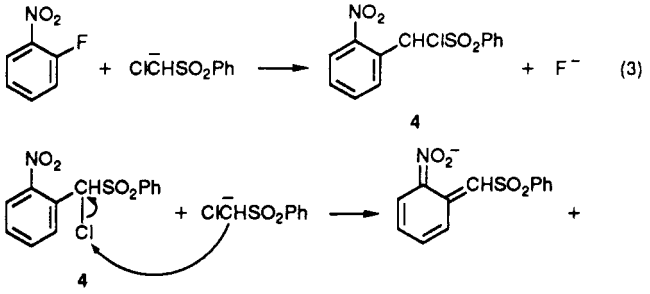
to give 4 (eq 3), which in turn undergoes halogen abstraction by the anion of 1 (eq 4). This latter step should



(3)

(4)

compete favorably with the analogous attack on 1 of Scheme I (forming methyl phenyl sulfone), since the resonance-stabilized nitrophenyl-substituted carbanion should be a better leaving group than $PhSO_2CH_2^-$. We thus favor Scheme I for the disproportionation of eq 2 and suggest that, in the presence of 2-fluoronitrobenzene, chloromethyl phenyl sulfone reacts according to a mechanism which comprises Scheme I and eqs 3–4.

In the case of bromomethyl phenyl sulfone, which gave the reduced product 3 in slight excess of the stoichiometric 50% yield required by the mechanism of Scheme I, there is probably a minor radical reaction component. $PhSO_2CH_2Br$ is a better one-electron acceptor than $PhSO_2CH_2Cl$,[11a] and the ease of fragmentation of the carbon–halogen bond in radical anions of haloderivatives follows the order Br > Cl. Thus, in this case (eq 2, X = Br), steps 1–4 of Scheme II probably provide a competing route for reductive dehalogenation of $PhSO_2CH_2Br$ to 3.

In conclusion, we believe that reaction 2 is an example of nucleophilic attack on halogen by an sp^3 hybridized carbanion. Precedents of carbon anions as nucleophiles in X-philic reactions commonly involve aryl anions as in the "halogen dance" of polyhalobenzenes.[13]

Experimental Section

GC analyses were performed on a Varian 3700 gas chromatograph interfaced to a Varian 401 Vista Series integrator and equipped with a 1.8 m × 2 mm i.d. glass column packed with 10% Carbowax 20 M on Chromosorb Z-DMCS. A Hewlett-Packard 5890 GC-5970 MSD system was used for GC–MS analysis, with a 15-m fused silica capillary column of polymethylsiloxane bonded phase. ^1H NMR spectra were recorded on a 200-MHz Bruker spectrometer.

Materials. DMSO (reagent grade product from Merck) was fractionally distilled and stored over molecular sieves (4 Å). *t*-BuOK (Aldrich) was sublimed before use. $PhSO_2CH_2Cl$ (1),[2b] $PhSO_2CH_2Br$,[2b] $PhSO_2CHCl_2$,[14] and $PhSO_2CHBr_2$[14] were prepared and purified according to published procedures.

$PhSO_2CHCl_2$: mp 59–60 °C (lit. mp 59 °C.[15] *NOTE*: higher melting point values have also been reported; 81.5–83 °C,[14] 79–81 °C[16]); ^1H NMR ($CDCl_3$) δ 6.25 (s, 1 H), 7.59–7.70 (m, 2 H), 7.74–7.84 (m, 1 H), 8.00–8.07 (m, 2 H); MS *m/z* (relative intensity) 225 (<1, M^+), 141 (16), 125 (3), 77 (100), 51 (70).

$PhSO_2CHBr_2$: mp 78–79 °C (lit. mp 78 °C.[17] *NOTE*: higher melting point values have also been reported; 114.5–115 °C[14]); ^1H NMR ($CDCl_3$) δ 6.24 (s, 1 H), 7.57–7.68 (m, 2 H), 7.72–7.83 (m, 1 H), 8.02–8.10 (m, 2 H); MS *m/z* (relative intensity) 314 (<1, M^+), 141 (10), 125 (47), 77 (100), 51 (90).

