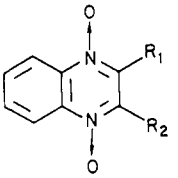
Table I[c]



	R_1	R_2		R_1	R_2	yield, %		R_1	R_2	yield, %
1a	CH_3	H	**1b**	CH_2Br	H	56[b]	**1c**	CH_2NO_3	H	56
3a	$-(CH_2)_4-$		**4a**	$BrCH(CH_2)_2$	CHBr	87[a]	**5a**	$CHNO_3(CH_2)_2$	$CHNO_3$	97
3b	$-(CH_2)_5-$		**4b**	$BrCH(CH_2)_3$	CHBr	70[b]	**5b**	$CHNO_3(CH_2)_3$	$CHNO_3$	70
3c	$COCH_3$	CH_3	**4c**	$COCH_3$	CH_2Br	70[a]	**5c**	$COCH_3$	CH_2NO_3	82
3d	$CH_2C_6H_5$	C_6H_5	**4d**	$CHBrC_6H_5$	C_6H_5	70[b]	**5d**	$CHNO_3C_6H_5$	C_6H_5	90
3e	COC_6H_5	CH_3	**4e**	COC_6H_6	CH_2Br	65[b]	**5e**	COC_6H_5	CH_2NO_3	71

[a] CH_3OH as solvent. [b] $CH_3COOC_2H_5$ as solvent. [c] Satisfactory analyses (±0.3% for C, H, N, and Br if present) were recorded for **4b,d** and **5a,b,d**. Compounds **1c**, **5c**, and **5e** could not be obtained in analytical purity.

2-(Bromobenzyl)-3-phenylquinoxaline 1,4-Dioxide (4d). The same procedure as for **4b** was followed using 2-benzyl-3-phenylquinoxaline 1,4-dioxide[5] (**3d**, 1.29 g, in 75 mL of ethyl acetate) and bromine (0.64 g, in 10 mL of ethyl acetate); reaction time 4 h. **4d**: 1.12 g (70%); mp 178–180 °C; IR (cm^{-1}) 3100, 3020, 1600, 1510, 1490, 1440, 1360, 1335, 1290, 1270, 1085, 1020, 1000, 990, 965, 890, 855, 815, 765, 750, 715, 700, 660.

***trans*-1,4-Dibromo-1,2,3,4-tetrahydrophenazine 5,10-Dioxide (4a).** To a magnetically stirred suspension of 1,2,3,4-tetrahydrophenazine 5,10-dioxide (**3a**, 3.20 g) in methanol (30 mL) was added bromine (5.64 g) dropwise. Stirring was continued in the dark for 5 days at room temperature. The resulting yellow precipitate was collected by suction filtration, washed with cold CH_3OH and ether, and recrystallized from CH_3OH–$CHCl_3$. **4a**: 5.11 g (87%); mp 179–181 °C (lit.[7] mp 171–173 °C).

Preparation of Quinoxaline 1,4-Dioxide Nitrate Esters. General Procedure. A solution of silver nitrate (7.1 mmol) and the specific bromo derivative (**1b**, **4a–e**; 1.3 mmol) in CH_3CN (30 mL) was stirred in the dark at room temperataure for 1.5 h unless otherwise specified. The solution was filtered and the precipitate was washed twice with $CHCl_3$ (30 mL each). The combined filtrates were concentrated. Ethyl acetate (100 mL) was added to the concentrate and any precipitate formed was filtered out. The ethyl acetate solution was washed twice with water (50 mL each), the organic layer was dried, and ethyl acetate was evaprated under reduced pressure to yield products **1c** and **5a–e** which were recrystallized from $CHCl_3$–CH_3OH (Table I).

1c (R_1 = CH_2NO_3, R_2 = H): mp 137–139 °C; yield 56%; IR (cm^{-1}) 3100, 3030, 1660, 1640, 1550, 1510, 1370, 1355, 1285, 1270, 1240, 1160, 1095, 1045, 1000, 975, 945, 860, 850, 785, 755, 710, 660; NMR δ 5.90 (s, 2 H), 8.00 (m, 2 H), 8.63 (m, 3 H).

5a (R_1,R_2 = $-CHNO_3(CH_2)_2CHNO_3-$): mp 205–207 °C dec; yield 97%; reaction time 20 min; IR (cm^{-1}) 3100, 3000, 1650, 1515, 1445, 1370, 1330, 1315, 1275, 1100, 1015, 940, 910, 845, 785, 670; NMR δ 2.3 (br s, 4 H), 6.8 (br s, 2 H), 7.9 (m, 2 H), 8.6 (m, 2 H).

