Spontaneous free radical/spin adduct formation and 1,3-dipolar molecular addition in reactions of cyanohalocarbons and *C*-phenyl *N*-*tert*-butyl nitrone (PBN)

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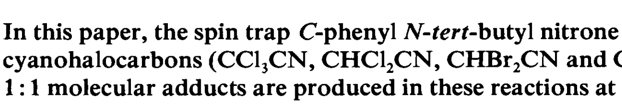
In this paper, the spin trap *C*-phenyl *N*-*tert*-butyl nitrone ‡ (PBN) is reported to react with cyanohalocarbons (CCl_3CN, $CHCl_2CN$, $CHBr_2CN$ and CH_2BrCN) in a molecular reaction. Some 1 : 1 molecular adducts are produced in these reactions at room temperature in hexane *via* 1,3-dipolar cycloaddition. These addition compounds have been studied by GC–MS and MS–MS spectrometry.

At the same time, various free radicals are formed spontaneously from these systems. These radicals are detected by EPR spin trapping techniques and assigned as follows: carbon-centred radical ($^{\bullet}CH_2CN$ and $^{\bullet}CHBrCN$) spin adducts, nitrogen-centred radical ($^{\bullet}N{=}C{=}CCl_2$, $^{\bullet}N{=}C{=}CHCl$ and $^{\bullet}N{=}C{=}CHBr$) spin adducts, oxygen-centred radical spin adducts and benzoyl-*tert*-butylaminoxyl.

Introduction

The [3 + 2] cycloaddition reactions of 1,3-dipoles have been intensely investigated in the last two decades[1,2] and their importance in natural product synthesis has been thoroughly established.[3] This reaction is defined as the reaction of a 1,3-dipole adding across a dipolarophile, which might be a double or a triple bond. The resulting product is a five-membered ring heterocycle. Nitrones commonly used in spin trapping may undergo 1,3-dipolar addition reactions with certain alkenes because of their 1,3-dipolar character. Numerous examples exist in the literature of reactions involving nitrones and alkenes and alkynes,[4] *e.g.* isoxazolidines are known to be formed in reaction (1).


(1)

In attempts to detect free radicals by the spin-trapping technique,[5] possible 1,3-dipolar addition reactions between compounds which can function as 1,3-dipolarophiles and nitrone spin traps have been largely ignored. If no new spin adducts are formed by 1,3-dipolar addition reactions, this practice may be justified. The only factor influencing the outcome of the experiment might be a diminished local concentration of the spin trap.

However if the 1,3-dipolar addition reaction leads to new reactive radicals, this process may constitute the worst of all possibilities; namely the probe generates reactive free radicals in the system it is sent to probe! As more use is made of nitrones as spin traps, the chemistry of possible molecular reactions with these compounds should be investigated. In this paper *C*-phenyl *N*-*tert*-butyl nitrone (PBN) is reported to react with cyanohalomethanes in a molecular reaction and at the same time various spin adducts are formed. The results obtained to date on this system are described.

One of the first observations of this type was between a peracid and PBN. Thus *m*-chloroperbenzoic acid when mixed with PBN in benzene gave a strong electron paramagnetic resonance (EPR) spectrum which was interpreted and assigned as follows: the *m*-chlorobenzoyloxyl adduct of PBN, benzoyl-*tert*-butylaminoxyl (PBNOX), the hydroxyl and *m*-cholorophenyl adducts of PBN and di-*tert*-butylaminoxyl.[6] Thus it is clear that mixing this peracid with PBN produces a variety of free radicals: some very reactive, *e.g.* the benzoyloxyl radical, and some more persistent and unreactive, *e.g.* the aminoxyl radicals. In this sense this system could be viewed as a case of a 'molecule assisted free-radical reaction' where two non-radical molecules combine to produce radicals after mixing.[7] This paper attempts to explore the possibility that cyanohalocarbons and PBN also undergo reactions which could be called 'molecule assisted free radical formation'.

There is another variation of this phenomenon which can apply to this case, namely the metal ion assisted addition of water to the nitrone producing the hydroxyl adduct of the spin trap.[8] Thus, if a transition metal in a higher oxidation state complexes with the oxygen atom of the nitrone and serves as a Lewis acid catalyst for the addition of nucleophilic water to the carbon atom of the nitrone followed by oxidation of the thus-formed hydroxylamine, the spin adduct is a new free radical produced by the combination of two non-radical molecules, or 'metal-ion assisted molecular addition' with free radical formation. Our group is studying ways to recognize situations where molecule assisted free radical formation occurs leading to EPR and MS detected spin adducts.[9]

In this paper we report on reaction chemistry between trichloro-, dichloro-, dibromo- or bromo-cyanomethane and PBN as studied by EPR spectroscopy, tandem mass spectrometry (MS–MS) and gas chromatography mass spectrometry (GC–MS).

Experimental

Materials

PBN, [$^2H_{14}$]PBN and [$^2H_9$,α-^{13}C]PBN were obtained from OMRF Spin Trap Source.[10] The hexane used was HPLC grade.

CCl_3CN (98% purity), $CHCl_2CN$ (98% purity), $CHBr_2CN$ (95% purity) and CH_2BrCN (97% purity) were purchased from Aldrich and used without purification.

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‡ IUPAC name: *N*-benzylidene-*tert*-butylamine *N*-oxide.

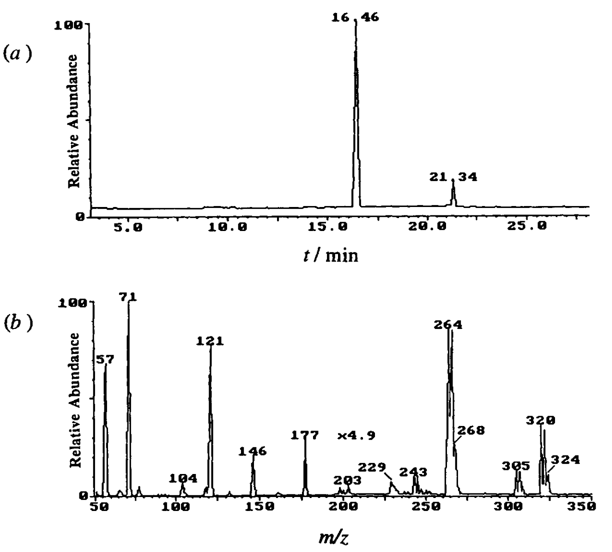


Fig. 1 (*a*) TIC gas chromatogram recorded from the reaction mixture of PBN and CCl_3CN in hexane after 2 h. (*b*) EI (15 eV) mass spectrum at the retention time of 21.34 min.

