hydroxylamine **7b**, which was immediately condensed with 4-acetoxybutanal to give the (*Z*)-nitrone **8b**.[13] Thermal cyclization (80%), ester hydrolysis, mesylation, and N–O bond cleavage gave the indolizidine **11b** in excellent yield. Conversion to 205A (**2**) required epimerization at C-8 and deoxygenation. This was achieved by oxidation[14] to the aldehyde **21b**, base-catalyzed epimerization[5,15] to the equatorial aldehyde **22b**, and reduction to the epimeric alcohol **23b**. Mesylation and displacement[16] with Super-Hydride gave (±)-205A (**2**).[11b,17] Lindlar reduction of 205A (**2**) afforded (±)-207A (**3**).[11b]

An asymmetric synthesis of the 5,8-disubstituted indolizidine alkaloids can, in principle, be achieved by using an enantiomerically pure *N*-alkenylhydroxylamine precursor **7**. This approach would depend on the hitherto unexplored formation of such α-chiral *N*-alkenylnitrones[18] and their use in intramolecular cycloadditions without loss of stereochemical integrity. Spurred on by the prospect of oxidizing chiral amines to chiral hydroxylamines,[19] we prepared the enantiomerically pure amine **34** in 53% overall yield from (*S*)-5-(hydroxymethyl)-2-pyrrolidone (**25**)[20] by a chain-extension sequence (Scheme IV).[21] Noteworthy was the novel use of the Ireland debenzylation procedure[22] for the removal of the benzyloxycarbamate protecting group [**33** → **34**] (95%). Formation of the imine **35**, selective oxidation to the oxaziridine **36**, and cleavage with hydroxylamine gave the chiral *N*-alkenylhydroxylamine **7d**. Application of the previously described intramolecular nitrone methodology and subsequent elaboration (Scheme IV) gave enantiomerically pure (−)-209B (**4**) in ten steps (15% overall yield from **34**).[23]

In summary, the *N*-alkenylnitrones **8** have been shown to serve as extremely efficient precursors for the stereocontrolled construction of enantiomerically pure 5,8-disubstituted indolizidine alkaloids by a general strategy which should make these compounds readily available for biological evaluation.[17]

Acknowledgment. We thank the S.E.R.C. (U.K.) for supporting this work, I.C.I. Pharmaceuticals (A.L.S.) and the Rohm and Haas Company (S.F.W.) for the award of CASE studentships, and Drs. J. W. Daly and T. Spande (NIH) for a preprint of ref 1c. A.L.S. is the recipient of a Sidney Sussex College research studentship.

Supplementary Material Available: Spectra (NMR, IR, MS) of new compounds described in this paper (5 pages). Ordering information is given on any current masthead page.

(13) A typical procedure for the conversion **6b** → **8b** and subsequent cyclization to **9b** is illustrated as follows. A solution of oxime **6b** (1.59 g, 9.64 mmol) in methanol (40 mL) was cooled to −10 °C under argon and treated with methyl orange indicator (5 drops) and sodium cyanoborohydride (0.91 g, 14.46 mmol). Hydrochloric acid (6 M solution in water/methanol) was added dropwise with stirring to maintain a red coloration until reduction was complete (ca. 30 min). The solution was made strongly alkaline with 20% aqueous sodium hydroxide solution, poured into saturated aqueous sodium chloride solution containing ice (50 mL), and extracted with dichloromethane (4 × 50 mL). The organic extracts were added directly to a solution of 4-acetoxybutanal (2.1 g, 16.1 mmol) in dry dichloromethane (20 mL) containing anhydrous $MgSO_4$ at 0 °C with stirring. After 1 h, the solution was filtered and evaporated in vacuo to give the crude nitrone **8b**, which was dissolved in dry toluene (250 mL) and refluxed under argon under Dean–Stark conditions for 15 h. Evaporation in vacuo and purification by flash chromatography on silica (hexane/ether 5:1 → 3:1) gave isoxazolidine **9b** (1.70 g, 63%) as a pale yellow liquid.

(14) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480–2482.

(15) The two epimeric aldehydes were readily distinguished in the ^1H NMR spectrum by the characteristic aldehyde signals (δ_{ax} CHO 10.0 (d, J = 2.0 Hz), δ_{eq} CHO 9.65 (d, J = 2.0 Hz)). Integration of the ^1H NMR spectrum of the equilibrium mixture indicated the ratio **22b**/**21b** = 16.7:1. The aldehydes were not easily separated, but the corresponding 8-hydroxymethyl compounds were readily separated by flash chromatography on silica eluting with EtOAc/NH_3 mixtures.

