Table II. Physical and Spectral Data for Compounds 4a, 6a, 12, 13, and 14

compd	mp, °C	IR, cm^{-1}	^1H NMR, δ	elemental analysis found, %	elemental analysis calcd, %
4a[a]	124–126 dec (CH_2Cl_2/*n*-pentane)	1550, 1345 (vs, NO_2) 1400, 1200 (vs, OSO_2)	8.17 (s, 2 H, arom), 7.90–6.75 (m, 15 H, arom), 6.23 (d, 1 H, C=CH, J = 11 Hz), 5.39 (d, 1 H, Ph_2CH, J = 11 Hz)	C 57.86 H 3.22 N 7.35 S 5.71	C 57.75 N 3.38 N 7.48 S 5.70
6a	118–120 dec (CH_2Cl_2/*n*-pentane)	1560, 1360 (vs, NO_2) 1410, 1210 (vs, OSO_2)	8.63 (s, 2 H, aromatic), 7.83–6.66 (m, 5 H, aromatic), 5.62 and 5.37 (AB q, 2 H, $C=CH_2$, J_{AB} = 4 Hz)	C 42.27 H 2.26 N 10.55 S 8.38	C 42.53 H 2.28 N 10.63 S 8.10
12	high boiling, pale yellow liquid	2210 (vw, C≡C)	7.41–6.97 (m, 10 H, arom), 4.95 (t, 1 H, $C{\equiv}CCHPh_2$, J = 2.2 Hz), 2.26 (m, 2 H, $C{\equiv}CCH_2$), 1.42 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.91 (m, 3 H, CH_3)	C 91.4 H 8.1	C 91.8 H 8.1
13	high boiling, pale yellow liquid	1710 (vs, C=O)	7.90–6.74 (m, 10 H, arom), 4.60 (t, 1 H, Ph_2CH, J = 7.3 Hz), 3.14 (d, 2 H, $COCH_2$, J = 7.3 Hz), 2.31 (m, 2 H, RCH_2CO), 1.43 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.87 (m, 3 H, CH_3)	C 85.0 H 7.95	C 85.6 H 8.3
14	109–111 dec (CH_2Cl_2/*n*-pentane)	1550, 1345 (vs, NO_2) 1380, 1200 (vs, OSO_2)	8.66 (s, 2 H, arom), 5.04 and 4.93 (AB q, 2 H, $C=CH_2$, J_{AB} = 3.5, J_{BCH_2} = 1.1, $J_{ACH_2} \approx 0$ Hz), 2.48 (m, 2 H, $C=CCH_2$), 1.48 (m, 4 H, $CH_2(CH_2)_2CH_3$), 0.92 (m, 3 H, CH_3)	C 38.0 H 3.5 N 10.8 S 9.0	C 38.4 H 3.5 N 11.2 S 8.5

[a] The *E* configuration is suggested on the basis of the ^1H NMR data by comparison with compounds of similar structure.[9,15,16]

and the excess of the starting 1-alkyne itself, which are more or less able to act selectively as proton scavengers, is also consistent with the proposed reaction scheme.

The above results suggest that direct alkylation of terminal alkynes, in particular arylacetylenes, under electrophilic conditions is a viable path, even though further experiments are needed in order to define scope and limitations of the reaction and its merits in comparison with alternative routes.

Experimental Section

Phenylacetylene, 1-hexyne, *cis*-stilbene, diphenylmethyl chloride and silver triflate were commercial products. Cyclohexene oxide and silver 2,4,6-trinitrobenzenesulfonate were prepared according to liaterature methods.[13,14] Melting points are uncorrected. ^1H NMR spectra were taken at 60 MHz on Varian EM 360 A or Brucker-Spectrospin WP 60 spectrometers, using $CDCl_3$ as a solvent; chemical shifts are given in δ relative to Me_4Si as internal standard. IR spectra were recorded (KBr pellets or liquid films) on a Perkin-Elmer 457 spectrometer.

General Procedure. A solution of the alkyl or phenylalkyl chloride (R^2Cl) in anhydrous dichloromethane (30 mL) was added dropwise to a stirred suspension of the appropriate silve salt (AgX, equimolar amounts with respect to R^2 Cl) in a solution of the 1-alkyne ($R^1C{\equiv}CH$) in the same solvent (35 mL), at room temperature.

The reaction mixture was refluxed for the time indicated in Table I, and the products that were insoluble in CH_2Cl_2 (AgCl and the sulfonic acid HX) were filtered off.

The dichloromethane solution was concentrated under reduced pressure, and sulfonates **4a,b**, **6a,b**, and **14** were fractionally preciptated by slow addition of anhydrous *n*-pentane at 0 °C.