Sample preparation

0.2 M of each cyanomethane was mixed with 0.15 M PBN (or $[^2H_{14}]$PBN or $[^2H_9, {}^{13}C]$PBN) in hexane at room temperature.

For the CCl_3CN and PBN or $CHCl_2CN$ and PBN systems, CCl_3CN or $CHCl_2CN$ were completely soluble in hexane. A 1 ml sample was bubbled with N_2 for 15 min and investigated by EPR spectroscopy. A 5–10 µl sample was used for EI MS–MS measurement and a 1–2 µl sample was sufficient for GC–MS measurement.

For the system of $CHBr_2CN$ or CH_2BrCN and PBN, $CHBr_2CN$ and CH_2BrCN were not completely soluble in hexane. The reaction mixture was bubbled with N_2 for 15 min. Then both the hexane layer and the cyanomethane layer were studied by EPR spectroscopy. The 5–10 µl hexane layer was investigated by EI MS–MS.

The reaction mixtures of cyanohalocarbons (CCl_3CN, $CHCl_2CN$ and $CHBr_2CN$) and PBN can be chromatographed on silica gel with CH_2Cl_2 as the eluent. The 1 : 1 molecular adducts of cyanohalocarbons and PBN were obtained. The yields increase as the reaction time increases.

The yield for CCl_3CN–PBN increases from 10 to 85% as the reaction time increases from 1 h to a week; mp 93–95 °C. GC–MS shows less than 2% impurity. EI MS (70 eV): *m*/*z* (relative intensity), 57 (100.0%), 71 (12.5), 77 (21.7), 104 (12.1), 121 (39.4), 177 (1.9), 198 (2.1), 200 (1.4), 202 (0.2), 263 (1.0), 264 (1.6), 265 (1.2), 266 (1.5), 267 (0.6), 268 (0.5), 320 (1.5), 322 (1.5) and 324 (0.5).

The yield for $CHCl_2CN$–PBN increases from 2 to 35% as the reaction time increases from 1 h to a week; mp 57–59 °C. GC–MS shows less than 3% impurity. EI MS (70 eV): *m*/*z* (relative intensity), 57 (100.0%), 71 (10.9), 77 (21.8), 89 (7.2), 104 (15.2), 121 (54.2), 177 (5.1), 229 (1.5), 230 (2.4), 231 (1.4), 232 (1.6), 233 (0.5), 234 (0.3), 271 (0.5), 273 (0.3), 286 (2.1), 288 (1.4) and 290 (0.2).

The yield for $CHBr_2CN$–PBN was less than 5% after 3 days reaction. EI MS (70 eV): *m*/*z* (relative intensity), 57 (100.0%), 71 (12.0), 77 (44.8), 89 (12.7), 104 (23.1), 121 (59.7), 177 (22.2), 208 (6.3), 210 (6.2), 317 (1.0), 318 (1.8), 319 (2.1), 320 (2.3), 321 (1.4), 322 (1.2), 374 (1.6), 376 (3.2) and 378 (1.6).

The 1 : 1 adduct of CH_2BrCN–PBN was not isolated because of its very low yield.

Mass spectrometric analysis

EI mass spectra were obtained with a VG-Fisons Quattro triple stage quadrupole mass spectrometer. A direct mixture analysis was performed using an insertion probe. The source temperature was 180 °C. The electron energy employed was 15 or 70 eV. The probe temperature was 20–30 °C.

Argon was used for the collision induced dissociation (CID). The collision energy for MS–MS analysis was 100 eV.

GC–MS spectra were recorded with a Hewlett-Packard 5890 series II GC interfaced directly with the VG-Fisons Quattro triple stage quadrupole mass spectrometer. The mode of ionization was EI at 70 or 15 eV. Chromatographic separation was carried out with a Quadrex Corporation 0.25 mm × 30 m methyl 5% phenyl fused silica capillary column with the temperature programmed from 55 to 220 °C at 7° min^{-1}. Helium was used as the carrier gas.

EPR measurements

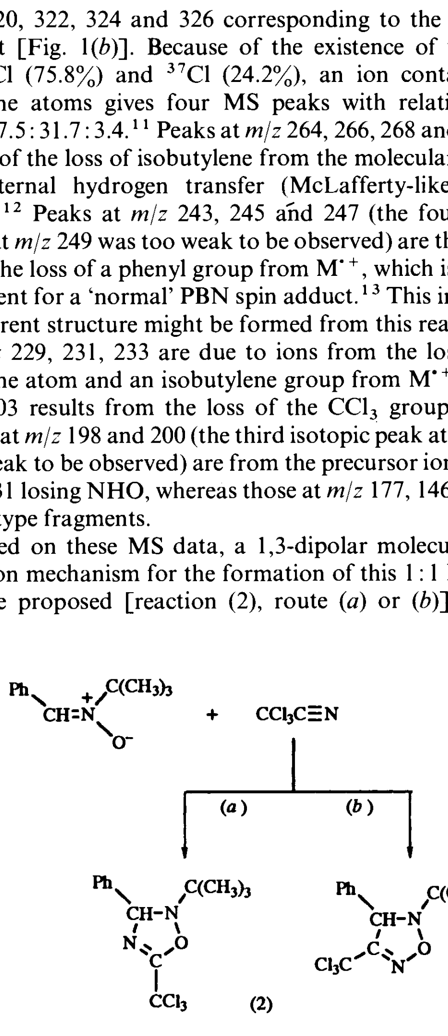
EPR spectra were recorded using a Bruker ER300E spectrometer with 100 kHz field modulation. Round quartz sample cells with 3.5 mm id were employed for the analysis of the hexane layer sample. Capillary glass tubes with 1 mm id were used for the measurement of the cyanomethane layer.