5b (R_1,R_2 = $-CHNO_3(CH_2)_3CHNO_3$): mp 196–198 °C yield 70%; IR (cm^{-1}) 3080, 2940, 1640, 1500, 1445, 1355, 1320, 1275, 1110, 1070, 1045, 980, 955, 915, 855, 800, 770, 660; NMR δ 2.03 (br s, 6 H), 7.2 (m, 2 H), 7.9 (m, 2 H), 8.6 (m, 2 H).

5c (R_1 = $COCH_3$, R_2 = CH_2NO_2): mp 136–138 °C dec; yield 82%; IR (cm^{-1}) 3110, 2960, 2940, 1715, 1665, 1605, 1445, 1430, 1375, 1340, 1290, 1270, 1105, 1055, 980, 955, 855, 790, 760, 700, 690; NMR δ 2.80 (s, 3 H), 5.86 (s, 2 H), 7.93 (m, 2 H), 8.63 (m, 2 H).

5d (R_1 = $CHNO_3C_6H_5$, R_2 = C_6H_5): mp 138–140 °C dec; yield 90%; IR (cm^{-1}) 3060, 1640, 1495, 1455, 1445, 1365, 1325, 1280, 1270, 1090, 1025, 1050, 995, 980, 940, 925, 905, 860, 845, 785, 770, 730, 715, 705, 670.

5e (R_1 = COC_6H_5, R_2 = CH_2NO_3): mp 177–180 °C; yield 71%; IR (cm^{-1}) 3100, 3050, 1655, 1600, 1585, 1510, 1440, 1430, 1330, 1275, 1245, 1185, 1170, 1110, 1065, 1030, 1010, 950, 880, 840, 820, 790, 760, 740, 710, 690, 665; NMR δ 5.86 (s, 2 H), 7.80 (m, 7 H), 8.70 (m, 2 H).

Methyl (Quinoxalinylmethylene)carbazate (Mecadox, 2). A solution of 2-[(nitrooxy)methyl]quinoxaline 1,4-dioxide (**1c**, 1.52 g) and methyl carbazate (3.24 g) in dichloromethane (15 mL) was heated on a steam bath to dissolve the starting materials. The reaction mixture was allowed to stand overnight at room temperature. The product precipitated out and was collected, washed with dichloromethane, and recrystallized from ethanol: 1.60 g (96%); mp 243–245 °C; IR (cm^{-1}) 3220, 1755, 1555, 1535, 1445, 1385, 1335, 1245, 1205, 1160, 1135, 1095, 1055, 995, 845, 795, 775. The product was identical with an authentic sample (mmp, TLC, IR) prepared by an independent method.[8]

1-Hydroxyphenazine 5,10-Dioxide (8). A solution of 1,4-bis(nitrooxy)-1,2,3,4-tetrahydrophenazine 5,10-dioxide (**5a**, 0.17 g) and triethylamine (0.14 mL) in dichloromethane (5 mL) was refluxed for 35 min. The dichloromethane was evaporated and product **8** was isolated by TLC: 0.06 g (55%); mp 187–189 °C (lit.[9] mp 184–185 °C).

2-Benzoyl-3-phenylquinoxaline 1,4-Dioxide (9). The same procedure used in the preparation of **8** was followed with 2-[[(phenyloxy)nitros]oxy]-3-phenylquinoxaline 1,4-dioxide (**5d**, 0.13 g) and triethylamine (0.25 mL) in 5 mL of dichloromethane; reaction time 1.25 h. Product **9** was purified by TLC: 0.08 g (72%); 228–230 °C (lit.[10] mp 234 °C).

Registry No. **1a**, 6639-86-7; **1b**, 18080-66-5; **1c**, 93222-85-6; **2**, 6804-07-5; **3b**, 18965-43-0; **3c**, 13297-17-1; **3d**, 53326-80-0; **3e**, 19803-53-3; **4a**, 93222-83-4; **4b**, 18965-53-2; **4c**, 60949-39-5; **4d**, 93222-84-5; **4e**, 62686-03-7; **5a**, 93222-86-7; **5b**, 93222-87-8; **5c**, 93222-88-9; **5d**, 93222-89-0; **5e**, 93222-90-3; **8**, 18274-55-0; **9**, 13494-38-7; silver nitrate, 7761-88-8; methyl carbazate, 6294-89-9; dichloromethane, 75-09-2.

