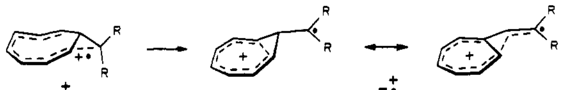
mode of reaction. One-electron oxidation of the cyclopropane group often gives rise to "trimethylene" radical cations.[9] In the present case, the observed rearrangement requires cleavage of one cyclopropane bond (C_8–C_9) and bond formation between C_9 and C_5, amounting to a major conformational change. A possible mechanism is shown in Scheme I.

Some insight into the nature of the radical cation preceding **2a** is provided by the CIDNP effects observed during the irradiation of chloranil with **1a** in acetone-d_6, in which **2a** was the only polarized product.[11] The bridgehead protons (2.1 ppm) show emission whereas the olefinic protons (6.0 ppm) and those alternating between cyclopropane and olefinic character (4.4 ppm) show enhanced absorption. However, the polarization differs from that generated in an authentic sample of **2a**. The signal at 4.4 ppm shows much weaker enhancement, and the doublet at 7.65 ppm (fluorene *o*-H) appears in enhanced absorption. These differences are consistent with the involvement of at least one additional intermediate as a short-lived precursor to $\mathbf{2a}^{\cdot+}$.[11]

The observed CIDNP effects rule out that $\mathbf{1a}^{\cdot+}$ is responsible for the altered polarization of **2a**, since its involvement in the spin-sorting process would cause polarization for regenerated **1a**, which we did not observe. Although our results are not sufficient to identify the intermediate, we note that a singly linked species, such as $\mathbf{5a}^{\cdot+}$, is an attractive candidate to explain the rearrangement.

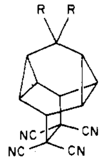


$1^{+\cdot}$ $5^{+\cdot}$

To some extent, $\mathbf{5a}^{\cdot+}$ might play a role in the formation of **3a** as indicated by the moderate, but not negligible, solvent polarity dependence. On the other hand, an exciplex intermediate may maintain more or less the boat configuration of **1a**, giving rise mainly to **3a** and **4a**, or regenerating **1a**, because of a lower degree of charge separation.

The difference between the rearrangements of **1a** and **1b** can be explained in terms of a lower rate of the bond formation of $\mathbf{1b}^{\cdot+}$ to give $\mathbf{2b}^{\cdot+}$ probably because of relatively larger steric hindrance of the diphenylmethyl group compared to the planar fluorenyl group.

Similar skeletal rearrangements were observed when the electron donor–acceptor (EDA) complex of **1a** with tetracyanoethylene (TCNE), was irradiated. This system has charge-transfer (CT) absorption maxima at 402 and 568 nm in dichloromethane, which can be ascribed to the interaction of the fluorene moiety with TCNE. This assignment follows (a) from the similarity of the above CT absorption to that exhibited by fluorene itself with TCNE (λ_{max} 420, 560 nm) and (b) from its lack of compatibility with the much weaker CT band of the system bicyclo[6.1.0]nonatriene/TCNE (λ_{max} 400, 490 nm). Irradiation (>400 nm) of **1a**/TCNE in dichloromethane under argon gave rise to two TCNE adducts, **6a** and **7a**, in 44 and 27% yields,[7] respectively, at 89% conversion.



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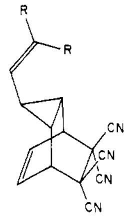

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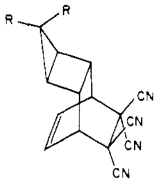
Similarly, irradiation of **1a**/TCNE in nitromethane gave **6a** (8%) and **7a** (7% at 35% conversion). In contrast, the thermal reaction of **1a** with TCNE in refluxing acetonitrile gave **8a** as sole product in 80% yield. The striking difference between photochemical and thermal reactions further supports the operation of a photoinduced electron-transfer mechanism. The cycloadducts **6a** and **7a** could be secondary products from the dark reaction of TCNE with **2a** and **3a** or they could be formed by direct interaction of the TCNE radical anion with $\mathbf{1a}^{\cdot+}$ or a rearranged radical cation.



