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SYNTHESIS AND REARRANGEMENT OF CYCLOADDUCTS FROM TRIMETHYLSILANECARBONITRILE OXIDE

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Abstract - The cycloadducts from trimethylsilanecarbonitrile oxide and ethylenic or acetylenic compounds easily rearrange to open-chain intermediates, which, in turn, are hydrolysed respectively to β-hydroxynitriles and β-oxonitriles. The cycloadducts of the same nitrile oxide with sulfur dioxide and sulfinylamines are unstable, too, leading respectively to trimethylsilylisocyanate and trimethylsilylcarbodiimides. All these reactions are of preparative interest, in comparison with previous methods.

Trimethylsilanecarbonitrile oxide (1), unlike common aliphatic and aromatic nitrile oxides, does not dimerize to the corresponding furoxan, therefore is remarkably stable. However, the nitrile oxide (1) resembles the parent compounds in their 1,3-dipolar behaviour, as shown by two preliminary examples.[1] Cycloadditions are now extended to a wider range of ethylenic and acetylenic compounds and to other unsaturated substrates, namely sulfur dioxide and *N*-sulfinylamines. The observed regioselectivities, illustrated in the Scheme, are the same as found for the cycloadducts of fulminic acid[2] or of other nitrile oxides to the same substrates.[3]

A common feature in the behaviour of all the primary cycloadducts is their thermal instability: only the 4,5-dihydroisoxazoles (3) can be evidenced (3c) or isolated [(3a) and (3b)], but on heating they undergo ring-opening with cleavage of the N-O bond. The other cycloadducts (7) and (11) cannot even be evidenced during the reaction and directly the rearranged products, respectively (8) and (12), are obtained.

CYCLOADDITIONS TO ETHYLENIC BONDS

Only one regioisomer is evidenced (n.m.r.) in the reactions of the nitrile oxide (1) with styrene (2a) and with methyl methacrylate (2b): the structures of the adducts

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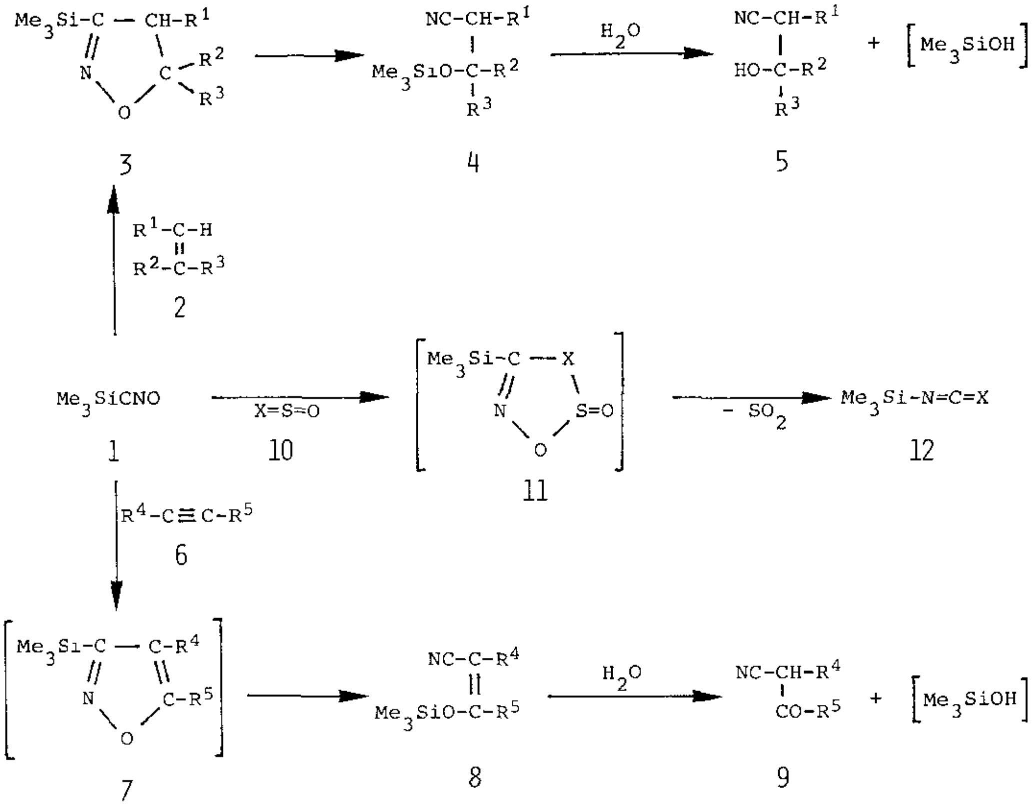
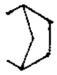


