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C-NITROSO COMPOUNDS—XXXI[a]

THE ADDITION OF α-CHLORONITROSO COMPOUNDS TO OLEFINS CONTAINING ALLYLIC HYDROGEN

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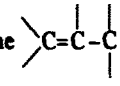
Abstract—α-Chloronitrosoadamantane **1a** gives upon reaction with 2-phenylpropene at room temperature virtually quantitatively a stable ketonitrone salt, the α,α-adamantylidene-N-(2-phenyl)prop-1-en-3-yl nitrone hydrochloride **2a**. Evidence for the structure of the crystalline product is based on microanalytical data and spectroscopic properties, together with degradation studies. Similar aliphatic ketonitrone hydrochlorides have been obtained from reaction of 2-phenylpropene with other α-chloronitroso compounds **1b–1e** (73–91%), and from α-chloronitrosoadamantane and a series of allylic olefins (76–95%). Rearrangement of an intermediary N-α-chloroalkyl-N-alkenylhydroxylamine, which has been initially formed by an ene-type process between the reactants, can explain formation of the product.

Reactions between aromatic nitroso compounds and allylic olefins have been studied already in 1910, by Alessandri.[1] The nature of such reactions has remained obscure for a long time, and only recently Knight and coworkers were able to present compelling evidence for an addition-hydrogen-abstraction process ("ene" reaction) leading, in first instance, to a labile N-aryl-N-alkenylhydroxylamine.[2,3]

Only in exceptional cases has it been possible to isolate the hydroxylamine.[4,5] Under normal conditions it reacts further by competing pathways: thermal decomposition, rearrangement, dehydration, and redox and condensation processes with the nitroso compound. This accounts for secondary products as diverse as nitrones,[1,6] amines,[6,7] anils,[8] azoxyarenes,[9] oxime ethers,[10] and isoxazolines.[11]

In the aliphatic series only perfluoronitrosoalkanes are known to give substantial amounts of well-defined products. For instance, the ene insertion product derived from isobutene and trifluoronitrosomethane[12] was virtually quantitatively obtained. As far as we know, only one report has been recorded concerning the ene reaction of non-fluorinated nitroso compounds. Roberts[13] found that small amounts of N-alkyl-N-alkenylhydroxylamines, which are rather easily oxidized to nitroxides, are formed upon reaction of *t*-nitrosobutane or caryophyllene nitrosite with a nine-membered cyclic olefin (caryophyllene), containing a reactive strained *trans*-tri-substituted double bond.

In view of our interest in routes leading to N-α-chloroalkylhydroxylamines, we have now investigated reactions between the easily obtainable α-chloronitroso compounds (through chlorination of the corresponding oximes) with olefins containing the  system.

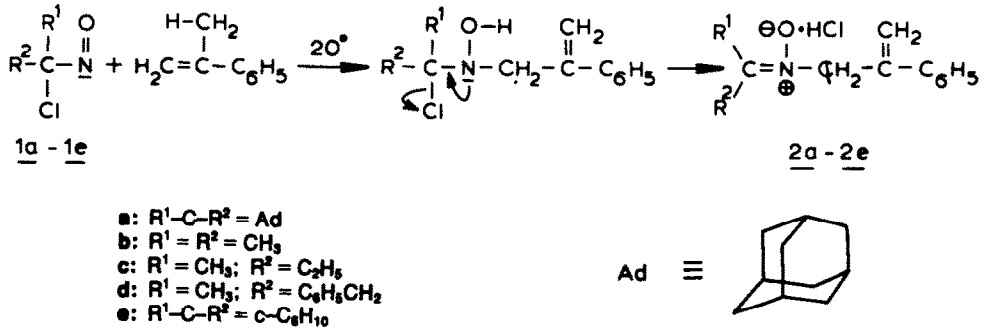
RESULTS AND DISCUSSION

Reaction of 2-phenylpropene with α-chloronitroso compounds. In order to illustrate possible reactivities of α-chloronitroso compounds towards allylic olefins, α-chloronitrosoadamantane (AdClNO) and 2-phenylpropene were, in first instance, employed as the substrates.

