), and 1 mL of HCl (5%) was added with stirring. After 30 min, the reaction mixture was washed with aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. Chromatography (silica gel, 1:1 benzene–diethyl ether) of the residue gave the corresponding carbinols **12a** and **12b**.

The ^1H NMR spectrum of **11a** showed the following peaks: δ 0.12 (s, 9 H, $OSiMe_3$), 2.17 (d, 3 H, =CMe, J = 1.0 Hz), 5.97 (s, 1 H, aliphatic CH), 7.62 (m, 6 H, ArH, =CH).

The ^1H NMR spectrum of **11b** showed the following peaks: δ 0.07 (s, 9 H, $OSiMe_3$), 1.00 (dd, 6 H, $CHMe_2$), 2.16 (m, 1 H, aliphatic CH), 2.18 (d, 3 H, =CMe, J = 1.1 Hz), 4.47 (d, 1 H, aliphatic CH), 7.4 (q, 1 H, =CH, J = 1.1 Hz).

The carbinol **12a** (0.25 g, 41%) showed spectroscopic characteristics (IR, NMR, MS) identical with those of compound **4b** obtained from lithiooxazole (see above).

The carbinol **12b** (0.37 g, 74%) showed the following data: bp 65–66 °C (0.8 mmHg); IR (film) 3450, 1605, 1560 cm^{-1}; ^1H NMR δ 0.95 (dd, 6 H, $CHMe_2$), 2.16 (m, 1 H, $CHMe_2$), 2.17 (d, 3 H, =CMe, J = 1.2 Hz), 4.47 (d, 1 H, CHOH), 7.37 (q, 1 H, =CH, J = 1.1 Hz). Anal. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.02. Found: C, 61.93; H, 8.41; N, 9.04.

Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Chiral Aldehydes 13 and 14. General Procedure. A mixture of oxazole **6a** (0.5 g, 3.2 mmol) and the aldehyde (6.4 mmol) was stirred at room temperature for the time listed in Table I. The crude reaction mixture was diluted with 40 mL of THF and treated with 1.3 equiv of Bu_4NF. After the mixture was stirred for 1 h, the solvent was removed under vacuum. The residue was diluted with 30 mL of ethyl acetate and washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried over anydrous Na_2SO_4, and the solvent was removed under vacuum. The residue was chromatographed (silica gel, 7:3 petroleum ether–ethyl acetate).

The reaction with D-glyceraldehyde **13** gave 0.44 g (65%) of a mixture of diastereomers **15a** and **15b** in 3.7:1 molar ratio: oil; ^1H NMR ($CDCl_3$, D_2O) δ 1.35 (s, 3 H), 1.42 (s, 3 H), 2.15 (d, 3 H, J = 1.0 Hz), 3.9–4.65 (m, 3 H), 4.75 (d, 1 H, CHOD), 7.3 (q, 1 H, J = 1.0 Hz).

The mixture of **15a** and **15b** was dissolved in 20 mL of dry dichloromethane, treated with 1.1 equiv of Et_3N and 1.1 equiv of acetyl chloride, and then stirred for 8 h. The usual workup gave a mixture of the *O*-acetate of the anti adduct **15a** and syn adduct **15b**.

15a (*O*-acetyl derivative): IR (film) 2980, 2920, 1750, 1600, 1560, 1370 cm^{-1}; ^1H NMR δ 1.36 (s, 3 H), 1.38 (s, 3 H), 2.15 (m, 6 H), 4.08 (m, 2 H), 4.56 (m, 1 H), 5.85 (d, 1 H, J = 5.55 Hz, methyne proton), 7.3 (q, 1 H, J = 1.0 Hz). The methyne proton of **15b** (*O*-acetyl derivative) showed a doublet centered at δ 5.83 (J = 7.65 Hz).

