α-Nitration of Ketones *via* Enol Silyl Ethers. Radical Cations as Reactive Intermediates in Thermal and Photochemical Processes

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Highly colored (red) solutions of various enol silyl ethers and tetranitromethane (TNM) are readily bleached to afford good yields of α-nitro ketones in the dark at room temperature or below. Spectral analysis show the red colors to be associated with the intermolecular 1:1 electron donor−acceptor (EDA) complexes between the enol silyl ether and TNM. The formation of similar vividly colored EDA complexes with other electron acceptors (such as chloranil, tetracyanobenzene, tetracyanoquinodimethane, *etc.*) readily establish enol silyl ethers to be excellent electron donors. The deliberate irradiation of the diagnostic (red) charge-transfer absorption bands of the EDA complexes of enol silyl ethers and TNM at −40 °C affords directly the same α-nitro ketones, under conditions in which the thermal reaction is too slow to compete. A common pathway is discussed in which the electron transfer from the enol silyl ether (ESE) to TNM results in the radical ion triad [$ESE^{\bullet+}$, $NO_2^{\bullet}$, $C(NO_2)_3^-$]. A subsequent fast homolytic coupling of the cation radical of the enol silyl ether with $NO_2^{\bullet}$ leads to the α-nitro ketones. The use of time-resolved spectroscopy and the disparate behavior of the isomeric enol silyl ethers of α- and *β*-tetralones as well as of 2-methylcyclohexanone strongly support cation radicals ($ESE^{\bullet+}$) as the critical intermediate in thermal and photoinduced electron-transfer as described in Schemes 1 and 2, respectively.

Introduction

Various α-nitro ketones are widely utilized as synthetic intermediates[1−3] since they are excellent precursors for carbon to carbon bond-forming reactions owing to the powerful activation of the α-hydrogen atom by the combined effect of the nitro and carbonyl groups.[4,5] Furthermore, the facile cleavage of the C−C bond between the carbonyl and the nitro-substituted carbon atom in α-nitro ketones can be exploited in the synthesis of ring-enlarged cycloalkanones.[6,7] Although general methods for the efficient preparation of α-nitro ketones are desirable, the most direct route involving the electrophilic nitration of ketones (with nitric acid) suffers from a variety of oxidative byproducts.[8] Alternatively, the conversion of ketones to their enolates,[9] enol acetates,[10] and enol ethers,[11] coupled with milder nitrating agents such as alkyl nitrates, nitryl chloride, and acyl nitrates, *etc.*, does facilitate the α-nitration of ketones, but their use has generally met with limited success.[12] Interestingly, the keto−enol tautomerization effectively converts a (relatively electron-poor) carbonyl acceptor into a (correspondingly electron-rich) olefinic donor;[13] such an umpolung allows the conventional nucleophilic additions at the carbonyl center (*e.g.* Grignard reaction) to be readily replaced by electrophilic substitution at the α-carbon (*e.g.* bromination) of ketones, aldehydes, esters, *etc.*[14] Especially noteworthy in this regard are the facile α-substitutions of enol silyl ethers with *N*-bromosuccinimide,[15,16] nitronium[17] and diazonium[18] salts, chloranil[19] and DDQ,[20] silver oxide,[21] lead tetraacetate,[22] vanadium oxytrichloride,[23] ceric ammonium nitrate,[24] *etc.* The wide diversity of such reagents (that includes cationic and neutral electrophiles as well as strong and weak 1-electron oxidants) raises the question as to whether a unified mechanistic formulation is applicable to enol silyl ethers as electron donors in general.[25]

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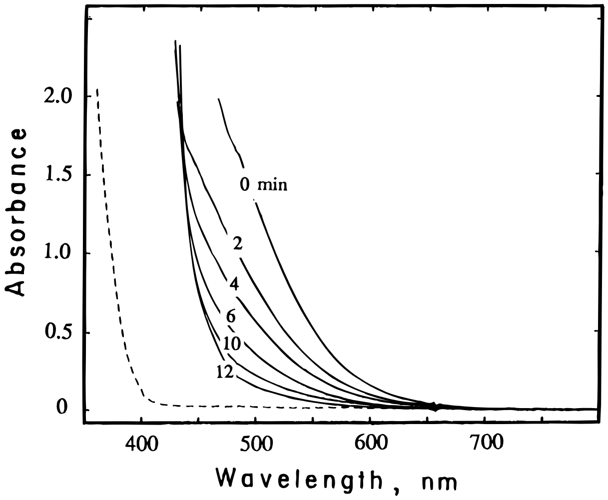
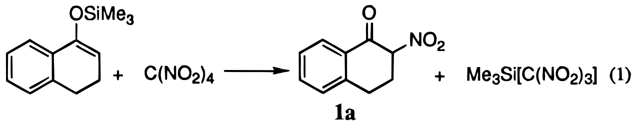


Figure 1. Typical bleaching of the red coloration obtained from 0.2 M enol silyl ether **1a** and 0.22 M TNM in dichloromethane at the indicated times, and the UV–vis spectrum of TNM alone (- - -).