2 through 5

a: $R^1 = R^2 = H$; $R^3 = Ph$

b: $R^1 = H$; $R^2 = Me$; $R^3 = COOMe$

c: R^1-R^2=  ; $R^3 = H$

6 through 9

d: $R^4 = R^5 = COOMe$

e: $R^4 = H$; $R^5 = Ph$

10 through 12

f: X = O

g: X = N-Ph

h: X = N-(4-MeC_6H_4)

i: X = N-(4-$NO_2C_6H_4$)

(3a) and (3b) are established on the basis of their n.m.r. spectral data and of the loss of the fragment CH_2CN, observed in the mass spectra of the nitriles (4a) and (4b). In the cycloaddition to norbornene (2c), the sole *exo*-approach is observed, as indicated by the coupling of each isoxazoline H-atom with the adjacent bridge-head H-atoms, undetectable in the adduct (3c) and lower than 2 Hz in the evolution products (4c) and (5c).

The rearrangement of the cycloadducts (3) to the silylethers (4) is slowed down by dilution: thus, almost pure adducts (3a) and (3b) could be obtained from the reactions in boiling benzene, and the adduct (3c) was detected if the preparation was carried out in 0.4 M solution, not in 1 M solution. Attempted kinetic measurements (^1H n.m.r., 80°C in benzene) of the rearrangement of the adduct (3a) to the silylether (4a) did not give clean results; however, slowing down of the process by dilution was confirmed.

CYCLOADDITIONS TO ACETYLENIC BONDS

3-Trimethylsilylisoxazoles (7) are apparently less stable than 3-trimethylsilyl-4,5-dihydroisoxazoles (3), since, from the reactions of the nitrile oxide (1) with acetylenic compounds (6), directly the rearranged products (8) are evidenced by ^1H n.m.r. spectroscopy. In addition, these are handled with difficulty, owing to their immediate hydrolysis even with atmospheric moisture. With a monosubstituted acetylene, like phenylacetylene (6e), a considerable amount of the adduct with fulminic acid is produced, due to the reaction $Me_3SiCNO + Ph\text{-}C{\equiv}CH \longrightarrow HCNO + Ph\text{-}C{\equiv}C\text{-}SiMe_3$ (cycloadditions on the last compound are slower, so they do not occur significantly).

CYCLOADDITIONS TO S=O AND S=N BONDS

Aromatic nitrile oxides are known to react with sulfur dioxide to give isolable cycloadducts, which in turn decompose thermally to sulfur dioxide and arylisocyanates.[4,5] The same reaction sequence, carried out on trimethylsilanecarbonitrile oxide (1), afforded quantitatively trimethylsilylisocyanate (12f), but the intermediate 5-trimethylsilyl-1,3,2,4-dioxathiazole S-oxide (11f) was not detected.

Similarly, the nitrile oxide (1) reacts with *N*-sulfinylamines (10g-i), as other nitrile oxides do,[6] but again the cycloadducts (11g-i) are unstable, yielding spontaneously the carbodiimides (12g-i) and sulfur dioxide. The last compound converts part of the nitrile oxide (1) into the isocyanate (12f), as reported above, thus mixtures of the products (12f) and (12g-i) are in general obtained. However, yields of the carbodiimides (12 g-i) are increased to acceptable values (12g, 79%; 12h, 30%; 12i, about 60%, impure) by adding very slowly an excess of nitrile oxide (1).

DISCUSSION

The intermediate cycloadducts (3), (7), and (11) appear to be much less stable than known analogous heterocycles bearing various substituents instead of the trimethylsilyl group.

Isoxazole derivatives are in general thermally stable, and only 3-unsubstituted compounds are isomerized by bases in the cold (isoxazoles) or on heating (4,5-dihydroisoxazoles). Kinetic studies on 4-aryl and 5-arylisoxazoles have shown that isomerization occurs by a second-order concerted process;[7] similarly, the isomerization of the cycloadduct (3a) to the nitrile (4a) is not a first-order reaction, though its mechanism is not yet fully understood. Possibly, more than one path is operating, involving an additional molecule of either the adduct (3a), or the product (4a), or some impurity, like (5a).