Results and discussion

Mass spectrometric studies

CCl_3CN + PBN. When CCl_3CN was mixed with PBN in hexane, a 1 : 1 adduct was formed and was stable enough to be detected by GC–MS. The total ion current (TIC) gas chromatogram of this reaction mixture shows two peaks at retention time *t* = 16.46 and 21.34 min [Fig. 1(*a*)]. These two peaks were assigned by their corresponding mass spectra. The peak at *t* = 16.46 min is from unreacted PBN. The peak at *t* = 21.34 min was assigned to the 1 : 1 molecular adduct of CCl_3CN and PBN based on the observation of isotopic peaks at *m*/*z* 320, 322, 324 and 326 corresponding to the mass of the adduct [Fig. 1(*b*)]. Because of the existence of the isotopes of ^{35}Cl (75.8%) and ^{37}Cl (24.2%), an ion containing three chlorine atoms gives four MS peaks with relative intensity 100 : 97.5 : 31.7 : 3.4.[11] Peaks at *m*/*z* 264, 266, 268 and 270 are the result of the loss of isobutylene from the molecular ions ($M^{\bullet+}$) by internal hydrogen transfer (McLafferty-like rearrangement).[12] Peaks at *m*/*z* 243, 245 and 247 (the fourth isotopic peak at *m*/*z* 249 was too weak to be observed) are the fragments from the loss of a phenyl group from $M^{\bullet+}$, which is an unusual fragment for a 'normal' PBN spin adduct.[13] This indicates that a different structure might be formed from this reaction. Peaks at *m*/*z* 229, 231, 233 are due to ions from the loss of both a chlorine atom and an isobutylene group from $M^{\bullet+}$. The ion at *m*/*z* 203 results from the loss of the CCl_3 group from $M^{\bullet+}$. Peaks at *m*/*z* 198 and 200 (the third isotopic peak at *m*/*z* 202 was too weak to be observed) are from the precursor ions at *m*/*z* 229 and 231 losing NHO, whereas those at *m*/*z* 177, 146 and 121 are PBN-type fragments.

Based on these MS data, a 1,3-dipolar molecular addition reaction mechanism for the formation of this 1 : 1 PBN adduct can be proposed [reaction (2), route (*a*) or (*b*)]. From this



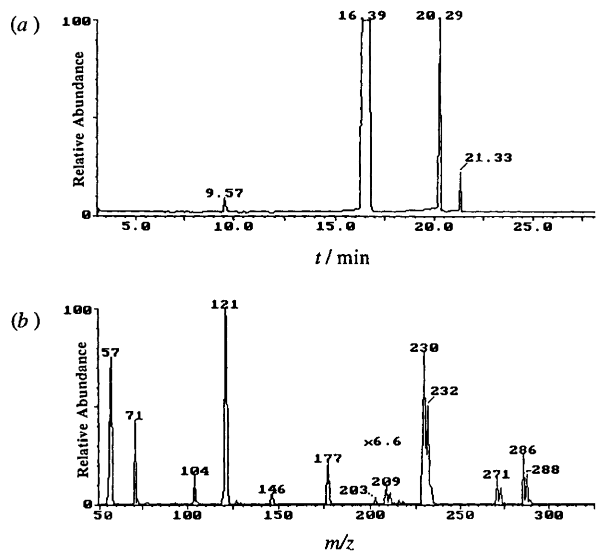
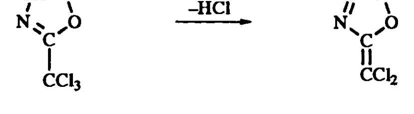


Fig. 2 (*a*) TIC gas chromatogram recorded from the reaction mixture of PBN and $CHCl_2CN$ in hexane after 12 h. (*b*) EI (15 eV) mass spectrum at a retention time of 20.29 min.

reaction, two different structures might be formed. However route (*a*) seems more likely based on the following arguments. Since PBN spin adducts usually produce an abundant fragment by EI, namely *m*/*z* 57 (*tert*-butyl group), a scan of the precursors of *m*/*z* 57 was recorded during MS–MS analysis to find ions potentially due to PBN spin adducts. In addition to the peaks at *m*/*z* 320, 322, 324 and 326 ($M^{\bullet +}$), *m*/*z* 243, 245 and 247 $[M - Ph]^+$ and *m*/*z* 203 $[M - CCl_3]^+$, another ion was observed at *m*/*z* 284, 286 and 288 in the precursor spectrum of *m*/*z* 57. This is not a fragment of $M^{\bullet +}$ because it was not observed in the GC–MS spectrum of PBN–CCl_3CN. It was also not observed in the product ion spectra of *m*/*z* 320, 322 and 324, indicating that it is not produced by the CID process. It might be the loss of HCl from the 1:1 adduct from route (*a*) [reaction (3)]. The relative intensity of the isotopic peaks indicates that this ion contains two chlorine atoms (the relative intensity is 100:65.0:10.6 for an ion containing two chlorine atoms).



(3)

This structure is probably stabilized by conjugation after losing HCl. No other spin adducts were observed in such precursor ion spectra, probably because their concentration is too low to be detected.

$CHCl_2CN$ + PBN. Similarly to CCl_3CN, when $CHCl_2CN$ is mixed with PBN in hexane at room temperature the formation of a 1:1 adduct results. The TIC gas chromatogram of this system shows four peaks at retention time t = 9.57, 16.39, 20.29 and 21.33 min, respectively [Fig. 2(*a*)]. Again the peak at t = 16.39 min is due to unreacted PBN. The mass spectrum of the peak at t = 9.57 min gives a molecular ion at *m*/*z* 161 which might be assigned to Ph–CH=N–$C(CH_3)_3$. Comparing with Fig. 1(*a*) and its corresponding mass spectra, the peak at t = 21.33 min is known to be the 1:1 adduct of CCl_3CN and PBN, which indicates that the chemical $CHCl_2CN$ is not pure (label purity 98%); it might contain some CCl_3CN as an impurity.

By the observation of isotopic peaks at *m*/*z* 286, 288 and 290 with the relative intensity similar to two chlorine ions [Fig. 2(*b*)] the peak at t = 20.29 min is assigned to the 1:1 adduct of $CHCl_2CN$ and PBN, which is the major product detected from this system by GC–MS. The area ratio of the two peaks at t = 20.29 min (due to $CHCl_2CN$–PBN) and 21.33 min (due to CCl_3CN–PBN) in the TIC gas chromatogram is *ca.* 100:12. A larger amount of CCl_3CN was detected than we expected based on the label purity (98%). This is because the amount of $CHCl_2CN$ used was in excess in the system, and CCl_3CN is more reactive than $CHCl_2CN$ (see yields in the Experimental section). In Fig. 2(*b*), peaks at *m*/*z* 271, 273 and 275 are the fragments of the loss of the methyl group from the molecular ions $M^{\bullet +}$. Peaks at *m*/*z* 230, 232 and 234 are attributed to fragments due to the loss of isobutylene from $M^{\bullet +}$. Losing isobutylene and β-H results in the fragments at *m*/*z* 229, 231 and 233. Peaks at *m*/*z* 209, 211 and 213 are fragments of the loss of a phenyl group. The peak at *m*/*z* 203 is assigned to the ion from the loss of a $CHCl_2$ group.