In this report, we report a facile method for the preparation of a variety of α-nitro ketones in good to excellent yields by the thermal as well as the photochemical nitration of readily available enol silyl ethers with tetranitromethane.[26] We focus in this study on (a) the structural effects of enol silyl ethers on their reactivity with such a mild nitrating agent as tetranitromethane[27] and (b) the spectroscopic identification of the accompanying color changes and the reactive intermediates that play a critical role in the α-nitration of enol silyl ethers.

Results

Thermal α-Nitration of Ketones *via* Enol Silyl Ethers. When a solution of the enol trimethylsilyl (TMS) ether of α-tetralone **1a** in anhydrous dichloromethane was mixed with 1 equiv of tetranitromethane (TNM) under an argon atmosphere at room temperature, the solution immediately took on a bright red coloration. Upon standing in the dark, the solution progressively bleached to a yellow solution over the course of ~10 min, as shown by the corresponding spectral changes in Figure 1. In a simple workup procedure, the reaction mixture was extracted repeatedly with water until the washings were colorless. The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo* to afford the crystalline 2-nitro-α-tetralone **1a** in essentially quantitative yield. In order to identify the accompanying trinitromethyl moiety in the reaction mixture, the yellow-colored aqueous washings were examined by UV–vis spectroscopy and by HPLC analysis. Spectroscopic analysis of the dark-yellow aqueous extracts (after dilution by water) indicated the presence of 1 equiv of trinitromethide [$C(NO_2)_3^-$: $\lambda_{max} = 350$ nm, $\epsilon_{max} = 14000$ M^{-1} cm^{-1}].[28] The identity of the trinitromethide was confirmed by comparison with an authentic sample[28] using the HPLC method (see Experimental Section). Furthermore, HPLC analysis was used to monitor the progress of the nitration reaction and establish the 1:1 molar stoichiometry between 2-nitro-α-tetralone **1a** and trinitromethide, *i.e.*



[The trimethylsilyl derivative of trinitromethide as presented in eq 1 was isolated as a highly labile yellow solid. However, an attempt to obtain a single crystal suitable for X-ray crystallography resulted in a violent explosion and further studies were suspended.] With this simple procedure, the enol silyl ethers derived from various types of ketones listed in Table 1 were converted to the corresponding α-nitro ketones in fair to excellent yields. It is noteworthy that every α-nitro ketone was accompanied by 1 equiv of trinitromethide to confirm the general stoichiometry in eq 1.

Effect of Solvent. The efficiency of the nitration reaction was rather insensitive to solvent variation, since comparable yields of α-nitro ketones were obtainable in either acetonitrile, dichloromethane, or *n*-pentane. For example, when a solution of α-tetralone enol silyl ether **1a** in *n*-pentane was mixed with 1 equiv of tetranitromethane at room temperature, the solution immediately took on the characteristic red coloration. Upon standing shortly, the solution progressively bleached as the yellow crystals of 2-nitro-α-tetralones **1a** were readily precipitated in quantitative yields (see Experimental Section).

Effect of Ketone Structure. The nitration of the enol silyl ethers in Table 1 qualitatively occurred at varying rates and efficiencies that largely depended on the number and location of various substituents. However in every case, a transient reddish coloration which changed to yellow with time, was a common, unmistakable feature of this transformation. Indeed, such a color change provided a convenient visual indicator for the progress of the nitration reaction, as illustrated by the spectral changes in Figure 1. Thus the dark-red colors derived from α-tetralone enol silyl ethers (**1a**–**c**) and TNM were rapidly discharged within minutes to afford the corresponding 2-nitro-α-tetralones (**1a**–**c**) in essentially quantitative yields. Also, the enol silyl ethers of the acyclic 1-phenylketones (such as acetophenone and its analogs **2a**–**d**) afforded excellent yields of 2-nitro-1-phenylketones (**2a**–**d**) with concomitant bleaching of the red color over the course of 5–6 h (see Table 1). In a similar vein, the cycloalkanone enol silyl ethers (**3a**–**e**) afforded good yields of 2-nitrocycloalkanones in relatively slow reactions, as indicated by the gradual bleaching of the color over a 16-h period. [Note that the isolation of the labile α-nitrocyclopentanone was hampered due to interference from its facile ring cleavage.[29]] On the other hand, the enol silyl ethers of acyclic ketones **4a** and **4b** afforded only poor yields of α-nitro ketones in significantly slower nitrations with TNM (see Table 1).