(7) Gordon, P. N.; Kent, R. E.; Ursprung, J. J. U.S. Pat. 2291937, 1960; *Chem. Abstr.* **1960**, *54*, 15411b.
(8) Issidorides, C. H.; Saikali, J., unpublished results.
(9) Issidorides, C. H.; Atfah, M. A.; Sabonji, J. J.; Sidani, A. R.; Haddadin, M. J. *Tetrahedron* **1978**, *34*, 217.
(10) Issidorides, C. H.; Haddadin, M. J. *J. Org. Chem.* **1966**, *31*, 4067.

Heteroacylsilanes: Synthesis and Synthetic Potentialities of New Nucleophilic Acylation Agents

Alfredo Ricci, Alessandro Degl'Innocenti,* Stefano Chimichi, Mariella Fiorenza, and Gabriele Rossini

Centro di Studio del C.N.R. sulla Chimica e la Struttura dei Composti Eterociclici e loro Applicazioni, c/o Istituto di Chimica Organica dell'Universitâ, I-50121 Firenze, Italy

Hans Jurgen Bestmann

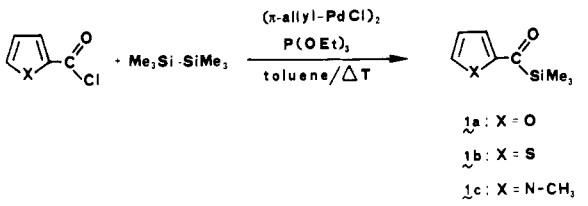
Institut für Organische Chemie der Universitat der Erlangen-Nürnberg, D-852 Erlangen, FRG

Received March 12, 1984

As a part of our continuing interest in the chemistry of acylsilanes, we describe here the first synthesis dealing with the hitherto unknown class of heteroacylsilanes and the

0022-3263/85/1950-0130$01.50/0

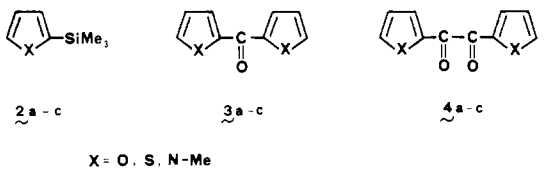
Scheme I



preliminary results on their potential use as nucleophilic heteroacylation agents.

The high reactivity of five-membered heterocyclic rings toward brominating and metalating agents, coupled with the easy desilylation of the target compounds prevented use of the previously reported methods, based mainly upon the hydrolysis of (*gem*-dibromobenzyl)trimethylsilanes[1] and on the Corey–Seebach procedure[2] for the synthesis of 2-furoyl- (**1a**), 2-thenoyl- (**1b**), and (2-*N*-methylpyrroyl)-trimethylsilane (**1c**).[3] However, the transition metal catalyst based procedure of forming C–Si bonds, first described by Atwell and Bokerman[4] and further developed by other authors,[5] proved (Scheme 1) to be suitable for the synthesis of **1a–c**, starting from the corresponding acyl chlorides.

Among the transition-metal catalysts, the $(\pi\text{-allyl-PdCl})_2$ complex and $(CH_3COO)_2Pd$ appeared to be the most effective, whereas the use of $(PPh_3)_2PdI_2$ or $(PPh_3)_4Pd$ led to a sizeable lowering of yields. All these reactions were run in the presence of 10% $P(OEt)_3$ and 5% of the catalyst, with toluene as solvent. Yields ranged from 50% to 70% and (see Experimental Section) the products were isolated by column chromatography. Careful GC/MS analysis of the crude reaction mixtures, revealed, besides **1a–c**, byproducts (**2a–c**, **3a–c**, **4a–c**) whose relative



amounts were related to the nature of the catalyst as well as that of the heterocyclic ring. Attempted silylation of pyridine-2-carbonyl chloride according to the previously outlined procedure failed, and not even traces of the expected ketone were detected by GC/MS analysis.[6]

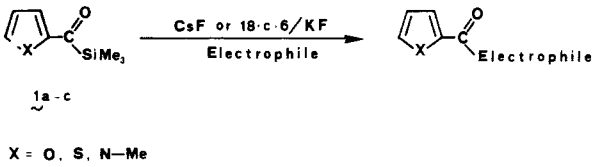
The new heteroacylsilanes showed unusual spectroscopic features, some of them previously noticed[7] in the case of aroylsilanes and of the aliphatic analogues. The ^{13}C and ^{29}Si NMR chemical shifts of **1a–c** collected in Table I together with those of reference compounds are strongly indicative of an unexpectedly low electron density on the carbonyl carbon, whereas the high upfield shift of the ^{29}Si