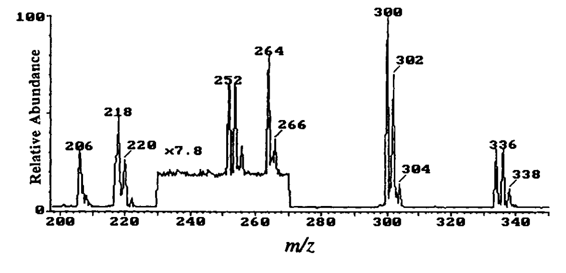
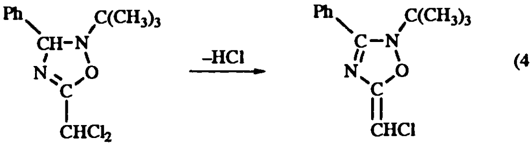


Fig. 3 Precursor ion spectrum of *m*/*z* 66 recorded during the EI (15 eV) MS–MS analysis of the reaction mixture of $[^2H_{14}]$PBN and $CHCl_2CN$ in hexane after 2 h

Therefore, we conclude that a similar structure of a 1:1 adduct between $CHCl_2CN$ and PBN was formed in this reaction system [route (*a*) or (*b*)]. Because of this five-membered ring structure, observation of the fragments due to the loss of phenyl, $CHCl_2$ groups and isobutylene from $M^{\bullet +}$ might be possible.

When $[^2H_{14}]$PBN was used instead of PBN, a precursor ion scan of *m*/*z* 66 ($C_4D_9{}^+$) was recorded (Fig. 3). Peaks at *m*/*z* 300, 302 and 304 are from the molecular ion of the 1:1 adduct of $CHCl_2CN$ and $[^2H_{14}]$PBN. Compared with $CHCl_2CN$–PBN, these peaks shift 14 Da from *m*/*z* 286, 288 and 290, respectively. Peaks at *m*/*z* 218, 220 and 222 are the fragments from loss of phenyl from the molecular ions. Peaks at *m*/*z* 334, 336, 338 and 340 are attributed to the 1:1 adduct of CCl_3CN and $[^2H_{14}]$PBN since CCl_3CN appears to be an impurity in commercial $CHCl_2CN$ (these peaks also shift 14 Da). Ions at *m*/*z* 252, 254 and 256 are the result of the loss of phenyl from the molecular ion of CCl_3CN–$[^2H_{14}]$PBN. Loss of $CHCl_2$ and CCl_3 groups from each corresponding molecular ion gives the fragment at *m*/*z* 217. Ions containing one chlorine (relative intensity 100:32.5) were observed at *m*/*z* 264 and 266, which might be assigned to another molecular ion $M_1{}^{\bullet +}$ produced by loss of HCl from the 1:1 adduct [reaction (4)]. Again two compounds could be formed in this 1:1 molecular addition reaction [route (*a*) or (*b*) in reaction (1)], however only one would form a stable molecule as the result of the loss of HCl from this 1:1 adduct. The corresponding structure is shown in reaction (4).



(4)

$CHBr_2CN$ + PBN. A 1:1 adduct was observed in both the EI mass spectrum [Fig. 4(*a*)] and the precursor ion spectrum of *m*/*z* 57 [Fig. 4(*b*)] when $CHBr_2CN$ was mixed with PBN in hexane. For an ion which contains two bromine atoms, three isotopic peaks are expected with relative intensity 51:100:49 because of the existence of the isotope of ^{79}Br (50.5%) and ^{81}Br (49.5%). Therefore, in Fig. 4(*a*), the isotopic peaks at *m*/*z* 374, 376 and 378 are from the 1:1 adduct of $CHBr_2CN$ and PBN.

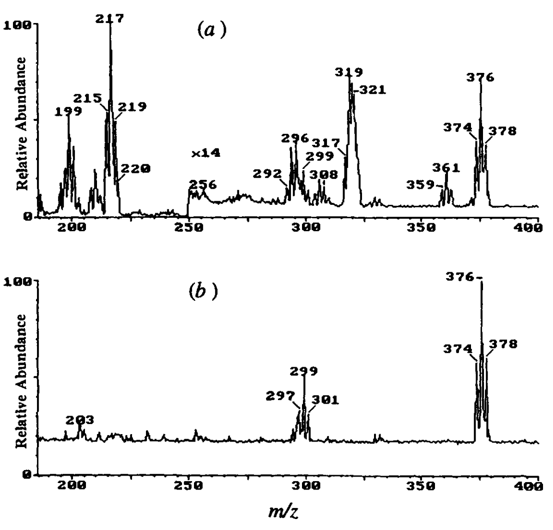


Fig. 4 (*a*) EI (70 eV) mass spectrum of the reaction mixture of PBN and $CHBr_2CN$ in hexane after 2 h. (*b*) Precursor ion spectrum of *m*/*z* 57 recorded during the EI (70 eV) MS–MS analysis of the reaction mixture of PBN and $CHBr_2CN$ in hexane after 2 h.

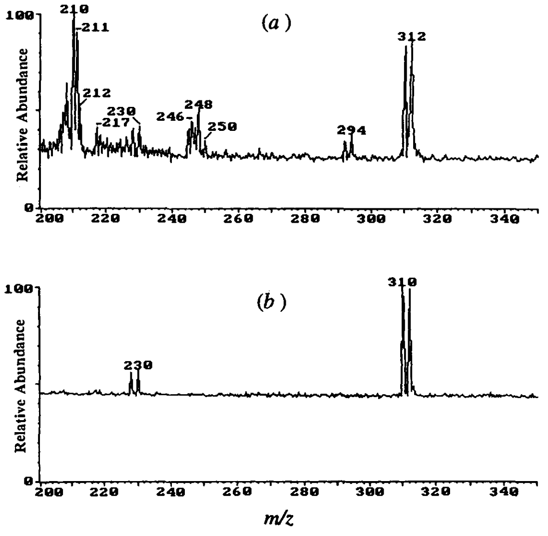
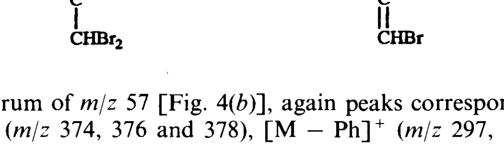


Fig. 5 (*a*) EI (15 eV) mass spectrum recorded from the reaction mixture of $[^2H_{14}]$PBN and CH_2BrCN in hexane after 2 h. (*b*) Precursor ion spectrum of *m*/*z* 66 recorded during the EI (15 eV) MS–MS analysis of the reaction mixture of $[^2H_{14}]$PBN and CH_2BrCN in hexane after 2 h.