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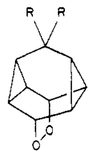

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Of particular interest is the fact that irradiation of **1a**/TCNE in oxygen-saturated nitromethane gave reduced yields of **6a** (3%) and **7a** (3%), together with an endo peroxide (**9a**, 11% yield at 24% conversion), which was also obtained directly from **2a** in excellent yield. Since the yields of **6a** and **7a** are reduced in favor of **9a**, but their ratio is not changed substantially, it is likely that molecular oxygen has intercepted (an) intermediate(s) on the pathway to **6a** and **7a**, the most likely species being $\mathbf{1a}^{\cdot+}$ and/or $\mathbf{5a}^{\cdot+}$. Additional work is in progress to further delineate the mechanism of the light-induced adduct formation with TCNE and to probe the details of the interesting photooxygenation reaction.

Registry No. **1a**, 114672-75-2; **1b**, 118864-83-8; **2a**, 114552-66-8; **3a**, 118724-11-1; **3b**, 100064-25-3; **4a**, 39520-18-8; **6a**, 118724-12-2; **7a**, 118724-13-3; **8a**, 118724-14-4; **9a**, 118760-91-1; DCA, 1217-45-4; DCN, 3029-30-9; TCA, 80721-78-4; TCNAQ, 106580-24-9; CA, 118-75-2; TNF, 129-79-3; TCNE, 670-54-2.

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Synthesis, Redox Behavior, and Spin-Trap Properties of 2,6-Di-*tert*-butylnitrosobenzene (DTBN)

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Introduction

The spin-trap technique is now one of the most powerful tools to investigate the role of transient paramagnetic

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species in chemical and biological processes.[1] This technique is a simple expedient whereby short-lived reactive free radicals may be transformed into more persistent paramagnetic species, which are easily characterized by using ESR spectroscopy. Nitroso compounds and nitrones, which afford nitroxides, are the most useful spin-traps. However complications can occur due to the possible formation of nitroxides other than those deriving from the radical reaction under investigation.[1] Alternatives[2] to nitroso compounds and nitrones have been mentioned from time to time but have been shown to offer more limited interest as free radical scavengers.

Water-soluble nitroso compounds are very attractive to study the occurrence of free radicals in water[3] or in biological processes.[4] We have investigated different routes to obtain this kind of nitroso compound, which should also retain the necessary structural features to behave as useful spin-traps.[1,5]

During the course of this research, we prepared the 2,6 di-*tert*-butylaniline with the aim of introducing an water-soluble substituent at the para position. Our approach failed, but the 2,6 di-*tert*-butylaniline was easily oxidized to the corresponding nitroso derivative. This new nitroso compound was tested as a spin-trapping agent in organic solvents. The results obtained and their comparison with those obtained with the well-known 2,4,6-tri-*tert*-butylnitrosobenzene[6] (TTBN) are interesting and deserve comment.

Results and Discussion

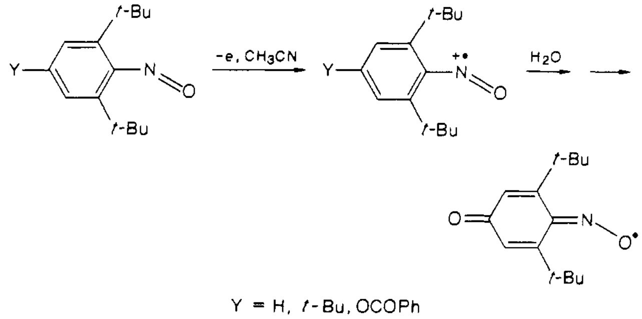
Redox Behavior. We and others have pointed out the possibility for arylnitroso compounds to be involved in electron-transfer processes[7] during the course of a spin-trapping (ST) experiment. Accordingly the redox behavior of a ST agent is a very important aspect to be taken into account when a ST experiment is considered. Cyclic voltammetry experiments showed that DTBN can be reduced or oxidized on a platinum electrode in acetonitrile by using tetrabutyl ammonium hexafluorophosphate as supporting electrolyte. A reduction was apparent at −1.3 V versus SCE. The ratio of the anodic to the cathodic peak current is 0.3 at 100 mV s^{-1}. The peak separation is close to 280 mV, thus indicating a rather slow electron transfer. The oxidation of DTBN occurs at +1.56 V versus SCE. The low value of the ratio of the cathodic to the anodic peak current (0.15 at 100 mV s^{-1}) indicates that the oxidation process generates a short-lived species. The peak separation is close to 310 mV, and this value like in the case of the reduction process suggests a slow electron transfer. The reduction and the oxidation peak currents of DTBN are very close to those observed during the monoelectronic reduction of 2,4,6-tri-*tert*-butylnitrosobenzene (TTBN).[8] This result supports the occurrence of monoelectronic transfers yielding the corresponding ion radicals. This conclusion was confirmed by the ESR detection of DTBN$^{\bullet+}$ and DTBN^{-} during the in situ electrochemical oxidation or reduction of DTBN.