Table I. Spectral Data of Heteroacylsilanes

compd	^{13}C NMR,[a] $\delta_{C=O}$	^{29}Si NMR,[a] δ	IR,[b] $\nu_{C=O}$
1a	220.7[c]	−6.3[c]	1590
1b	223.1	−6.9	1580
1c	220.0	−8.8	1575
$PhCOSi(CH_3)_3$	234.2[d]	−7.9[d]	1617[d]
$PhCOCH_2Si(CH_3)_3$	197.5	2.3	1670[e]
$PhCOC(CH_3)_3$	206.9[f]		1680[g]
$PhCH_2Si(CH_3)_3$		1.2[h]	

[a] Spectra recorded in C_6D_6 (ppm) with respect to internal Me_4Si. [b] ν in cm^{-1}, as film liquid. [c] In $CDCl_3$. [d] Lit. 236.7, ref 7b. [e] Lutsenko, I. F.; Baukov, Yu. I.; Dudukina, O. V.; Kramarova, E. N. *J. Organomet. Chem.* **1968**, *11*, 35. [f] Dhami, K. S.; Stothers, J. B. *Can. J. Chem.* **1965**, *43*, 479. [g] Adelfang, J. L.; Hess, P. H.; Cromwell, N. H. *J. Org. Chem.* **1961**, *26*, 1402. [h] 0.4 (neat), Chuy, N. D.; Chvalovsky, V.; Schraml, J.; Magi, M.; Lipmaa, E. *Collect. Czech. Chem. Commun.* **1977**, *42*, 306.

Scheme II



of **1a–c** compared with that of benzyltrimethylsilane suggests abnormally high electron density on the silicon atom. Also the IR frequencies collected in Table I support the inadequacy of the ketonic structure for a description of the ground-state features of compounds **1a–c**.[8]

The behavior of aroylsilanes and allied substrates as nucleophilic acylation agents, being outlined in one of our previous papers[9] and shortly after by Heathcock et al.,[10] we thought it worthwhile to extend this reversed polarity reaction to the synthetically attractive transfer of pyrroyl, thenoyl, and furoyl anions by reacting **1a–c** under F^- catalysis with a variety of representative carbon electrophiles (Scheme II).

Satisfactory, although not optimized, yields of the products of nucleophilic heteroacyl transfer were obtained for furoyl- and thenoyltrimethylsilane (Table II), whereas only trace amounts (<10%) of the expected products were revealed by GC/MS analysis with pyrroyltrimethylsilane which was recovered unchanged from the reaction mixture. This lack of reactivity is more likely due to steric rather than electronic effects. In fact, according to a previously reported mechanism the attack of the F^- ion in this class of compounds is expected to take place at the carbonyl carbon[11] which in the case of **1c** is much more sterically hindered due to the presence of the $Si(CH_3)_3$ and NCH_3 groups.

With most reactive electrophiles such as benzaldehyde a clean transfer of the heteroacyl moiety was observed, whereas with aliphatic aldehydes the reaction proved to be successful only when long chain derivatives such as butyraldehyde were used in 1,3-dimethylimidazolidin-2-one (DMI) as solvent, (entry 4 in Table II). Any attempt at functionalizing acetaldehyde failed, the main reaction being desilylation of the acylsilane.

Reactions of compounds **1a–c** with ketones according to Scheme II were also unsuccessful.

(1) (a) Brook, A. G. *Adv. Organomet. Chem.* **1968**, *7*, 95. (b) Degl'Innocenti, A.; Walton, D. R. M.; Seconi, G.; Pirazzini, G.; Ricci, A. *Tetrahedron Lett.* **1980**, *21*, 3927.

(2) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434.

(3) Only in the case of thiophene derivative was the bromination based procedure partially successful (yields ca. 25%).

(4) Atwell, W.; Bokerman, G. N. U.S. Pat. 3 772 347, 1973.

(5) (a) Eaborn, C.; Griffiths, R. W.; Pidcock, A. *J. Organomet. Chem.* **1982**, *225*, 331. (b) Yamamoto, K.; Suzuki, S.; Tsuji, J. *Tetrahedron Lett.* **1980**, *21*, 1653.

(6) The difficulties in getting the pure pyridine-2-carbonyl chloride, coupled with the expected high reactivity of the C-Si bond, might be responsible for the failure of this reaction.