Product Studies. Finely powdered KOH (3.7 g, 70 mmol) was added to a solution of 1 (1.8 g, 9.5 mmol) in 19 mL of DMSO. After being stirred for 1 h, the mixture was poured in dilute aqueous HCl and extracted with $CHCl_3$. The crude product (1.7 g) was subjected to low-pressure column chromatography (eluent: petroleum ether/chloroform mixtures) and yielded 0.39 g (2.5 mmol, 26% yield) of methyl phenyl sulfone (2) and 0.46 g (2.0 mmol, 22% yield) of dichloromethyl phenyl sulfone (3). The same procedure was used when *t*-BuOK was used as the base, and also in the reactions of bromomethyl phenyl sulfone, except that with this substrate the reaction was quenched after one min. The recovered products had melting points (cf. values above) and spectral properties equal to those of authentic samples.

The products of the reaction between 2-fluoronitrobenzene and chloromethyl phenyl sulfone were characterized by HRGC–MS analysis, and, when possible, by the coincidence of retention times and mass spectra with those of authentic samples. Notably, eq 1 describes the product distribution at very short reaction times; most of these products rapidly undergo further reactions.

Kinetic Experiments. To a solution of 1 (1.14 g, 6 mmol in 2 mL of DMSO) contained in a vessel thermostatted at 25 °C was added 18 mL of a previously thermostatted 0.31 M *t*-BuOK DMSO solution in DMSO. Next, 1.0-mL aliquots were withdrawn with graduated pipettes at desired times and quenched with ca. 1 mL of dilute aqueous HCl (2%). After addition of 5.0 mL of a CH_2Cl_2 solution containing dibenzyl ether, used as GC internal standard, the layers were separated, and the organic layer was subjected to GC analysis.

Acknowledgment. We are grateful to the reviewers for their helpful comments. Financial support by the Ministero della Pubblica Istruzione (Fondi 40% e Fondi 60%) and by the Italian National Council of Research (Strategic Project "Single Electron Transfer") is gratefully acknowledged.

Registry No. 1, 7205-98-3; 2, 31540-74-6; 3, 3112-85-4; 4, 127354-27-2; $PhSO_2CH_2Br$, 19169-90-5; $PhSO_2CHBr_2$, 16003-66-0; *o*-$FC_6H_4NO_2$, 1493-27-2; *o*-$C_2NC_6H_4CH_2SO_2Ph$, 69709-34-8; 2-fluoro-6-[(phenylsulfonyl)methyl]nirobenzene, 127354-25-0; 2-fluoro-4-[(phenylsulfonyl)methyl]nitrobenzene, 127354-26-1.

(13) Bunnett, J. F. *Acc. Chem. Res.* **1972**, *11*, 139.
(14) Middelbos, W.; Strating, J.; Zwanenburg, B. *Tetrahedron Lett.* **1971**, *4*, 351.
(15) Otto, R. *J. Prakt. Chem.* **1889**, *40*, 505.
(16) Grossert, J. S.; Dubey, P. K.; Gill, G. H.; Cameron, T. S.; Gardner, P. A. *Can. J. Chem.* **1984**, *62*, 798.
(17) Troeger, J.; Hille, W. *J. Prakt. Chem.* **1905**, *71*, 201.

Reaction of Aryl and Alkyl Nitro Compounds with 2-Butenylmagnesium Chloride: Synthesis of a New Class of Nitrones

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Nitrones have received great attention during recent years because they have been revealed as important intermediates in organic synthesis. Indeed nitrones are versatile 1,3-dipoles useful for the construction of nitrogen heterocycles, which are largely present in natural products like alkaloids and β-lactams.[1] Some of them, e.g. phenyl-*tert*-butylnitrone have also been used as spin-trapping reagents and utilized in studies concerning radical pro-

(1) For reviews of properties and synthetic utilization of nitrones, see: (a) Padwa, A. *1,3-Dipolar Cycloadditions Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2. (b) Breuer, E. *The Chemistry of Amino, Nitroso and Nitro Compounds*; Patai, S., Ed.; Wiley: New York, 1982; p 459. (c) Tufariello, J. J. *Acc. Chem. Res.* **1979**, *12*, 396. (d) Black, D. St. C.; Crozier, R. F.; Davis, V. C. *Synthesis* **1975**, 205. (e) Hamer, J.; Macaluso, A. *Chem. Rev.* **1964**, 473.