The time for the visual color change (required to obtain the isolated yields of α-nitro ketones listed in Table 1) provided a qualitative measure of the reactivities of

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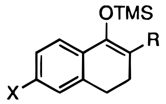
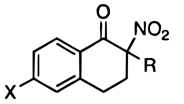
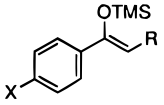
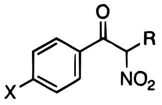
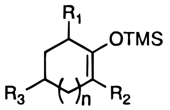
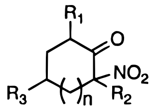
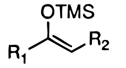
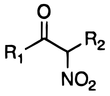
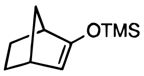
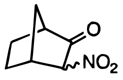
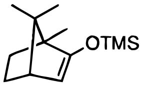
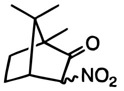
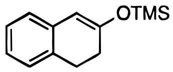
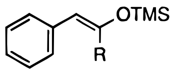
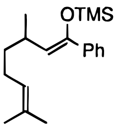
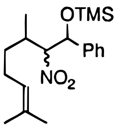
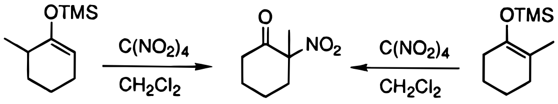
Table 1. Thermal Nitration of Enol Silyl Ethers with Tetranitromethane

No.	Enol Silyl Ether	α-Nitroketone	Time (h)	Yield (%)[a]
1				
1a	X = H, R = H		0.17	95
1b	X = OMe, R = H		0.01	97
1c	X = H, R = Me		0.17	92
2				
2a	X = H, R = H		6	87
2b	X = H, R = Me		6	90
2c	X = H, R = *n*-Bu		6	93
2d	X = H R = $PhCH_2$		6	91
2e	X = NO_2, R = H		16	85
3				
3a	R_1 = H R_2 = H R_3 = H n = 1		16	70
3b	R_1 = H R_2 = H R_3 = *t*-Bu n = 1		16	70
3c	R_1 = Me R_2 = H R_3 = H n = 1		16	76
3d	R_1 = H R_2 = Me R_3 = H n = 1		16	68
3e	R_1 = H R_2 = H R_3 = H n = 2		16	70
3f	R_1 = H R_2 = H R_3 = H n = 0		5	95[b]
4				
4a	R_1 = *n*-Pr, R_2 = Et		72	20
4b	R_1 = *t*-Bu R_2 = H		168	25
5			0.5	60[c]
6			0.3	54[c]
7			--	d
8				
8a	R = Me		--	d
8b	R = CH_2Ph		--	d
9			8	78[d]

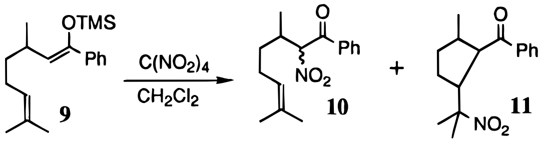
[a] Isolated Yields. [b] Nitrocyclopentanone not isolated; estimated from ^1H NMR. [c] Reaction at -30 °C. [d] See text.

various enol silyl ethers towards TNM. On this basis, the methoxy-substituted α-tetralone enol silyl ether **1b** reacted at least 1 order of magnitude faster than either derivative **1a** or **1c**. In contrast, the nitro-substituted acetophenone derivative **2e** reacted much slower than the parent acetophenone derivative **2a**. The effect of ring strain was shown in the enol silyl ether derivatives of norbornanone (**5**) and camphor (**6**), both of which resulted in the corresponding α-nitro ketones *via* the rapid bleaching of the color even at −30 °C. It is noteworthy that nitrations with TNM were not regiospecific, since the kinetic and thermodynamic enol silyl ethers of methylcyclohexanone **3c** and **3d**, respectively, yielded the same 2-methyl-2-nitrocyclohexanone, *i.e.*