When a solution of AdClNO **1a** in an excess of 2-phenylpropene is stirred at room temperature, a white precipitate is formed. As indicated by the disappearance of the blue colour of the nitroso compound, completion of the reaction takes about 10 days. By filtration a high yield (96%) of a crystalline product can be isolated, while analysis of the mother liquor only reveals traces of adamantanone and predominantly unreacted olefin. The product has an element composition of $C_{19}H_{24}(Cl)NO$, suggesting a 1:1 adduct of nitroso compound and olefin. Its structure is formulated as α,α-adamantylidene-N-(2-phenyl)prop-1-en-3-yl nitrone hydrochloride[b] **2a** (eqn (1), R^1–C–R^2=Ad) on the basis of spectroscopic data (see Table 2). Dominant absorption bands for the hydrochloride salt function (1750–2870 cm^{-1}), and the C=C and C=N double bonds (1630–1680 cm^{-1}) are observed in the IR spectrum. The 100 MHz NMR spectrum contains six bands (δ 2, 3.10, 3.87, 5.35, 5.59 and 7.38 ppm) of relative intensities 12:1:1:2:2:5. The bands at 3.10 and 3.87 ppm are particularly broad (width at half-height *ca.* 8 cps), and are assigned to the hydrogen nuclei at the bridgehead positions of the adamantylidene skeleton next to the nitrone group. Their difference in chemical shift is due to the non-symmetrically substituted exocyclic C=N bond. All other hydrogens of the adamantylidene skeleton are present as a broad band around 2 ppm. The sharp singlet

[a]Part XXX in this series see *Recl. Trav. Chim. Pays-Bas* **96**, 237 (1977).

[b]In the *Chemical Abstracts* nomenclature of nitrones the sp^2 carbon is part of the nitrone group, and the substituents attached to it get the suffix α, while the substituent attached to nitrogen is prefixed by N.[14,15] For cyclic nitrones this is not very convenient, and therefore we introduce for these the α,α-cycloalkylidene nomenclature for simplicity. For instance, we call c-$(CH_2)_5$C=N(→O(R) an α,α-cyclohexylidene nitrone, rather than an α,α-cyclo-pentamethylene nitrone. This is especially simplifying for "adamantylidene" nitrones.



Scheme 1.

at 5.35 ppm is assigned to the methylene group, and its low field position is consistent with the adjacent electron deficient nitrogen center. The band at 5.59 ppm shows signs of unresolved structure, which may be due to (i) different chemical shifts for the two vinylic hydrogens, or to (ii) weak coupling (*ca.* 1 cps) between both. Finally, the band at 7.38 ppm shows the aromatic hydrogens.

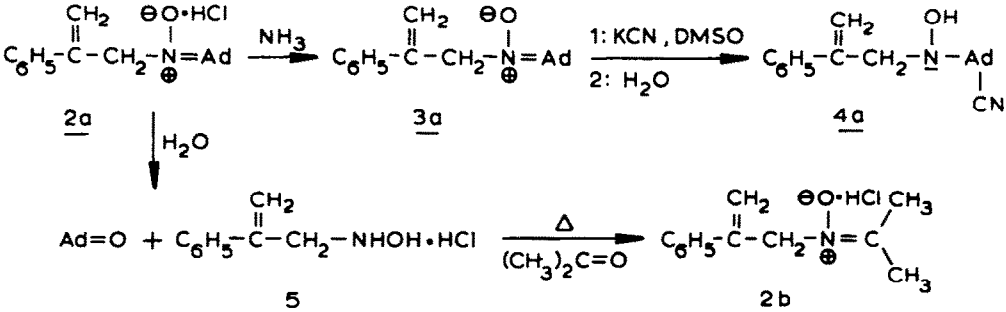
Nitrone hydrochloride **2a** most likely originates from an initially formed N-α-*chloro*alkyl-N-alkenylhydroxylamine, by heterolytic expulsion of chlorine (see Scheme 1). The lability of chlorine in the α-position of a mobile nitrogen lone pair is well known.[16] Thus, in contrast with previous results, we obtain a single and stable product from a nitroso compound and an allylic olefin. The intermediary hydroxylamine is most likely safeguarded from complex secondary reactions, because of the efficient formation of the insoluble nitrone salt. That we really are dealing with an initial ene reaction involving the shift of a double bond, is concluded from a reaction with α-trideuteriomethylstyrene: exclusively the product is obtained with a deuterated vinylidene (*not* methylene) group.

The structure of **2a** could be substantiated by chemical modification (see Scheme 2). With ammonia in diethyl ether, the hydrochloride salt is quantitatively converted into the free nitrone **3a**. Potassium cyanide can be added to **3a** in DMSO solution, to give N-(2-cyanoadamantyl-2)-N-(2-phenyl)prop-1-en-3-ylhydroxylamine **4a** (37%) after aqueous work-up. It is noteworthy that **4a** is formally the ene adduct of 2-cyano-2-nitrosoadamantane and 2-phenylpropene.

Nitrone hydrochloride **2a** is soluble in cold water, and rapid extraction of the aqueous solution with chloroform furnishes the nitrone in the acid free form, hence illustrating its low basicity. The nitrone is then only hydrolyzed to a minor extent (<5%), whereas after prolonged hydrolysis (15 h) at room temperature complete hydrolytic cleavage can be achieved. In this way hydroxylamine hydrochloride **5** (84%) and adamantanone (96%) are obtained. Heating of **5** for 3 h in refluxing acetone under thorough exclusion of moisture, gives after cooling of the homogeneous reaction mixture to −10° crystals of α,α-dimethyl-N-(2-phenyl)prop-1-en-3-yl nitrone hydrochloride **2b** (30%). This is one of the few examples of the synthesis of a simple non-conjugated ketonitrone via condensation of a hydroxylamine and a ketone.[17–20] Alternatively, **2b** could be obtained directly by reaction of 2-chloro-2-nitrosopropane **1b** with 2-phenylpropene (*vide infra*).