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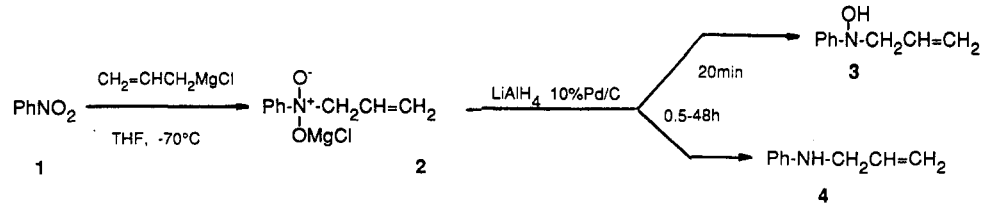
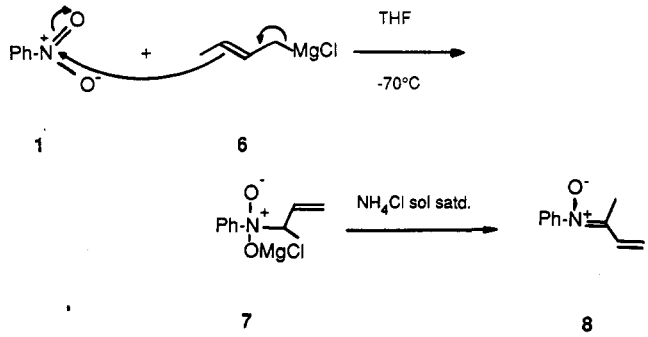
Scheme I



1 2 3 4

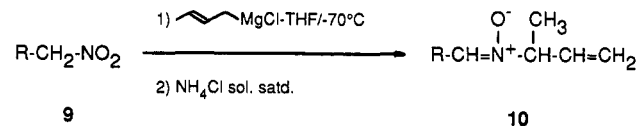
Scheme II



1 6 7 8

8	Ph	E:Z	YIELDS %
a	2-$CH_3C_6H_4$	95:5	59
b	2-ClC_6H_4	97:3	85
c	2,6-$CH_3C_6H_3$	95:5	78
d	2-BrC_6H_4	98:2	65
e	4-ClC_6H_4	99:1	82
f	2-Naphtyl	99:1	71

Scheme III



9 10

10	R	E:Z	YIELDS %
a	Ph	2:98	77
b	n-C_5H_{11}	3:97	90
c	n-C_3H_7	3:97	58

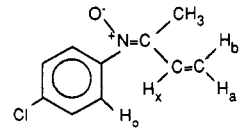
cesses.[2] The classical methods for the preparation of nitrones involve condensation of carbonyl compounds with substituted hydroxylamines[1,3] or direct oxidation of hydroxylamines.[4] However, the main trouble concerning those methods often resides in the preparation of the nitrogenous substrate. More recently other systems have been set up to synthesize this class of compounds: oxidation of secondary amines with hydrogen peroxide–sodium tungstate,[5] reaction of alkyl triflates with aldoxime-*o*-trimethylsilyl ethers[6] and reaction of α-chloronitroso compounds with Grignard reagents.[7] α-Aroyl-*N*-phenylnitrones have been prepared by silver oxide oxidation of the adducts of silyl enol ethers with nitrosobenzene.[8] To sum up there is a continuing need to develop new and versatile procedures for the synthesis of nitrones.

During our studies we noted that in contrast to alkyl Grignard reagents[9] the allylmagnesium chloride reacts with nitroarenes via 1,2-addition to the nitro group[10] (Scheme I). An intermediate **2** is probably formed, but our attempts to trap or isolate it were unsuccessful. Anyway the in situ treatment of the reaction mixture for 20 min with $LiAlH_4$ in the presence of catalytic amount of 10% Pd/C gives *N*-Allyl-*N*-phenylhydroxylamines **3** while prolonged reaction times (0.5–48 h), in the same conditions, affords *N*-allylanilines **4** in moderate to good yields.

In order to broaden the synthetic utility of this reaction, we decided to test the reactivity of other allyl Grignard reagents, and so we observed that reaction of nitroarenes with 2-butenylmagnesium chloride[11] **6** could give an intermediate **7**, which upon decomposition with NH_4Cl saturated solution afforded a stable compound having the structure **8** (Scheme II).