Peaks at *m*/*z* 359, 361 and 363 are due to $[M - CH_3]^+$. Peaks at *m*/*z* 318, 320 and 322 are attributed to $[M - C_4H_8]^+$. Peaks at *m*/*z* 317, 319 and 321 are the result of loss of isobutylene and β-H from $M^{\cdot+}$. Peaks at *m*/*z* 297, 299 and 301 are the result of the loss of phenyl group from $M^{\cdot+}$. Again in this system another molecule which could be produced by loss of HBr from the 1 : 1 adduct was also observed at *m*/*z* 294 and 296 with a relative intensity of 1 : 1, indicating similar ring structures are formed in this system [reaction (5)]. In the precursor ion spectrum of *m*/*z* 57 [Fig. 4(*b*)], again peaks corresponding to $M^{\cdot+}$ (*m*/*z* 374, 376 and 378), $[M - Ph]^+$ (*m*/*z* 297, 299 and 301), $[M - CHBr_2]$ (*m*/*z* 203) and $M_1^{\cdot+}$ (*m*/*z* 294 and 296) were observed.



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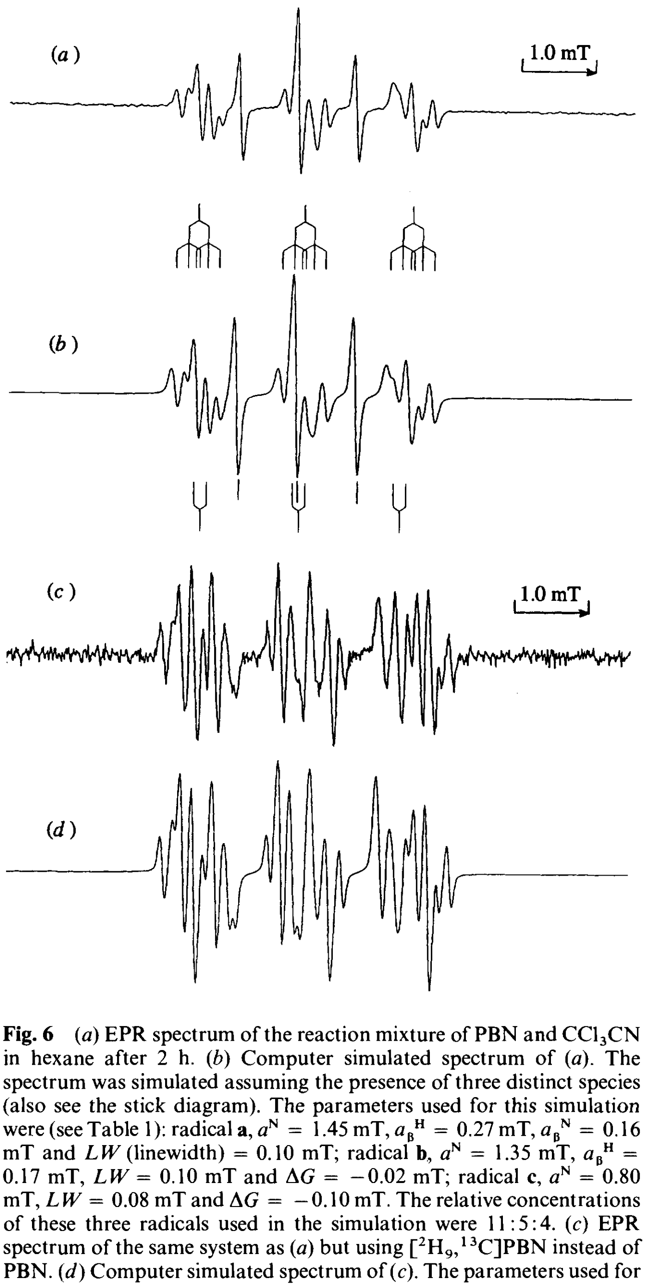


Fig. 6 (*a*) EPR spectrum of the reaction mixture of PBN and CCl_3CN in hexane after 2 h. (*b*) Computer simulated spectrum of (*a*). The spectrum was simulated assuming the presence of three distinct species (also see the stick diagram). The parameters used for this simulation were (see Table 1): radical **a**, a^N = 1.45 mT, a_β^H = 0.27 mT, a_β^N = 0.16 mT and *LW* (linewidth) = 0.10 mT; radical **b**, a^N = 1.35 mT, a_β^H = 0.17 mT, *LW* = 0.10 mT and ΔG = −0.02 mT; radical **c**, a^N = 0.80 mT, *LW* = 0.08 mT and ΔG = −0.10 mT. The relative concentrations of these three radicals used in the simulation were 11 : 5 : 4. (*c*) EPR spectrum of the same system as (*a*) but using $[^2H_9,^{13}C]$PBN instead of PBN. (*d*) Computer simulated spectrum of (*c*). The parameters used for this simulation were: radical **a**, a^N = 1.45 mT, a_β^H = 0.27 mT, a_β^N = 0.16 mT, a_α^C = 0.40 mT and *LW* = 0.07 mT; radical **b**, a^N = 1.35 mT, a_β^H = 0.17 mT, a_α^C = 0.46 mT, *LW* = 0.10 mT and ΔG = −0.02 mT; the relative concentrations of these two radicals used in the simulation were 10 : 17.

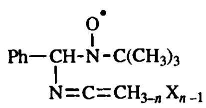
CH_2BrCN + PBN. A 1 : 1 adduct was also observed in the mass spectrum [Fig. 5(*a*)] when CH_2BrCN was mixed with $[^2H_{14}]$PBN in hexane. However it was found that the intensity of peaks corresponding to the molecular ions of this 1 : 1 adduct was weaker than those of the other three systems, indicating that when fewer chlorine or bromine atoms exist in the cyanomethane a weaker molecular addition reaction occurs. The relative intensity of isotopic peaks of an ion which contains one bromine atom is known to be 100 : 98.