In order to establish the scope of this new and convenient route to aliphatic ketonitrones, 2-phenylpropene was allowed to react with a series of α-chloronitroso compounds **1b–1e** (see Scheme 1). In generally somewhat faster reactions than with AdCINO **1a** (e.g. completion with **1b** requires only 12 h), high yields of analogous nitrone hydrochlorides were obtained as white powders (73–91%; see Table 1), with the exception of the cyclohexylidene derivative **2e**, which was obtained as a viscous yellow oil. No reaction occurred with the crowded α-chloronitroso compounds 2,2-dimethyl-3-chloro-3-nitrosobutane and 2,2,6,6-tetramethyl-1-chloro-1-nitrosocyclohexane, presumably for steric reasons.

Spectroscopic properties of the new nitrones are very similar and in full accord with the proposed structures. It is noteworthy, that non-symmetrical nitrones (i.e. $R^1 \neq R^2$) can exist, in principle, in two isomeric configurations.[14,15] The NMR spectrum of the α-methyl-α-benzyl derivative **2d** clearly indicates the presence of two such isomers in a ratio of approximately 3:1. On the other hand, the spectrum of the α-methyl-α-ethyl derivative **2c**, can be fully interpreted by assuming the presence of only one isomer (see Table 1).



Scheme 2.

Table 1. Yields and spectroscopic properties of nitrone hydrochlorides $R^1R^2C=N(-O\cdot HCl)CH_2C(=CH_2)C_6H_5$ 2b–2e

Nitrone	R^1	R^2	Yield (%)	IR ($CHCl_3$); ν_{max} in cm^{-1}	NMR ($CDCl_3$); δ in ppm
2b*	CH_3	CH_3	91	3450 (m), 2900-1740 (s), 1680-1660 (w), 1635 (w), 1500 (s), 1450 (s)	2.43 (s, CH_3), 2.52 (s, CH_3), 5.40 (broad s, CH_2 and HC:), 5.59 (s, HC:), 7.35 (m, Ar), 12.35 (OH)
2c*	CH_3	C_2H_5	79	3450 (w), 2870-1740 (s), 1670 (m), 1638 (w), 1500 (s), 1450 (s)	1.09 (t, CH_3, J = 7.5), 2.38 (s, CH_3), 2.81 (q, CH_2, J = 7.5), 5.41 (s, CH_2 and HC:), 5.55 (s, HC:), 7.35 (m, Ar), 11.25 (OH)
2d	CH_3	$C_6H_5CH_2$	73	3480 (w), 2900-1780 (s), 1680 (w), 1645 (w), 1510 (s), 1460 (s)	2.25† and 2.32 (s, CH_3), 4.05 and 4.14† (s, CH_2), 5.49 (m, CH_2 and H_2C:), 7.30 (m, 2Ar), 10.35 (OH)
2e	c-C_6H_{10}		76	3450 (w), 2850-1740 (s), 1670-1630 (m), 1500 (m), 1460 (s)	1.63 (m, $(CH_2)_3$), 2.70 (m, CH_2), 2.92 (m, CH_2), 5.39 (s, CH_2), 5.45 (s, HC:), 5.65 (s, HC:), 7.37 (m, Ar), 11.13 (OH)

* These nitrone derivatives could be obtained in an analytically pure form as white crystals, by crystallization from acetone and 2-butanone, respectively.

† These signals represent the major isomer.

Table 2. Yields (%), spectroscopic and analytical data of α,α-adamantylidene nitrone hydrochlorides 2a and 7a–7l, obtained by reaction of AdCINO with various mono-olefins containing substituents R^3CH_2[a], R^4 and R^5