Table I. ESR Parameters for DTBN$^{\bullet-}$ and DTBN$^{\bullet+}$ Generated in Situ by Electrolysis

radical	solvent	A_N, G	A_H, G	g^a
DTBN$^{\bullet-}$	CH_3CN	10.3	1.25 (2 H_m) 2.50 (H_p)	2.0066
TTBN$^{\bullet-}$	DMF	9.55	1.25 (2 H_m)	2.0068
PhNO$^{\bullet-}$	CH_3CN	8.34	1.03 (2 H_m) 3.91 (H_p)	
PhNO$^{\bullet-\,b}$	planar	7.2	0.97 (H_m), 0.98 (H_m) −2.0 (H_p)	
	perpendicular	12.5	0.5 (2 H_m) +0.05 (H_p)	
DTBN$^{\bullet+}$	CH_3CN	37.2^c	3.7 (1 H_m)^c	2.0015^d
TTBN$^{\bullet+}$	CH_3CN	36.0	0.92 (9 H) 3.5 (1 H_m)	2.0017

^{a} +0.0002. ^{b} INDO calculations. ^{c} Obtained by computer simulation. ^{d} +0.0004.

Scheme I



The ESR features of these ionic species are listed in Table I. The magnitudes of the hyperfine coupling constants and g factor for DTBN$^{\bullet+}$, are characteristic of a σ radical and are comparable to those reported for other nitrosobenzene radical cations.[7c,8,9] The ESR spectrum of DTBN$^{\bullet+}$ was always superimposed with the ESR spectrum of an iminoxyl radical (A_N = 34.0 G, A_H = 3.7 G (1 H_m), A_H = 0.5 G (1 H_m), A_H = 0.12 G (9 H), A_H = 0.58 G (9 H), g = 2.0039). This iminoxyl radical presumably results from the attack by residual water at the para position of DTBN$^{\bullet+}$ and corresponds to the 4-oxo-2,6-di-*tert*-butyl-1,4-dihydrobenzene-1-iminoxyl (Scheme I).

For Y = H, even at low temperature, the ESR signal of the iminoxyl radical was always stronger than that of the radical cation. However, the reverse was observed when the para position was substituted with a *tert*-butyl group (Y = *t*-Bu) while only the iminoxyl radical was detectable when Y = OCOPh.

The transformation of an arylnitroso cation radical to an iminoxyl radical has been previously clearly established for the pentamethoxynitrosobenzene (PMNB).[10] Elec-

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Table II. ESR Parameters (Gauss, Benzene, 298 K) for Several Spin Adducts Formed from DTBN

trapped radical	radical source	spin adduct	DTBN[a] A_N	DTBN[a] A_H	TTBN[6] A_N	TTBN[6] A_H
CH_3	A[d]	**1**	13.0	12.2 (3 H) 0.7 (2 H_m)	13.03	12.33 (3 H) 0.81 (2 H_m)
CH_2CH_3	A	**2**	13.4	18.0 (2 H) 0.7 (2 H_m)	13.46	17.99 (2 H) 0.83 (2 H_m)
$CH_2CH{=}CH_2$	A	**3**	13.2	16.5 (2 H) 0.7 (2 H_m)	13.40	16.42 (2 H) 0.84 (2 H_m)
$HC(CH_3)_2$	B[e]	**4**[f]	13.2	22.0 (1 H)	13.29	22.19 (1 H) 0.76 (2 H_m)
		5[f]	10.9	1.9 (3 H) 5.5 (H_p)	11.01	1.82 (3 H)
$C(CH_3)_3$	A	**6**[f]	10.3	2.0 (2 H_m) 5.5 (H_p)	10.26	1.90 (2 H_m)
$C(O)C(CH_3)_3$	B	**7**[g]	7.5	0.5 (2 H_m)	g = 2.0068	
$C(O)CH(CH_3)_2$	B	**8**[g]	7.5		g = 2.0067	
SCH_2CH_3	EtSH +TBHN[b]	**9**	16.0		g = 2.0069	
$P(O)(OEt)_2$	$HP(O)(OEt)_2$ +DBPO[c]	**10**	8.7	16.5 (1 P)	g = 2.0065	

[a] g = 2.0060 + 0.0002. [b] TBHN = *tert*-butyl hyponitrite. [c] Di-*tert*-butyl peroxide. [d] RBr + *n*-Bu_3SnH + TBHN. [e] RC(O)H + TBHN. [f] Temperature below 303–313 K. [g] Temperature above 313 K.

trochemical oxidation of DMF solution of PMNB yields an intense ESR spectrum (A_N = 33.1 G, g = 2.0053), attributable to the 4-oxo-2,3,5,6-tetramethoxy-1,4-dihydrobenzene-1-iminoxyl. However if the electrochemical oxidation is conducted in very thoroughly dried acetonitrile at 243 K, only the radical cation $PMNB^{\bullet+}$ is observed (A_N = 34.0 G, A_H = 0.7 G (3 H, meta OMe), g = 2.0034).