The reaction of **6a** with 2-phenylpropanal (**14**) gave 0.42 g (60%) of a mixture of diastereomers **16a** and **16b** (ratio from ^1H NMR spectrum 1:2.2). Crystallization of the crude reaction mixture from dichloromethane–petroleum ether gave the syn diastereomer **16b**: mp 103–105 °C; IR (KBr) 3200, 1605, 1555 cm^{-1}; ^1H NMR ($CDCl_3$, D_2O) δ 1.36 (d, 3 H, J = 7.1 Hz), 2.08 (d, 3 H, J = 1.0 Hz), 3.3 (m, 1 H, J = 7.1, 5.9 Hz), 4.8 (d, 1 H, J = 5.9 Hz), 7.17 (s, 5 H, ArH), 7.2 (q, 1 H, J = 1.0 Hz). Anal. Calcd for $C_{13}H_{15}NO_2$:

C, 71.86; H, 6.96; N, 6.45. Found: C, 71.89; H, 6.94; N, 6.46.

The mother liquor was concentrated to give the anti diastereomer **16a**: ^{1}H NMR ($CDCl_3$, D_2O) δ 1.2 (d, 3 H, J = 7.1 Hz), 2.07 (d, 3 H, J = 1.0 Hz), 3.28 (m, 1 H, J = 7.1, 7.95 Hz), 4.75 (d, 1 H, J = 7.95 Hz), 7.15 (s, 5 H), 7.23 (q, 1 H, J = 1.0 Hz). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.83; H, 6.97; N, 6.43.

Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Acyl Chlorides. General Procedure. A solution of the oxazole **6a** (0.5 g, 3.2 mmol) and the acyl chloride (6.4 mmol) in benzene (dichloromethane was used for acetyl chloride) (20 mL) was refluxed (room temperature for acetyl chloride) for the time listed in Table II. The reaction mixture, unless otherwise stated, was washed with aqueous $NaHCO_3$ and dried over Na_2SO_4, and the solvent was distilled. The product was isolated by distillation or chromatography.

For R = Me, distillation gave 0.32 g (80%) of 2-acetyl-4-methyloxazole (**17a**): bp 43–44 °C (1 mmHg); IR (film) 1700 (C=O) cm^{-1}; ^{1}H NMR δ 2.3 (d, 3 H, =CMe, J = 0.8 Hz), 2.67 (s, 3 H, COMe), 7.65 (q, 1 H, =CH, J = 0.8 Hz). Anal. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.62; H, 5.63; N, 11.15.

For R = Ph, the reaction mixture was treated with 40% potassium hydroxide and benzyltriethylammonium chloride. After 20 min the organic layer was separated, dried over anhydrous Na_2SO_4, and chromatographed (silica gel, 1:1 *n*-hexane–diethyl ether) to give 0.24 g (40%) of 2-benzoyl-4-methyloxazole (**17b**): mp 65–67 °C (from benzene–*n*-hexane); IR (KBr) 1650 (C=O), 1570 cm^{-1}; ^{1}H NMR δ 2.38 (d, 3 H, =CMe, J = 1.0 Hz), 7.7 (m, 4 H, ArH, =CH), 8.6 (m, 2 H, ArH); mass spectrum, m/e (relative intensity) 187 (M^+, 36), 159 (15), 105 (100), 77 (94). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.55; H, 4.89; N, 7.44.

For R = OEt, distillation gave 0.42 g (84%) of 2-carbethoxy-4-methyloxazole (**17c**): bp 102–104 °C (from diethyl ether–*n*-hexane); IR (film) 1740 (COOEt) cm^{-1}; ^{1}H NMR δ 1.45 (t, 3 H, COOEt, J = 7 Hz), 2.3 (d, 3 H, =CMe, J = 1.4 Hz), 4.5 (q, 2 H, COOEt, J = 7 Hz), 7.65 (q, 1 H, =CH, J = 1.4 Hz). Anal. Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.23; H, 5.83; N, 9.06.

