areas, but the low melting point of *cis*-[2.1.1] and *cis*-azobenzene necessitated correcting for the heat of fusion of one or both isomers. Thus for *cis*-[2.1.1], $\Delta H(\text{cis,s} \rightarrow \text{trans,s}) = \Delta H(\text{cis,l} \rightarrow \text{trans,l}) + \Delta H(\text{cis,s} \rightarrow \text{cis,l}) - \Delta H(\text{trans,s} \rightarrow \text{trans,l})$. Darkening of the *cis*-[2.1.1] samples was noticed when the pans were opened after the DSC runs. However, the fact that the preisomerization base line extrapolates to the postisomerization base line speaks for the absence of deep-seated decomposition.

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"Spontaneous" Formation of Radicals from Nitroso Compounds. Inadvertent Photolysis vs. Molecule Assisted Homolysis[1]

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Abstract: The formation of radicals by a "spontaneous" reaction between nitroso compounds and certain organic materials has often been reported in the literature and has generally been ascribed to a process of molecule assisted homolysis (MAH). Some selected "spontaneous" radical-forming processes involving trifluoronitrosomethane, nitrosobenzene, and 2,4,6-trichloronitrosobenzene have been reexamined. In many cases it has been found that the radicals are formed only when the sample is exposed to ordinary laboratory light. It is suggested that the role of light on other "spontaneous" radical-forming reactions should be investigated.

Introduction

Pryor and co-workers[3] have identified three types of polymolecular process by which radicals are produced from the interaction of closed-shell (i.e., singlet) molecules. These are: molecule assisted homolysis (MAH), in which acceleration of a single bond homolysis is caused by the interaction of one molecule with another; interactions of two π systems leading to diradicals; and one-electron transfer reactions in which a donor and an acceptor exchange an electron to produce two radicals or radical ions.[4] The mechanisms of many such processes are still not firmly established. Particularly intriguing is the "spontaneous" formation of free radicals which has often been observed when nitroso compounds are mixed with other organic compounds at ambient temperatures.[5–23] These reactions have been studied by EPR spectroscopy.[24,25] With certain exceptions the radicals have been correctly identified as nitroxides, though not all the nitroxides have had

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(1) Issued as N.R.C.C. No. 19555.

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their structures assigned correctly (vide infra)! The formation of nitroxides is not unexpected since nitroso compounds are widely used as "spin-traps",[26] viz.

$$R\cdot + R'N{=}O \rightarrow R'(R)N{-}O\cdot \qquad (1)$$

In certain "spontaneous" radical forming reactions of nitroso compounds it seems probable that genuine MAH processes are involved, for example, their reactions with hydroxylamines.[14,16,17,23] For two of these processes both the kinetic and thermodynamic parameters have been measured:[14]

$$Me_3CN{=}O + Me_3CNHOH \rightleftharpoons 2Me_3CNHO\cdot \qquad (2)$$

$$C_6H_5N{=}O + C_6H_5NHOH \rightleftharpoons 2C_6H_5NHO\cdot \qquad (3)$$

If we make the reasonable assumption that the O–H bond strength in *N*-alkyl hydroxylamines is the same as that in *N,N*-dialkyl hydroxylamines (viz. ca 71 kcal/mol[27,28]), then the measured value of ΔH for reaction 2 (viz 10.4 kcal/mol[14]) yields $D[\mathrm{Me_3CN(\dot{O})\text{-}H}] \approx 61$ kcal/mol. A similar value has been obtained[14] for $D[\mathrm{CH_3N(\dot{O})\text{-}H}]$ from the heats of formation of CH_3NO and CH_3NHOH.[29] What this means is that alkyl nitroso compounds can only "abstract" hydrogen atoms that are very weakly bound indeed: i.e., only from compounds, XH, which give highly stabilized[30] radicals, X·.[31a]

$$R'N{=}O + XH \rightarrow R'NHO\cdot + X\cdot \qquad (4)$$

Although there are no data available from which values of, for example, $D[\mathrm{CF_3N(\dot{O})\text{-}H}]$ or $D[\mathrm{C_6H_5N(\dot{O})\text{-}H}]$ could be estimated,[31b] we do not think that they will differ grossly from the value of 61 kcal/mol estimated for alkyl nitroxides. *A simple MAH, i.e., reacton 4, can therefore be ruled out on thermodynamic ground for most of the reported, ambient-temperature, thermal, "spontaneous" radical-forming reactions involving nitroso compounds.* It is the purpose of the present paper to show, by using a few carefully selected examples, that at least some "spontaneous" radical-forming reactions involving CF_3NO and nitroso aromatics are due to inadvertent photolysis of the nitroso compound.