(16) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669–1671.

(17) The pharmacology of 205A will be communicated in due course.

(18) A few α-chiral nitrones have been prepared and used in intramolecular cycloaddition reactions. These were, however, C-alkenylnitrones and hence did not require the formation of α-chiral *N*-alkenylhydroxylamines. See: Wovkulich, P. M.; Uskoković, M. R. *J. Am. Chem. Soc.* **1981**, *103*, 3958–3959. Baggiolini, E. G.; Lee, H. L.; Pizzolato, G.; Uskoković, M. R. *J. Am. Chem. Soc.* **1982**, *104*, 6460–6462.

(19) Grundke, G.; Keese, W.; Rimpler, M. *Synthesis* **1987**, 1115–1116, and references cited therein.

(20) Silverman, R. B.; Levy, M. A. *J. Org. Chem.* **1980**, *45*, 815–818.

(21) (a) Cuprate displacement of tosylate: Johnson, C. R.; Dutra, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7777–7782, 7783–7788. (b) The aldehyde **32** was found to be in the form of the corresponding hemi-aminal. (c) Wittig olefination: Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128–1129.

(22) Ireland, R. E.; Smith, M. G. *J. Am. Chem. Soc.* **1988**, *110*, 854–860.

(23) $[\alpha]^{22}_D$ = −94.3°, *c* 1.85, MeOH. The enantiomeric excess was judged to be >95% by chiral shift studies on **9d**. The optical rotation of the natural 209B is not available at present due to insufficient material having been isolated.

Intramolecular Reactions of 2-*O*-Organosilyl Glycosides: Highly Stereoselective Synthesis of *C*-Furanosides

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Received July 25, 1988

Our investigations on the Lewis acid-mediated reactions of substituted sugars have demonstrated that glycofuranosides bearing, at *O*-2, a carbon nucleophilic substituent such as a benzyl[2] or an allyl[3] group, undergo readily internal *C*-glycosidation, a reaction that leads to "cyclic" 1,2-*cis*-*C*-furanosides. These results suggested that an intramolecular process might provide a reliable approach to the stereoselective synthesis of *C*-furanosides. The stereochemical outcome of the reactions of glycofuranosyl derivatives with *C*-nucleophiles such as allyltrimethylsilane,[4] silyl enol ethers,[5] or activated aromatic systems[5e,6] is indeed largely unpredictable, and the availability of a stereocontrolled approach to *C*-furanosides, which constitute important precursors of *C*-nucleosides,[7] aryl *C*-glycosides,[8] and polyethers[9] antibiotics, is highly desirable.

We therefore looked for substituents that would make the general process represented in Scheme I feasible. In particular, on the basis of the well-documented chemistry of aryl- and vinylsilanes, which undergo ipso substitution in reactions with electrophiles,[10] a functionalized organosilyl substituent appeared to be an appropriate candidate. Initial investigations were not very encouraging as the 2-*O*-phenyldimethylsilyl derivative of xylofuranoside **1** led, on reaction with tin(IV) chloride, to the expected α-*C*-glycosylated benzene in 18% yield only as well as to a large amount of desilylated, anomerized xylofuranoside α-**1** (65%) and to the cyclic dimer of **1**, compound **2**[11] (8%). However, we considered that the low yield of the internal reaction was due

(1) Present address: Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt.

(2) (a) Martin, O. R. *Tetrahedron Lett.* **1985**, *26*, 2055. (b) Martin, O. R.; Mahnken, R. E. *J. Chem. Soc., Chem. Commun.* **1986**, 497. (c) Martin, O. R. *Carbohydr. Res.* **1987**, *171*, 211.

(3) Martin, O. R.; Kurz, K. G. Unpublished results.

(4) (a) Kozikowski, A. P.; Sorgi, K. L. *Tetrahedron Lett.* **1982**, *23*, 2281; **1983**, *24*, 1563. (b) Cupps, T. L.; Wise, D. L.; Townsend, L. B. *J. Org. Chem.* **1982**, *47*, 5115. (c) Wilcox, C. S.; Otoski, R. M. *Tetrahedron Lett.* **1986**, *27*, 1011. (d) Bennek, J. A.; Gray, G. R. *J. Org. Chem.* **1987**, *52*, 892.