(7) (a) Ramsey, B. G.; Brook, A. G.; Bassindale, A. R.; Bock, M. *J. Organomet. Chem.* **1974**, *11*, 751. (b) Dexheimer, E. M.; Buell, G. R.; Le Croix, C. *Spectrosc. Lett.* **1978**, *11*, 751.

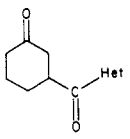
(8) Ab initio calculations now in progress seems to point out that a carbenoid like structure might also be worth taking into consideration.

(9) Degl'Innocenti, A.; Pike, S.; Walton, D. R. M.; Seconi, G.; Ricci A.; Fiorenza, M. *J. Chem. Soc.; Chem. Commun.* **1980**, 1201.

(10) Schinzer, D.; Heathcock, C. H. *Tetrahedron Lett.* **1981**, *22*, 1881.

(11) Pietropaolo, D.; Fiorenza, M.; Ricci, A.; Taddei, M.; *J. Organomet. Chem.* **1980**, *197*, 7.

Table II. Reactions of Heteroacylsilanes 1a-c with Carbon Electrophiles

entry	compd[a]	electrophile	catlyst[b]/condns[c]	product	% yield[e]	MS (M^+), m/e	ref
1	1a	PhCHO	CsF/rt, 6 h	HO O PhCHC-Het	68[f]	202	13
2	1b	5	CsF/rt, 6 h	11a-c	60[f]	218	14
3	1c		CsF/reflux, 20 h		10	215	
4	1a	$CH_3(CH_2)_2CHO$ 6	CsF/rt, 3 h[d]	HO O $CH_3(CH_2)_2CHC$-Het 12a	55	168	15
5	1a	 7	CsF/reflux, 12 h	 13a, b	30	192	
6	1b		CsF/reflux, 10 h		40	208	
7	1a	$PhCOCH_2Br$	CsF/reflux, 12 h	$PhCOCH_2COHet$	40	214	16
8	1b	8	CsF/reflux, 12 h	14a-c	50	230	17
9	1a	$PhCH_2Br$	18.C.6/KF/rt, 10 h	$PhCH_2COHet$	45	186	18
10	1b	9	18.C.6/KF/rt, 10 h	15a-c	50	202	19
11	1c		CsF/reflux, 20 h		<10	199	
12	1a	$PhCH{=}CHCH_2I$ 10	CsF/rt, 3 h[d]	O $PhCH{=}CHCH_2C$-Het 16a	45	212	

[a] 1:1 molar ratio of the reagents. [b] 10% molar with respect to the reagents. [c] Unless otherwise specified all reactions were run in anhydrous THF. [d] Reaction run in 1,3-dimethylimidazolidin-2-one (DMI) as solvent. [e] Determined by quantitative GC/MS analysis. [f] Isolated yield of chromatographically pure product.

When less reactive electrophiles such as 2-cyclohexenone were used, thenil and furil were formed besides the expected products,[12] thus lowering the overall yields of the reactions. In this case interaction of the heteroacyl anion with the electrophile occurred in a regioselective fashion at position 3 (entries 5 and 6 in Table II).

Finally, reactions employing allyl bromide as an electrophile afforded complex reaction mixtures in which ca. 2% of the expected product was present besides unreacted starting material and sizeable amounts of unidentified byproducts. Much better results were achieved however when the reaction was performed in DMI employing phenyl allyl iodide as an electrophile.

Experimental Section

General Methods. ^1H, ^{13}C, and ^{29}Si nuclear magnetic resonance spectra were obtained on Perkin-Elmer R-32 or Varian FT-80A spectrometers, infrared spectra on a Perkin-Elmer 283 spectrophotometer, and mass spectra on a Varian MAT 112 or HP 5970A apparatus. NMR spectra were measured in CCl_4, $CDCl_3$, or C_6D_6 solutions, and, when not otherwise specified, IR spectra were recorded as neat liquids.

Starting materials were commercially available except for 2-*N*-methylpyrrolecarbonyl chloride which was obtained from the corresponding acid by treatment under reflux with an excess of $SOCl_2$ in dimethoxyethane, bp 84 °C (1 mmHg).

THF was freshly distilled from $LiAlH_4$ and toluene from sodium. All reactions were run under an atmosphere of dry nitrogen.

GC analyses were performed on a 5% OV 101 column on Chromosorb and preparative chromatography on a Jobin Yvon Chromatospac Prep. 10 with Merck 60H silica gel as the stationary phase. Column chromatography was carried out on silica gel grade 923 or "Florisil".

Elemental analyses were performed on a Perkin-Elmer 240C apparatus.