For R = CO_2Me, chromatography (silica gel, 1:1 cyclohexane–diethyl ether) gave 0.12 g (30%) of methyl 2-(4-methyloxazol-2-yl)-2-oxoethanoate (**17d**): mp 64–66 °C (from diethyl ether–*n*-hexane); IR (CCl_4) 1755, 1705 cm^{-1}; ^{1}H NMR δ 2.35 (d, 3 H, =CMe, J = 1.4 Hz), 4.1 (s, 3 H, OMe), 7.87 (q, 1 H, =CH, J = 1.4 Hz); mass spectrum, m/e (relative intensity) 169 (M^+, 55), 141 (9), 128 (55), 110 (100). Anal. Calcd for $C_7H_7NO_4$: C, 49.71; H, 4.17; N, 8.28. Found: C, 49.73; H, 4.15; N, 8.30.

Reactions of 5-Phenyl-2-(trimethylsilyl)oxazole (6b) with Acyl Chlorides. General Procedure. The oxazole **6b** (0.5 g, 2.3 mmol) was treated with a large excess of acyl chloride under the conditions indicated in Table II. Workup of the reaction mixture (aqueous $NaHCO_3$, anhydrous Na_2SO_4) gave after chromatography (silica gel, 9:1 dichloromethane–ethyl acetate) the corresponding products **17** and in some cases the open-chain derivatives **18**.

2-Acetyl-5-phenyloxazole (**17e**): 0.137 g, 32%; mp 83–84 °C (from benzene–*n*-hexane); IR (KBr) 1680 (C=O) cm^{-1}; ^{1}H NMR δ 2.67 (s, 3 H, COMe), 7.37–7.46 (m, 3 H, ArH), 7.5 (s, 1 H, =CH), 7.68–7.82 (m, 2 H, ArH); mass spectrum, m/e (relative intensity) 187 (M^+, 100), 145 (84), 117 (44), 105 (35), 91 (40). Anal. Calcd for $C_{11}H_9NO_2$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.55; H, 4.87; N, 7.51.

2-Benzoyl-5-phenyloxazole (**17f**): 0.166 g, 29%; mp 132–133 °C (from benzene–*n*-hexane); IR (CCl_4) 1670 (C=O) cm^{-1}; ^{1}H NMR δ 7.37–7.9 (m, 8 H, ArH), 7.6 (s, 1 H, =CH), 8.37–8.52 (m, 2 H, ArH); mass spectrum, m/e (relative intensity) 249 (M^+, 82), 221 (12), 105 (100), 91 (66), 77 (84). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.09; H, 4.45; N, 5.64. Found: C, 77.11; H, 4.47; N, 5.61.

2-Carbethoxy-5-phenyloxazole (**17g**): 0.065 g, 13%, oil; IR (CCl_4) 1745 (C=O) cm^{-1}; ^{1}H NMR δ 1.46 (t, 3 H, OEt), 4.5 (q, 2 H, OEt), 7.32–7.8 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 217 (M^+, 100), 189 (7), 173 (11), 116 (38), 15 (85), 91 (40), 77 (46). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.39; H, 5.12; N, 6.47.

N-Formylamide **18g**: 0.092 g, 17%; oil; IR (CCl_4) 1755 (C=O), 1705 (C=O) cm^{-1}; ^{1}H NMR δ 1.32 (t, 3 H, OEt), 4.37 (d, 2 H, OEt), 5.05 (s, 2 H, $COCH_2N$), 7.25–8.02 (m, 5 H, ArH), 9.32 (s, 1 H, CHO); mass spectrum, m/e (relative intensity) 235 (M^+, 16), 217 (16), 189 (11), 161 (9), 145 (10), 118 (78), 105 (100), 91 (47), 77 (80). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.37; N, 5.95. Found: C, 61.23; H, 5.34; N, 5.98.