In Fig. 5(*a*), the molecular ion of the 1 : 1 adduct of CH_2BrCN and $[^2H_{14}]$PBN was observed at *m*/*z* 310 and 312. Peaks at *m*/*z* 246 and 248 are the result of the loss of isobutylene from $M^{\cdot+}$. Peaks at *m*/*z* 245 and 247 correspond to ions due to the loss of isobutylene and β-H from $M^{\cdot+}$. Fig. 5(*b*) is the precursor ion spectrum of *m*/*z* 66. Peaks at *m*/*z* 228 and 230 in Fig. 5(*b*) are the result of loss of $[^2H_5]$phenyl from $M^{\cdot+}$, which are also observed in Fig. 5(*a*). No peak corresponding to a molecular ion due to

Table 1 EPR hyperfine splitting constants of PBN spin adducts

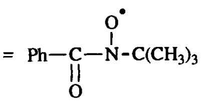
	a^N/mT	$a_\alpha{}^C$/mT	$a_\beta{}^H$/mT	$a_\beta{}^N$/mT	$a_\gamma{}^H$/mT
PBN-CCl_3CN (see Fig. 6)					
a	1.45	0.40	0.27	0.16	
b	1.35	0.46	0.17		
c	0.80				
PBN-$CHCl_2CN$					
a	1.47		0.27	0.16	
d	1.49	0.57	0.35		
b	1.40	0.46	0.21		
c	0.80				
PBN-$CHBr_2CN$					
a	1.48		0.19	0.19	
d	1.46	0.61	0.31		
c	0.80				
PBN-CH_2BrCN (see Fig. 7)					
d	1.48	0.58	0.40		0.06
b	1.39	0.49	0.17		
c	0.80				

a



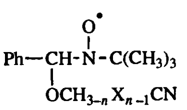
$Ph{-}CH(N{=}C{=}CH_{3-n}X_{n-1}){-}N(O^\bullet){-}C(CH_3)_3$

c PBNOX =



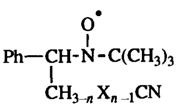
$Ph{-}C({=}O){-}N(O^\bullet){-}C(CH_3)_3$

b



$Ph{-}CH(OCH_{3-n}X_{n-1}CN){-}N(O^\bullet){-}C(CH_3)_3$

d



$Ph{-}CH(CH_{3-n}X_{n-1}CN){-}N(O^\bullet){-}C(CH_3)_3$

the loss of HBr from the 1 : 1 adduct was observed in this system, indicating that the loss of HBr needs at least two bromine atoms.

EPR studies

CCl_3CN + PBN. When CCl_3CN is mixed with PBN in hexane, the EPR spectrum shown in Fig. 6(*a*) is obtained. It consists of three different PBN spin adducts (SAs). Based on the analysis of their splitting patterns, they are tentatively assigned as follows: PBNOX (triplet, a_N = 0.80 mT), an oxygen-centred radical SA (triplet of doublets, a_N = 1.35 mT, $a_\beta{}^H$ = 0.17 mT) and a nitrogen-centred radical SA ($^\bullet N{=}C{=}CCl_2$, a_N = 1.45 mT, $a_\beta{}^H$ = 0.27 mT, $a_\beta{}^N$ = 0.16 mT) (Table 1). The assignment of the oxygen-centred radical was confirmed by observing that the intensity of this triplet of doublets increased after the system was bubbled with O_2 for 20 min.

A similar nitrogen-centred radical precursor has been recognized before, namely $^\bullet N{=}C{=}C(CH_3)_2$, produced by the thermolysis of azobisisobutyronitrile (AIBN).[14] AIBN has been used as a radical initiator in the polymer industry since the 1950s. It thermally decomposes to give a pair of cyanoalkyl radicals, $^\bullet C(CH_3)_2CN$ and N_2. This carbon-centred radical has another resonance form, namely $^\bullet N{=}C{=}C(CH_3)_2$, a nitrogen-centred radical. The formation of such a nitrogen-centred radical is clear from the 'head to tail' dimer $CN(CH_3)_2C{-}N{=}C{=}C(CH_3)_2$, produced by simply coupling these two resonance forms.

In our system, $^\bullet N{=}C{=}CCl_2$ is another resonance form of the radical $^\bullet CCl_2CN$, which could be produced by its reaction with PBN. The computer simulated spectrum obtained by using the above hyperfine splitting constants shown in Fig. 6(*b*) is in good agreement with the experimental observation.

The α-^{13}C-labelled PBN is an improved spin trap for EPR spectral identification of transient radicals.[15] It was found that the α-^{13}C hyperfine splitting (HFS) constants of SAs provides a better indication of the group that was the radical than only the N and β-H HFS. For example, all α-^{13}C HFS constants for oxygen-, nitrogen- and sulfur-centred radical SAs are between 0.30 and 0.50 mT; carbon-centred radical SAs are between 0.50 and 0.60 mT.