2-Furoyltrimethylsilane (1a). A dry, nitrogen-purged round-bottomed flask is charged with 0.041 g (0.112 mmol) of $(\pi$-allyl-$PdCl)_2$, 0.073 g (0.075 mL, 0.44 mmol) of freshly distilled $P(OEt)_3$, and 0.68 g (0.96 mL, 4.7 mmol) of hexamethyldisilane, the mixture is stirred for 5 min, and a 0.584-g (0.441 mL, 4.4 mmol) sample of 2-furoyl chloride and 1.5 mL of toluene are then added via a syringe. The homogeneous solution thus obtained is refluxed for 6 h and then cooled, and the progression of the reaction was monitored by GC. The obtained mixture is taken up in ether, filtered, and chromatographed by using pentane/ether [5:1 v/v] as the eluent. After a short forerun of unidentified material, 2-furoyltrimethylsilane is collected and the solvent evaporated to obtain a greenish yellow oil: 0.443 g (60% yield); IR (neat) 3120, 2960, 1590, 1250, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.24 (s, 9 H, $Si(CH_3)_3$), 6.48 (dd, $J_{4,5}$ = 1.9 Hz, $J_{4,3}$ = 3.8 Hz, 1 H, H-4), 6.92 (d, $J_{5,3}$ = 1.9 Hz, 1 H, H-5), 7.56 (d, $J_{3,5}$ = 3.8 Hz, 1 H, H-3); ^{13}C NMR ($CDCl_3$) δ 220.7 (C=O), 158.8 (C-2), 145.8 (C-5), 113.9 (C-3),[20] 112.0 (C-4),[20], -2.45 ($Si(CH_3)_3$). Anal. Calcd for $C_8H_{12}O_2Si$: C, 57.09; H, 7.20. Found: C, 57.16; H, 7.38.

2-Thenoyltrimethylsilane (1b). Following the procedure described for **1a**, from 0.879 g of 2-thenoyl chloride were obtained, after purification by elution on silica gel with pentane/ether (5:1 v/v) as the eluent, 0.405 g (50% yield) of 2-thenoyltrimethylsilane: IR (neat) 3100, 2960, 1580, 1250, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.19 (s, 9 H, $Si(CH_3)_3$), 6.91 (dd, $J_{4,5}$ = 5 Hz, $J_{4,3}$ = 4 Hz, 1 H, H-4), 7.26 (dd, $J_{5,4}$ = 5 Hz, $J_{5,3}$ = 1 Hz, 1 H, H-5), 7.67 (dd, $J_{3,4}$ = 4 Hz, $J_{3,5}$ = 1 Hz, 1 H, H-4); ^{13}C NMR (C_6D_6) δ 223.1 (C=O), 151.3 (C-2), 132.7 (C-5),[20] 132.3 (C-3),[20] 128.0 (C-4), -1.8 ($Si(CH_3)_3$). Anal. Calcd for $C_8H_{12}OSSi$: C, 52.13; H, 6.56. Found: C, 51.94; H, 6.83.

[(1-Methyl-2-pyrrolyl)carbonyl]trimethylsilane (1c). A 2.0-g (14 mmol) sample of *N*-methylpyrrole-2-carbonyl chloride was reacted as for **1a** to give 1.25 g (50% yield) of the silylated ketone after elution on Florisil with pentane/ether (5:1 v/v) as the eluent: IR (neat) 3120, 2960, 1575, 1250, 840 cm^{-1}; ^1H NMR (CCl_4) δ 0.25 (s, 9 H, $Si(CH_3)_3$), 3.82 (s, 3 H, NCH_3), 6.03 (dd, $J_{4,5}$ = 2.6 Hz, $J_{4,3}$ = 1.8 Hz, 1 H, H-4), 6.63 (dd, $J_{5,4}$ = 3.0 Hz, $J_{5,3}$ =

(12) Variable amounts of benzil were also formed in the reactions of acylsilane and carbon electrophiles.

(13) Okuzumi, T. *Nippon Kagaku Zasshi* **1961**, *82*, 1235-40; *Chem. Abstr.* **1962**, *57*, 15090d.

(14) Wright, W. B.; Marsico, J. W.; Marsico, J. W. U.S. Pat. 4 283 334, 1981.

(15) Stetter, H.; Daembkes, G. *Synthesis* **1977**, 403.

(16) Lesiak, T.; Nielek, S. *Rocz. Chem.* **1970**, *44*, 2467.

(17) Harris, S. R.; Levine, R. *J. Am. Chem. Soc.* **1948**, *70*, 3360.