This reaction therefore represents an easy and straightfoward synthesis of a new class of nitrones. Good yields were indeed obtained for a significant variety of starting aromatic nitro compounds. In addition the reaction proceeds with high stereoselectivity since the *E* isomer is almost exclusively formed ($E/Z > 95:5$). Stereochemical assignements have been made after examining some literature data available for arylnitrones of similar structure.[7] In these molecules the methyl group has a chemical shift of δ 1.76–1.91 ppm in the *Z* configuration while the deshielding effect of the oxygen causes a lower field absorption (δ 2.25–2.31 ppm) in the *E* structure. A similar behavior has been found in structures **8a–f** in which the methyl group has δ 2.35–2.45 ppm, while in the spectrum of compound **8a** it is possible to observe a small signal at δ 1.90 ppm due to the methyl of the *Z* isomer present in amount of about 5%.[12]

The *E* configuration has been also confirmed by evaluating the intramolecular NOE's effect which have been measured by a ROESY experiment[13] on structure **8e**.



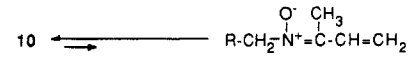
8e

(2) Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 31.
(3) Tennant, G. In *Comprehnsive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 2, p 500.
(4) Murahashi, S.; Mitsui, H.; Watanabe, T.; Zenki, S. *Tetrahedron Lett.* **1983**, *24*, 1049. For recent electrochemical method, see: Shono, T.; Matsumura, Y.; Inoue, K. *J. Org. Chem.* **1986**, *51*, 549.
(5) Mitsui, H.; Zenki, S.; Shiota, T.; Murahashi, S. *J. Chem. Soc., Chem. Commun.* **1984**, 874.
(6) Lebel, N. A.; Balasubramanian, N. *Tetrahedron Lett.* **1985**, *26*, 4331.
(7) Schenk, C.; Beekes, M. L.; Van der Drift, J. A. M.; Th. De Boer, J. *Recl. Trav. Chim. Pays-Bas* **1980**, *99*, 278.
(8) Sasaki, T.; Mori, K.; Ohno, M. *Synthesis* **1985**, 279.
(9) Bartoli, G. *Acc. Chem. Res.* **1984**, *17*, 109. Bartoli, G.; Bosco, M.; Dalpozzo, R.; Todesco, P. E. *J. Org. Chem.* **1986**, *51*, 3694.
(10) Bartoli, G.; Marcantoni, E.; Bosco, M.; Dalpozzo, R. *Tetrahedron Lett.* **1988**, *29*, 2251.
(11) This Grignard reagent can be prepared starting from both 2-chloro-3-butene or chloro-2-butene: Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 7075.
(12) A downfield absorption (Δδ = 0.4 ppm) can also be observed for the vinyl protons in the *Z* configuration.
(13) Kessler, H.; Griesinger, C.; Kerssenbaum, R.; Wagner, K.; Ernst, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 607.

Remarkable cross-peaks have been detected between the two geminal vinylic protons H_a–H_b, the methyl group and H_b and finally between H_b and H_o in the aromatic ring. This demonstrates that the molecule in its preferred conformation has the H_b proton almost equidistant from the methyl group and the H_o proton in the ring, and this is possible only in the *E* configuration. Furthermore the lack of any effect between the methyl and the protons of the aromatic ring rules out the hypothesis of a Z configuration.

The experimental data at disposal strenghten our conviction about the formation of an intermediate hydroxylamine *N*-oxide magnesium salt **7**, which in protic conditions undergo an elimination of a water molecule to give the nitrone. A slight exess of the Grignard reagent (1.1 equiv) is used in our reaction; a major amount of reagent or prolonged reaction times does not affect the overall yields of products.

Since alkyl Grignard reagents add to nitrones in a 1,3-fashion[14] giving hydroxylamines, the absence of such kind of products in the reaction mixture could exclude the direct formation of nitrones upon addition of the reagent on the substrate. This method works well even with aliphatic nitro compounds but in this case the isolated product is of type **10** (Scheme III). At present we are not able to say compound **10** is directly formed from decomposition of the intermediate **7** or if a Behrend-type equilibrium operates.[15]



11

A similar high degree of stereoselectivity has been observed with this class of compounds since the *Z* isomer is preferentially formed. For example configuration of **10a** has been established to be *Z* by comparison of similar structures[16] in which the two protons in positions 2, 6 in the aromatic ring exhibit a lower field shift (δ 8.20 ppm) compared with the others (δ 7.4 ppm), owing to their proximity to the oxigen in the *Z* structure.