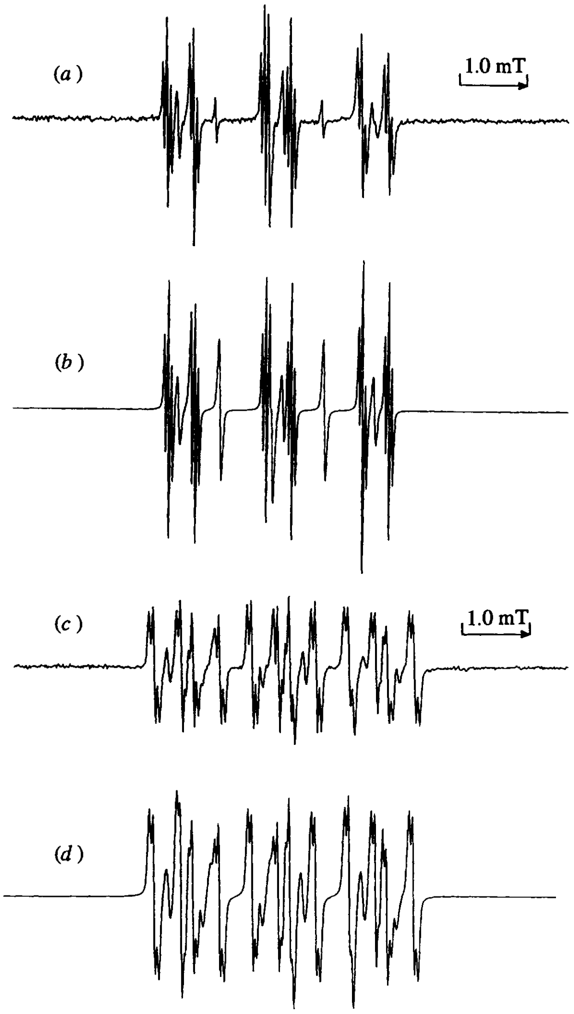


Fig. 7 (*a*) EPR spectrum recorded from the CH_2BrCN layer of the reaction mixture of [$^2H_{14}$]PBN and CH_2BrCN in hexane after 2 h reaction. (*b*) Computer simulated spectrum of (*a*). The parameters used for this simulation were (see Table 1): radical **d**, a^N = 1.48 mT, $a_\beta{}^H$ = 0.40 mT, $a_\gamma{}^H$ = 0.06 mT and *LW* = 0.03 mT; radical **b**, a^N = 1.39 mT, $a_\beta{}^H$ = 0.17 mT, *LW* = 0.05 mT and ΔG = −0.03 mT; radical **c**, a^N = 0.80 mT, *LW* = 0.05 mT and ΔG = −0.10 mT. The relative concentrations of these three radicals used in the simulation were 3 : 1 : 1. (*c*) EPR spectrum from the same system as (*a*) but using [$^2H_9$,^{13}C]PBN instead of PBN. (*d*) Computer simulated spectrum of (*c*). The parameters used for this simulation were: radical **d**, a^N = 1.48 mT, $a_\beta{}^H$ = 0.40 mT, $a_\gamma{}^H$ = 0.06 mT, $a_\alpha{}^C$ = 0.58 mT and *LW* = 0.05 mT; radical **b**, a^N = 1.39 mT, $a_\beta{}^H$ = 0.17 mT, $a_\alpha{}^C$ = 0.49 mT, *LW* = 0.07 mT and ΔG = −0.03 mT; the relative concentrations of these two radicals used in the simulation were 5 : 1.

To confirm the above assignment, [$^2H_9$,α-^{13}C]PBN was used instead of PBN. The α-^{13}C HFS constant for the nitrogen-centred radical SA ($^\bullet N{=}C{=}CCl_2$) is 0.40 mT, and for the oxygen-centred radical SA, α-^{13}C HFS is 0.46 mT [Fig. 6(*c*)]. These values are consistent with the reference data for nitrogen-centred and oxygen-centred radical SAs.[15] The simulated spectrum is shown in Fig. 6(*d*).

$CHCl_2CN$ + PBN. The EPR spectrum recorded from this system consisted of two different radical spin adducts. By analysis of the splitting patterns in the EPR spectrum, these spin adducts were assigned as follows: PBNOX (triplet, a_N = 0.80 mT) and an oxygen-centred radical SA (a triplet of doublets, a_N = 1.40 mT and $a_\beta{}^H$ = 0.21 mT) (Table 1). It was found that the sensitivity and resolution of the EPR spectrum can be improved by using deuteriated PBN.[16] Using [$^2H_{14}$]PBN instead of PBN, a third spin adduct was observed and assigned to the nitrogen-centred radical SA ($^{\bullet}N{=}C{=}CHCl$, a_N = 1.47 mT, $a_\beta{}^H$ = 0.27 mT and $a_\beta{}^N$ = 0.16 mT). The signals from these nitrogen-centred radical SAs are very weak. Because their splitting constants are almost the same as those of $^{\bullet}N{=}C{=}CCl_2$ formed in the system of CCl_3CN and PBN, and as CCl_3CN is known from MS to be an impurity of $CHCl_2CN$, it might be considered that some of these nitrogen-centred radicals are formed from CCl_3CN and PBN.

The oxygen-centred radicals were identified by bubbling the system with O_2, since the intensity of the signals due to the oxygen-centred radicals increased after the system was bubbled with O_2 for 20 min. This assignment was also confirmed by using [$^2H_9$,α-^{13}C]PBN instead of PBN since the α-^{13}C HFS constant of the oxygen-centred radical SA is 0.46 mT.

The carbon-centred radical SA sometimes was also observed by EPR spectromety in this system when [$^2H_9$,α-^{13}C]PBN was used. The α-^{13}C HFS constant for this carbon-centred radical SA is 0.57 mT. The β-H HFS constant is 0.35 mT. However the observation of this carbon-centred radical SA is very dependent on the sample preparation and the amount of O_2 present in the system.

$CHBr_2CN$ + PBN. The EPR spectrum recorded in this system is composed of two different spin adducts: PBNOX (triplet) and a triplet of doublets. The triplet of doublets is known to be a carbon-centred radical SA based on an α-^{13}C PBN experiment, because the α-^{13}C HFS constant is 0.61 mT (Table 1). A nitrogen-centred radical SA ($^{\bullet}N{=}C{=}CHBr$) was also observed when [$^2H_{14}$]PBN was used.

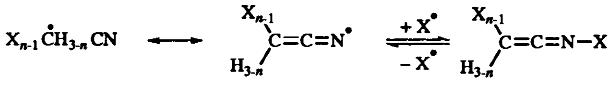
Because the linewidth of the triplet of doublets of the carbon-centred radical is quite wide, the signals from the oxygen-centred radical SA might not be observed.

CH_2BrCN + PBN. Fig. 7(*a*) is the EPR spectrum recorded from the system of [$^2H_{14}$]PBN and CH_2BrCN. In this system [$^2H_{14}$]PBN was used to observe the small splitting from the γ-H. In addition to PBNOX and an oxygen-centred radical SA, a carbon-centred radical ($^{\bullet}CH_2CN$) spin adduct was observed. Its HFS constants are a_N = 1.48 mT, $a_\beta{}^H$ = 0.40 mT and $a_\gamma{}^H$ = 0.06 mT (Table 1). These values are different from those in the other three systems in that a nitrogen-centred radical is observed. Therefore, in the formation of the nitrogen-centred radical SA in this reaction, cyanomethane may need at least two chlorine atoms or two bromine atoms. When [$^2H_9$,α-^{13}C]PBN was used instead of [$^2H_{14}$]PBN, the HFS constant of α-^{13}C for the carbon-centred radical SA was 0.58 mT [Fig. 7(*c*)]; for the oxygen-centred radical SA, the α-^{13}C HFS constant is 0.49 mT. Fig. 7(*b*) and (*d*) are the computer simulated spectra. The experimental fit is quite acceptable.

Mechanisms

This is the first study of the reaction between cyanohalocarbons and PBN and it is too early to know the details of the mechanisms involved in the production of spin adducts and the molecular complexes. It is our assumption that the cyanohalocarbons are spontaneously losing a halogen in the presence of PBN [reaction (6)] to produce a carbon-centred radical at room temperature which is trapped by PBN in hexane. Moreover the possibility of an *N*-haloimine structure is suggested by the fact that apparently *N*-centred radical SAs are detected [reaction (7)]. The fact that oxygen-centred SAs are detected in greater amounts when the halocarbons are exposed to oxygen supports this proposal. However, room light does not seem to be a factor since experiments in the dark or in the absence of room light did not change the results.