3c **3d** (2)

The efficiency of the nitration reaction prompted us to examine the enol silyl ether **9** (with a tethered olefinic group) derived from citronellal.[30] Treatment of a solution of **9** in dichloromethane with tetranitromethane instantaneously led to the characteristic red coloration, which on standing (in the dark) progressively bleached to a yellow colored solution. Aqueous workup afforded a pair of diastereomeric α-nitro ketones **10** in excellent yields; but no cyclized product **11** was detected (<0.1%), *i.e.*



9 **10** **11** (3)

Comparative Reactivity of α- and β-Tetralone Enol Silyl Ethers. Although the characteristic red coloration of α-tetralone enol silyl ether **1a** and TNM in dichloromethane rapidly bleached on standing to afford a quantitative yield of 2-nitro-α-tetralone, the similar red coloration of the isomeric β-tetralone enol silyl ether **7** and TNM persisted at 25 °C for hours without any noticeable change. After standing in the dark for ~12 h, the enol silyl ether **7** was recovered unchanged; upon aqueous workup and spectral analysis the aqueous layer showed the presence of very little nitroform (<0.05 equiv, ~5%, see Experimental Section). Such a dramatic difference in the reactivity between a pair of isomeric enol silyl ethers with tetranitromethane was not restricted only to α- and β-tetralone derivatives **1a** and **7**. A similar difference in the reactivity was observed with other isomeric pairs of acyclic enol silyl ethers derived from 1-phenyl ketone *versus* 2-phenyl ketone, such as **8a** compared to **2b**, or **8b** compared to **2d**. Thus, 1-phenyl ketone enol silyl ethers 2b and 2d afforded excellent yields of the corresponding α-nitro ketones, whereas both of the isomeric 2-phenyl ketone enol silyl ethers **8a** and **8b** did not react under the same conditions (see Table 1).

Photochemical Nitration of Enol Silyl Ethers. The persistence of the colored solutions of enol silyl ethers (especially those derived from the relatively unreactive cycloalkanones **3a**−**e** and the acyclic ketones **4a**−**b**) in

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(30) (a) Similar cyclizations have been effected with ceric ammonium nitrate (CAN) as the 1-electron oxidant. (b) Snider, B. B, Kwon, T. *J. Org. Chem.* **1992**, *57*, 2399.

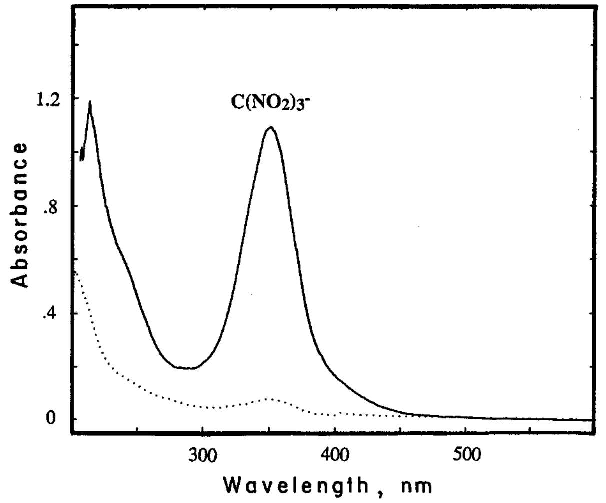
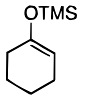
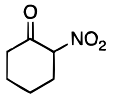
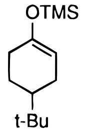
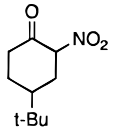
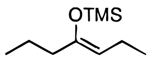
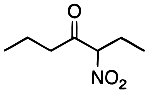
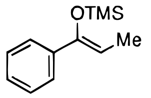
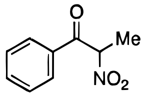
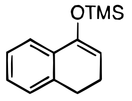
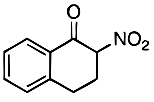
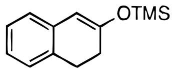
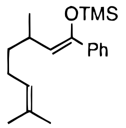
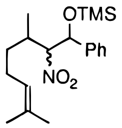


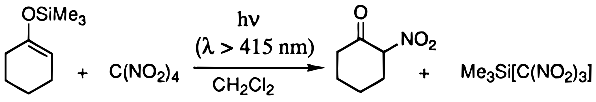
Figure 2. Spectral comparison of the trinitromethide concentration in the aqueous extract of the photolysate (—) and the dark control (····) after the photonitration with λ > 415 nm of 0.2 M enol silyl ether **3a** and 0.22 M TNM in dichloromethane at −40 °C.