All products prepared are stable for some days if stored at 0 °C; after this time they undergo a dimerization or polymerization process which is much more enhanced for nitrones derived from aliphatic nitro compounds. The limit of this procedure resides in the necessity of employing substituted allyl Grignard reagents in order to have stable and isolable products. Indeed the hydrolysis of the assumed intermediate **2** using allylmagnesium chloride in similar conditions gives a liquid which on standing rapidly became a vitreous solid having an obscure NMR and IR spectra but the same elemental analysis of the corresponding nitrone structure.

In conclusion an easy method to synthesize in good yields a new class of nitrones has been made ready. Further studies on their reactivity and synthetic utilization are in progress.

Experimental Section

Microanalyses were performed using a C, H, N analyzer Model 185 from Hewlett-Packard Co.; IR spectra were recorded with a Perkin-Elmer 257 spectrophotometer. NMR spectra were recorded at 300 MHz on a Varian VXR 300. ^{1}H NMR shifts are given in parts per million from Me_4Si in $CDCl_3$. ROESY experiment has been run on a $CDCl_3$ solution 10^{-2} M. A time-shared spin-lock pulse has been used.[13] Data points have been collected into two matrixes of 1024 × 1024; 256 increments have been used with 16 transients each; mixing time 0.8; spectral window was of 1733 Hz in both dimensions. Mass spectra were obtained using a Hewlett-Packard GC/MS 5988. UV spectra were recorded with a Perkin-Elmer Coleman 575 spectrophotometer. Reaction progress was monitored by TLC or GLC on a Carlo Erba Fractovap 4160, using capillary column of duran glass (0.32 mm × 25 mt) stationary phase OV1 (film tickness 0.4–0.45 nm). Melting points are uncorrected and were determined by a Büchi apparatus. Column chromatography was performed on Merck Silica gel (0.040–0.063 mm) eluting with hexane–ethyl acetate–ethanol, 6:3:1. All chemicals used are commercial exept phenylnitromethane, which has been prepared as described.[17] THF was dried by refluxing it over sodium wire until the blue color of benzophenone ketyl persisted and then distilling it into a dry receiver under nitrogen atmosphere. 2-Butenylmagnesium chloride was prepared as described[11] and titrated before use.[18]

Preparation of Nitrones 8a–f and 10a–c: General Procedure. A 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, dropping funnel, reflux condenser, and thermometer was charged under Nitrogen atmosphere with the appropriate nitro compound (5 mmol) dissolved in dry THF (30 mL). The solution was cooled at −70 °C, and 2-butenylmagnesium chloride (5.5 mmol) was added dropwise. After about 15 min the mixture was quenched with saturated aqueous amonium chloride, extracted with ether, and dried over magnesium sulfate. Solvent was evaporated under reduced pressure, and the crude product was purified by column chromatography.

(*E*)-α-Ethenyl-α-methyl-*N*-(2-methylphenyl)nitrone (8a): oil; yield 59%; IR (neat, cm^{-1}) 1520 (C=N), 1165 (N—O); ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 3 H, Ar-CH_3), 2.40 (s, 3 H, N=CCH_3), 5.22 (d, 1 H, =CH_2, J_{ax} = 11.20 Hz), 5.52 (d, 1 H, =CH_2, J_{bx} = 17.10 Hz), 6.15 (dd, 1 H, CH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz), 7.15–7.30 (m, 4 H, arom); mass spectrum, *m/e* 174 (M^+), 174, 143, 132, 104, 91, 79, 77, 65. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.30; H, 7.55; N, 7.80.

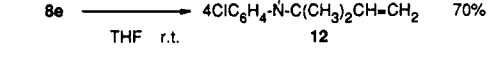
(*E*)-α-Ethenyl-α-methyl-*N*-(2-chlorophenyl)nitrone (8b): oil; yield 85%; IR (neat, cm^{-1}) 1580 (C=N), 1060 (N—O); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H, N=CCH_3), 5.10 (d, 1 H, =CH_2, J_{ax} = 11.20 Hz), 5.42 (d, 1 H, =CH_2, J_{bx} = 17.10 Hz), 5.98 (dd, 1 H, CH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz), 6.90–7.50 (m, 4 H, arom); mass spectrum, *m/e* 197 $(M + 2)^+$, 195 (M^+), 154, 152, 127, 125, 111, 90, 75, 51, 39. Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.40; H, 4.12; N, 7.16. Found: C, 6105; H, 4.11; N, 7.17.