Compound	R^4	R^5	Yield[b]	IR ($CHCl_3$), ν_{max} in cm^{-1}	NMR[c,d], δ in ppm	Element analysis[e]
2a	C_6H_5	H	96	3470(w),2870-1750(s),1660(m),1505(m),1460(s)	3.10(broad s,AdH),3.87(broad s,AdH),5.35(s,CH_2),5.59(s,H_2C:),7.38(m,Ar)	Calcd: C 71.92; H 7.57; Cl 11.04; N 4.41 Found: C 71.77; H 7.45; Cl 11.11; N 4.58
7a	p-FC_6H_4	H	90	3370(w),2800-1750(s),1625(w),1595(m),1500(s),1440(s)	3.13(broad s,AdH),3.87(broad s,AdH),5.36(s,CH_2),5.53(s,HC:),5.57(s,HC:),7.25(m,Ar)	Calcd: C 67.95; H 6.85; F 5.66; Cl 10.58; N 4.17 Found: C 68.04; H 6.95; F 5.70; Cl 10.56; N 4.26
7b	p-$CH_3C_6H_4$	H	89	3440(m),2700-1800(s),1650(m),1520(m),1455(s)	2.34(s,CH_3),3.14(broad s,AdH),3.87(broad s,AdH),5.35(s,CH_2),5.50(s,HC:),5.57(s,HC:),7.16(d,Ar,J=8,2H),7.32(d,Ar,J=8,2H)	Calcd: C 72.50; H 7.85; Cl 10.72; N 4.23 Found: C 72.44: H 7.96; Cl 10.87; N 4.14
7c	p-$NO_2C_6H_4$	H	93	3450(w),2800-1800(s),1640(w),1600(m),1530(s),1458(m),1350(s)	3.38(broad s,AdH),3.68(broad s,AdH),5.50(s,CH_2),5.67(s,HC:),5.92(s,HC:),7.87(d,Ar,J=8.5,2H),8.28(d,Ar,J=8.5,2H)	Calcd: C 62.89; H 6.34; Cl 9.79; N 7.72 Found: C 62.86; H 6.22; Cl 9.96; N 7.83
7d	p-$CH_3OC_6H_4$	H	76	3400(w),2800-1750(s),1650(w),1610(m),1510(s),1455(m),1250(s),1210(s)	3.13(broad s,AdH),3.84(broad s,AdH),3.77(s,CH_3),5.31(s,CH_2),5.40(s,HC:),5.49(s,HC:),6.87(d,Ar,J=9,2H),7.38(d,Ar,J=9,2H)	Calcd: C 69.16; H 7.49; Cl 10.23; N 4.03 Found: C 69.09; H 7.49; Cl 10.10; N 4.03

7e	H	H	76	3460(w),2850-1760(s),1650 (m),1615(w),1516(s),1500 (s),1460(s),1258(s)	3.37(broad s,AdH),3.87(broad s,AdH),5.11(d,CH_2,J=6),5.95 (s,CH_2O_2),6.38(m,HC:CH),6.80 (m,Ar)	Calcd: C 66.57; H 6.[illegible]; Cl 9.82; N 3.90 Found: C 66.49; H 6.84; Cl 10.03; N 4.23
7f	CH_3	C_2H_5	64 (91)	3460(m),2850-1700(s),1630 (m),1460(s)	1.03(t,CH_3,J=7),1.87(s,CH_3), 3.49(broad s,AdH),3.98(broad s,AdH),4.90(t,CH,J=6),5.18 (s,H_2C:)	Calcd: C 67.84; H 9.18; Cl 12.54; N 4.94 Found: C 67.68; H 9.06; Cl 12.43; N 5.06
7g	CH_3	CH_3	21 (95)	3470(m),2840-1760(s),1630 (m),1460(s)	1.70(d,CH_3,J=7),1.85(s,CH_3), 3.33(broad s,AdH),3.96(broad s,AdH),5.06(q,CH,J=7),5.09 (s,H_2C:)	Calcd: C 66.91; H 8.93; Cl 13.20; N 5.20 Found: C 66.67; H 8.96; Cl 13.26; N 5.17
7h	CH_3	H	33 (80)	3400(m),2800-1800(s),1650 (m),1450(s)	1.91(s,CH_3),3.22(broad s, AdH),3.96(broad s,AdH),4.97 (s,CH_2),5.11(s,HC:),5.17(s, HC:)	Calcd: C 65.88; H 8.63; Cl 13.90; N 5.49 Found: C 65.97; H 8.68; Cl 14.02; N 5.35
7i	c-C_3H_5	H	57 (95)	3495(w),2870-1760(s),1660 (m),1465(s)	0.60(m,$(CH_2)_2$),1.35(m,CH), 3.27(broad s,AdH),3.91(broad s,AdH),4.96(s,CH_2),5.00(s, HC:),5.05(s,HC:)	Calcd: C 68.32; H 8.54; Cl 12.63; N 4.98 Found: C 68.19; H 8.47; Cl 12.58; N 5.08

[a] R^3 is hydrogen in all cases, except for 7e where it is m,p-$CH_2O_2C_6H_3$.

[b] Values in parenthesis show yields corrected for recovered starting material 1a (i.e. AdClNO).

[c] All NMR spectra have been recorded in $CDCl_3$ solution, with the exception of the nitro derivative 7c, which was run in DMSO-d_6.