Methyl 2-(5-phenyloxazol-2-yl)-2-oxoethanoate (**17h**): 0.122 g, 23%; oil; IR (CCl_4) 1755 (C=O), 1700 (C=O) cm^{-1}; ^{1}H NMR δ 4.00 (s, 3 H, OMe), 7.35–7.85 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 231 (M^+, 100), 205 (32), 172 (90), 105 (44), 77 (90). Anal. Calcd for $C_{12}H_9NO_4$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.32; H, 3.95; N, 6.04.

Methyl 4-(5-phenyloxazol-2-yl)-2-oxoethanoate (**17i**): 0.178 g, 30%; mp 130–131 °C (from diethyl ether–cyclohexane); IR (film) 1745, 1715 cm^{-1}; ^{1}H NMR δ 2.77 (t, 2 H, J = 7 Hz, CH_2), 3.41 (t, 2 H, J = 7 Hz, CH_2), 3.67 (s, 3 H, OMe), 7.3–7.75 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 259 (M^+, 100), 228 (40), 200 (11), 172 (25), 115 (83). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.86; H, 5.05; N, 5.40. Found: C, 64.82; H, 5.03; N, 5.43.

2-Hexanoyl-5-phenyloxazole (**17l**): 0.14 g, 25%; mp 74–76 °C (from diethyl ether–cyclohexane); IR (CCl_4) 2925, 1695 cm^{-1}; ^{1}H NMR δ 0.9 (t, 3 H, Me), 1.37 (m, 4 H, 2 CH_2), 1.78 (m, 2 H, CH_2), 3.06 (t, 2 H, $COCH_2$), 7.25–7.8 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 243 (M^+, 100), 215 (21), 200 (9), 186 (70), 172 (40), 159 (45). Anal. Calcd for $C_{15}H_{17}NO_2$: C, 74.04; H, 7.04; N, 5.76. Found: C, 74.01; H, 7.02; N, 5.79.

N-Formylamide **18l**: 0.22 g 37%; oil; IR (film) 2915, 1705, 1670 cm^{-1}; ^{1}H NMR δ 1.5–3.0 (m, 7 H, aliphatic CH), 2.32 (m, 2 H, aliphatic CH), 2.57 (t, 2 H, aliphatic CH), 5.08 (s, 2 H, $PhCOCH_2$), 7.3–7.95 (m, 5 H, ArH). 9.45 (s, 1 H, NCHO); mass spectrum, m/e (relative intensity) 261 (M^+, 7), 243 (6), 187 (9), 120 (13), 105 (100), 99 (20), 77 (40). Anal. Calcd for $C_{15}H_{19}NO_3$: C, 68.94; H, 7.33; N, 5.36. Found: C, 68.91; H, 7.34; N, 5.38.

2-(9-Octadecenoyl)-5-phenyloxazole (**17m**): 0.56 g, 60%; oil; IR (CCl_4) 2910, 2850, 1695 cm^{-1}; ^{1}H NMR δ 0.8–2.22 (m, 29 H, aliphatic CH), 3.03 (t, 2 H, $COCH_2$), 5.3 (m, 2 H, =CH), 7.3–7.77 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 409 (M^+, 52), 381 (72), 186 (92), 172 (45), 159 (58), 146 (100). Anal. Calcd for $C_{27}H_{39}NO_2$: C, 79.17; H, 9.60; N, 3.42. Found: C, 79.21; H, 9.58; N, 3.41.

Reaction of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Dichloroketene (DCK). A solution of dichloroacetyl chloride (0.28 g, 1.61 mmol) in *n*-hexane (30 mL) was added to a solution of the oxazole **6a** (0.25 g, 1.61 mmol) and triethylamine (0.162 g, 1.61 mmol) in the same solvent (50 mL). After the mixture was stirred for 1 h, the solvent was removed under vacuum. The ^{1}H NMR spectrum of the crude mixture showed the presence of the 2:1 adduct **20a** and the ketone **21a** in 1:1.2 ratio. Chromatography (silica gel, 7:3 petroleum ether–diethyl ether) gave 100 mg (32%) of the ketone **21a**: oil; IR (film) 1725 (C=O) cm^{-1}; ^{1}H NMR δ 2.32 (d, 3 H, =CMe, J = 1.2 Hz), 7.17 (s, 1 H, aliphatic CH), 7.85 (q, 1 H, =CH, J = 1.2 Hz); mass spectrum, m/e (relative intensity) 193 (M^+, 70), 110 (96), 83 (100). Anal. Calcd for $C_6H_5Cl_2NO_2$: C, 37.15; H, 2.60; N, 7.22. Found: C, 37.18; H, 2.61; N, 7.20.