(*E*)-α-Ethenyl-α-methyl-*N*-(2,6-dimethylphenyl)nitrone (8c): oil; yield 78%; IR (neat, cm^{-1}) 1520 (C=N), 1165 (N—O); ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3 H, $ArCH_3$), 2.20 (s, 3 H, $ArCH_3$), 2.40 (s, 3 H, N=CCH_3), 5.23 (d, 1 H, =CH_2, J_{ax} = 11.20 Hz), 5.53 (d, 1 H, =CH_2, J_{bx} = 17.10 Hz), 6.08 (dd, 1 H, CH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz), 6.95–7.25 (m, 3 H, arom); mass spectrum, *m/e* 189 (M^+), 172, 157, 131, 118, 91, 77, 65, 42. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.10; H, 7.95; N, 7.42.

(*E*)-α-Ethenyl-α-methyl-*N*-(2-bromophenyl)nitrone (8d): mp 90 °C (petroleum ether); yield 65%; IR (KBr, cm^{-1}) 1525 (C=N), 1170 (N—O); ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3 H, N=CCH_3), 5.29 (d, 1 H, =CH_2, J_{ax} = 11.20 Hz), 5.58 (d, 1 H, =CH_2, J_{bx} = 17.10 Hz), 6.12 (dd, 1 H, CH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz), 7.25–7.47 (m, 3 H, arom), 7.64–7.69 (m, 1 H, arom); mass spectrum, *m/e* 242 $(M + 2)^+$, 240 (M^+), 238, 222, 200, 198, 167, 90, 75, 51, 42, 39. Anal. Calcd for $C_{10}H_{10}BrNO$: C, 50.02; H, 4.20; N, 5.83. Found: C, 50.21; H, 4.28; N, 5.72. UV λ_{max} 286 nm (ϵ 36988).

(*E*)-α-Ethenyl-α-methyl-*N*-(4-chlorophenyl)nitrone (8e): mp 83 °C (petroleum ether); yield 82%; IR (KBr, cm^{-1}) 1570 (C=N, 1165 (N—O); ^{1}H NMR ($CDCl_3$) δ 2.35 (s, 3 H, N=CCH_3), 5.28 (d, 1 H, =CH_2, J_{ax} = 11.20 Hz), 5.54 (d, 1 H, =CH_2, J_{bx} = 17.10 Hz), 6.31 (dd, 1 H, CH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz),

(14) Reaction of compound **8e** with MeMgCl in THF at room temperature gave the hydroxylamine product **12**.



For further examples, see refs 2b, p 532; 2e, p 488; 5.

(15) See ref 2b, p 474.

(16) Koyano, K.; Suzuki, H. *Terahedron Lett.* **1968**, 1859.

(17) Kornblum, N.; Smiley, R. A.; Blackwood, R. K.; Iffland, D. C. *J. Am. Chem. Soc.* **1955**, *77*, 6269.

(18) Bergbreiter, D. E.; Pendergrass, E. *J. Org. Chem.* **1981**, *46*, 219.

7.35 (dd, 4 H, arom, $J_{aa'xx'}$ = 6.70 Hz); mass spectrum *m/e* 197 $(M + 2)^+$, 195 (M^+), 166, 152, 127, 111, 83, 75, 42. Anal. Calcd for $C_{10}H_{10}ClNO$: C, 61.39; H, 5.15; N, 7.16. Found: C, 61.22; H, 5.30; N, 7.09; UV λ_{max} 298 nm (ϵ 20 670).

(*E*)-α-Ethenyl-α-methyl-*N*-(2-naphthyl)nitrone (8f): oil; yield 71%; IR (neat, cm^{-1}) 1505 (C=N), 1050 (N—O); ^1H NMR ($CDCl_3$) δ 2.45 (s, 3 H, N=CCH_3), 5.23 (d, 1 H, C=CH_2, J_{ax} = 11.20 Hz), 5.55 (d, 1 H, C=CH_2, J_{bx} = 17.10 Hz), 6.41 (dd, 1 H, N=CCH=C, J_{ax} = 11.20 Hz, J_{bx} = 17.10 Hz), 7.40–7.80 (m, 7 H, arom); mass spectrum, *m/e* 211 (M^+), 182, 166, 128, 115, 77, 63, 39. Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.30; H, 6.44; N, 6.50.

