scribed in a first approximation as the lowest unoccupied (LU) MO of the pyridinium ion. However, the replacement of a CH group by an NH^+ group is such a strong perturbation that it imposes local "C_{2v}" symmetry on the levels of the substituted ring. Since there is a near node at the meta position in the LUMO of the pyridinium ion, only the 2 and 4 isomers are able to mix a significant contribution from the π orbitals of the central bond into their LUMO's. The lowest energy transition is therefore strong in both 2- and 4-$StPH^+$, but weak in 3-$StPH^+$.

Acknowledgment. Support by NATQ Grant 1190 and stimulating interactions with Drs. Birks, Mazzucato, and Orlandi are gratefully acknowledged.

References and Notes

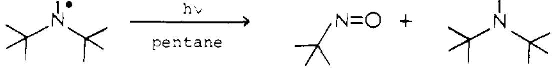
(1) (a) Presented in part at an informal symposium on Internal Rotation in Excited Organic Molecules, University of Cambridge, England, Aug 10–11, 1978, Abstract No. 10. (b) Issued as NRCC No. 17346.
(2) G. Favini, S. Fasone, and M. Raimondi, *Gazz. Chim. Ital.*, **97**, 1434 (1967).
(3) P. Bortolus, G. Cauzzo, U. Mazzucato, and G. Galiazzo, *Z. Phys. Chem. (Frankfurt am Main)*, **51**, 264 (1966); **63**, 29 (1969).
(4) D. G. Whitten and M. T. McCall, *J. Am. Chem. Soc.*, **91**, 5097 (1969).
(5) Y. J. Lee, D. G. Whitten, and L. Pedersen, *J. Am. Chem. Soc.*, **93**, 6330 (1971).
(6) D. G. Whitten and Y. J. Lee, *J. Am. Chem. Soc.*, **94**, 9142 (1972).
(7) G. Favaro, U. Mazzucato, and F. Masetti, *J. Phys. Chem.*, **77**, 601 (1973).
(8) G. Bartocci, P. Bortolus, and U. Mazzucato, *J. Phys. Chem.*, **77**, 605 (1973).
(9) G. Bartocci and U. Mazzucato, *Chem. Phys. Lett.*, **47**, 541 (1977).
(10) (a) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968). (b) Basic program: Program 174.0 "CNDO/S", Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. (c) Parameterization: R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26**, 131 (1972). (d) Geometries: all angles 120°; bond lengths (in ångstroms), CC and CN 1.45 (single), 1.39 (aromatic), and 1.33 (double), CH 1.10, NH 1.00.
(11) L. Pedersen, D. G. Whitten, and M. T. McCall, *Chem. Phys. Lett.*, **3**, 569 (1969).
(12) G. Distefano, U. Mazzucato, A. Modelli, S. Pignatoro, and G. Orlandi, *J. Chem. Soc., Faraday Trans. 2*, **71**, 1583 (1975).
(13) K. Nishimoto and N. Mataga, *Z. Phys. Chem. (Frankfurt am Main)*, **12**, 335 (1957); **13**, 140 (1957).
(14) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 767 (1953).
(15) O. Chalvet, H. H. Jaffé, and J. C. Rayez, *Photochem. Photobiol.*, **26**, 353 (1977).

Allan R. Gregory,* Willem Siebrand, Digby F. Williams
Division of Chemistry, National Research Council of Canada
Ottawa, Canada K1A 0R6
Received June 12, 1978

Electron-Transfer Photochemistry of Di-*tert*-butyl Nitroxide

Sir:

Although nitroxides, especially di-*tert*-butyl nitroxide (DTBN), have been extensively investigated as quenchers of electronically excited species, little is known about their photochemical reactivity. We have previously shown that DTBN is inert in its n,π^* doublet state and is reactive in its π,π^* doublet state.[1] When the π,π^* doublet state is populated by irradiation at 254 nm in pentane solvent, DTBN cleaves to *tert*-butyl radical and 2-methyl-2-nitrosopropane ($\phi_{\text{destruction}}$ = 0.21). The *tert*-butyl radical is scavenged by DTBN to give



di-*tert*-butyl-*tert*-butoxyamine. Two modes of photochemical reactivity of some cyclic nitroxides, hydrogen atom abstraction[2-4] and fragmentation[5] with loss of nitric oxide, have also been reported.