[d] In all cases the typical broad signals of the adamantyl group were observed at δ 1.55-2.40. The chemical shift of the hydrogen nuclei at the bridgehead positions next to the nitrone moiety are given separately for each nitrone as AdH.

[e] Derivatives 2a, 7b and 7e were purified by crystallization from acetonitrile. All other derivatives were obtained in an analytically pure form directly from the reaction mixture.

Reaction of AdClNO *with various allylic olefins.* The adamantylidene nitrone hydrochloride **2a** was of somewhat greater purity and stability than the analogues derived from the other α-chloronitroso compounds. We therefore elaborated this new synthetic route in particular for the sythesis of adamantylidene nitrones.

On reaction of AdClNO **1a** with the α-methylstyrenes **6a–6d**, carrying different *para* substituents, high yields of the expected nitrone hydrochlorides **7a–7d** were obtained in pentane or in diethyl ether solution, after varying reaction times (76–93%; see Table 2).

Safrole **6e**, which contains a double bond not in conjugation with the phenyl group, gave in a relatively fast reaction a high yield of the crystalline adamantylidene nitrone hydrochloride **7e** (76% after 3 days), in which the double bond is shifted to an electronically favourable direction, i.e. in conjugation with the phenyl group. It should ne noted that the NMR spectrum of **7e** is rather complex, apparently due to the presence of *E–Z* isomers of the olefinic double bond system, as becomes more evident from spectra of a degradation product (see below).

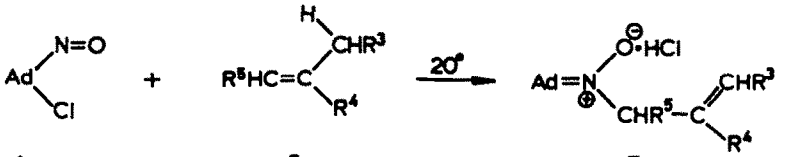
Olefins exclusively containing aliphatic substituents R (i.e. **6f–6i**) have also been made to react with AdClNO **1a**. Conversions were very slow in pentane solution at room temperature, and even after 27 days incomplete. Apart from unreacted starting material, the adamantylidene nitrone hydrochlorides **7f–7i** were virtually the only products (see Table 2). The structure of the nitrone hydrochlorides derived from 2-methylpentene-2 **6f** and 2-methylbutene-2 **6g** again shows that product formation occurs with rearrangement of the double bond. It is noteworthy that these olefins have two types of allylic hydrogen; in principle, this can lead to different (isomeric) nitrones. Thorough spectral analysis indicates that in both cases only one of the possible isomers is formed: the one with the nitrone group attached to the originally least substituted site of the olefinic double bond.

With the nitrone hydrochlorides **7e**, **7f** and **7i**, derived from safrole, 2-methylpentene-2 and 2-cyclopropylpropene, respectively, some typical degradation reactions were carried out. The corresponding free nitrones **8** could be obtained from the salts by means of ammonia, or by rapid extraction of an aqueous solution with chloroform. Hydrolysis furnished almost quantitatively equimolar amounts of adamantanone and hydroxylamine **9** (see Scheme 4). Spectroscopic properties of the free nitrones **8** and hydroxylamines **9** are given in the experimental section, where the NMR spectrum of hydroxylamine **9e** (R^3 = m,p-$CH_2O_2C_6H_3$, R^4=R^5=H) clearly indicates the presence of the *Z* and *E* isomer in a ratio of 2:7.

EXPERIMENTAL

IR spectra were recorded on a Unicam SP200 or a Perkin Elmer 257 spectrophotometer. The ^{1}H NMR spectra were measured on a Varian A60, A60D or HA100 instrument, and were usually obtained from solutions in deuteriochloroform, with TMS ($\delta = 0$) as an internal standard. MS spectra were determined on an AEI MS-902 or a Varian MAT-711 instrument. M.ps are uncorrected and were taken on a Reichert m.p. apparatus.

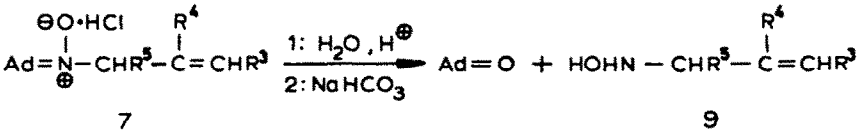
α-Chloronitrosoadamantane[21] **1a**, 2-chloro-2-nitrosopropane[22] **1b**, 2-chloro-2-nitrosobutane[22] **1c**, 1-phenyl-2-chloro-2-nitrosopropane[22] **1d** and α-chloronitrosocyclohexane[23] **1e** were prepared by the action of chlorine on the appropriate oximes, according to literature methods, and were purified prior to use, by distillation or by chromatography (silica gel/n-pentane). Safrole **6e**, 2-methylpentene-2 **6f** and isobutene **6h** were Fluka products. 2-Phenylpropene and 2-methylbutene-2 **6g** were also commercially available (E. Merck). 2-Cyclopropylpropene **6i** was synthesized according to the procedure of Volkenburgh *et al.* (yield 30%. B.p. 70–71°; lit.[24] 70.4°). This involves the addition of CH_3MgI to methylcyclopropyl ketone, followed by dehydration (H_2SO_4) of the formed tertiary alcohol. 4-Fluoro- **6a** (54%), 4-methyl- **6b** (50%) and 4-methoxy-α-methylstyrene **6d** (63%) were similarly prepared from the corresponding substituted acetophenones.[25] 4-Nitro-α-methylstyrene **6c** was prepared from 4-nitrocumene, by bromination with NBS and subsequent base (KOH) catalysed elimination of HBr from 2-(4-nitrophenyl)-2-bromopropane (yield 32%. M.p.