In retrospect, it is astonishing that so many examples of "spontaneous" radical-forming reactions involving nitroso compounds have been proposed and, apparently, accepted. The irradiation of *monomeric* nitroso compounds with light of a suitable wavelength is well known to cause C–N bond homolysis, followed by nitroxide formation.[15,32-42]

$$R'N{=}O \xrightarrow{h\nu} R'\cdot + NO \qquad (5)$$

$$R'\cdot + R'N{=}O \rightarrow R'_2NO\cdot \qquad (6)$$

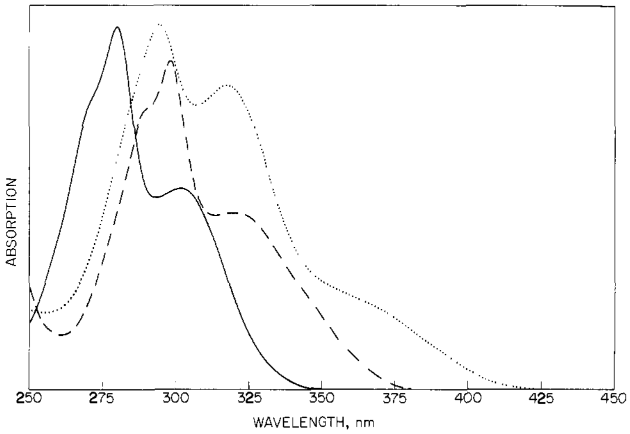

Figure 1. Light absorption from 250 to 450 nm in $CFCl_3$: (—) nitrosobenzene, (---) 2,4,6-trichloronitrosobenzene, (···) 2,3,5,6-tetramethylnitrosobenzene. Relative and absolute extinction coefficients were not determined.

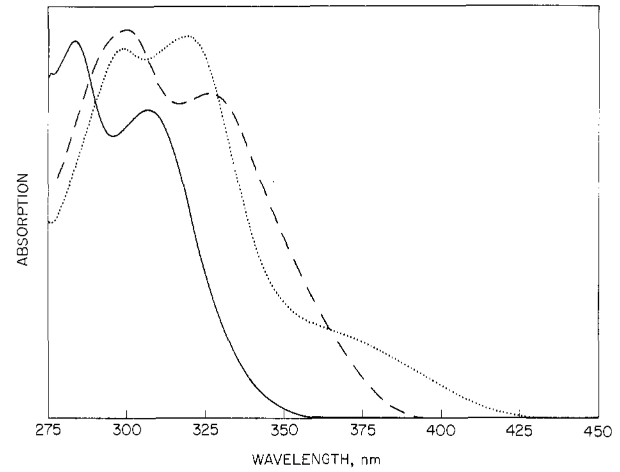

Figure 2. Light absorption from 275 to 450 nm in benzene: (—) nitrosobenzene, (---) 2,4,6-trichloronitrosobenzene, (···) 2,3,5,6-tetramethylnitrosobenzene. Relative and absolute extinction coefficients were not determined.