The reductive electrolysis of DTBN in the cavity of the ESR spectrometer yielded first the ESR spectrum of the 2,6-di-*tert*-butylphenyl hydronitroxide (A_N = 12.2 G, A_H = 14.0 G, A_H = 0.7 G (2 H_m)), which disappeared after a few minutes of electrolysis and was replaced by a new spectrum which was assigned to $DTBN^{\bullet-}$ (Table I). For this species the delocalization of the unpaired electron is partially inhibited by the steric hindrance of the ortho *tert*-butyl substituents, and thus the nitrogen splitting increases and the para hydrogen splitting decreases compared to those observed for the nitrosobenzene radical anion. However, it is worth noting that for $DTBN^{\bullet-}$ the coupling with the meta hydrogens (A_{H_m} = 1.25 G), is significantly higher than that observed for $PhNO^{\bullet-}$ (A_{H_m} = 1.0 G). This result suggests that in the nonplanar conformation of $DTBN^{\bullet-}$, the decrease of the unpaired electron delocalization is balanced by a contribution of the s meta hydrogen orbitals to the SOMO. The existence of this long-range hyperfine interaction was supported by the results of INDO calculations performed on the planar and perpendicular conformations of $PhNO^{\bullet-}$ (Table I).

Spin Trapping. Table II summarizes the observed ESR parameters for a number of adduct radicals generated by trapping short-lived free radicals with DTBN in benzene. DTBN like TTBN presents two spin-trapping sites, the nitrogen and oxygen atoms of the nitroso group. The regioselectivity of the radical addition was governed by the bulk of the trapped radical and was shown to be the same for the two nitroso compounds. The two sorts of spin adduct (nitroxide or *N*-alkoxyanilino radicals) exhibited exactly the same ESR features whether they were obtained from TTBN or DTBN.

The DTBN's para hydrogen was completely "invisible" in the ESR spectra of the nitroxide spin adducts. This result supports the orthogonality of the aromatic ring π system with that of the nitroxyl function, and thus the coupling with the meta hydrogens should be only the result of a s meta hydrogen orbital contribution to the SOMO. The existence of this preferred orthogonal conformation was already proposed for the nitroxide spin adducts arising from TTBN.[6] The *N*-alkoxyanilino radicals obtained with DTBN showed a large coupling with the para hydrogen (Table II). The magnitude of this coupling is very close to that observed for *N*-alkoxyanilino radicals unsubstituted at the phenyl ring ($Ph\dot{N}Ot\text{-}Bu$, A_N = 10.95 G, A_{H_p} = 5.06 G), thus suggesting that these radicals remain planar even when the phenyl ring is substituted by two ortho *tert*-butyl groups.

Conclusion

DTBN and TTBN exhibit the same redox behavior. 4-Oxo-2,6-di-*tert*-butyl-1,4-dihydrobenzene-1-iminoxyl results from the addition of water at the para position of $DTBN^{\bullet+}$. DTBN and TTBN present the same reactivity toward free radical trapping. We never observed any evidence of a free radical addition at the para position of DTBN. The magnitude of the para hydrogen hyperfine coupling for the free radicals obtained from DTBN depends only on the extent of unpaired electron delocalization into the aromatic ring. However, the meta hydrogen hyperfine coupling results both from the unpaired electron delocalization and a long-range hyperfine interaction, which reaches its maximum value when the π system of the free radical center is orthogonal to the aromatic π system.

Experimental Section

2,6-Di-*tert*-butylnitrosobenzene (DTBN). To an ice-cooled dichloromethane solution (5 mL) of 2,6-di-*tert*-butylaniline[11] (0.13 g) was added dropwise with stirring 2 molar equiv of peroxybenzoic acid in the same solvent (10 mL). After being kept at 0 °C overnight, the reaction mixture was shaken with aqueous carbonate. The organic layer was dried, and the solvent was evaporated. The crude product was purified by means of column chromatography on silica gel. The nitroso compound was eluted with petroleum ether and collected in the monomeric form as a blue liquid (yield 75%): ^1H NMR (CCl_4) δ 1.15 (s, 18 H), 7.18 (m, 3 H). Anal. Calcd for $C_{14}H_{21}NO$: C, 76.71; H, 21.58; N, 6.39. Found: C, 76.22; H, 21.38; N, 6.15.