Table 2. Photochemical Nitration of Enol Silyl Ethers with Tetranitromethane in Dichloromethane at −40 °C

No.	Enol Silyl Ether	α-Nitroketone	Time (h)	Yield (%)[a]
3a			1.0	73
3b			1.0	76
4a			1.5	64
2b			0.5	96
1a			0.5[b]	98[c]
7		d	3.0	e
9			0.8	72

[a] Isolated Yields. [b] Reaction carried out at -78 °C. [c] Dark control showed a 17 % yield of α-nitroketone, see Text. [d] A mixture of products. [e] See Experimental Section.

the dark, in comparison to those solutions that were exposed to room light, prompted us to examine the effect of *deliberate* irradiation. Thus, photochemical studies were carried out with filtered actinic radiation from a medium pressure 500-W mercury lamp equipped with a sharp Pyrex cutoff filter that allowed only light with λ > 415 nm to be transmitted. [Note that under these conditions, neither tetranitromethane nor enol silyl ethers were excited since they only absorb below 400 nm.] In each case, the photoactivated transformation of enol silyl ethers with TNM were carried out at low temperatures (typically <−40 °C) at which the thermal reactions (*vide supra*) were too slow to compete. For example, the irradiation of an orange-red dichloromethane solution of cyclohexanone enol silyl ether **3a** and TNM in a dry ice/acetonitrile bath (under an argon atmosphere) resulted in the continuous bleach of the color over the course of 1 h, to finally yield a yellow solution. An identical solution of enol ether **3a** and TNM was also prepared but kept protected from light alongside the irradiated solution at the same temperature and for the same irradiation period. The UV−vis analysis of this (dark) control showed no spectral change. The simultaneous workup of the (dark) control and the photolysate by removal of the solvent and excess TNM *in vacuo*, followed by the aqueous treatment of the residues (after redissolution in dichloromethane) was followed by quantitative GC and HPLC analysis using the internal standard method (see Experimental Section). Although the enol ether **3a** from the unirradiated solution remained wholly intact, HPLC analysis of the photolysate indicated that α-nitrocyclohexanone (**3a**) was formed in 73% yield. The spectral properties and GC-MS behavior of α-nitrocyclohexanone (**3a**) coincided with those of an authentic sample prepared independently.[10a] The subsequent spectrophotometric analysis of the aqueous extracts from the photolysate revealed that 1 equiv of nitroform accompanied the formation of α-nitrocyclohexanone (see Figure 2). By contrast, the aqueous extracts from the dark control showed the presence of only traces of nitroform. Accordingly, the stoichiometry for the photochemical nitration of enol silyl ether of cyclohexanone with TNM was described as



(4)

The photochemical nitrations of other silyl enol ethers with TNM at low temperatures (−40 °C) are included in Table 2. It is noteworthy that irradiation for a rather short duration (1−2 h) was generally sufficient to obtain good yields of α-nitro ketones, that otherwise required much longer periods for preparation in the dark at 25 °C (compare Tables 1 and 2). Furthermore, the dark-red solution of the reactive α-tetralone enol silyl ether **1a** and TNM was bleached within 20 min even at −78 °C, and the analysis of photolysate showed the formation of 2-nitro-α-tetralone **1a** in >98% yield. [By comparison, the (dark) control at this temperature showed only a 17% yield of α-nitro ketone **1a**, see Experimental Section]. On the other hand, the intensely colored solution of the isomeric β-tetralone enol silyl ether **7** and TNM upon irradiation at 25 °C bleached rather sluggishly to afford a pale brown solution. Aqueous workup, followed by GC and GC-MS analysis showed that a complex mixture of products was formed. Notably, enol silyl ether **7** was completely consumed. Although no β-nitro ketone was detected in the crude reaction mixture (see Experimental Section) spectral analysis of the aqueous washings showed that substantial amounts of nitroform (0.45 equiv) was produced.