For 2-methyl-2-nitrosopropane the C–N bond strength, $D[\mathrm{Me_3C\text{-}NO}]$, has been estimated to be 39.5 kcal/mol,[43] which means that light having a wavelength ≤725 nm can, in principle, cleave this bond. The blue color of $Me_3CN{=}O$ is due to an absorption band having $\lambda_{max} \sim 680$ nm and $\epsilon \sim 10\ \mathrm{M^{-1}\ cm^{-1}}$,[44] and the photocleavage of $Me_3CN{=}O$ with visible (red) light (to form di-*tert*-butyl nitroxide) is a facile process.[15,32] Trifluoronitrosomethane ($D[\mathrm{CF_3\text{-}NO}] \leq 33$ kcal/mol)[45] also yields radicals upon irradiation with visible light.[34-37] For nitrosobenzene, however, $D[\mathrm{C_6H_5\text{-}NO}]$ is ca. 51.5 kcal/mol,[46] so that the light must have a wavelength ≲555 nm for C–N cleavage to occur,[47] but there is no detectable absorption at this wavelength.[48] This

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(31) (a) For example, taking $D[\mathrm{R'N(\dot{O})\text{-}H}] = 61$ kcal/mol and assuming $A_4 = 10^8\ \mathrm{M\ s^{-1}}$, then at 298 K, k_4 would be ≤25, 1×10^{-6}, and $5 \times 10^{-14}\ \mathrm{M^{-1}\ s^{-1}}$ for $D[\mathrm{X\text{-}H}] = 70$, 80, and 90 kcal/mol, respectively. (b) ΔH for reaction 3 is 7.2 kcal/mol.[14]

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(40) The claimed[41] stability of certain sterically hindered nitrosoaromatics towards UV irradiation has been shown to be in error.[42]

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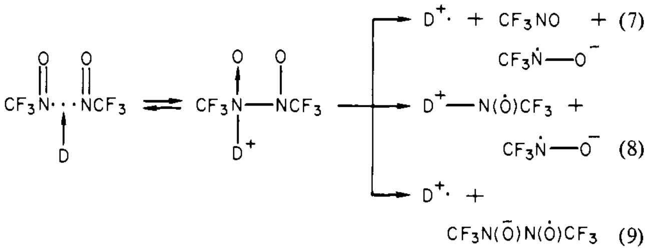
(47) It is therefore hardly surprising that nitrosobenzene does not exhibit "any photochemical activity with 730-nm excitation".[39]

has led to the idea that *only* UV light (i.e., light with λ <ca. 380–400 nm) can convert nitrosobenzene and other nitrosoaromatics into nitroxide radicals.[15,32,33,38–42] This idea is somewhat misleading because the strong UV absorption band of aromatic nitroso compounds actually tails into, or almost into, the visible region of the spectrum (see Figures 1 and 2). At high gain even nitrosobenzene was found to have a small but measurable absorption "tail" up to ca. 370–380 nm. Since "normal" laboratory illumination (whether from diffuse daylight, from fluorescent lights, or even from some tungsten filament lamps) contains some light having λ <380 nm, there is obviously a possibility that aryl–NO bonds can be cleaved by "visible" light. Though both light absorption and light intensity will be weak, C–N cleavage (if it occurred) should be observed eventually by EPR spectroscopy provided the nitroxide radicals which are produced are sufficiently persistent.

Finally, it should be noted that even when "spontaneous" radical formation has been reported to occur in the dark, it is improbable the light was rigorously excluded at all stages of sample preparation.

Results and Discussion

Trifluoronitrosomethane. Ginsburg and co-workers[6] used EPR spectroscopy to study radical formation from CF_3NO and an astonishing variety of organic compounds including, e.g., alkanes, alkenes, alkyl aromatics, aldehydes, amines, ethers, nitrosamines, phosphites, etc. With *all* of these substrates *one* of the radicals observed had $a^F(3\ F) = a^N$, but the magnitude of this hyperfine splitting (hfs) varied from 10.2 to 14.2 G! This radical was always assigned the radical-anion structure, $CF_3\dot{N}{-}O^-$, and it was suggested that it was formed by an electron transfer from some donor molecule, D (eq 7–9) With many hydrogen-containing organic substrates (e.g., ethanol, toluene, styrene, benzaldehyde, etc.), the spectrum assigned to $CF_3\dot{N}{-}O^-$ showed an *additional* doublet ($S = {}^1/_2$) splitting varying from 2.2 to 3.5 G, which was attributed to the formation of a "hydrogen bond".