ESR Spectra. X-band ESR spectra were measured on a Varian E_9 instrument. An inverted U-type mixing cell was used

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for all the spin trapping experiments. The radical ions were generated in situ by using a special electrochemical cell.[8a]

Registry No. DTBN, 118921-33-8; DTBN$^{\bullet-}$, 118921-34-9; DTBN^{+}, 119008-54-7; TTBN, 24973-59-9; PMNB, 84802-28-8; PMNB^{+}, 118921-35-0; TTBN^{-}, 61278-22-6; TTBN^{+}, 34530-62-6; PhNO$^{\bullet-}$, 34480-22-3; CH_3, 2229-07-4; CH_2CH_3, 2025-56-1; $CH_2C{-}H{=}CH_2$, 1981-80-2; $CH(CH_3)_2$, 2025-55-0; $C(CH_3)_3$, 1605-73-8; $C(O)C(CH_3)_3$, 50694-27-4; $C(O)CH(CH_3)_2$, 35586-36-8; SCH_2CH_3, 14836-22-7; $P(O)(OEt)_2$, 31682-65-2; 4-oxo-2,6-di-*tert*-butyl-1,4-dihydrobenzene-1-iminoxyl, 118921-37-2; 4-oxo-2,3,5,6-tetramethoxy-1,4-dihydrobenzene-1-iminoxyl, 118921-38-3; 2,6-di-*tert*-butylaniline, 2909-83-3; 4-(benzoyloxy)-2,6-di-*tert*-butylnitrosobenzene, 25798-70-3; 2,6-di-*tert*-butylphenylhydronitroxide, 118921-36-1.

Single-Step Reductive Isomerization of Unsaturated Polycyclics to $C_{4n+6}H_{4n+12}$ Diamondoid Cage Hydrocarbons with Sodium Borohydride/Triflic Acid[1]

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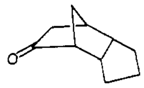
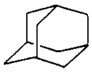
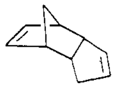
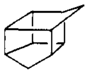
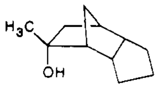
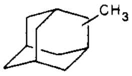
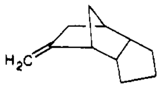
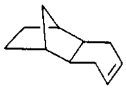
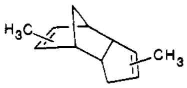
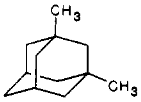
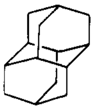
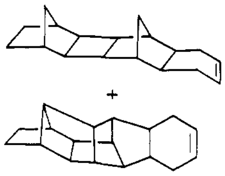
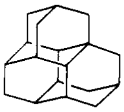
Introduction

Following the first isolation of adamantane and diamantane by Landa et al. from crude oil[2a] and Prelog's subsequent multistep synthesis,[2b] substantial interest arose in adamantanoid polycyclic cage hydrocarbons of $C_{4n+6}H_{4n+12}$ composition.[3] Adamantane, diamantane, and later triamantane were prepared in 19,[4-6] 65,[7-14] and 60%[15-18] yield, respectively, by Lewis acid ($AlCl_3$, $AlBr_3$, $AlBr_3$–sludge) catalyzed isomerization of their various strained polycyclic saturated precursors.

Table I

R′H (reactant)	RH (product)	yield,[a] %
		95
		96
		97
		92
		95
		90
		90
		99
		92

[a] Isolated yield. [b] 1-Methyladamantane was the major product.

Subsequent developments[19-22] led to an improved (60%) yield of adamantane by gas-phase isomerization of isomeric trimethylenenorbornane ($C_{10}H_{16}$) precursors over chlorinated platina.[23] We have recently reported that the polycyclic cage hydrocarbons, adamantane and diamantane, can be conveniently prepared in quantitative yield by isomerization of their corresponding hydrogenated (saturated) precursors with $B(OTf)_3$, $B(OTf)_3$–CF_3SO_3H, and SbF_5–CF_3SO_3H superacids, either neat or in Freon-113 solution.[24-26] Near quantitative isomerization of isomeric

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