Spectral Characterization of the Transient Colors Observed during the Nitration of Enol Silyl Ethers with Tetranitromethane. The addition of TNM to cyclohexanone enol silyl ether (**3a**) resulted in

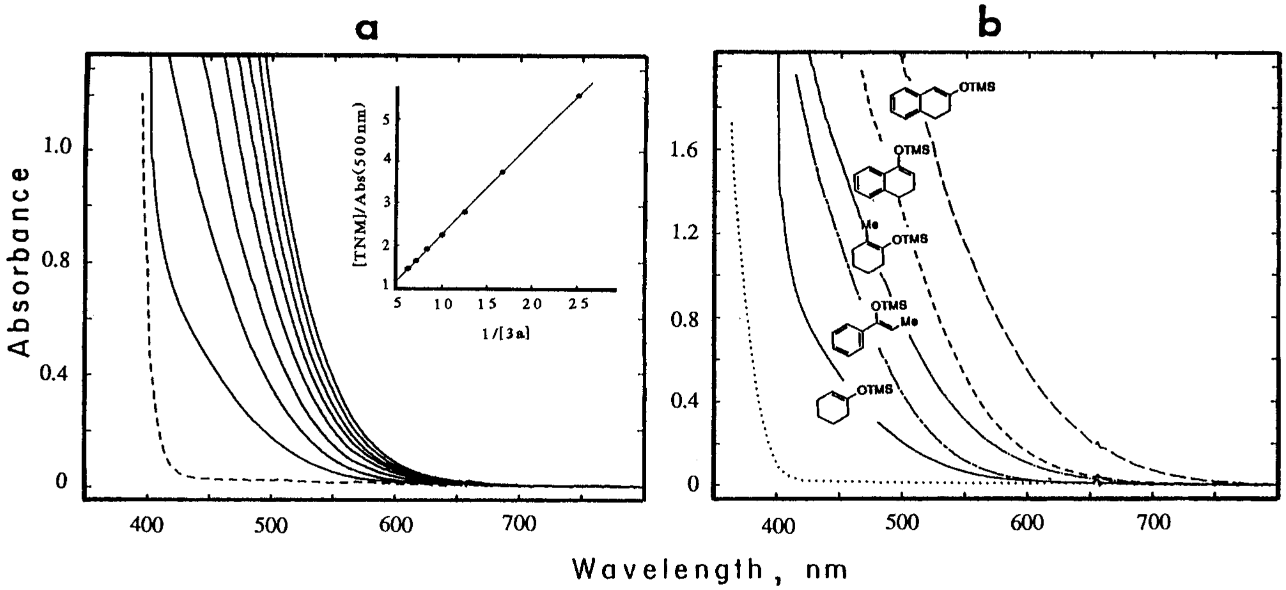
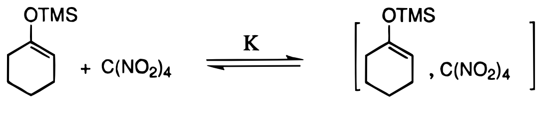


Figure 3. Charge-transfer spectra of the EDA complexes of enol silyl ethers with TNM. (a) Spectral changes accompanying the incremental addition of cyclohexanone enol silyl ether **3a** (0.02−0.2 M) to 2.0 M TNM (- - -) in dichloromethane at −15 °C. Inset: Benesi−Hildebrand plot. (b) Comparative charge-transfer absorption spectra obtained from the addition of 0.2 M enol silyl ethers **3a**, **7**, **1a**, **3d**, and **2b** to 0.2 M TNM (····) as indicated.

an instantaneous coloration which varied from deep yellow to wine red depending on the concentration of each component. For example, the absorption spectrum of TNM in dichloromethane solution underwent the successive changes shown in Figure 3a upon the incremental addition of enol ether **3a** at −15 °C. When the absorbance change was measured at 450 nm (A_{450}) as a function of the enol silyl ether concentration [**3a**] according to the Benesi−Hildebrand treatment,[31] *i.e.*

$$\frac{[\mathrm{TNM}]}{A_{450}} = \frac{1}{\epsilon_{450}} + \frac{1}{K_{\mathrm{EDA}}\epsilon_{450}}\frac{1}{[\mathbf{3a}]} \qquad (5)$$

the linear correlation shown in the inset of Figure 3a yielded the formation constant of $K = 0.24\ \mathrm{M}^{-1}$ and the extinction coefficient of $\epsilon_{450} = 19\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$. Such values of K and ϵ are indeed typical for the spontaneous formation of electron donor−acceptor (EDA) complexes of tetranitromethane when the TNM acceptor was exposed to various types of electron donors (including arenes, alkenes, *etc.*),[32] *e.g.*



(6)