We have examined the radicals formed "spontanously" from CF_3NO and some alcohols and ethers in $CFCl_3$ (or in CF_2Cl_2) as solvent at room temperature. All samples were prepared using high-vacuum techniques. Under normal laboratory conditions and in the absence of organic substrates a relatively strong spectrum of the extremely persistent $(CF_3)_2NO\cdot$ radical was obtained.[49] A similar sample prepared as nearly "in the dark" as practicable (including all handling of CF_3NO in the dark) gave a barely detectable signal of $(CF_3)_2NO\cdot$ which did not change with time. However, if while the sample remained in the cavity of the EPR spectrometer the laboratory lights were turned on, or daylight was allowed into the lab, the signal due to $(CF_3)_2NO\cdot$ rapidly grew in strength.

Samples containing ethanol (typically, $CF_3NO{:}C_2H_5OH{:}CFCl_3{::}$ca. 1:4:15 v/v) did not give $(CF_3)_2NO\cdot$. Instead, a spectrum was obtained which at room temperature[50,51] had the following hfs: $a^N = 11.2$ G; $a^F(3\ F) = 10.65$ G; $a^H(1\ H) = 2.8$ G (due to H not F because C_2D_5OD gave $a^D = 0.4$ G); $a^H(1\ H) = 0.3$ G[52] (due to H because it is not observed with C_2D_5OD). Ginsburg observed the larger but not the smaller of these two H hfs's. The signal due to this radical was intense when the sample was prepared normally, but was almost undetectable for samples prepared in the dark. The radical cannot be a "hydrogen-bonded" $CF_3\dot{N}{-}O^-$ since, for one thing, it has too many hfs's. More significantly, methanol yields a similar radical with $a^N = 10.8$ G, $a^F(3\ F) = 10.0$ G, $a^H(2\ H) = 3.7$ G, and $a^H(1\ H) = 0.2$ G,[52] and isopropyl alcohol a radical with $a^N = 12.1$ G, $a^F(3\ F) = 12.1$ G, and no detectable hydrogen hfs (≤ 0.3 G). With *tert*-butyl alcohol only $(CF_3)_2NO\cdot$ was formed, and some of this radical was also produced with C_2D_5OD (though not with C_2H_5OH).

All the alcohol-derived radicals have $g = 2.0067$ which identifies them as nitroxides. We have assigned them the $CF_3N(\dot{O})C(R_1R_2)OH$ structure[51] and propose that they are formed by reactions 10–12. It is clear that radical formation from CF_3NO

$$CF_3NO \xrightarrow[\text{light}]{\text{visible}} CF_3\cdot + NO \xrightarrow{CF_3NO} (CF_3)_2N\dot{O} \quad (10)$$

$$CF_3\cdot \text{ and/or } (CF_3)_2NO\cdot + R_1R_2CHOH \rightarrow R_1R_2\dot{C}OH \quad (11)$$

$$R_1R_2\dot{C}OH \xrightarrow{CF_3NO} CF_3N(\dot{O})C(R_1R_2)OH \quad (12)$$

and alcohols is not "spontaneous" but is, instead, due to inadvertent photlysis. The same holds true for ethers. That is, CF_3NO and many ethers in Freon solvents form $CF_3N(\dot{O})C(R_1R_2)OR$ radicals in the presence of visible light but not in the dark.[51]

It is not our intention to imply that *all* examples of "spontaneous" radical formation from CF_3NO are due to inadvertent photolysis. Thus, Haszeldine and co-workers[7] have shown that with acetylacetone in CCl_4 the radicals $CF_3N(\dot{O})CH(COCH_3)_2$ and $CF_3N(\dot{O})C(COCH_3){=}C(OH)CH_3$ were formed at $[CF_3NO]/[(CH_3CO)_2CH_2]$ ratios < 3:1. The reaction mechanism was suggested to involve reaction of the diketone with CF_3NO to form a carbanion which, by a nucleophilic reaction with a second molecule of CF_3NO, forms a hydroxylamine anion,[25] which is then oxidized to form the simple nitroxide and its tautomer. We have confirmed that the radicals described by Haszeldine et al.[7] are formed in the dark and that the blue color of the CF_3NO is lost in a few hours at room temperature.[53] It should, however, be added that under normal laboratory lighting conditions the EPR signal intensities are much enhanced which indicates that the same radicals can be formed by photolysis.