(18) Tagaki, S.; Yasuda, H.; Kono, M. *Yakugaku Zasshi* **1961**, *81*, 1559–63; *Chem. Abstr.* **1962**, *57* 16581i.

(19) Meth-Cohn, O.; Gronowitz, S. *Acta Chem. Scand.* **1966**, *20*, 1577.

(20) These assignments may be reversed.

1.0 Hz, 1 H, H-5), 6.87 (dd, $J_{3,4}$ = 1.6 Hz, $J_{3,5}$ = 1.0 Hz, 1 H, H-3); ^{13}C NMR (C_6D_6) δ 220.0 (C=O), 136.2 (C-2), 130.2 (C-5),[20] 121.7 (C-3),[20] 108.2 (C-4), 37.4 (NCH_3), -1.4 ($Si(CH_3)_3$). Anal. Calcd for $C_9H_{15}NOSi$: C, 59.61; H, 8.35. Found: C, 59.30; H, 8.30.

General Procedure for the Reaction of the Heteroacylsilanes 1a-c with Electrophiles. A dry, nitrogen-purged flask is charged with CsF (0.055 mmol) (dried for 3 h at 150 °C under high vacuum) and THF (1 mL). Equimolar amounts (0.55 mmol) of the acylsilane and of the electrophile dissolved in THF (1 mL) are then added, and the mixture is stirred and eventually refluxed. Reaction progress is monitored by GC, and the obtained mixtures are analyzed by GC/MS analysis.

Reaction of 2-Thenoyltrimethylsilane (1b) with Benzaldehyde. To a stirred suspension of CsF (0.008 g, 0.055 mmol) in 1 mL of anhydrous THF is added dropwise a solution of **1b** (0.10 g, 0.55 mmol) and benzaldehyde (0.058 g, 0.55 mmol) in 1 mL of THF. The mixture is stirred for 6 h at room temperature, then taken up in ether, and washed 3 times with water, and the organic layer is dried over Na_2SO_4. Evaporation of the solvent affords a gummy solid, which when washed with cold ether (1 mL) gives **11a** (0.08 g, 68%); IR (KBr) 3440, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.40 (d, $^3J_{CH-OH}$ = 5 Hz, 1 H, OH), 5.75 (d, $^3J_{CH-OH}$ = 5 Hz, 1 H, CH), 6.97-7.72 (m, 8 H, aromatic and heterocyclic H).

Registry No. **1a**, 80671-28-9; **1b**, 88372-95-6; **1c**, 93303-99-2; **4a**, 492-94-4; **4b**, 7333-07-5; **5**, 100-52-7; **6**, 123-72-8; **7**, 52844-25-4; **8**, 70-11-1; **9**, 100-39-0; **10**, 59625-54-6; **11a**, 36715-43-2; **11b**, 36715-42-1; **11c**, 93304-00-8; **12a**, 20894-97-7; **13a**, 93304-01-9; **13b**, 93304-02-0; **14a**, 5910-23-6; **14b**, 10471-74-6; **15a**, 86607-65-0; **15b**, 13196-28-6; **15c**, 93304-03-1; **16a**, 93304-04-2; DMI, 80-73-9; $PhCOSi(CH_3)_3$, 5908-41-8; $PhCOCH_2Si(CH_3)_3$, 13735-78-9; $((\pi\text{-allyl})PdCl)_2$, 12012-95-2; hexamethyldisilane, 1450-14-2; 2-furoyl chloride, 527-69-5; 2-thenoyl chloride, 5271-67-0; *N*-methylpyrrole-2-carbonyl chloride, 26214-68-6.

Reduction of α,β-Unsaturated Nitro Compounds with Boron Hydrides: A New Route to N-Substituted Hydroxylamines

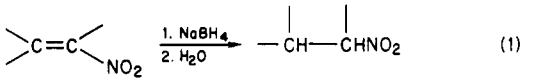
M. Soubei Mourad, Rajender S. Varma, and George W. Kabalka*

Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600

Received April 11, 1984

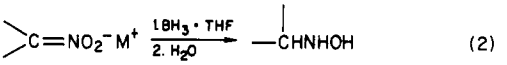
In connection with our ongoing program directed toward the synthesis of radiolabeled amphetamine derivatives,[1] we required a convenient method for the preparation of hydroxylamines. A survey of the literature indicated that the most convenient syntheses of N-substituted hydroxylamines involved the reduction of conjugated nitroalkenes.[2,3] Other methods include the reduction of oximes[4] and nitro salts[5] or the oxidation of amines.[6] The latter methods are involved and are not readily amenable to the synthesis of the desired target molecules.