The 2:1 adduct **20a** showed the following ^{1}H NMR data: δ 2.27 (d, 3 H, =CMe, J = 1.4 Hz), 6.41 (s, 1 H, aliphatic CH), 7.62 (q, 1 H, =CH, J = 1.4 Hz).

Reaction of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with *tert*-Butylcyanoketene (TBCK). A solution of the oxazole **6a** (0.25 g, 1.61 mmol) in benzene (15 mL) was added to a solution of the ketene (3.22 mmol) prepared according to the literature procedure[35] in benzene (10 mL). After 15 min, the solvent was evaporated and the ^{1}H NMR spectrum of the crude mixture showed the presence of the 2:1 adduct **20b** and the silyl enol ether **19b** in 2:1 ratio. Chromatography of the reaction mixture (silica gel, 7:3 diethyl ether–petroleum ether) gave 212 mg (64%) of the ketone **21b**. Crystallization from *n*-hexane of the reaction mixture obtained from another experiment carried out as detailed above gave 130 mg (25%) of the 2:1 adduct **20b**.

Silyl enol ether **19b**: ^{1}H NMR δ 0.22 (s, 9 H, $OSiMe_3$), 1.33 (s, 9 H, CMe_3), 2.21 (d, 3 H, =CMe, J = 1.4 Hz), 7.53 (q, 1 H, =CH, J = 1.4 Hz).

2:1 adduct **20b**: mp 74–75 °C (from *n*-hexane); IR (KBr) 2220 (C≡N), 2200 (C≡N), 1780 (–COO–), 1610, 1590 cm^{-1}; ^{1}H NMR

δ 1.33 (s, 9 H, CMe_3), 1.41 (s, 9 H, CMe_3), 2.25 (d, 3 H, =CMe, J = 1.6 Hz), 3.56 (s, 1 H, aliphatic CH), 7.55 (q, 1 H, =CH, J = 1.6 Hz). Anal. Calcd for $C_{18}H_{23}N_3O_3$: C, 65.63; H, 7.04; N, 12.76. Found: C, 65.67; H, 7.00; N, 12.75.

Ketone **21b**: mp 29–31 °C (from *n*-hexane); IR (film) 2220 (C≡N), 1710 (C=O), 1580 cm^{-1}; ^1H NMR δ 1.18 (s, 9 H, CMe_3), 2.28 (d, 3 H, =CMe, J = 1.0 Hz), 4.78 (s, 1 H, aliphatic CH), 7.63 (q, 1 H, =CH, J = 1.0 Hz); mass spectrum, m/e (relative intensity) 206 (M^+, 13), 191 (6), 150 (71), 110 (100). Anal. Calcd for $C_{11}H_{14}N_2O_2$: C, 64.06; H, 6.84; N, 13.58. Found: C, 64.09; H, 6.83; N, 13.55.

Reaction of 5-Phenyl-2-(trimethylsilyl)oxazole (6b) with Dichloroketene (DCK). A solution of dichloroacetyl chloride (0.34 g, 2.3 mmol) in *n*-hexane (50 mL) was slowly added to a solution of the oxazole **6b** (0.25 g, 1.15 mmol) and triethylamine (0.233 g, 2.3 mmol) in the same solvent (100 mL). After the mixture was stirred for 2 h, the solvent was removed under vacuum and the residue chromatographed (silica gel, 6:2:2 cyclohexane–ethyl acetate–benzene) to give 0.23 g (80%) of the ketone **21c**: mp 106–109 °C (from dichloromethane–*n*-hexane); IR (KBr) 1700 (C=O) cm^{-1}; ^1H NMR δ 7.18 (s, 1 H, aliphatic CH), 7.51–7.9 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 255 (M^+, 43), 172 (100), 116 (66), 105 (33), 77 (40). Anal. Calcd for $C_{11}H_7Cl_2NO_2$: C, 51.59; H, 2.75; N, 5.47. Found: C, 51.62; H, 2.74; N, 5.46.