Nitrosoaromatics. 1. Nitrosobenzene. Samples of commercial nitrosobenzene, or of nitrosobenzene recrystallized in the dark, which have been dissolved in a Freon solvent in the absence of light, show a weak EPR spectrum of diphenyl nitroxide ($a^N = 9.80$ G, $a^H(6\ H) = 1.80$ G, $a^H(4\ H) = 0.88$ G[32,38]). This spectrum does not grow in the dark, nor, under normal lighting conditions (diffuse daylight, fluorescent, or tungsten filament lamps), does it increase appreciably while the sample remains in the EPR cavity.[54] If, however, such a sample is removed from the cavity and kept in the light for a few minutes, or if a sample is made up in the light, the intensity of the diphenyl nitroxide signal is greatly enhanced.[55] This we attribute to light absorption by the "tail" of the C_6H_5NO UV absorption band (see Introduction).

$$C_6H_5NO \xrightarrow[\text{light}]{\text{visible}} C_6H_5\cdot + NO \xrightarrow{C_6H_5NO} (C_6H_5)_2NO\cdot \quad (13)$$

The "spontaneous" formation of radicals in nitrosobenzene-containing systems has been reported fairly frequently but, since no particular efforts seem to have been made to exclude light, we

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[48] The blue band of C_6H_5NO has λ_{max} 760 nm and ϵ 44 M^{-1} cm^{-1} in heptane. See: Tabei, K.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 965.

[49] Ginsburg[6k] also observed this radical in the absence of hydrogen-containing organic compounds.

[50] The N and F hfs's show a pronounced temperature dependence. Full EPR data for this and related radicals will be published elsewhere.[51]

[51] Chatgilialoglu, C.; Ingold, K. U. *Can. J. Chem.* in press.

[52] Resolved only at lower temperatures.[51]

[53] Under similar, i.e., dark, conditions with ethanol or diethyl ether the blue color persists for weeks.

[54] All samples were examined in a Varian E-104 EPR spectrometer. For comparison, a sample containing ca. 10^{-3} M Me_3CNO gave $(Me_3C)_2NO\cdot$ at a rate of ca. 10^{-5} M/h when left in the cavity under normal lighting conditions.

[55] A sample containing ca. 10^{-1} M C_6H_5NO formed $(C_6H_5)_2NO\cdot$ at a rate of ca. 5×10^{-6} M/h when left outside the cavity under normal lighting conditions.

think it probable that many examples are due to inadvertent photolysis of the sample. For brevity the following discussion is restricted to the recent report by Camaggi et al.[20] that: "Degassed solutions in benzene of hexamethylditin and nitrosobenzene gave an intense ESR spectrum even without irradiation". The main radical was identified as $C_6H_5N(\dot{O})CH_2Sn(CH_3)_2Sn(CH_3)_3$ (**1**) and a small amount of diphenyl nitroxide was also present. An MAH process was tentatively suggested but it was noted that the reaction "does not happen if nitrosobenzene is replaced by nitroso(*tert*)butane". We find that there is no reaction between nitrosobenzene and hexamethylditin at room temperature in the dark, but that both **1** and diphenyl nitroxide were formed in the light in relative concentrations that depend on the relative concentrations of the two reagents. The reaction mechanism is obvious (reaction 13 followed by reactions 14 and 15). We suggest that

$$C_6H_5\cdot + (CH_3)_3SnSn(CH_3)_3 \rightarrow C_6H_6 + \dot{C}H_2Sn(CH_3)_2Sn(CH_3)_3 \quad (14)$$

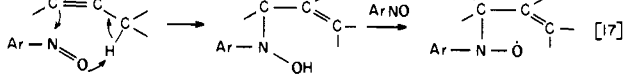
$$C_6H_5NO + \dot{C}H_2Sn(CH_3)_2Sn(CH_3)_3 \rightarrow \underset{\mathbf{1}}{C_6H_5N(\dot{O})CH_2Sn(CH_3)_2Sn(CH_3)_3} \quad (15)$$

the *tert*-butyl radical, which would be formed from $(CH_3)_3CNO$, would be insufficiently reactive for the necessary H-atom abstraction.