Since catalytic hydrogenation of conjugated nitroalkenes is reported to be a complex reaction,[2] we investigated the reduction of conjugated nitroalkenes utilizing lithium aluminum hydride.[3] Unfortunately, in our hands, mixtures were obtained under a variety of conditions. We then investigated the reduction of conjugated nitroalkenes with boron hydrides. It had been reported that the sodium borohyride reduction of α,β-unsaturated nitroalkenes produces the corresponding nitroalkanes (eq 1).[7] In a later



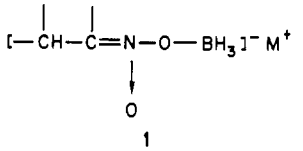
(1)

study, Feuer reported[5] that nitro salts (nitronates) are readily reduced to hydroxylamines by borane complexes, eq 2 (i.e., the nitro compounds are unreactive). These



(2)

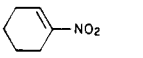
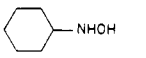
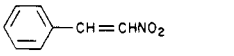
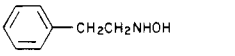
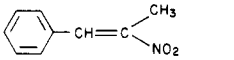
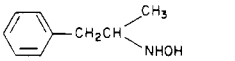
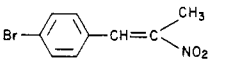
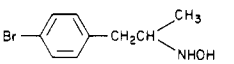
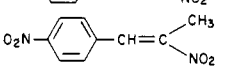
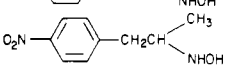
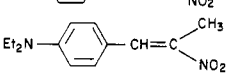
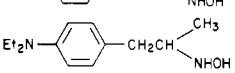
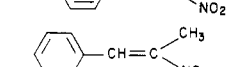
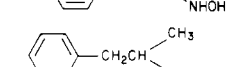
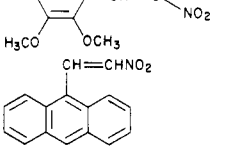
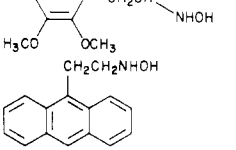
reactions presumably occur through a common intermediate 1, which can then be hydrolyzed directly to nitroalkane or reduced with a borane complex to yield hydroxylamine after hydrolysis. It occurred to us that these reactions could be utilized to prepare the desired hydroxylamine directly from the conjugated nitroalkenes.



1

We have found that sodium borohydride catalyzes the reaction of borane complexes with α,β-unsaturated nitro compounds. The reaction is straightforward. A catalytic amount of sodium borohydride is added to a normally unreactive mixture of the α,β-unsaturated nitro compound and the borane complex at room temperature. The pure

Table I. Reduction of α,β-Unsaturated Nitro Compounds with BH_3•THF and Sodium Borohydride (Catalytic Amount)

starting material	product	time, h	yield,[a] %
		0.5	85
		1	80
		2	74
		1	78
		1.5	77
		3	85
		1	70
		1	74

[a] Isolated yield.

(1) Kabalka, G. W. *Acc. Chem. Res.* **1984**, *17*, 215 and references cited therein.
(2) Coutts, R. T.; Malicky, J. L. *Can. J. Chem.* **1974**, *52*, 395.
(3) Gilsdorf, R. T.; Nord, F. F. *J. Am. Chem. Soc.* **1952**, *74*, 1837.
(4) (a) Feuer, H.; Vincent, B. F., Jr.; Bartlett, R. S. *J. Org. Chem.* **1965**, *30*, 2877. (b) Gribble, G. W.; Leiby, R. W.; Sheeha, M. N. *Synthesis* **1977**, 856. (c) Benington, F.; Morin, R. D.; Clark, L. C., Jr. *J. Med. Chem.* **1965**, *8*, 100.
(5) Feuer, H.; Bartlett, R. S.; Vincent, B. F., Jr.; Anderson, R. S. *J. Org. Chem.* **1965**, *30*, 2880.
(6) (a) Beckett, A. H.; Coutts, R. T.; Ogunbona, F. A. *Tetrahedron* **1973**, *29*, 4189. (b) Beckett, A. H.; Haya, K.; Jones, G. R.; Morgan, P. H. *Tetrahedron* **1975**, *31*, 1531.
(7) Shechter, H.; Ley, D. E.; Roberson, E. B., Jr. *J. Am. Chem. Soc.* **1956**, *78*, 4984.

0022-3263/85/1950-0133$01.50/0