The reaction sequence converting an olefinic compound into the corresponding

β-hydroxynitrile upon nitrile oxide cycloaddition, followed by ring-opening of the intermediate 4,5-dihydroisoxazole derivative, has been employed on preparative purposes. As a consequence of the stereospecificity of the cycloaddition, the cyanohydroxylation is expected to occur *cis*-stereospecifically. Removal of the 3-substituent, such as H,[2] COOEt,[8] or $PhSO_2$,[9] was achieved in rather drastic conditions (strong bases and heating). The analogous process, starting from trimethylsilanecarbonitrile oxide (1), is carried out under milder conditions (gentle warming, if any; no base required) with improvement of both yield and purity of the products (5). For instance, the cyanohydroxynorbornane (5c) prepared *via* fulminic acid has been described as a low-melting solid (m.p. 35-38°C)[2] and later, *via* benzenesulfonylcarbonitrile oxide, as an oil "which refused to crystallize".[9] By the present method, the same compound (5c) is obtained as a solid, m.p. 84-85°C; however, the spectra (i.r., ^{1}H and ^{13}C n.m.r.) of the three samples are identical, thus indicating that the difference in the melting points is a matter of purity.

EXPERIMENTAL

Melting points were determined on a RCH Kofler apparatus. Vacuum distillations were carried out by a Büchi GKR-50 Kugelrohr distillator: the oven temperature is reported. I.r. spectra were recorded with a Perkin-Elmer 283 spectrophotometer, ^{1}H n.m.r. spectra with a Perkin-Elmer R 32 spectrometer (90 MHz), ^{13}C and ^{29}Si n.m.r. spectra with a Varian FT-80 A spectrometer (respectively 20 and 15.801 MHz). N.m.r. shifts (deuteriochloroform solutions) are given in p.p.m. from TMS and were evaluated using chloroform as i.s. for ^{1}H (unless otherwise stated) and deuteriochloroform as a secondary reference for ^{13}C; coupling constants (J) are in hertz. Mass spectra were recorded with a LKB-2091 spectrometer by gas-chromatographic inlet (3% OV 17 2m glass column, electron energy 20 eV),unless otherwise stated. Microanalyses were carried out with a Perkin-Elmer 240 C elemental analyzer.

Trimethylsilanecarbonitrile oxide (1) was prepared as previously reported.[1]

3-*Trimethylsilyl*-4,5-*dihydro*-5-*phenylisoxazole* (3a).

A solution of the nitrile oxide (1) (0.01 mol) and styrene (2a) (0.01 mol) in anhydrous benzene (10 ml) was refluxed 24 h, then concentrated *in vacuo* to afford the crude adduct (3a), over 90% pure (^{1}H n.m.r. control). ^{1}H n.m.r. (i.s. cyclohexane) 0.27 (s, 9H); AXY system: 2.95 (H_Y), 3.41 (H_X, J_{XY} 17.1), 5.38 (H_A, J_{AY} 8, J_{AX} 11.5); 7.3 to 7.4 (aromatic). ^{13}C n.m.r. -2.4 (q,$^{1}J_{CH}$ 120), 49.1 (t, $^{1}J_{CH}$ 135), 78.3 (d,$^{1}J_{CH}$ 150),125.4, 127.5, and 128.3 (all d, Ar-C), 141.7 (s, Ar-C), and 159.6 (s). ^{29}Si n.m.r. -6.3 .

3-[(*Trimethylsilyl*)*oxy*]-3-*phenylpropionitrile* (4a).

The crude adduct (3a), prepared as above, was heated at 100°C for 24 h (yield crude 80%), then distilled at 130°C and 0.2 torr: yield 58%. Found: C,66.53; H,7.64; N,6.81. $C_{12}H_{17}NOSi$ requires C,65.70; H,7.81; N,6.38 %. *m/z* 204 (50%, $M^{+\cdot}$ - Me), 179 (100 , $M^{+\cdot}$- CH_2CN), 163(13), 149(3), 135(5), 130(4), 105(4), 104(4), 103(5), 102(5), 98(32), 82(11), 77(11), 75(64, Me_2SiOH^+), 73(52, Me_3Si^+), 70(4), 61(2.5), 51(3.5), 47(4), 45(8.5), 43(6). I.r. (liquid film) $\nu_{C\equiv N}$ 2255 cm^{-1}. ^1H n.m.r. (i.s. cyclohexane) 0.1 (s, 9H), 2.64 (d, J 6, 2H), 4.98 (t, J 6, 1H), 7.35 to 7.5 (m, 5H). ^{13}C n.m.r. - 0.4 (q, $^1J_{CH}$119), 29.2 (t, $^1J_{CH}$136), 70.5 (d, $^1J_{CH}$143), 117.2 (m, $^2J_{CH}$9.0, $^3J_{CH}$ 4.6, C≡N), 125.2, 128.0, and 128.3 (all d, Ar-C), 141.6 (s, Ar-C). ^{29}Si n.m.r. 20.5 .