2. A Ring-Substituted Nitrosobenzene. Mulvey and Waters[18] have reported that 2,4,6-trichloronitrosobenzene (hereafter ArNO) in benzene yields nitroxide radicals when mixed with a wide variety of olefins. Subsequently, Waters[19] reported that radicals are formed from ArNO and many other types of organic compounds including enolizable carbonyl compounds (some of which *may* have reacted with the nitroso function via a nucleophilic attack of the carbanion; vide supra), hydroxylamines, thiols, and phenols (some of which *may* have reacted via a genuine MAH process). The results with the olefins[18] are the more interesting. The nitroxides formed initially had spectra which were interpreted as indicative "that the trichloronitrosobenzene had added to each olefin at the carbon atom indicative of a free radical and not a polar addition to the C=C bond".[18] A reaction mechanism was proposed involving the initial formation of a reactive biradical (**2**) which, by subseqent reaction, yielded the observed nitroxides, viz.

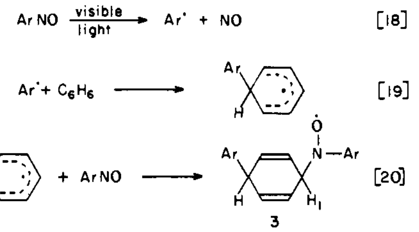
$$ArN{=}O + CH_2{=}CHR \xrightarrow{\text{slow}} \underset{\mathbf{2}}{ArN(\dot{O})CH_2\dot{C}HR} \quad (16)$$

We believe that few, if any, of the olefins studied by Mulvey and Waters react with ArNO by this mechanism. Those olefins having a suitable structure probably react at least in part by a cyclic "ene" addition[56] and subsequent oxidation of the hydroxylamine by the nitroso compound,[56,57] viz., eq 17. This mechanism[8,57] was considered by Mulvey and Waters[18] but was rejected because they found that many olefins which could not undergo "ene" addition also gave nitroxides and that these were formed within a few minutes after admixture under nitrogen of ArNO in benzene and the olefin. We have examined some of these "problem" olefins and we find that *they do not react with ArNO under the reported experimental conditions. Instead, the nitroxide that is formed is the spin adduct of a cyclohexadienyl radical derived from the benzene solvent and that this occurs only in the presence of light.*



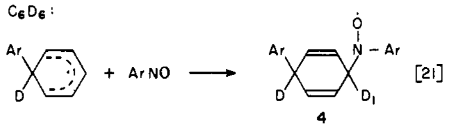
In benzene ArNO gives no radicals *in the dark*. *Brief* exposure to visible light gives a nitroxide ($g = 2.0062$) to which we assign structure **3** *because* in perdeuteriobenzene we obtain **4** which shows, splitting by one deuterium instead of one hydrogen, *plus* additional splitting due to the two meta hydrogens of the N-bonded trichlorobenzene moiety which are now resolved because of the narrower line width. In C_6D_6, ArNO gave a second radical which shows only a nitrogen hfs and to which we assign structure **5** by analogy with the nitrosodurene/aryl/C_6D_6 derived radicals of Suehiro et al.[58,59] In $CFCl_3$ no radicals are formed in the dark, but in visible light we obtained bis(trichlorophenyl) nitroxide (**6**). This last radical has been claimed to have been produced by UV irradiation of ArNO in benzene,[41b] but the reported N hfs (9.57 G) makes it clear that the radical observed was the nondeuterated analogue of **5**.

In C_6H_6:

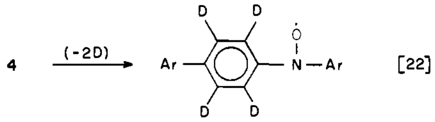


$a^N = 12.55$ G; a^{H_1}(1H) = 5.30 G; $a^{H_{meta}}$(2H) not resolved.