After filtration of the sulfonates, the solution was evaporated and the residue was chromatographed on silica gel. Elution with light petroleum yielded alkynes **3**, **9**, and **12**; further elution with light petroleum containing 3–5% diethyl ether afforded the ketones **5**, **7**, and **13**.

In this procedure, stirring and rate of addition of the chloride R^2Cl are critical. In one experiment, performed with a very low rate of addition of diphenylmethyl chloride to equimolar amounts of silver 2,4,6-trinitrobenzenesulfonate and phenylacetylene in dichloromethane, the product distribution changed significantly (see Table I).

The reaction products **3**, **4b**, **5**, **6b**, **9**, and **7** were identified by comparison with authentic samples prepared by literature methods.[9] Physical and spectral data for the new compounds isolated are reported in Table II.

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Registry No. **1**, 536-74-3; **2a**, 51117-47-6; **2b**, 5435-24-5; **2c**, 82951-42-6; **3**, 5467-43-6; **4a**, 82963-10-8; **4b**, 51117-52-3; **5**, 606-86-0; **6a**, 82951-43-7; **8**, 82951-44-8; **11**, 693-02-7; **12**, 82951-47-1; **13**, 82951-45-9; **14**, 82951-46-0; silver 2,4,6-trinitrobenzenesulfonate, 18681-53-3; silver tosylate, 16836-95-6; silver triflate, 2923-28-6; *tert*-butyl chloride, 507-20-0; diphenylmethyl chloride, 90-99-3.

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Conformational Studies by Dynamic Nuclear Magnetic Resonance. 23.[1] Stereodynamics of Cyclic Sulfinylhydrazines

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Restricted rotation about the NN bond can be detected by NMR in molecules where conjugative effects produce partial double bond character. Compounds of the general formula $R_2NN{=}X$ frequently display slow NN rotation, owing to the contribution of structures of the type $R_2N^+{=}N{-}X^-$.

(1) Part 22: Lunazzi, L.; Macciantelli, D.; Spinelli, D.; Consiglio, G., *J. Org. Chem.* **1982**, *47*, 3759.

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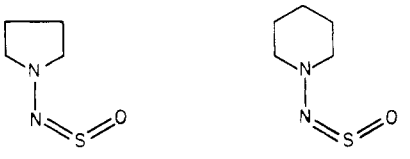
Table I. Free Energies of Activation for the NN Rotation of Derivatives 1-4[a]

parameter	compd 1	2	3	4
$\Delta H^{\ddagger}$, kcal mol^{-1}	11.7	9.9	8.0	8.2
temp range, °C	-28	-63, -77	-102, -106	-97, -101
solvent	$CDCl_3$	CHF_2Cl	CHF_2Cl	CHF_2Cl/ $CHFCl_2$

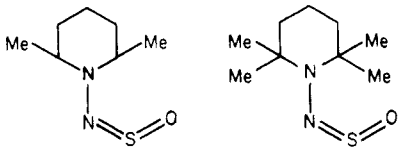
[a] Estimated error ±0.1 kcal mol^{-1}. Since there are two (in 1, 2) or three pairs (3, 4) of nonequivalent carbons with different chemical shift differences, the coalescence points lie within the temperature ranges indicated in the table (see also the Experimental Section).

Examples include the cases X = O (*N*-nitroso amines[2-6]), X = NAr (triazenes[7-10]), and X = CR_2 (hydrazones[3,6,11,12]). Recently we found that also for X = SO (sulfinylhydrazines[13]) restricted NN rotation can be observed, and in the present work are presented the results concerning some cyclic sulfinylhydrazines (compounds 1-4).



1

2



3

4

At temperatures lower than -30 °C the ^{13}C NMR spectra of derivatives 1-3 display two different signals for the carbons that do not lie along the NN axis. These splittings are not present at room temperature and depend upon the asymmetry generated by restricted NN rotation. Each compounds has two (1, 2) or three (3, 4) pairs of nonequivalent ^{13}C lines that, having different shift separations, coalesce at different temperatures. The free energies of activation for NN rotation can thus be measured at two or three different coalescence temperatures: the $\Delta G^{\ddagger}$ values obtained in this way for each compound were found to be equal, within ±0.1 kcal mol^{-1}. One can see (Table I) that the $\Delta G^{\ddagger}$ value for the derivative 1 is larger than for the six-membered analogue 2. Since the cisoid[13,14] NSO moiety is coplanar, or nearly so, with the dynamically averaged plane of the rings, the steric interactions in the ground state are expected to be larger in the six- with respect to the five-membered ring. On the other hand, the energy of the transition state (where the NSO plane is perpendicular to the dynamic plane of the ring) should be almost equal in 1 and 2. As a consequence the energy difference (i.e., the rotational barrier) is larger in 1 with respect to 2.