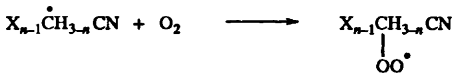
$$X_nCH_{3-n}CN \rightleftharpoons X_{n-1}\dot{C}H_{3-n}CN + X^{\bullet}(\tfrac{1}{2}X_2) \quad (6)$$



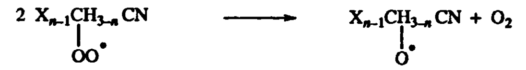
$$X_{n-1}\dot{C}H_{3-n}CN \longleftrightarrow (X_{n-1})(H_{3-n})C{=}C{=}N^{\bullet} \underset{-X^{\bullet}}{\overset{+X^{\bullet}}{\rightleftharpoons}} (X_{n-1})(H_{3-n})C{=}C{=}N{-}X$$

(7)

The structure of the oxygen-centred radical is assumed to be simply the cyanohaloalkyloxyl radical formed from the peroxyl radical [reactions (8) and (9)] but we do not have proof of this structure.

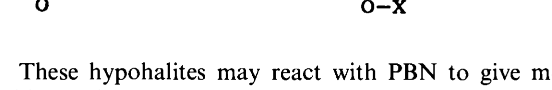


$$X_{n-1}\dot{C}H_{3-n}CN + O_2 \longrightarrow X_{n-1}C(OO^{\bullet})H_{3-n}CN \quad (8)$$



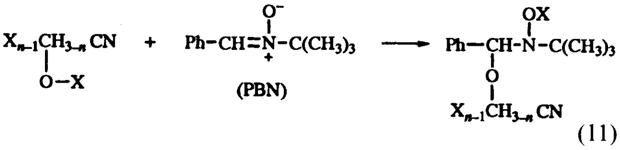
$$2\,X_{n-1}C(OO^{\bullet})H_{3-n}CN \longrightarrow X_{n-1}C(O^{\bullet})H_{3-n}CN + O_2 \quad (9)$$

Of course this spontaneous radical formation should be happening all the time in the liquid cyanohalomethane if this proposed mechanism is right. In the presence of air, oxygenation should occur and perhaps hypohalites form [reaction (10)].

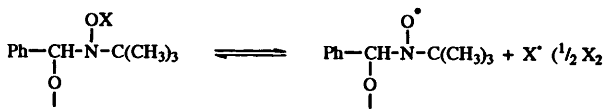


$$X_{n-1}C(O^{\bullet})H_{3-n}CN + X_2 \longrightarrow X_{n-1}C(O{-}X)H_{3-n}CN + X^{\bullet}\,(\tfrac{1}{2}X_2) \quad (10)$$

These hypohalites may react with PBN to give molecular adducts with the halogen attached to the hydroxylamine oxygen [reaction (11)]. Halogen atoms attached to the hydroxylamine oxygen are labile and dissociation probably occurs [reaction (12)]. Perhaps this is the origin of some of the oxygen-centred radical SAs. It is known that sodium hypochlorite and 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) react to give the hydroxyl adduct of DMPO spontaneously[17] and *tert*-butyl hypochlorite reacts with PBN to give the *tert*-butoxyl adduct.[18]

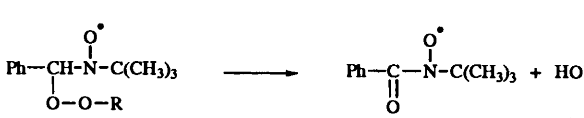


$$X_{n-1}C(O{-}X)H_{3-n}CN + \underset{(PBN)}{Ph{-}CH{=}\overset{+}{N}(O^-){-}C(CH_3)_3} \longrightarrow Ph{-}CH(O{-}X_{n-1}CH_{3-n}CN){-}N(OX){-}C(CH_3)_3 \quad (11)$$

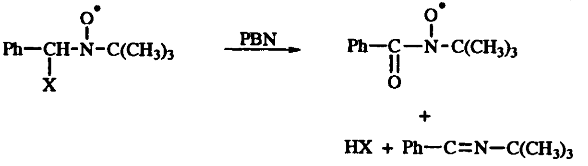


$$Ph{-}CH(O{-}X_{n-1}CH_{3-n}CN){-}N(OX){-}C(CH_3)_3 \rightleftharpoons Ph{-}CH(O{-}X_{n-1}CH_{3-n}CN){-}N(O^{\bullet}){-}C(CH_3)_3 + X^{\bullet}\,(\tfrac{1}{2}X_2) \quad (12)$$

The formation of PBNOX is a product of peroxyl radicals[19] or halogen atoms.[20] Since both these radical intermediates are probably present in this system, a specific reaction route cannot be selected [reactions (13) and (14)].



$$Ph{-}CH(O{-}O{-}R){-}N(O^{\bullet}){-}C(CH_3)_3 \longrightarrow Ph{-}C({=}O){-}N(O^{\bullet}){-}C(CH_3)_3 + HOR \quad (13)$$



$$Ph{-}CH(X){-}N(O^{\bullet}){-}C(CH_3)_3 \xrightarrow{PBN} Ph{-}C({=}O){-}N(O^{\bullet}){-}C(CH_3)_3 + HX + Ph{-}C{=}N{-}C(CH_3)_3 \quad (14)$$

Conclusions

Free radicals are produced spontaneously from the system of cyanohalocarbons (CCl_3CN, $CHCl_2CN$, $CHBr_2CN$ and CH_2BrCN) and PBN. Several SAs were formed in these systems and detected by EPR spectroscopy. They are carbon-centred radical SAs ($^•CHClCN$, $^•CHBrCN$ and $^•CH_2CN$), nitrogen-centred radical SAs ($^•N{=}C{=}CCl_2$, $^•N{=}C{=}CHCl$ and $^•N{=}C{=}CHBr$), oxygen-centred radical SAs and PBNOX. To form the nitrogen-centred radical, cyanomethane needs at least two Cl or Br atoms at the α-carbon of the cyanomethyl function.

In addition 1:1 molecular adducts were formed in these systems. MS fragmentation patterns for these 1:1 adducts are different from those of the 'normal' PBN spin adduct. The fragment corresponding to the loss of the phenyl group from the molecular ions is always observed. Therefore a structure with a five-membered ring is proposed. The formation mechanism could be [3+2] cycloaddition, where PBN is a 1,3-dipole and the cyano group behaves like a dipolarophile because of the existence of the chlorine or bromine atoms.

Another species might be produced by the loss of HCl or HBr from the corresponding 1:1 adduct. These may have stable structures, because losing HCl or HBr results in a good conjugated heterocyclic system.

Based on the above observation, it is known that PBN reacts with cyanohalocarbons not only to produce non-radical products (1:1 adducts), but also to produce radicals. Therefore PBN cannot be used as a spin probe to study systems containing cyanohalocarbons or compounds of similar chemical structure.

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