(5) (a) Ogawa, T.; Pernet, A. G.; Hanessian, S. *Tetrahedron Lett.* **1973**, 3543. (b) Yokoyama, Y. S.; Inoue, T.; Kuwajima, I. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 553. (c) Reetz, M. T.; Müller-Starke, H. *Liebigs Ann. Chem.* **1983**, 1726. (d) Araki, Y.; Watanabe, K.; Kuan, F.-H.; Itoh, K.; Kobayashi, N.; Ishido, Y. *Carbohydr. Res.* **1984**, *127*, C5. (e) Stewart, A. O.; Williams, R. M. *J. Am. Chem. Soc.* **1985**, *107*, 4289.

(6) (a) Kalvoda, L. *Coll. Czech. Chem. Commun.* **1973**, *38*, 1679. (b) Schmidt, R. R.; Hoffmann, M. *Tetrahedron Lett.* **1982**, *23*, 409.

(7) Hanessian, S.; Pernet, A. G. *Adv. Carbohydr. Chem. Biochem.* **1976**, *33*, 111.

(8) Hacksell, U.; Daves, G. D. *Progress Med. Chem.* **1985**, *22*, 1.

(9) Boivin, T. L. B. *Tetrahedron* **1987**, *43*, 3309 and references cited.

(10) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(11) This compound (**2**) is the tetra-*O*-(4-chlorobenzyl) derivative of 1,2′-anhydro-2-*O*-(α-D-xylofuranosyl)-α-D-xylofuranose. Details on its structure are provided in the Supplementary Material.

0002-7863/88/1510-8698$01.50/0

Scheme I

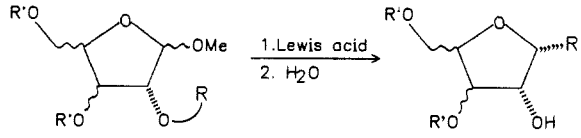
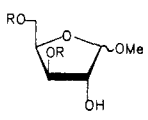
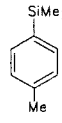
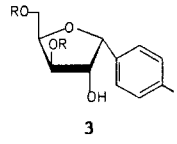
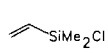
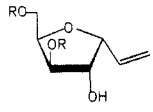
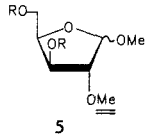
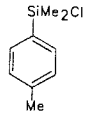
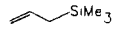
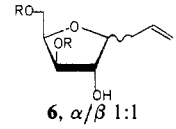
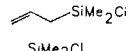
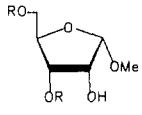
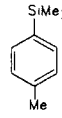
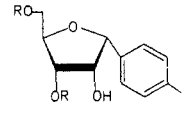
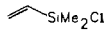
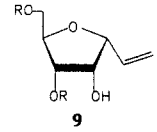
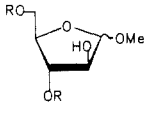
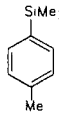
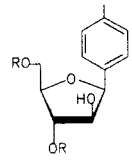


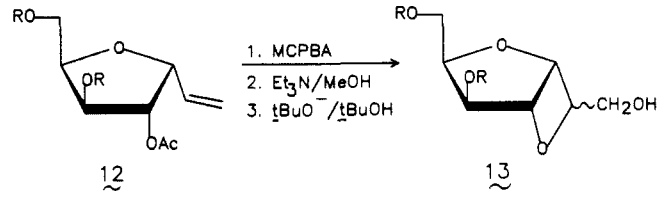
Table I. $SnCl_4$-Mediated Reactions of Glycosides **1**, **7**, and **10** with Organosilyl Reagents

glycoside[d]	reagent[a]	product(s)[b,d]	yield[c] (%)
 **1**		 **3**	72
1		 **4**	35
 **5**		no C-glycosides	
1		 **6**, α/β 1:1	78
1		**6**, α/β 1:5	58
 **7**		 **8**	35
7		 **9**	29
 **10**		 **11**	48

[a] Conditions: 2 mol equiv of silylating agent and 1–2 equiv of $SnCl_4$ in CH_2Cl_2 for 2 h at room temperature (12 h for **4** and **9**). [b] Dimer **2** formed in the case of **3** and **4** only (less than 10%). [c] Yields are for isolated products and have not been optimized. [d] R = *p*-chlorobenzyl.