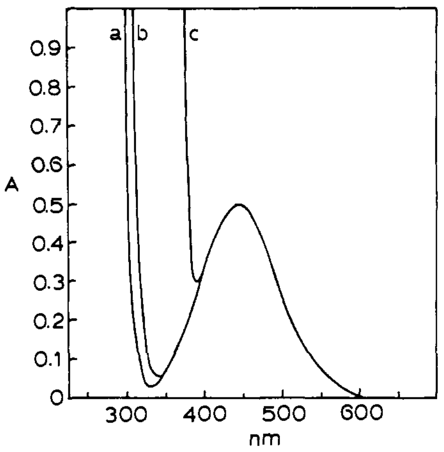
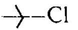


Figure 1. UV-visible absorption spectra of 0.05 M di-*tert*-butyl nitroxide in (a) pentane or methylene chloride, (b) chloroform, and (c) carbon tetrachloride solvents.

Table I. Observed and Calculated Quantum Yields

product	observed quantum yield[a]	quantum yield expression[b]	calculated quantum yield
 Cl	0.30	$\beta(1-\alpha)$	
 NO	0.85	$\beta(1+\alpha)$	0.85
1	0.56	β	0.58
2	0.27	$\alpha\beta$	0.27
isobutylene	0.55	$2\alpha\beta$	0.54

[a] Quantum yields were measured at 366 nm with a 0.10 M solution of DTBN in argon degassed carbon tetrachloride. [b] The symbol α = 0.47 represents the fraction of di-*tert*-butyloxoammonium chloride which decomposes to isobutylene and hydrogen chloride. The symbol β = 0.58 represents the quantum yield of reaction of the charge transfer excited state (see Scheme I).

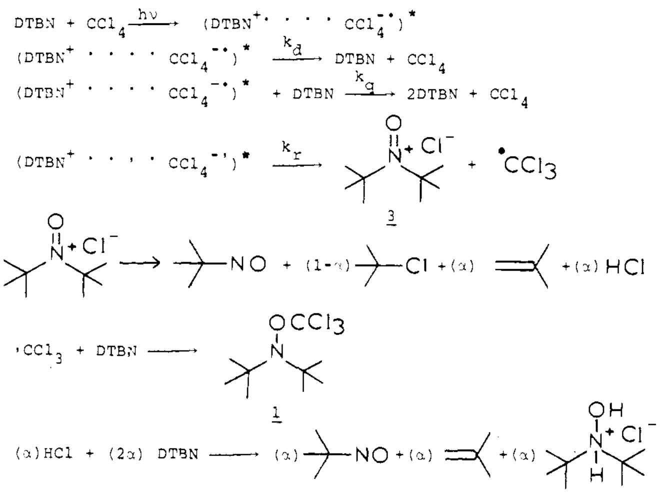
We now report that di-*tert*-butyl nitroxide weakly interacts by contact charge transfer[6] with carbon tetrachloride and that irradiation of the DTBN-CCl_4 charge-transfer band results in very efficient one-electron transfer to carbon tetrachloride.

The UV-visible spectrum of di-*tert*-butyl nitroxide in pentane solvent shows an n–π^* band at 460 nm (ϵ 8.9) and a π–π^* band at 238 nm (ϵ 2580).[7] A 0.05 M solution of DTBN in pentane solvent is almost transparent in the region between 310 and 370 nm. A 0.05 M solution of DTBN in carbon tetrachloride solvent, however, shows appreciable absorption in the 310–370 nm region in addition to the n–π^* band at 460 nm (see Figure 1). In methylene chloride solvent there is no additional absorption in the 310–370 nm region relative to pentane solvent, and in chloroform solvent there is an intermediate level of absorption in this region. We attribute the additional absorption in the region 310–370 nm to a contact charge-transfer interaction.[6] Contact charge transfer between nitroxides and halocarbons has also been observed by ^{13}C NMR spectroscopy.[8]