Similarly, the other substituted enol silyl ethers in Table 1 afforded red solutions of varying intensity when mixed with TNM. In each case, the colors attendant upon the exposure of the various enol silyl ethers to TNM were associated with the appearance of new broad absorption bands (see Figure 3b), since neither TNM nor the enol silyl ethers absorbed in the visible region above 400 nm. Unfortunately, the quantitative treatment of these new (tailing) absorptions was hampered owing to the absence of distinct spectral maxima (see Figure 3b). Accordingly, in order to establish the viability of the EDA complex in eq 6, we examined the formation of analogous charge-transfer complexes of enol silyl ethers with other commonly used π-acceptors, such as chloranil (CA), tetracyanobenzene (TCNB), and tetracyanoquinodimethane (TCNQ). Fortunately, these acceptors led to well-resolved absorption bands with enol silyl ethers (as electron donors) sufficient to identify the transient colors as follows.

Electron Donor−Acceptor Complexes of Enol Silyl Ethers with π-Acceptors. The visual indication of enol silyl ethers as electron donors derives from the vivid charge-transfer colors that were observed when enol silyl ethers were exposed to various electron acceptors.[33] For example, an intense orange coloration developed immediately when chloranil (CA) was added to a solution of cyclohexanone enol silyl ether **1a** in dichloromethane under an argon atmosphere at 25 °C. Figure 4a shows the progressive growth of the spectral absorbance with incremental additions of the ether **1a**. Spectrophotometric analysis by the Benesi and Hildebrand method in eq 5, under conditions in which [CA] ≫ [**1a**], yielded a linear plot (see inset of Figure 4a) with a typical correlation coefficient of >0.99. From the slope and intercept, the values of the formation constant and extinction coefficient were obtained as $K_{\mathrm{CT}} = 1.1\ \mathrm{M}^{-1}$ and $\epsilon_{460} = 416\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$, respectively.[34] The other substituted enol silyl ethers listed in Table 3 and chloranil similarly afforded brightly colored solutions of varying shades of red, blue, and green. The quantitative effect of the color changes is illustrated in Figure 4b by the systematic spectral shifts of the well-defined new absorption bands of chloranil with the enol silyl ethers of cyclohexanone, methylcyclohexanone, and β-tetralone. [Note that neither chloranil nor the enol silyl ethers absorbed beyond $\lambda = 400$ nm.] These well-resolved, but featureless absorption bands were

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[31] (a) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703. (b) Foster, R. *Mol. Complexes* **1974**, *2*, 107.

[32] Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235 and 7824.

[33] (a) Rathore, R.; Kochi, J. K. *Tetrahedron Lett.* **1994**, *35*, 8577. (b) Bockman, T. M.; Perrier, S.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1993**, 595.

[34] The values of the formation constants K_{EDA} of enol silyl ether/chloranil complexes were uniformly small (~1−3 M^{-1}),[33a] characteristic of typical π−π electron donor−acceptor complexes; see also Foster, R. F. in ref 41.

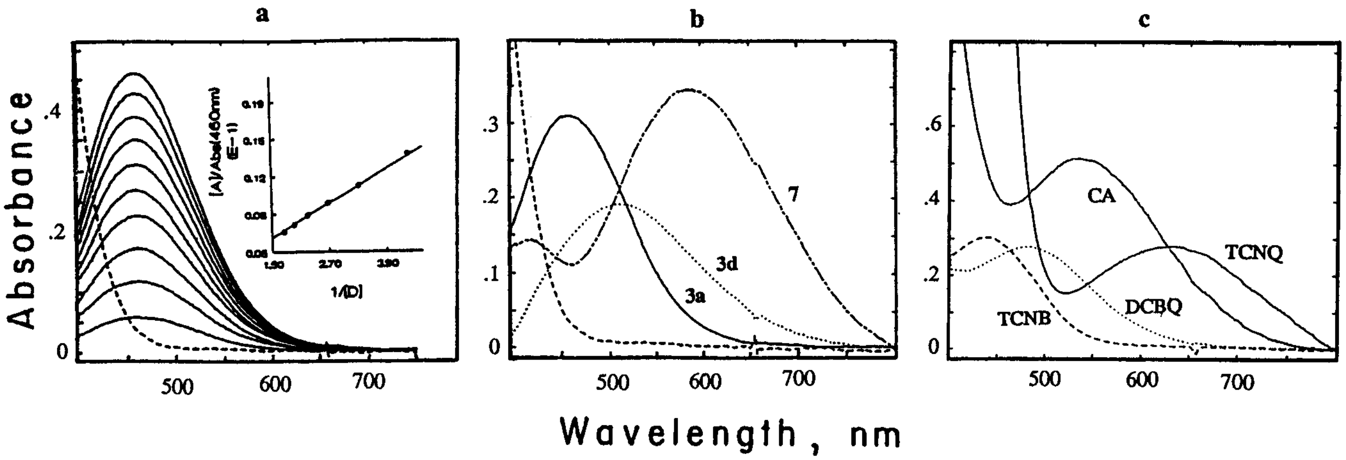
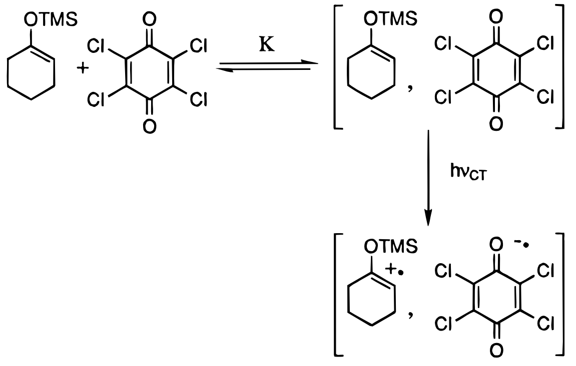