3-*Hydroxy*-3-*phenylpropionitrile* (5a).

A solution of the crude cycloadduct (3a) in methanol containing 10% water (10 ml) was refluxed 15 minutes. After concentration *in vacuo* the product (96%, crude) was distilled at 180°C and 0.5 torr (lit.[10] not reported), yield 65%. Found: C, 72.54; H,6.00; N,9.90. C_9H_9NO requires C,73.45; H,6.16; N,9.52%. I.r. (liquid film) ν_{OH}3450 broad , $\nu_{C\equiv N}$ 2250 cm^{-1}. ^1H n.m.r. (i.s. cyclohexane) 2.64 (d, J 6.5), 3.53(br s), 4.93 (t, J 6.5), 7.36 (s). ^{13}C n.m.r. 27.4 (t, $^1J_{CH}$ 136.5), 69.25 (d, $^1J_{CH}$ 148), 117.3 (m, $^2J_{CH}$ 9.3, $^3J_{CH}$ 4.9, C≡N), 125.3, 128.2, and 128.4 (all d, Ar-C), 140.9 (s, Ar-C).

5-*Methoxycarbonyl*-5-*methyl*-3-*trimethylsilyl*-4,5-*dihydroisoxazole* (3b).

This cycloadduct was prepared by the same procedure described for the adduct (3a), as previously reported.[1]

3-*Methoxycarbonyl*-3 [*(trimethylsilyl)oxy*] *butyronitrile* (4b).

The adduct (3b) was heated at 100°C for 4h and the silylether collected by distillation at 90°C and 0.1 torr: yield 70%. Found: C, 50.00; H, 7.76; N, 6.77 . $C_9H_{17}NO_3Si$ requires C,50.20; H,7.96; N,6.50 %. *m/z* 200(37%, $M^{+\cdot}$- Me), 172(35), 160 (6, $M^{+\cdot}$- Me - CH_2CN), 156(80, $M^{+\cdot}$- COOMe), 148 (metastable ion, 200 ⟶ 172), 145(8), 140(7), 114(7), 105(8), 98(15), 89(100, Me_3SiO^+), 75(31, Me_2SiOH^+), 73(93, Me_3Si^+), 59(32, $COOMe^+$ or Me_2SiH^+), 47 (8), 45 (34), 43 (40), 29 (6). I.r.(liquid film) $\nu_{C\equiv N}$ 2250 cm^{-1}. ^1H n.m.r. 0.04 (s, 9H), 1.44 (s, 3H), 2.62 (s, 2H), 3.64 (s, 3H). ^{13}C n.m.r. 1.35 (q, $^1J_{CH}$ 119, Me_3), 25.7 (q, $^1J_{CH}$ 129, Me), 30.4 (t, $^1J_{CH}$ 137, CH_2), 52.35 (q, $^1J_{CH}$ 148, OMe), 74.6 (s, quaternary C), 116.2 (t, $^2J_{CH}$ 9.7, C≡N), 172.5 (s, O=C-O). ^{29}Si n.m.r. 15.8 .

3-*Hydroxy*-3-*methoxycarbonylbutyronitrile* (5b).

The adduct (3b) was hydrolyzed by the procedure described above for the hydrolysis of 3a, or as reported previously.[1]

3a,4,5,6,7,7a-*Hexahydro*-4,7-*methano*-3-*trimethylsilylbenz* [d] *isoxazole* (3c).

The adduct (3c) was only evidenced in solution, as complete rearrangement to the silylether (4c) occurred during removal of the solvent.

A solution of the nitrile oxide (1) (4 mmol) and of norbornene (2c) (4 mmol) in deuteriochloroform (10 ml), after 24 h reflux, contained the adduct (3c) as the main product. ^{1}H n.m.r. 0.20 (s, 9H), multiplets between 0.8 and 1.6 (three CH$_2$), 2.22 and 2.44 (both broad s, bridgehead CH), 3.13 (d, J 9, 3a-H), 4.18 (d, J 9, 7a-H). ^{13}C n.m.r. (^{1}H decoupled) - 1.7 (Me$_3$), 23.6, 27.8, 31.9, 38.9, 42.5, 64.3, and 83.4 (norbornane system), 135.2 (3-C). ^{29}Si n.m.r. - 6.5 .