primarily to a competitive and *reversible* desilylation of the substrate promoted by the Lewis acid to form, in particular, phenyldimethylchlorosilane. Thus, increasing the concentration of the silylating species should make the process more efficient. Indeed, direct treatment of xylofuranosides **1** with an excess of silylating agent (4-fold excess of *p*-tolyldimethylchlorosilane) in the presence of tin(IV) chloride afforded the corresponding α-xylofuranosyltoluene **3** stereospecifically and in higher yield (72%).[12] Similar results were obtained from ribo- and arabinofuranosides **7**[13] and **10**[14] (Table I); furthermore, the process

Scheme II



R= p-chlorobenzyl

was also successful with vinyldimethylchlorosilane, which gave the highly versatile vinyl α-*C*-furanosides **4** and **9** from glycosides **1** and **7**, albeit in lower yield.

Two experiments established that the *C*-glycosidation step must be intramolecular: thus, reaction of the 2-*O*-methyl analogue of **1**, glycoside **5**, with *p*-tolyldimethylchlorosilane did not give any *C*-glycosylated toluene under the same conditions. Furthermore, the presence of the leaving group on the organosilane is indispensable for the success of the reaction:[15] no *C*-glycosylated benzene was obtained, for example, with phenyltrimethylsilane under identical conditions. Thus, the 2-*O*-organosilyl derivative must be formed in situ, and the *C*-glycosidation occurs by way of an intramolecular electrophilic substitution of the silyl group, which leads exclusively to the 1,2-*cis*-*C*-furanosides. This process, which constitutes a conceptually novel approach to stereoselective *C*-glycosidation, is particularly remarkable since the 2-*O*-substituted intermediate does not have to be isolated and no activation of the glycosidic function is required.

Although allylsilanes react with electrophiles by way of a different mechanism (substitution with rearrangement),[10] the *C*-allylation of furanosides by a related process was also investigated. With allyltrimethylsilane in the presence of tin(IV) chloride, the intermolecular *C*-allylation of **1**, to give *C*-glycosides **6**, proceeded in high yield (Table I) but without any stereoselectivity. By contrast, the reaction of **1** with allyldimethylchlorosilane afforded predominantly the β-anomer of **6**. This result is again consistent with an intramolecular process: we believe, indeed, that a 2-*O*-allyldimethylsilyl derivative of **1** is formed in situ and then undergoes an $SnCl_4$-promoted internal allylic substitution of the silyl group, by way of a seven-membered cyclic transition state (or intermediate). As shown by molecular models, the formation of a 1,2-*trans*-*C*-glycoside by this mechanism should be much more favorable than that of the 1,2-*cis*-isomer, for both steric and electronic reasons; in particular, the C–Si bond can remain aligned with the π-orbital of the unsaturated system throughout the reaction pathway, a stereoelectronic requirement for the allylic displacement to occur. Thus, the stereoselectivity achieved with the allylsilyl substituent contrasts sharply with that of the aryl- and vinylsilyl systems and provides a complementary approach to 1,2-*trans*-*C*-furanosides.

The stereochemistry of the *C*-glycosyl compounds was assigned on the basis of a detailed analysis of their NMR parameters; in particular, the ^1H chemical shift of the acetyl-methyl signal is a useful probe of the anomeric configuration of the 2-*O*-acetylated aryl *C*-furanosides (δ 1.65–1.85 ppm in 1,2-cis isomers vs 2.0–2.2 in normal acetates, in $CDCl_3$). Furthermore, the 1,2-cis relationship of the substituents on the *C*-vinyl compounds was confirmed by the conversion of the acetate of **4** (**12**) into the 2,4;3,6-dianhydroalditol **13** (Scheme II).[16]

Thus, the reaction of glycofuranosides having a free hydroxyl group at C-2 with functionalized organochlorosilanes, in the

(12) The final product is readily separated by flash chromatography from slow-moving byproducts (partially debenzylated analogues of **3**, 7%) and from a small amount of fast-moving dimer **2** (8%).

(13) Martin, O. R.; Kurz, K. G.; Rao, S. P. *J. Org. Chem.* **1987**, *52*, 2922.

(14) Martin, O. R.; Rao, S. P.; El-Shenawy, H. A.; Kurz, K. G.; Cutler, A. B. *J. Org. Chem.* **1988**, *53*, 3287.

(15) The best results (TLC quantitative) were obtained with *p*-tolylmethyldichlorosilane. Formation of dark, polymeric material on aqueous processing of the reaction mixture made, however, the isolation of the final product difficult with this reagent.