Reaction of 5-Phenyl-2-(trimethylsilyl)oxazole (6b) with *tert*-Butylcyanoketene (TBCK). To a solution of the oxazole **6b** (0.43 g, 1.98 mmol) in benzene (10 mL) was slowly added (1 h) a solution of the ketene (3.9 mmol) prepared according to the literature procedure[35] in benzene (30 mL). After the mixture was stirred for 2 h at room temperature, the solvent was removed under vacuum and the residue chromatographed (silica gel, 6:2:2 cyclohexane–ethyl acetate–benzene) to give 0.42 g (80%) of the ketone **21d**: mp 102–104 °C (from dichloromethane–*n*-hexane); IR (KBr) 2230 (C≡N), 1700 (C=O) cm^{-1}; ^1H NMR δ 1.23 (s, 9 H, CMe_3), 4.91 (s, 1 H, aliphatic CH), 7.62–7.95 (m, 6 H, ArH, =CH); mass spectrum, m/e (relative intensity) 268 (M^+, 43), 253 (5), 212 (100), 172 (54), 116 (45), 105 (25), 102 (29), 77 (23). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44. Found: C, 71.67; H, 6.03; N, 10.46.

Reactions of 4-Methyl-2-(trimethylsilyl)oxazole (6a) with Heteroaryl Cations 23a–e. General Procedure. To a solution of the selected azaryl **22** (2 mmol) in dichloromethane (30 mL) at 0 °C was added a solution of ethyl chloroformate (0.22 g, 2 mmol) in the same solvent (5 mL). After 30 min, a solution of the oxazole **6a** (0.31 g, 2 mmol) in dichloromethane (10 mL) was added. The reaction mixture was stirred for the time listed in Table IV and the solvent evaporated under vacuum. Flash chromatography (silica gel, 9:1 dichloromethane–diethyl ether) of the crude reaction mixture gave the adduct **24**.

Adduct **24a**: oil; IR (film) 3100, 2970, 2920, 1715 (N–CO_2Et), 1600 cm^{-1}; ^1H NMR δ 1.3 (t, 3 H, CO_2Et), 2.2 (d, 3 H, =CMe, J = 0.4 Hz), 4.23 (q, 2 H, CO_2Et), 5.6 (d, 1 H, =CH, J = 3.6 Hz), 6.63 (s, 2 H, aliphatic CH, =CH), 7.33 (q, 1 H, =CH, J = 0.4 Hz). Anal. Calcd for $C_{10}H_{12}N_2O_3S$: C, 49.99; H, 5.03; N, 11.66. Found: C, 49.95; H, 5.01; N, 11.68.

Adduct **24b**: oil; IR (film) 2980, 2930, 1720 (N–CO_2Et), 1585 cm^{-1}; ^1H NMR δ 1.3 (t, 3 H, CO_2Et), 2.15 (d, 3 H, =CMe, J = 1.6 Hz), 4.35 (q, 2 H, CO_2Et), 6.9 (s, 1 H, aliphatic CH), 7.07–7.34 (m, 5 H, ArH, =CH), 7.97 (m, 1 H, ArH). Anal. Calcd for $C_{14}H_{14}N_2O_3S$: C, 57.91; H, 4.86; N, 9.65. Found: C, 57.94; H, 4.85; N, 9.62.