(*Z*)-α-Phenyl-*N*-(1-buten-3-yl)nitrone (10a): oil; yield 77%; IR (neat, cm^{-1}) 1450 (C=N), 1140 (N—O); ^1H NMR ($CDCl_3$) δ 2.65 (d, 3 H, CH_3, *J* = 6.70 Hz), 4.55 (quint, 1 H, NCH, *J* = 6.70 Hz), 5.30–5.43 (m, 2 H, =CH_2), 6.10–6.25 (m, 1 H, NCH=C), 7.35–7.45 (m, 3 H, arom + 1 H, ArCH=), 8.20–8.25 (m, 2 H, arom ortho); mass spectrum, *m/e* 175 (M^+), 145, 121, 104, 89, 77, 55, 39. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.39; H, 7.47; N, 7.99. Found: C, 75.14; H, 7.32; N, 7.87.

(*Z*)-α-*n*-Pentyl-*N*-(1-buten-3-yl)nitrone (10b): oil; yield 90%; IR (neat, cm^{-1}) 1590 (C=N), 1165 (N—O); ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, CH_3CH$_2$, *J* = 7.35 Hz), 1.10–1.25 (m, 6 H, $CH_2CH_2CH_2$), 1.45 (d, 3 H, NCHCH_3, *J* = 6.75 Hz), 2.35–2.45 (m, 2 H, CH_2CH=N), 4.30 (quint, 1 H, NCH, *J* = 6.75 Hz), 5.15–5.30 (m, 2 H, =CH_2), 5.95–6.10 (m, 1 H, CH=C), 6.65 (t, 1 H, CH=N, *J* = 4.65 Hz); mass spectrum, *m/e* 169 (M^+), 152, 126, 98, 57, 55, 43, 41, 39. Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 70.78; H, 11.21; N, 8.12.

(*Z*)-α-*n*-Propyl-*N*-(1-buten-3-yl)nitrone (10c): oil; yield 58%; IR (neat, cm^{-1}) 1560 (C=N), 1165 (N—O); H NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3CH$_2$, *J* = 7.35 Hz, 1.20–1.30 (m, 2 H, CH_3CH_2), 155 (d, 3 H, NCHCH_3, *J* = 6.75 Hz), 2.40–2.50 (m, 2 H, $C_2H_5CH_2$), 4.40 (quint, 1 H, NCH, *J* = 6.75 Hz), 5.25–5.30 (m, 2 H, =CH_2), 6.00–6.15 (m, 1 H, C*H*=CH_2), 6.62 (t, 1 H, CH=N, *J* = 4.65 Hz); mass spectrum, *m/e* 141 (M^+), 124, 98, 82, 72, 55, 41, 39. Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.70; N, 9.91. Found: C, 67.85; H, 10.89; N, 9.75.

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Registry No. **1a**, 88-72-2; **1b**, 88-73-3; **1c**, 81-20-9; **1d**, 577-19-5; **1e**, 100-00-5; **1f**, 581-89-5; **8a**, 127279-63-4; **8b**, 127279-64-5; **8c**, 127309-72-2; **8d**, 127279-65-6; **8e**, 127279-66-7; **8f**, 127279-67-8; **9** (R = Ph), 622-42-4; **9** (R = *n*-C_5H_{11}), 646-14-0; **9** (R = *n*-C_3H_7), 627-05-4; **10a**, 127279-68-9; **10b**, 127279-69-0; **10c**, 127279-70-3; **12**, 127279-71-4; $H_3CCH=CHCH_2MgCl$, 6088-88-6.