(16) The formation of oxetanes has been observed by Buchanan and coworkers[17] in related systems: 5,6-anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose as well as the β-L-ido isomer lead to 3,5-anhydro derivatives on reaction with a base. This behavior is consistent with Baldwin's rules for ring closure.

(17) Buchanan, J. G.; Oakes, E. M. *Carbohydr. Res.* **1965**, *1*, 242.

presence of $SnCl_4$, provides the corresponding *C*-glycosyl compounds in one step and highly stereoselectively. Since the starting furanosides are readily available in the ribo,[13] xylo,[14] and arabino[14] series, this process constitutes a simple, highly useful methodology for the synthesis of *C*-furanosides of well-defined stereochemistry.

Acknowledgment. Support from the National Institutes of Health for this research (Grant GM38710) and from the U.S. Department of Education for the purchase of a high field NMR spectrometer (Grant 2-20-1009) is gratefully acknowledged. We also thank Dean Marson for the preparation of compounds **10** and **11**.

Supplementary Material Available: Physical constants and spectroscopic data for the new compounds (or their acetates) (10 pages). Ordering information is given on any current masthead page.

"Photochemical" Azo Metathesis by $(CO)_5W{=}C(OCH_3)CH_3$. Isolation of a Zwitterionic Intermediate

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Stanford, California 94305

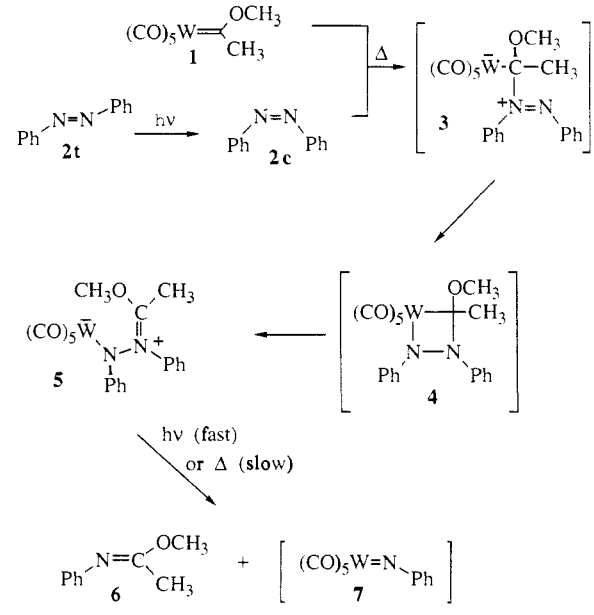
Received August 18, 1988

The photolysis of $(CO)_5Cr{=}C(OCH_3)CH_3$ and azobenzene has recently been reported to give mixtures of heterocycles (1,2- and 1,3-diazetidinones) and the azo metathesis product $PhN{=}C(OCH_3)CH_3$ (**6**).[1] The three products were suggested to arise from a common intermediate, a diazametallacycle arising from [2 + 2] cycloaddition of azobenzene to the carbene complex. We have examined the photochemical reaction of the related tungsten carbene $(CO)_5W{=}C(OCH_3)CH_3$ (**1**)[2] with azobenzene in benzene solution. In contrast to the chromium chemistry, the tungsten system does not give heterocycles. Only products of azo metathesis are observed. The primary photoprocess is trans–cis isomerization of azobenzene (**2t** → **2c**),[3] with the cis isomer undergoing thermal reaction with **1** to yield **5**, the first zwitterionic intermediate to be isolated from a metathesis system. Photolysis or thermolysis of **5** gives imidate **6**[4] (Scheme I) and products apparently deriving from low-valent tungsten nitrene **7**.

The UV–vis spectra of carbene **1**[5] and azobenzene[3] are quite similar, and irradiation of the reaction mixtures at wavelengths where one absorbs will also result in excitation of the other. *trans*-Azobenzene is known to undergo photoisomerization to the cis isomer, producing a photostationary state that is 37% cis, 63% trans.[6] Pure *cis*-azobenzene, isolated by the method of Cook,[7] undergoes a room temperature *thermal* reaction with carbene **1** which gives the same intermediate (**5**) and product (**6**) as photolysis of the reaction mixtures. It is thus not necessary to invoke photochemistry of the carbene in the metathesis process.