Irradiation of the n–π^* band of a 0.10 M solution of DTBN in carbon tetrachloride solvent results in no destruction; however, irradiation at 313 or 366 nm in the contact charge-transfer region results in efficient destruction of DTBN ($\phi_{\text{destruction}}$ = 1.7). The products of the photoreaction are 2-methyl-2-nitrosopropane, isobutylene, *tert*-butyl chloride, di-*tert*-butyltrichloromethoxyamine (**1**), and di-*tert*-butylhydroxylammonium chloride (**2**). Hexachloroethane is not formed, and the solution is not significantly paramagnetic upon completion of the reaction. The products together with their quantum yields of formation are summarized in Table

0002-7863/79/1501-1904$01.00/0

Scheme I



α = fraction of 3 that reacts by elimination = 0.47

$$\Phi_{reaction} = \frac{k_r}{k_r + k_d + k_q[DTBN]} = \beta = 0.58$$

$$\Phi_{DTBN\ destruction} = \beta(2+2\alpha) = 1.7$$

1. Di-*tert*-butyltrichloromethoxyamine (**1**) is an unstable[9] low-melting solid (mp 40-45 °C) which was characterized by IR (no N-H, O-H, or multiple bond stretching bands), ^1H NMR (CCl_4, singlet at δ 1.39 ppm), ^{13}C NMR (CCl_4, strong absorption at δ 30.3 and weak absorptions at 64.1 and 119.8 ppm), and mass spectrometry (70 eV, 25 °C) (*m/e* 190, 192, 194, and 196 ($M - CH_3 - C_4H_8$), 144 ($M - CCl_3$), and 128 ($M - OCCl_3$)). This alkoxyamine is unstable in the injection port of a gas chromatograph, decomposing to phosgene as the only volatile product which was identified by GC-mass spectrometry. The structural assignment for di-*tert*-butylhydroxylammonium chloride (**2**) was made by comparison of its spectral properties and chemical properties with those of the known compound.[10] In particular, treatment of **2** with sodium hydroxide followed by air oxidation yielded di-*tert*-butyl nitroxide.

The products and stoichiometry of the irradiation of DTBN in carbon tetrachloride solvent can be explained as shown in Scheme I. The primary photochemical event is electron transfer from DTBN to CCl_4 with formation of di-*tert*-butyloxoammonium chloride (**3**) and trichloromethyl radical. Di-*tert*-butyloxoammonium chloride is unstable and decomposes to 2-methyl-2-nitrosopropane, isobutylene, *tert*-butyl chloride, and hydrogen chloride by elimination and nucleophilic substitution. Cyclic oxoammonium halides have been reported as unstable products from oxidation of cyclic nitroxides by chlorine,[11] bromine,[12] nitrogen dioxide,[13] and peroxides.[14] The fraction of oxoammonium chloride that decomposes to isobutylene and hydrogen chloride is designated by the symbol α. DTBN has been reported to be reactive with hydrogen chloride[10,15] as shown in Scheme I. The trichloromethyl radical is efficiently scavenged by a second equivalent of DTBN to give the alkoxyamine **1**.

The mechanism predicts as observed that the quantum yield of formation of 2-methyl-2-nitrosopropane is exactly half of the quantum yield of destruction of DTBN. The quantum yield of reaction of the charge-transfer excited state (β) and the fraction of **3** decomposing by elimination (α) can be calculated from the quantum yields of destruction of DTBN and formation of *tert*-butyl chloride and are 0.58 and 0.47, respectively. Similarly, the quantum yields of formation of **1**, **2**, and isobutylene can be calculated. The observed and calculated quantum yields (Table I) agree well within the experimental error of our measurements.