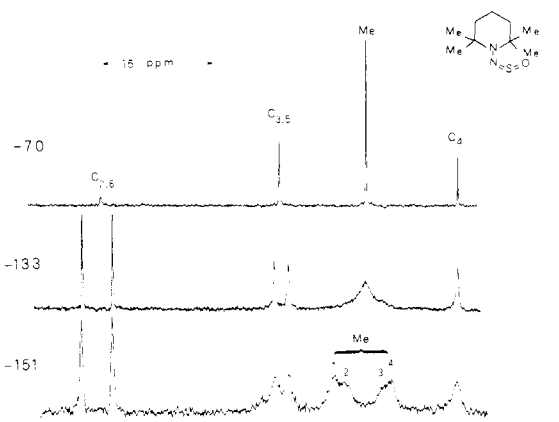


Figure 1. Dependence of the 25.16-MHz C-13 spectrum of 4 on the temperature. At -120 °C all the carbon signals are split in two, owing to the restricted NN rotation. At -130 °C the methyls broaden again and at -150 °C display an additional splitting (a total of four lines) due to the slow ring-reversal process,

Introduction of two *cis*-methyls in positions 2 and 6 of the pyperidyl ring (compound 3) makes the barrier even lower. To explain this fact, we must know the conformational arrangement of the two methyls in 3. Even at -155 °C no evidence was observed for the existence of two conformers. Since at these temperatures ring reversal is expected to be slow on the NMR time scale,[6,15] the absence of such an exchange indicates that we are dealing, essentially, with a single conformer, either axial or equatorial. In similar molecules containing the 2,6-*cis*-dimethylpyperidyl moiety, X-ray diffraction indicated that the methyls prefer to adopt the axial conformation to avoid the strong repulsive interactions between the equatorial methyls and the substituent.[10,15] Many other investigations on analogous molecules agree with such a conclusion.[16-19] As a consequence, the difference in the $\Delta G^{\ddagger}$ values between 2 and 3 (1.9 kcal mol^{-1}) represents an indication of the axial–axial repulsion of the methyl groups in this class of molecules.

It has been also shown that, when the steric hindrance is increased further with the introduction of two additional methyls, as in the 2,2,6,6-tetramethylpyperidyl (TMP) derivatives 4, there is the possibility that the substituent adopts a perpendicular, rather than a planar, conformation in the ground state.

Examples of such a modification of the conformational preference are hydrazones[3,6,11] and amidines[15] containing the TMP ring. The ring carbons C-3,5 and C-2,6 of the

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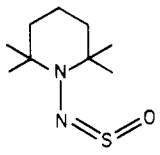
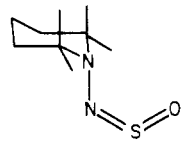


planar



perpendicular

TMP hydrazones and amidines display single NMR signals, even when the rotation is slow on the NMR time scale, because of the change of symmetry. On the other hand, we found that the ring carbons C-2,6 and C-3,5 of the TMP—N=S=O compound **4** become doublets, as in **2** and **3** (Figure 1). This means that the NSO moiety is still coplanar to the dynamic plane of the TMP ring (planar formula above), despite the large steric crowding. The conformational behavior of **4** is thus similar to that of the corresponding triazenes,[10] amides,[15] and *N*-nitroso amines[3,6,11] that remain planar and different from that of the corresponding hydrazones[3,6,11] and amidines[15] that become perpendicular.

It is also noteworthy to observe that the $\Delta G^{\ddagger}$ for NN rotation in **4** is equal to that of **3**, although there are, now, two methyls axial and two equatorial. The molecule, therefore, should experience not only the axial–axial repulsion but also the equatorial–substituent repulsion. To understand why the latter effect does not reduce the $\Delta G^{\ddagger}$ of **4** with respect to **3**, it might be argued that the TMP ring in **4** is a twisted chair, rather than a chair. In this way, in fact, both the axial–axial and equatorial–substituent repulsions can be, in part, relieved. This behavior parallels that observed in two similar situations[3,6,10] (i.e., TMP—N=N—Ph and TMP—N=NO).

In order to check whether this distorted conformation still allows distinction of the pseudoaxial from the pseudoequatorial methyls, we recorded the spectrum of **4** at the lowest attainable temperature. As shown in Figure 1, at −151 °C the four methyls yield four different signals. In fact, each pair of syn and anti methyls is now split further in two, because they are either in a pseudoaxial or in a pseudoequatorial situation.