3-exo-*Cyano*-2-exo-[*(trimethylsilyl)oxy*]*bicyclo*[2.2.1]*heptane* (4c).

A solution of the nitrile oxide (1) (0.01 mol) and norbornene (2c) (0.01 mol) in anhydrous benzene (10 ml) was refluxed 12 h, then fractionated to give the silylether (4c), b.p. 120°C at 0.2 torr, yield 83%. Found: C,63.23; H,9.01;N,6.64. C$_{11}$H$_{19}$NOSi requires C,63.10; H,9.15; N,6.69%. *m/z* 209(6%, M$^{+\cdot}$),194(100, M$^{+\cdot}$-Me), 181 (11), 180 (3), 167(5), 166(5), 153(5), 152(8), 139(5), 115(6), 113(5), 100(4), 93(7), 89(4), 75(14), 73(19, Me$_3$Si^{+}). I.r.(liquid film) $\nu_{C\equiv N}$ 2245 cm^{-1}. ^{1}H n.m.r. 0.02 (s, Me$_3$), multiplets between 0.8 and 1.5 (CH$_2$-CH$_2$), multiplet centered at 1.84 (bridge CH$_2$), 2.02 (br s, C*H*-CH-O), 2.42 (d, J 2, C*H*-CH-CN), 2.50 (dd, J 2, J 7, CH-CN), 3.67 (br d, J 7) . ^{13}C n.m.r. - 0.55 (q, $^{1}J_{CH}$ 118.5), 23.3, 27.5, and 33.5 (all t), 41.1, 42.1, 43.8, and 73.8 (all d), 118.6 (d, $^{2}J_{CH}$ 8.1, CN). ^{29}Si n.m.r. 18.0 .

3-exo-*Cyano*-2-exo-*hydroxybicyclo*[2.2.1]*heptane* (5c).

The crude silylether (4c), obtained as above after removal of the volatiles, was refluxed 15 minutes in methanol containing 10% water (10 ml). After concentration *in vacuo*, the residue solidified on cooling, yield 92% with respect to the starting materials (1) and (2c). Crystallised from diethyl ether and light petroleum (b.p.30-50°C), the product (5c) had m.p. 84-85°C (reported,[2] 35-38°C); yield 54%. Found:C,70.18; H,8.11; N,10.57. C$_8$H$_{11}$NO requires C,70.04; H,8.08; N,10.21%. *m/z* 136(1.5%, M$^{+\cdot}$- H), 118 (4, M$^{+\cdot}$ - H - H$_2$O), 109(15, M$^{+\cdot}$ - H - HCN), 108(21), 104(4), 94(13), 92(17),91(16), 82(7), 81(27), 80(37), 79(12), 77(5), 70(16), 68(36), 67(100, C$_5$H$_7$$^{+}$), 60(21),56(11), 55(9), 54(13), 53(19), 43(87), 41(35). I.r. (nujol mull) ν_{OH} 3430, $\nu_{C\equiv N}$ 2250 cm^{-1}. ^{1}H n.m.r. multiplet between 0.9 and 1.6 (CH$_2$-CH$_2$), multiplet centered at 1.88 (bridge CH$_2$), 2.25 (br s, bridgehead C*H*-CHOH), 2.53 (d, J 2, bridgehead C*H*-CHCN), 2.63 (dd, J 2, J 7, CH-CN), 2.95 (br s, OH), 3.87 (d, J 7, CH-O). ^{13}C n.m.r. 23.5, 27.3, and 33.6 (all t), 41.2, 41.4, and 43.1 (all d), 73.0 (d, CHOH), 119.0 (s, CN).

Dimethyl Cyano[*(trimethylsilyl)oxy*]*maleate* (8d).

A mixture of the nitrile oxide (1) and dimethyl acetylenedicarboxylate (6d), 1:1 molar ratio, was set aside under nitrogen for 3 days. The silylether (8d) was collected at 120°C and 0.06 torr; yield 86 %. I.r. (liquid film protected from atmosphere) $\nu_{C\equiv N}$ 2230 cm^{-1}. ^{1}H n.m.r. 0.28 (s, 9H), 3.73 and 3.82(both s, 3H each). ^{13}C n.m.r. - 0.43 (q, $^{1}J_{CH}$ 121), 52.3 (q, $^{1}J_{CH}$ 148), 52.8 (q, $^{1}J_{CH}$ 149), 90.8, 112.1, 161.7, 162.3, and 166.8 (all s). ^{29}Si n.m.r. 34.7 .