Di-*tert*-butyl nitroxide is an efficient quencher of electronically excited species at or near diffusion-controlled rates. The mechanism of quenching is generally thought to be either an electron-exchange relaxation process or vibrational quenching where a complex deactivates directly to ground state.[16] The charge-transfer excited state of DTBN-CCl_4 in principle can be quenched by DTBN via the electron-exchange mechanism, by vibrational quenching with the intermediacy of a complex, or by collisional energy transfer with formation of the lower energy, unreactive n,π* state. We have observed that the quantum yield of formation of 2-methyl-2-nitrosopropane is inversely related to the concentration of DTBN and propose, as shown in Scheme I, that DTBN is operating as a quencher of the DTBN-CCl_4 charge-transfer excited state. A plot of the reciprocal of the quantum yield of formation of 2-methyl-2-nitrosopropane vs. DTBN concentration is linear with slope of $0.24 \pm 0.03\ M^{-1}$ and intercept of 1.15 ± 0.02. From α, the slope and intercept of the quenching plot, and the assumption that DTBN quenches at a diffusion-controlled rate,[17] the rates of reaction of the charge-transfer excited state (k_r) and of internal conversion (k_d) can be calculated and are 3.1×10^{10} and $2.2 \times 10^{10}\ s^{-1}$, respectively. The rate of internal conversion is consistent with the anticipated short lifetime for the charge-transfer state which is actually an upper excited state.[18]

A possible alternate route to the oxoammonium chloride **3** is chlorine atom abstraction by excited DTBN to form a hypochlorite and the trichloromethyl radical. The hypochlorite might then react via an intramolecular redox process to give di-*tert*-butyloxoammonium chloride. We do not favor this process for the primary photochemical event for the following reasons. (1) The reaction does not occur from the n,π* state, the state associated with atom abstraction. (2) There is a charge-transfer interaction between DTBN and CCl_4 observed in the UV spectrum, and the degree of charge-transfer interaction with halogenated solvents parallels the half-wave electrode reduction potentials of the solvents.[19] (3) Ground-state DTBN is known to react as a one-electron reducing agent with easily reduced compounds such as peroxides.[14] (4) The photochemical reactivity described here is precedented in the photochemical reactions of amines with halogenated solvents which most likely occur by one-electron transfer.[20]

Currently we are actively investigating other examples of nitroxide photoelectron transfer and exploring possible chemical and biological applications.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health under grant GM-18349 for partial support of this research. D.R.A. thanks the University of Colorado for a Graduate Fellowship and the National Science Foundation for a Traineeship.

References and Notes

(1) D. R. Anderson and T. H. Koch, *Tetrahedron Lett.*, 3015 (1977).

(2) L. Call and E. F. Ullman, *Tetrahedron Lett.*, 961 (1973).

(3) J. F. W. Keana, R. J. Dinerstein, and F. Baitis, *J. Org. Chem.*, **36**, 209 (1971).

(4) J. A. Nelson, S. Chou, and T. A. Spencer, *J. Am. Chem. Soc.*, **97**, 648 (1975).

(5) J. F. W. Keana and F. Baitis, *Tetrahedron Lett.*, 365 (1968).

(6) E. M. Kosower, *Prog. Phys. Org. Chem.*, **3**, 81 (1965); A. K. Colter and M. R. J. Dack, *Mol. Complexes*, 1, 301 (1973); **2**, 1 (1974). R. S. Mulliken and W. B. Person, "Molecular Complexes" Wiley, New York, 1969.

(7) These configurational assignments have been previously discussed: O. Kikuchi, *Bull. Chem. Soc. Jpn.*, **42**, 47 (1969); A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, **53**, 333 (1970).

(8) I. Morishima, T. Inubushi, K. Endo, and T. Yonezawa, *Chem. Phys. Lett.*, **14**, 372 (1972); I. Morishima, T. Inubushi, K. Endo, T. Yonezawa, and K. Goto, *J. Am. Chem. Soc.*, **94**, 4812 (1972).

(9) Di-*tert*-butyltrichloromethoxyamine (1) decomposes slowly upon attempted isolation from CCl_4. When dissolved in more polar solvents, it rapidly and sometimes violently decomposes with the noticeable odor of phosgene.

(10) A. K. Hoffman and A. T. Henderson, *J. Am. Chem. Soc.*, **83**, 4671 (1961).