In C_6D_6:



$a^N = 12.55$ G; a^{D_1}(1D) = 0.8 G; $a^{H_{meta}}$(2H) = 0.8 G



5

$g = 2.0062$; $a^N = 9.55$ G

$$Ar^{\cdot} + ArNO \longrightarrow \underset{\mathbf{6}}{Ar_2N\dot{O}} \qquad [23]$$

$g = 2.0062$; $a^N = 8.65$ G; a^H(4H) = 0.60 G

When ArNO is mixed with *trans*-stilbene in C_6H_6 or in C_6D_6 no radicals are formed in the dark, but in visible light **3** is produced in C_6H_6 and **4** in C_6D_6 (Mulvey and Walters[18] report $a^N = 12.6$ G, $a^H = 5.9$ G, and for $ArNO–C_6H_6$–stilbene system). In $CFCl_3$ stilbene is apparently incorporated into the nitroxide formed in visible light since the radical shows splitting from one spin $^1/_2$ nucleus ($g = 2.0062$; $a^N = 13.00$ G; $a^H(1\ H) = 5.05$ G). We suggest the structure of this radical is $ArCH(C_6H_5)CH(C_6H_5)$-$N(\dot{O})Ar$. Similar results were obtained with triphenylethylene. That is, **3** was formed in C_6H_6 in the light (Mulvey and Walters[18] give $a^N = 12.70$ G, $a^H(1\ H) = 5.25$ G) and **4** was produced in C_6D_6. In the latter solvent **5** was also formed. In the ArNO–$CFCl_3$–triphenylethylene–visible light system a nitroxide showing only an N hfs (9.35 G) was formed.

Finally, and to emphasize that nitroso compounds can yield nitroxides by nonphotolytic processes, we note that *in the dark* ArNO and *cis*-butene gave a nitroxide which had $a^N = 12.66$ G, $a^H(1\ H) = 7.12$ G in both benzene and $CFCl_3$. The radical concentration decreased slowly with time and the concentration was not increased by exposure to visible light. We assign this radical the structure, $CH_2{=}CHCH(CH_3)N(\dot{O})Ar$, and take its formation in the dark to provide strong support for the "ene" addition/oxidation mechanism[8,56,57] of nitroxide formation.

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(56) Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556.

(57) Banks, R. E.; Barlow, M. G.; Haszeldine, R. N. *J. Chem. Soc.* **1965**, 4714.

(58) Suehiro, T.; Kamimori, M.; Tokumani, K.; Yoshida, M. *Chem. Lett.* **1976**, 531.

(59) Suehiro, T.; Kamimori, M.; Sakuragi, H.; Yoshida, M.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2594.

Conclusion

Many purported examples of "spontaneous" radical formation from nitroso compounds which have (explicitly or implicitly) been identified as MAH processes are actually due to inadvertent photolysis. We suggest that the role of ordinary laboratory light on other "spontaneous" radical-forming processes should be investigated.

Note Added in Proof: After submission of this manuscript a paper appeared describing the hydroxylamines formed in the ene reactions of CF_3NO with a variety of olefins and the nitroxides formed by oxidation of these hydroxylamines.[60] It was pointed out[60] that the previously postulated[6] involvement of ion radicals in these reactions was based upon doubtful EPR evidence and a misidentification of the products from allyl compounds. It was also pointed out[60] that the evidence for the postulated rate-determining formation of a diradical in the reactions of 2,4,6-trichloronitrosobenzene with olefins[18] was doubtful.

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(60) Barlow, M. G.; Haszeldine, R. N.; Murray, K. W. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1960.

Dication Ether Salts, R^+–O–R^+·$2CF_3SO_3^-$, from the Reaction of Trifluoromethanesulfonic Anhydride with Activated Ketones

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Abstract: Reaction of activated ketones with triflic anhydride (Tf_2O) in either CH_2Cl_2 or CCl_4 results in the formation of novel dication ether salts, R^+-O-R^+·$2O^-Tf$. Stabilized dications of the Hückel aromatic, 6π-heterocyclic, and substituted urea systems can all be prepared. The majority of these compounds are stable hygroscopic crystalline salts. They may be fully characterized by spectroscopic and chemical means. Hydrolysis results in the corresponding hydroxy salts and reaction with amines in the corresponding amino salts. These results are discussed in detail.