1a **6** **7**

	R^3	R^4	R^5		R^3	R^4	R^5
6/7 a:	H	p-F-C_6H_4	H	**6/7 f:**	H	CH_3	C_2H_5
b:	H	p-CH_3-C_6H_4	H	**g:**	H	CH_3	CH_3
c:	H	p-NO_2-C_6H_4	H	**h:**	H	CH_3	H
d:	H	p-CH_3O-C_6H_4	H	**i:**	H	c-C_3H_5	H
e:	m,p-$CH_2O_2C_6H_3$	H	H				

Scheme 3.



7 **9**

Scheme 4.

52–53°. lit.[26] 53–53.5°). The deuteriated α-methylstyrene was prepared from $PhCOCD_3$ by a Wittig reaction, following Ref. 27.

Formation of nitrone hydrochlorides. Reactions of α-chloronitroso compounds 1 with 2-phenylpropene were performed by dissolving 5 mmol of the nitroso compound in 25 mmol of the olefin. Stirring of the solution at 20° in the dark then furnished the nitrone hydrochloride as a white precipitate. Isolation of the solid was effected by filtration, and subsequent repeated trituration with anhydrous diethyl ether. When acetonitrile or chloroform was used as a co-solvent, no crystalline product was formed during the decolouration reaction. The same nitrone salt could then be obtained after removal of the solvent and excess of olefin at diminished pressure. From AdClNO and 2-phenylpropene this afforded a yield of 80% of nitrone **2a** after 2 days in acetonitrile, and a yield of 94% after 6 days in chloroform solution.

Reactions of AdClNO *with olefins* **6a–6i** were carried out with 0.5 M n-pentane or diethyl ether as apolar solvent. In all cases this furnished a crystalline product in the reaction mixture.

Isolation of free α,α-adamantylidene nitrones. The free nitrones could be obtained in an almost quantitative way, by addition of an excess of liquid ammonia to an emulsion of the nitrone salts (1.2 mmol) in 50 ml of diethyl ether, and stirring of the mixture at room temperature under careful anhydrous conditions, until all unreacted ammonia had evaporated spontaneously. Rapid removal of NH_4Cl by filtration and evaporation of the ether, furnished white crystalline α,α-adamantylidene nitrones. *Nitrone* **3a** *derived from 2-phenylpropene.* IR ($CHCl_3$): 1640 (w), 1608 (m), 1500 (w), 1460 (m), 1150 (s), 1100 (m) and 1082 (m) cm^{-1}. NMR ($CDCl_3$): δ 1.85 (broad s, Ad, 12H), 2.80 (broad s, AdH, 1H), 3.95 (broad s, AdH, 1H), 4.90 (s, CH_2, 2H), 5.36 (s, HC:, 1H), 5.52 (m, HC:, unres. couplings, 1H), 7.34 (m, Ar). *Nitrone* **8e** *derived from safrole.* IR ($CHCl_3$): 1650 (w), 1605 (m), 1505 (s), 1490 (s), 1450 (s), 1250 (s), 1145 (s) and 1040 (s) cm^{-1}. NMR ($CDCl_3$): δ 1.80 (broad s, Ad, 12H), 3.0 (broad s, AdH, 1H), 3.88 (broad s, AdH, 1H), 4.63 (d, CH_2, J = 6, 2H), 5.87 (s, CH_2O_2, 2H), 6.03–6.96 (m, Ar and HC:CH, 5H). *Nitrone* **8f** *derived from 2-methylpentene-2.* IR ($CHCl_3$): 1650 (w), 1580 (m), 1458 (s), 1150 (s), 1100 (s), 1090 (s), 1074 (s) and 908 (s) cm^{-1}. NMR ($CDCl_3$): δ 0.89 (t, CH_3, J = 7, 3H), 1.79 (m, CH_3–C:, unres. couplings), 1.87 (broad s, Ad), 2.25 (m, CH_2, 2H), 3.15 (broad s, AdH, 1H), 4.00 (broad s, AdH, 1H), 4.55 (m, CH_X, J_{AX} = 9, J_{BX} = 5, 1H), 4.98 (s, H_2C:, 2H). *Nitrone* **8i** *derived from 2-cyclopropylpropene.* IR ($CHCl_3$): 1650 (w), 1608 (m), 1460 (s), 1150 (s), 1100 (s), 1095 (s), 1080 (s) and 955 (m) cm^{-1}. NMR ($CDCl_3$): δ 0.30–0.84 (m, CH_2CH_2, 4H), 1.40 (m, CH, 1H), 1.90 (broad s, Ad, 12H), 2.91 (broad s, Ad, 1H), 3.96 (broad s, AdH, 1H), 4.57 (s, CH_2, 2H), 4.90 (m, H_2C:, unres. couplings, 2H).