Adduct **24c**: oil; IR (film) 3100, 2980, 2920, 1715 (N–CO_2Et), 1645, 1580 cm^{-1}; ^1H NMR δ 1.2 (t, 3 H, CO_2Et), 2.1 (d, 3 H, =CMe, J = 1.4 Hz), 4.2 (q, 2 H, CO_2Et), 5.3 (m, 1 H), 5.7 (br, 1 H), 6.0 (m, 2 H) 6.9 (br, 1 H), 7.9 (q, 1 H, =CH, J = 1.4 Hz). Anal. Calcd for $C_{12}H_{14}N_2O_3$: C, 61.52; H, 6.02; N, 11.96. Found: C, 61.56; H, 6.00; N, 11.93.

Adduct **24d**: oil; IR (film) 2960, 2920, 1705 (N–CO_2Et), 1600 cm^{-1}; ^1H NMR δ 1.29 (t, 3 H, CO_2Et), 2.07 (d, 3 H, =CMe, J = 1.6 Hz), 3.5 (q, 2 H, CO_2Et), 6.36 (s, 1 H, aliphatic CH), 6.76 (d, 1 H), 7.25 (m, 5 H, ArH), 7.67 (d, 1 H, ArH). Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.55; H, 5.66; N, 9.81.

Adduct **24e**: mp 96–98 °C (from diethyl ether–*n*-hexane); IR (KBr) 3130, 2970, 1710 (N–CO_2Et), 1640, 1600 cm^{-1}; ^1H NMR δ 1.3 (t, 3 H, CO_2Et) 2.04 (d, 3 H, =CMe, J = 1.4 Hz), 4.3 (q, 2 H, CO_2Et), 5.83 (d, 1 H, =CH, J = 6.0 Hz), 6.56 (br, 1 H, aliphatic CH), 7.0–7.4 (m, 6 H, ArH). Anal. Calcd for $C_{16}H_{16}N_2O_3$: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.61; H, 5.69; N, 9.83.

Oxidation of the Adducts 24a–e. General Procedure. A solution of the adduct **24** (2 mmol) and *o*-chloroanil (0.47 g, 2 mmol) in benzene (30 mL) was heated (room temperature for the adduct **24b**) for the time indicated in Table IV. The reaction mixture was washed with NaOH (5%), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue chromatographed (silica gel, 9:1 dichloromethane–diethyl ether) to give the azadiaryl **25**.

Product **25a**: mp 86–88 °C (from diethyl ether–*n*-hexane); IR (KBr) 3070, 1595 cm^{-1}; ^1H NMR δ 2.29 (d, 3 H, =CMe, J = 2.0 Hz), 7.55 (d, 1 H, =CH, J = 3.0 Hz), 7.59 (q, 1 H, =CH, J = 2.0 Hz), 8.04 (d, 1 H, =CH, J = 3.0 Hz). Anal. Calcd for $C_7H_6N_2OS$: C, 50.59; H, 3.64; N, 16.86. Found: C, 50.62; H, 3.63; N, 16.82.

Product **25b**: mp 88–90 °C (from diethyl ether–*n*-hexane); IR (KBr) 1590 cm^{-1}; ^1H NMR δ 2.35 (d, 3 H, =CMe, J = 1.6 Hz), 7.6 (m, 3 H, ArH), 8.04 (m , 1 H, ArH), 8.25 (m, 1 H, ArH). Anal. Calcd for $C_{11}H_8N_2OS$: C, 61.09; H, 3.73; N, 12.95. Found: C, 61.05; H, 3.74; N, 12.97.

Product **25c**: oil; IR (film) 2960, 1590 cm^{-1}; ^1H NMR δ 2.31 (d, 3 H, =CMe, J = 1.6 Hz), 7.42 (m, 1 H, ArH), 7.62 (q, 1 H, =CH, J = 1.6 Hz),7.9 (m, 1 H, ArH), 8.21 (m, 1 H, ArH), 8.84 (m, 1 H, ArH). Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.59. Found: C, 67.52; H, 5.00; N, 17.52.