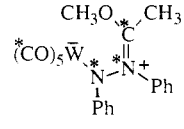
Upon mixing **2c** with a slight excess of **1** in benzene at room temperature, quantitative formation of zwitterion **5** can be observed by NMR. Under these conditions, **5** is stable for several hours in the dark. Evaporation of the solvent and washing with

Scheme I



pentane to remove unreacted starting material gives **5** as a red oil in 55% yield. For spectroscopic characterization of **5** we have prepared the ^{15}N and ^{13}C labeled compounds **5b–d** from isotopically enriched **1**[8] and **2**.[11]

The ^1H, ^{13}C, and ^{15}N NMR data[12] from compounds **5a–d**



5a *N = ^{14}N *C = ^{12}C
5b *N = ^{14}N *C = ^{13}C
5c *N = ^{15}N *C = ^{12}C
5d *N = ^{15}N *C = ^{13}C

support the zwitterionic structure for the intermediate. The ^{13}C chemical shift of 176.1 for the labeled carbon in **5b,d** suggests double bonding of nitrogen to the original carbene fragment, a feature confirmed by the 28 Hz ^{13}C–^{15}N coupling.[13] Observation of a 14 Hz coupling between the ^{15}N's in **5c,d** establishes that the N–N bond is intact.[14] IR data for **5**[15] are also consistent. The metal carbonyl region exhibits the characteristic pattern for $(CO)_5ML$, in agreement with the observation of two W–CO signals in the ^{13}C NMR. The C=N stretch is found at 1590 cm^{-1} and shifts to 1568 upon substitution with ^{15}N. The alternative structure **3** can be ruled out by comparison of the spectral data for the intermediate with that of the known phosphorus ylide **8** (vide infra). Also, no IR stretch between 1260 and 1500 cm^{-1} shifts upon ^{15}N substitution as would be expected for the N=N double bond of **3**. A saturated system such as metallacycle **4** is

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(2) Fischer, E. O.; Maasboel, A. *Chem. Ber.* **1967**, *100*, 2445–2456.
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(6) Quoted composition of photostationary state is for Pyrex-filtered irradiation from a mercury arc lamp. Fischer, E.; Frankel, M.; Wolovsky, R. *J. Chem. Phys.* **1955**, *23*, 1367.
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(8) **5b** and **5d** are 16% enriched in ^{13}C at the starred positions. The synthetic route to the enriched carbene began with reaction of $(CO)_5W(THF)$[9] with ^{13}CO to give $W(CO)_5(^{13}CO)$. The carbene was then prepared in the usual fashion.[10]
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(10) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. In *Inorganic Syntheses*; Wiley-Interscience: New York, 1979; Vol. XIX, pp 164–167.
(11) Synthesis of **5c** and **5d** utilized $[^{15}N_2]$azobenzene prepared by reductive coupling of $[^{15}N]$nitrobenzene. Coupling reaction: Bigelow, H. E.; Robinson, D. R. In *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 103.
(12) For **5a**: ^1H NMR (C_6D_6) δ 1.64 (s, 3 H), 2.45 (s, 3 H), 6.68 (t, 1 H), 6.82 (d, 2 H), 6.93 (m, 3 H), 7.20 (t, 2 H), 7.27 (d, 2 H); ^{13}C NMR (C_7D_8) δ 14.9, 59.3, 176.1, 199.2, 200.0. For **5c**: ^1H NMR (C_6D_6) 1.64 (d, $^1J_{NH}$ = 2.3 Hz); ^{15}N NMR (chemical shifts upfield of CH_3NO_2) 53.9 (d, $^1J_{NN}$ = 14 Hz), 58.0 (d). For **5d**: ^{13}C NMR δ 176.1 (d, $^1J_{CN}$ = 28 Hz).
(13) (a) Rabillier, C.; Ricolleau, G.; Martin, M. L.; Martin, G. L. *Nouv. J. Chim.* **1980**, *4*, 35–42. (b) Fritz, H.; Cierin, D.; Fleury, J.-P. *Org. Magn. Reson.* **1976**, *8*, 269–270.
(14) Schultheiss, H.; Fluck, E. *Z. Naturforsch. B.* **1977**, *32B*, 257–264.
(15) IR of **5a**: ν_{WCO} 2061 (m), 1913 (vs), 1860 (s); $\nu_{C=N}$ 1590 cm^{-1}. For **5c**: $\nu_{C=N}$ 1568 cm^{-1}.

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