Dimethyl cyanooxalacetate (9d), or tautomer, was obtained by hydrolysis of the silylether (8d) on exposure to atmospheric moisture, as already reported.[1]

3-[*(Trimethylsilyl)oxy*]*cinnamonitrile* (8e).

A solution of the nitrile oxide (1) (0.01 mol) and phenylacetylene (6e) (0.01 mol) in anhydrous benzene (10 ml) was refluxed 40 h, then concentrated *in vacuo*. The silylether (8e) was evidenced by ^{1}H n.m.r. as the major product, besides 5-phenyl=isoxazole, benzoylacetonitrile (9e), and residual phenylacetylene (respectively 30, 23, and 70% of the silylether). On distillation *in vacuo*, a fraction containing mainly the silylether (8e) was collected at 100°C and 0.03 torr. ^{1}H n.m.r. (i.s. cyclohexane) 0.43 (s, 9H), 5.19 (s, 1H), and 7.3 to 7.7 (m, 5H). ^{13}C n.m.r. 0.38 (q, $^1J_{CH}$ 120), 78.2 (d, $^1J_{CH}$ 173), 117.2 (s, CN), 168.3 (s, C-O); the aromatic carbon signals were not identified with certitude, owing to the impurities. ^{29}Si n.m.r. 27.6 .

Benzoylacetonitrile (9e).

The impure silylether (8e), obtained by distillation, solidified on exposure to the atmosphere. The crude product (9e) was washed throughly with light petroleum (b.p. 40-70°C) and dried: m.p. 68-77°C, yield 60%. Recrystallised twice from benzin (b.p. 80-100°C), m.p. 78-80°C (reported[11] 83°C), yield 25%. ^{1}H n.m.r. 4.09 (s, 2H), 7.35 to 8.05 (m, 5H). ^{13}C n.m.r. 29.3 (CH_2), 113.8 (CN), 128.3, 128.9, and 134.5 (Ar-CH), 134.1 (Ar-C), 187.1 (CO).

Trimethylsilylisocyanate (12f).

Dry sulfur dioxide was bubbled 3 min. into an ice-cold solution of trimethyl=silanecarbonitrile oxide (1) (1.15 g, 0.01 mol) in anhydrous diphenylether (5 ml). I.r. and ^{1}H n.m.r. spectra indicated that the reaction was complete. The isocyanate (12f) was collected by distillation at atmospheric pressure (bath, 220°C), yield 73%.

N-*Trimethylsilyl*-N'-*arylcarbodiimides* (12g-i).

A solution of trimethylsilanecarbonitrile oxide (1) in anhydrous benzene (0.01 mol in 5 ml) was added dropwise, during 6 h, to a refluxing solution of *N*-sulfinyl=amine (10g-i) in the same solvent (5mmol in 3 ml). After removal of the volatiles *in vacuo*, the carbodiimide (12g-i) was collected.

N-*Trimethylsilyl*-N'-*phenylcarbodiimide* (12g): b.p. 100-110°C at 2.5 torr, yield 79%. I.r. (benzene) $\nu_{N=C=N}$ 2170 cm^{-1}. The ^{13}C n.m.r. shifts were identical to the reported values.[12]

N-*Trimethylsilyl*-N'-4-*tolylcarbodiimide* (12h): b.p. 140°C at 2 torr, yield 30 %. *m/z* 204 (87%, $M^{+\cdot}$), 189 (100, $M^{+\cdot}$- Me), 73 (30, Me_3Si^+). I.r. (benzene) $\nu_{N=C=N}$ 2170 cm^{-1}. ^{1}H n.m.r.

0.32 (s, 9H), 2.32 (s, 3H), 7.03 (m, 4H). ^{13}C n.m.r. 0.77 and 20.66 (both q), 122.6 and 129.8 (both d), 130.1, 132.6, and 138.0 (all s).

N-*Trimethylsilyl*-N'-4-*nitrophenylcarbodiimide* (12i): b.p.150°C at 0.5 torr, yield 0.87 g, containing about 25% of the starting sulfinylamine (10i). I.r. (benzene) $\nu_{N=C=N}$ 2160 cm^{-1}. ^1H n.m.r. 0.26 (s, 9H), 6.94 and 8.05 (both d, J 10). The product was rapidly hydrolysed with atmospheric moisture to 4-nitrophenylcyanamide, identical to a sample prepared as described.[13]

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