The $\Delta G^{\ddagger}$ measured for the ring reversal process in **4** is 6.0 ± 0.2 kcal mol^{-1}, a value smaller than that of the unsubstituted 2,2,6,6-tetramethylpiperidine (i.e., 8.0 kcal mol^{-1}).[6] This might depend not only on the sp^2 contribution given to the ring nitrogen by the conjugation with NSO but also on the twisted arrangement that seems to lower further the barrier to ring reversal.

Experimental Section

The synthesis of derivative **2** has been previously reported:[20] the other compounds were obtained with the same method.[13,20] The hydrazines needed for the synthesis were prepared according to the literature.[3,6,11] The new compounds were identified by mass spectroscopy, and the expected molecular weights were obtained: **1**, *m/e* 132 (M$^+$); **3**, *m/e* 174 (M$^+$); **4**, *m/e* 202 (M$^+$).

The IR spectra also showed the typical[13] NSO bands: ν_{as} in the range 1170–1185 cm^{-1} (w) and ν_s in the range 1080–1090 cm^{-1} (vs). The ^{13}C NMR spectra gave the expected number and type of carbons: **1**, 55.0 (C-2,5), 23.3 ppm (C-3,4); **2**, 57.8 ppm (C-2,6); 26.0 (C-3,5), 23.7 ppm (C-4); **3**, 59.9 (C-2,6), 30.0 (C-3,5), 19.3 (Me 2,6), 13.0 ppm (C-4); **4**, 64.0 (C-2,6), 40.6 (C-3,5), 29.1 (Me-2,2,6,6), 16.9 ppm (C-4).

The elemental analysis of the three unknown products gave the following results. Found for **1**: C, 36.2; H, 6.2; N, 21.1 ($C_4H_8N_2SO$ requires: C, 36.3; H, 6.1; N, 21.2). Found for **3**: C, 48.4; H, 8.4; N, 16.0 ($C_7H_{14}N_2SO$ requires: C, 48.2; H, 8.1; N, 16.1). Found for **4**: C, 53.5; H, 9.2; N, 13.7 ($C_9H_{18}N_2SO$ requires: C, 53.4; H, 9.0; N, 13.8).

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The samples for running the low-temperature NMR spectra of compounds **2–4** were prepared by connecting a 10-mm tube, containing the compound, to a vacuum line; the gaseous solvents were then condensed in by means of liquid nitrogen. The tubes were subsequently sealed off and introduced into precooled probe of the spectrometer.

The temperature was monitored by a thermocouple inserted in a dummy tube before or after the spectral acquisition. The $\Delta G^{\ddagger}$ values were obtained for each compound at the various coalescence temperatures (see text) and the values averaged. In the case of **1** where the shift difference between carbons 2 and 5 is almost equal to that between carbons 3 and 4 there is a single coalescence temperature (−28 °C; see Table I). Therefore, to obtain additional data, we carried out a line-shape analysis at three different temperatures, and the averaged values were found to lie, as in the other cases, within ±0.1 kcal mol^{-1}. The spectra were recorded at 25.16 MHz (Varian XL-100) in the FT mode with a ^{19}F external lock.

Acknowledgment. The work has been supported by a grant of the Italian CNR, Rome.

Registry No. **1**, 82665-38-1; **2**, 82665-39-2; **3**, 82665-40-5; **4**, 82665-41-6.

Stereochemistry of Reduction of Cyclic and Bicyclic Ketones by Lithium Diisobutyl-*tert*-butylaluminum Hydride

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Although in the past decade considerable efforts have been devoted to the development of the hindered alkali metal trialkylborohydrides which allow stereoselective reduction of cyclic and bicyclic ketones,[1,2] there are relatively few reports in the literature on the use of alkali metal trialkylaluminum hydrides.[3,4]

Studies directed toward stereoselective reduction with lithium trialkylaluminum hydrides were briefly described by Kovács.[4b] Contrary to the high stereoselectivity exhibited by the hindered trialkylborohydrides,[2] the reduction of 4-*tert*-butylcyclohexanone with lithium diisobutyl-*tert*-butylaluminum hydride in ether–hexane (1:1) affords a 49:51 mixture of cis and trans isomers. However, in the stereoselective reduction of cyclic ketone during the total synthesis of aphidicolin by Trost,[4c] lithium diisobutyl-*tert*-butylaluminum hydride exhibits the same degree of stereoselectivity achieved with lithium tri-*sec*-butylborohydride.[5]

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