(11) V. A. Golubev and R. I. Zhdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 184

(1970).
(12) R. I. Zhdanov, V. A. Golubev, and E. G. Rozantsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **186** (1970); V. A. Golubev, G. N. Voronina, E. G. Rozantsev, *ibid.*, 2605 (1970).
(13) J. A. Nelson, S. Chou, and T. A. Spencer, *Chem. Commun.*, 1580 (1971); S. Chou, J. A. Nelson, and T. A. Spencer, *J. Org. Chem.*, **39**, 2356 (1974).
(14) J. A. Cella, J. A. Kelley, and E. F. Kenehan, *J. Org. Chem.*, **40**, 1860 (1975); B. Ganem, *ibid.*, **40**, 1998 (1975).
(15) S. B. Phillip and J. E. Keller, *J. Org. Chem.*, **35**, 2782 (1970); V. A. Golubev, V. D. Sen, I. V. Kulyk, and A. L. Aleksandrov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2235 (1975).
(16) R. E. Schwerzel and R. A. Caldwell, *J. Am. Chem. Soc.*, **95**, 1382 (1973); J. A. Green II and L. A. Singer, *J. Chem. Phys.*, **58**, 2690 (1973).
(17) A rate of 1.1×10^{10} M^{-1} s^{-1} was used for the rate of diffusion in CCl_4 at ambient temperature. S. L. Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, p 55.
(18) N. J. Turro, V. Ramamurthy, W. Cherry, and W. Farneth, *Chem. Rev.*, **78**, 125 (1978).
(19) The half-wave electrode reduction potentials vs. SCE for the halogenated solvents are as follows: CH_2Cl_2, −2.3, $CHCl_3$, −1.67, and CCl_4, −0.78 V. L. Meites, "Polarographic Techniques", Wiley, New York, 1965, pp 671–711.
(20) D. P. Stevens and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962).

David Richard Anderson, Joseph S. Keute
Harold L. Chapel, Tad H. Koch*
Department of Chemistry, University of Colorado
Boulder, Colorado 80309

Received October 20, 1978

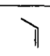
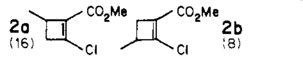
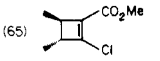
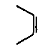
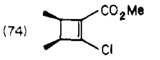
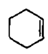
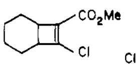
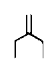
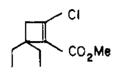
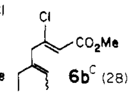
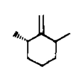
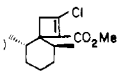
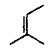
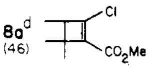
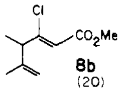
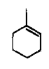
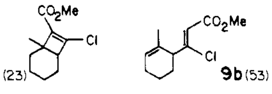
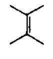
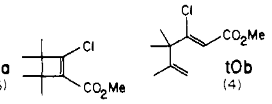
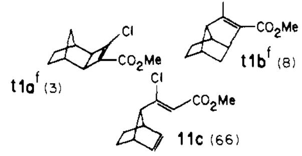
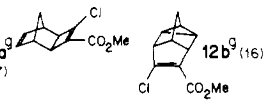
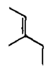
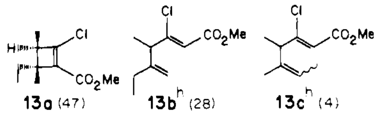
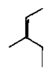
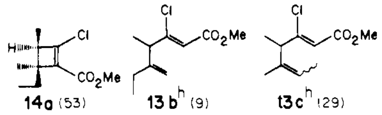
Aluminum Chloride Catalyzed Reactions of Methyl Chloropropiolate with Unactivated Alkenes

Sir:

We have recently reported that methyl propiolate undergoes aluminum chloride catalyzed ene reactions and/or stereospecific [2 + 2] cycloadditions with unactivated alkenes.[1] We report that this reaction can be extended to methyl chloropropiolate which gives rise stereospecifically to (*Z*)-3-chloro-2,5-alkadienoates via a regioselective ene reaction and to 2-chlorocyclobutene carboxylates via a stereospecific [2 + 2] cycloaddition (Figure 1). The resulting adducts are versatile synthetic intermediates which are not readily accessible by other routes.