Synthesis of 2,2,4,4-Tetranitroadamantane

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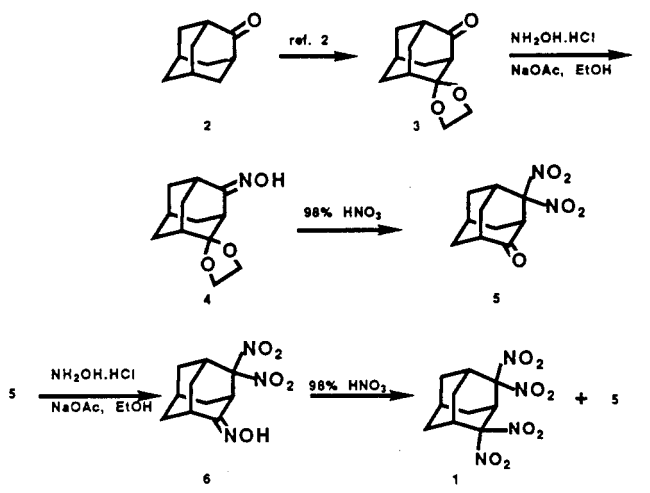
There is considerable current interest in the synthesis and chemistry of polynitropolycycles.[1] The compounds are primarily of interest because of their energetic properties, that is, they can function as explosives, propellants, and/or fuels. Since high density is an important property for these materials to possess, the incorporation of nitro group substituents in compact cage molecules can result in high energy-density materials. Polynitroadamantanes have received little attention. 1,3,5,7-Tetranitroadamantane was synthesized by oxidation of the corresponding amine.[1a] Recently, 2,2-dinitro- and 2,2,6,6-tetranitroadamantane have been synthesized[1j] from the corresponding oximes. Similar attempts aimed at the synthesis of 2,2,4,4-tetranitroadamantane (**1**) failed, apparently due to proximity effects. In order to synthesize higher polynitroadamantanes bearing geminal nitro groups, it is essential to overcome problems associated with steric crowding. A similar difficulty was encountered in the synthesis of 8,8,11,11-tetranitropentacyclo-[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane.[1h] It was shown that treating the carbonyls one at a time provided an easy solution to this problem. We now report a similar strategy that resulted in the synthesis of the title compound.

Scheme I



The starting material, 4,4-(ethylenedioxy)adamantan-2-one (**3**), was prepared from adamantan-2-one by known procedures[2] (Scheme I). Conversion of **3** to the corresponding oxime was achieved by using the conditions developed by Corey et al.[3] Treatment of **4** with 98% nitric acid in refluxing methylene chloride[4] gave 4,4-dinitroadamantan-2-one (**5**) in 35% yield. A transient blue-green color was observed initially, apparently due to formation of the corresponding nitroso compound. This color gradually faded as more nitric acid was added. Compound **5** was converted into the corresponding oxime **6** in 79%

(1) (a) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405. (b) Eaton, P. E.; RaviShankar, B. K.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185. (c) Marchand, A. P.; Suri, S. C. *J. Org. Chem.* **1984**, *49*, 4078. (d) Paquette, L. A.; Fischer, J. W.; Engel, P. *J. Org. Chem.* **1985**, *50*, 2524. (e) Paquette, L. A.; Nakamura, K.; Engel, P. *Chem. Ber.* **1986**, *119*, 3782. (f) Marchand, A. P.; Annapurna, G. S.; Vidyasagar, V.; Flippen-Anderson, J. L.; Gilardi, R.; George, C.; Ammon, H. L. *J. Org. Chem.* **1987**, *52*, 4781. (g) Marchand, A. P.; Sharma, G. V. M.; Annapurna, G. S.; Pednekar, P. R. *J. Org. Chem.* **1987**, *52*, 4784. (h) Marchand, A. P.; Arney, B. E., Jr.; Dave, P. R. *J. Org. Chem.* **1988**, *53*, 443. (i) Marchand, A. P.; Dave, P. R.; Rajapaksa, D.; Arney, B. E., Jr. *J. Org. Chem.* **1989**, *54*, 1769. (j) Archibald, T. G.; Baum, K. *J. Org. Chem.* **1988**, *53*, 4645. (k) Review: Marchand, A. P. *Tetrahedron* **1988**, *44*, 2377.

(2) (a) Faulkner, D.; McKervey, M. A. *J. Chem. Soc. C* **1971**, 3906. (b) Numan, H.; Wynberg, H. *J. Org. Chem.* **1978**, *43*, 2232.

(3) Corey, E. J.; Melvin, L. S.; Haslanger, M. F. *Tetrahedron Lett.* **1975**, 3117.

(4) Bull, J. R.; Jones, E. R. H.; Meakins, G. D. *J. Chem. Soc.* **1965**, 2601.

0022-3263/90/1955-4459$02.50/0