Synthesis of β,γ-unsaturated hydroxylamines. Nitrone hydrochloride **2a** or **7** was dissolved in dilute hydrochloric acid, and the solution was stirred overnight at room temperature. The formed adamantanone was subsequently removed by repeated extraction of the water layer with n-pentane. Neutralization ($NaHCO_3$) of the remaining water layer was followed by extraction with chloroform. Drying of the extracts ($MgSO_4$) and removal of the solvent at diminished pressure, gave the β,γ-unsaturated hydroxylamine. *2-Phenylprop-1-en-3-ylhydroxylamine* **5**. Yield 95%. White plates (PA 40–60/diethyl ether). M.p. 65–66.5°. IR ($CHCl_3$): 3670 (m), 3350 (s), 1638 (m), 1610 (w), 1585 (w), 1510 (m), 1030 (s) and 920 (m) cm^{-1}. NMR ($CDCl_3$): δ 3.88 (s, CH_2, 2H), 5.23 (d, HC:, J ~ 1, 1H), 5.44 (d, HC:, J ~ 1, 1H), 5.87 (NHOH), 7.30 (m, Ar). MS: *m/e* 149 (M^+). (Found: C, 72.32; H, 7.49; N, 9.54. $C_9H_{11}NO$ requires: C, 72.48; H, 7.38; N, 9.39%). *Hydroxylamine* **9e** (R^3 = m,p-$CH_2O_2C_6H_3$, R^4=R^5=H). Yield 70%. White plates (diethyl ether). M.p. 73–76°. IR ($CHCl_3$): 3650 (w), 3350 (m), 1663 (w), 1615 (w), 1518 (s), 1500 (s), 1255 (s) and 1044 (s) cm^{-1}. NMR ($CDCl_3$): δ 5.90 (s, CH_2O_2, 2H), 6.25 (NHOH), 6.80 (m, Ar, 3H), other protons, see below. MS: *m/e* 193 (M^+). (Found: C, 62.13; H, 5.63; N, 7.34. $C_{10}H_{11}NO_3$ requires: C, 62.17; H, 5.74; N, 7.25%). *Hydroxylamine* **9f** (R^3=H, R^4=CH_3, R^5=C_2H_5). Yield 64%. Colourless oil. IR ($CHCl_3$): 3640 (w), 3300 (s), 1650 (m), 1458 (s) and 900 (s) cm^{-1}. NMR ($CDCl_3$): δ 0.85 (t, CH_3, J = 7.5, 3H), 1.50 (m, CH_2, 2H), 1.70 (s, CH_3, 3H), 3.34 (m, CH, J_{AX} = 8, J_{BX} = 6, 1H), 4.93 (m, H_2C:, 2H), 6.07 (NHOH). The MS (70 eV) exhibits the following main peaks (*m/e* (composition, %)): 115 ($C_6H_{13}NO$, 2.3), 87 (C_4H_9NO, 15), 86 (C_4H_8NO, 100), 84 (C_4H_6NO, 6.8), 74 (C_3H_8NO, 19.5), 70 (C_4H_8N, 40), 68 (C_4H_6N, 20), 55 (C_3H_5, 61.6), 41 (C_3H_5, 85), 39 (C_3H_3, 27), 29 (C_2H_5, 16). *Hydroxylamine* **9i** (R^3=R^5=H, R^4=c-C_3H_5). Yield 100%. Colourless oil. IR ($CHCl_3$): 3650 (w), 3350 (s), 1650 (m), 1440 (m), 1022 (s) and 900 (s) cm^{-1}. NMR ($CDCl_3$): δ 0.30–0.91 (m, CH_2CH_2, 4H), 1.12–1.63 (m, CH, 1H), 3.56 (s, CH_2, 2H), 4.87 (s, H_2C:, 2H), 6.27 (NHOH). The MS (70 eV) exhibits the following main peaks (*m/e* (composition, %)): 113 ($C_6H_{11}NO$, 0.5), 96 ($C_6H_{10}N$, 30), 82 (C_6H_{10}, 44), 67 (C_5H_7, 60), 46 (CH_4NO, 100). *N-(2-phenyl)prop-1-en-3-yl-N-(2-cyanoadamantyl-2)hydroxylamine* **4a**. In 10 ml of dry (CaH_2) DMSO were dissolved 1 g (3.56 mmol) of free nitrone **3a** and a five-fold excess of potassium cyanide (1.35 g). After stirring this solution for 3 days at room temperature, 50 ml of water was added. Extraction of the water layer with small portions of diethyl ether and evaporation of the solvent after drying ($MgSO_4$), afforded 0.58 g of a pale yellow solid. Crystallization from ether then gave 0.41 g (1.33 mmol) of pure **4a** as white needles. Yield 37%. M.p. 131–132°. IR ($CHCl_3$): 3580 (s), 3380 (m), 2230 (w), 1630 (w), 1600 (w), 1495 (m), 1455 (s), 1100 (s) and 910 (m) cm^{-1}. NMR ($CDCl_3$): δ 1.33–2.38 (Ad, 14H), 3.81 (s, CH_2, 2H), 4.80 (s, OH), 5.37 (s, HC:, 1H), 5.42 (s, HC:, 1H), 7.31 (m, Ar). (Found: C, 77.82; H, 7.78; N, 9.13. $C_{20}H_{24}N_2O$ requires: C, 77.92; H, 7.79; N, 9.09%).