Carbocations are among the most ubiquitous reactive intermediates in chemistry. These electron-deficient species encompass a wide spectrum of structural features and possess a rich variety of chemical properties. Despite the ubiquitous nature and great variety of carbocations, bis(carbenium ions) linked by a single atom, **1a**, are to our knowledge unknown. Since coulombic

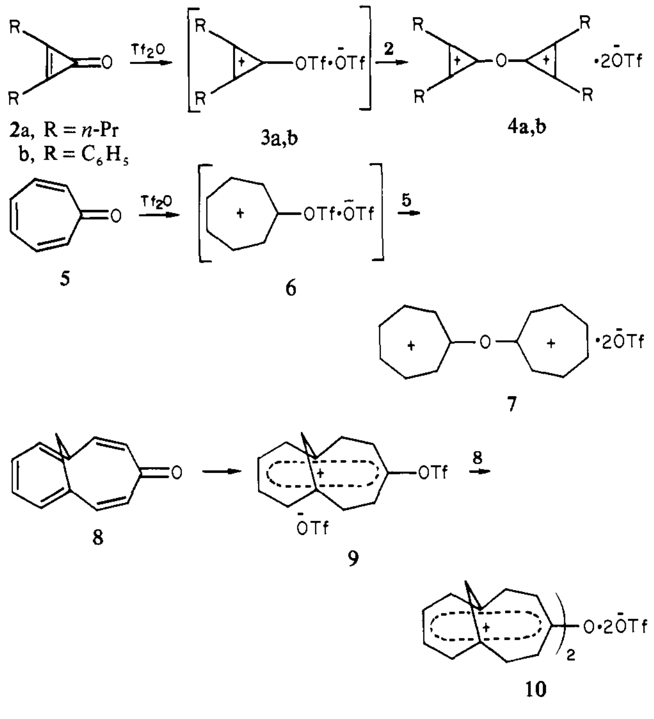
$$\underset{\mathbf{1a}}{R^+\text{–A–}R^+\cdot 2X^-} \qquad \underset{\mathbf{1b}}{R^+\text{–O–}R^+\cdot 2CF_3SO_3^-}$$

repulsion of two nearby concentrated like charges would result in considerable destabilization, species with highly delocalized carbenium ions linked by a heteroatom with lone-pair electrons would have the best chance of being observed. In this paper we report[1] the preparation, characterization, and some chemistry of remarkably stable, novel dication ether salts (**1b**), the first members of a class of new bis(carbenium ions) (**1a**).

Results and Discussion

A. Synthesis of Aromatic Cations of the Hückel Type. Addition of half an equivalent of triflic anhydride, $(CF_3SO_2)_2O$, Tf_2O, to a solution of the substituted cyclopropenones (**2**) or to tropone (**5**) in anhydrous CH_2Cl_2 or CCl_4 results in the rapid formation of the corresponding dication ether salts **4** and **7** as shown in Scheme I. Reaction most likely proceeds by initial sulfonation of these activated carbonyls to form monocations **3** and **6**. In the case of the cyclopropenones or tropone, the respective monocations could not be be isolated or observed even with inverse addition of the carbonyl to a large excess of Tf_2O. In contrast, reaction of Tf_2O with [11]annulenone **8** at room temperature yields only the monocation **9**. Cation **9** may be readily transformed into dication **10** by reaction with an equivalent amount of annulenone **8** at elevated temperature.

Scheme I



6π-Heteroaromatic Ions. Dimethylpyrone (**11**) xanthone (**13**), and *N*-methylpyridone (**15**) also react with triflic anhydride to give the respective dication ether salts **12**, **14**, and **17**, as shown in Scheme II. Once again reaction undoubtedly occurs via monotriflation and the intermediacy of monocations, but only in the case of *N*-methylpyridone (**15**) was the monocation isolable. Further reaction of monocation **16** at elevated temperatures results in dication **17**. In contrast to the above systems, reaction of

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(1) For a preliminary communication, see: Stang, P. J.; Maas, G.; Fisk, T. E. *J. Am. Chem. Soc.* **1980**, *102*, 6361-6362.

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