Methyl chloropropiolate (**1**) can be prepared in a single step from *trans*-1,2-dichloroethylene, methyllithium, and methyl chloroformate in 60–70% yield by a modification of Viehe's procedure,[2] making this versatile reagent readily available.[3,4] The products from the aluminum chloride catalyzed reactions of **1** with alkenes are shown in Table I. Cyclobutenes are the major products in most cases, while with methyl propiolate cyclobutenes are formed only from mono- and 1,2-disubstituted alkenes. The most significant effect of the chlorine is observed in the reactions of 2,3-dimethyl-2-butene (**10**) which gives exclusively ene adduct with methyl propiolate and 95% cyclobutene with **1**.

Table I. Reaction of Methyl Chloropropiolate with Alkenes

	ALKENE	MOLE %AlCl$_3$	REACTION TIME DAYS, (°C)	PRODUCTS (% YIELD)[a]
2		32	3 (25)	 **2a** (16) **2b** (8)
3		50	2 (25)	 **3a** (65)
4		70	2 (25)	 **4a** (74)
5		76	3 (25)	 **5a** (51)
6		50	2 (25)	 **6a**[b] (41)  **6b**[c] (28)
7		47	5 (4) 1 (25)	 **7a** (52)
8		45	3 (4) 1 (25)	 **8a**[d] (46)  **8b** (20)
9		22	27 (25)[e]	 **9a** (23) **9b** (53)
10		42	3 (4)	 **10a** (76) **10b** (4)
11		70	2 (25)	 **11a**[f] (3) **11b**[f] (8) **11c** (66)
12		38	5 (4) 2 (25)	 **12a**[g] (37) **12b**[g] (16)
13		66	3 (4) 1 (25)	 **13a** (47) **13b**[h] (28) **13c**[h] (4)
14		66	3 (4) 1 (25)	 **14a** (53) **13b**[h] (9) **13c**[h] (29)

[a] Methyl chloropropiolate is added to a stirred suspension of sublimed aluminum chloride in anhydrous benzene under nitrogen. After the aluminum chloride has dissolved, 1.1 equiv of alkene is added and the reaction is stirred for the time shown. The reaction is quenched in dilute hydrochloric acid. Cyclobutenes (less polar) are easily separable from ene adducts by chromatography on silica gel. All yields are for isolated pure compounds unless otherwise specified. Products were characterized by NMR, IR, and mass spectroscopy and elemental analysis. [b] Contains ~85–90% **6a** and 10–15% **13a** and **14a.** [c] Contains ~85–90% **6b** as a 1:1 mixture of isomers and 10–15% **13b** and **13c.** [d] Regiochemistry determined by conversion to **18.** [e] Similar yields are obtained in 2–3 days using more aluminum chloride. [f] Determined by analysis of NMR spectrum of a mixture **11a** and **11b.** [g] Small amounts of an unidentified compound, which may have a structure analogous to **11b**, were also formed. For similar results in the thermal reaction of chloropropiolonitrile with norbornadiene, see T. Sasaki, S. Eguschi, M. Sugimoto, and F. Hibi, *J. Org. Chem.*, **37**, 2317 (1972). [h] Determined by analysis of the NMR spectrum of a mixture of **13b** and **13c**.

A possible explanation for this follows from an examination of the transition state required for a concerted ene reaction (Figure 1). If $R = CH_3$ and $X = Cl$, severe steric strain retards the reaction. For methyl propiolate ($X = H$), the steric hindrance is apparently not severe. Reactions 13 and 14 were carried out to test this hypothesis. If the mechanism shown in Figure 1 is correct, then the hydrogen on the carbon trans to olefinic hydrogen should be transferred preferentially. In both cases the major ene adduct is the one expected from the less hindered transiton state (Figure 1: $R = H$, $R' = CH_3$). The minor isomer may result from isomerization of the starting alkene. As predicted, 1:1 mixtures of regioisomers are obtained from the reaction of **13** or **14** with methyl propiolate. Similar interactions may be responsible for the formation of a single ene adduct in case 9. This is a novel example of synthetically useful regioselectivity in an ene reaction, which should be applicable to the ene reactions of a variety of disubstituted acetylenes.

In addition to the regioselectivity studies which support a

0002-7863/79/1501-1906$01.00/0