REFERENCES

[1]L. Alessandri, *Gazz. Chim. Ital.* **51**, 129 (1921); and Refs. cited therein.

[2]G. T. Knight and B. Saville, *Cork Mechanisms Conference* No. 4, Kinsale, Republic of Ireland (1971).

[3]G. T. Knight and B. Pepper, *Tetrahedron* **27**, 2601 (1971).

[4]G. T. Knight, *J. Chem. Soc., Chem. Commun.* 1016 (1970).

[5]R. E. Banks, R. N. Haszeldine and P. J. Miller, *Tetrahedron Letters* 4417 (1970).

[6]G. T. Knight and B. Pepper, *J. Chem. Soc., Chem. Commun.* 1507 (1971).

[7]M. E. Cain, G. T. Knight and P. M. Lewis, *Chem. and Ind.* 126 (1970).

[8]L. S. Zherebkova, A. S. Shashkov, T. N. Dyumayeva, E. Ya. Devirts and F. A. Galil-Ogly, *Vysokomol. Soedin*, Ser. A **11**, 227 (1969) [*Chem. Abs.* **70**, 88671y (1969)].

[9]J. Hamer and A. Macaluso, *Tetrahedron Letters* 381 (1963).

[10]B. Pepper and M. Porter, *J. Chem. Soc., Chem. Commun.* 130 (1974).

[11]N. P. Kolak, *Diss. Abstr. Int. B*, 6921 (1972).

[12]R. E. Banks, M. G. Barlow and R. N. Haszeldine, *J. Chem. Soc.* 4714 (1965).

[13]W. B. Motherwell and J. S. Roberts, *J. Chem. Soc., Chem. Commun.* 329 (1972).

[14]J. Hamer and A. Macaluso, *Chem. Rev.* **64**, 473 (1964).

[15]G. R. Delpierre and M. Lamchen, *Quart. Rev. Chem. Soc.* **19**, 329 (1965).

[16]B. Zeeh and H. Metzger *Methoden der Organischen Chemie* (Edited by Houben–Weyl). Vol. 10–1, pp. 1207–1208. Georg Thieme Verlag, Stuttgart (1971).

[17]O. Exner, *Collect. Czech. Chem. Commun.* **16**, 258 (1951).

[18]G. Zinner and B. Geister, *Arch. Pharm.* **306**, 898 (1973).

[19]P. M. Weintraub and P. L. Tiernan, *J. Org. Chem.* **39**, 1061 (1974).

[20]D. H. R. Barton, M. J. Day, R. H. Hesse and M. M. Pechet, *J. Chem. Soc., Perkin Trans. I*, 1765 (1975).

[21]A. H. M. Kayen, L. R. Subramanian and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas* **90**, 866 (1971).

[22]M. Kosinski, *Lodz. Towarz. Nauk. Wijdzial III, Acta Chim.* **9**, 93 (1964); [*Chem. Abs.* **62**, 11674b (1965)].

[23]E. Müller, H. Metzger and D. Fries, *Chem. Ber.* **87**, 1449 (1954).

[24]Ross van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Am. Chem. Soc.* **71**, 172 (1949).

[25]J. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

[26]G. Brubacher and E. Suter, *Helv. Chim. Acta* **33**, 256 (1950).

[27]H. C. Volger, *Recl. Trav. Chim. Pays-Bas* **86**, 684 (1967).