Product **25d**: mp 107–109 °C (from diethyl ether–*n*-hexane); IR (KBr) 1585 cm^{-1}; ^1H NMR δ 2.22 (d, 3 H, =CMe, J = 1.6 Hz), 7.65 (m, 4 H, ArH, =CH), 8.21 (m, 3 H, ArH). Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.25; H, 4.77; N, 13.35.

Product **25e**: mp 64–66 °C (from diethyl ether–*n*-hexane); IR (KBr) 3050, 2930, 1600, 1590 cm^{-1}; ^1H NMR δ 2.4 (d, 3 H, =CMe, J = 1.6 Hz), 7.7–7.9 (m, 5 H, ArH), 8.75 (m, 1 H, ArH), 9.5 (m, 1 H, ArH). Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.33. Found: C, 74.30; H, 4.80; N, 13.35.

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Registry No. **1a**, 693-93-6; **1b**, 1006-68-4; **1c**, 1008-94-2; **1d**, 1011-51-4; **1e**, 70380-70-0; **1f**, 70380-73-3; (±)-**4b**, 108665-41-4; (*Z*)-**5a**, 90892-92-5; (*E*)-**5a**, 108665-42-5; (*Z*)-**5b**, 108665-43-6; (*Z*)-**5c**, 108665-45-8; (*Z*)-**5d**, 108665-47-0; (*Z*)-**5e**, 108665-49-2; (*Z*)-**5f**, 108665-50-5; (*Z*)-**5g**, 90892-91-4; **6a**, 90892-93-6; **6b**, 108665-44-7; **6c**, 108665-46-9; **6d**, 108665-48-1; **6f**, 108665-51-6; (±)-**11a**, 108665-52-7; (±)-**11b**, 108665-53-8; (±)-**12b**, 108665-54-9; **13**, 15186-48-8; (±)-**14**, 34713-70-7; **15a**, 104470-57-7; **15a** (acetate), 108665-57-2; **15b**, 104470-58-8; **15b** (acetate), 108665-58-3; (±)-**16a**, 108665-55-0; (±)-**16b**, 108665-56-1; **17a**, 90892-97-0; **17b**, 90892-98-1; **17c**, 90892-99-2; **17d**, 90893-00-8; **17e**, 108665-59-4; **17f**, 31970-74-8; **17g**, 13575-16-1; **17h**, 108665-60-7; **17i**, 108665-61-8; **17l**, 108665-62-9; **17m**, 108665-63-0; **18g**, 108665-64-1; **18l**, 108665-65-2; **19b**, 108665-67-4; **20a**, 91190-48-6; (±)-**20b**, 108665-66-3; **21a**, 91190-64-6; (±)-**21b**, 108665-68-5; **21c**, 108665-69-6; (±)-**21d**, 108665-70-9; **22a**, 288-47-1; **22b**, 95-16-9; **22c**, 110-86-1; **22d**, 91-22-5; **22e**, 119-65-3; (±)-**24a**, 108675-01-0; (±)-**24b**, 108665-71-0; (±)-**24c**, 108665-72-1; (±)-**24d**, 108665-73-2; (±)-**24e**, 108665-74-3; **25a**, 93472-33-4; **25b**, 93472-34-5; **25c**, 90417-11-1; **25d**, 91822-59-2; **25e**, 93472-37-8; TBCK, 29342-22-1; CH_3COCl, 75-36-5; PhCHO, 100-52-7; Me_3SiCl, 75-77-4; *i*-C_3H_7CHO, 78-84-2; PhCOCl, 98-88-4; EtOCOCl, 541-41-3; MeO_2CCOCl, 5781-53-3; $MeO_2C(CH_2)_2COCl$, 1490-25-1; $Me(CH_2)_4COCl$, 142-61-0; $Me(CH_2)_7CH{=}CH(CH_2)_7COCl$, 7378-94-1; $Cl_2CHCOCl$, 79-36-7.