Figure 4. Charge-transfer absorption spectra of enol silyl ether complexes with π-acceptors. (a) Spectral changes accompanying the incremental addition of cyclohexanone enol silyl ether **3a** (0.08–0.69 M) to 0.003 M chloranil in dichloromethane at 25 °C. Inset: Benesi–Hildebrand plot. (b) Charge-transfer absorption spectra of chloranil complexes of enol silyl ethers **3a**, **3d**, and **7** (as indicated) in dichloromethane at 25 °C. (c) Comparative charge-transfer spectra of the EDA complexes of enol silyl ether **1a** with tetracyanobenzene, 2,6-dichlorobenzoquinone, chloranil, and tetracyanoquinodimethane (as indicated) in dichloromethane at 25 °C.

characteristic of weak intermolecular EDA complexes in which the colors derived from the charge-transfer transition ($h\nu_{CT}$), for example as depicted in eq 7.[35]



(7)

In order to establish the generality of such intermolecular EDA complexes, we examined various enol silyl ethers with several electron acceptors of different acceptor strengths, such as tetracyanobenzene (TCNB), 2,6-dichlorobenzoquinone (DCBQ), chloranil (CA), and tetracyanoquinodimetane (TCNQ). For example, when a colorless solution of α-tetralone enol silyl ether in dichloromethane was mixed with either TCNB, DCBQ, CA, or TCNQ, the colorless solution immediately changed to orange (λ_{max} = 438 nm), red (λ_{max} = 486 nm), purple (λ_{max} = 538 nm), or green (λ_{max} = 628 nm), respectively, as illustrated in Figure 4c. The absorption maxima λ_{CT} obtained for the EDA complexes of various substituted enol silyl ethers and these electron acceptors in dichloromethane solutions are compiled in Table 3.

To gain further insight into the nature of the colored complexes of representative enol silyl ethers with various electron acceptors, the energies of the new absorption maxima ($h\nu/\lambda_{CT}$) of the enol silyl ether complexes of chloranil were plotted against those of the corresponding TCNB and TCNQ complexes. The excellent linear correlations with the slopes of 1.27 and 1.44 (r > 0.99) are illustrated in Figures 5a and 5b, respectively.

Since the enol silyl ether complexes with TNM did not exhibit well-defined absorption maxima (*vide supra*), a modified procedure[36] was used to evaluate the charge-transfer energies. Thus the relative charge-transfer energies were calculated from the wavelengths λ_{CT}' at which all TNM complexes exhibited the same arbitrary absorbance of 0.5 (under identical conditions of enol silyl ether and TNM concentrations.) As shown in Figure 5c, the relative charge-transfer energies ($h\nu_{CT}'$) of the various enol silyl ether complexes with TNM determined in this manner followed an excellent linear correlation with $h\nu_{CT}$ of the corresponding chloranil complexes (r = 0.99 for a slope of 1.13).

Spectral Observation of the Enol Silyl Ether Cation Radical as the Reactive Intermediate by Time-Resolved Spectroscopy. The temporal events following the photoexcitation of enol silyl ether complexes with TNM were directly examined by transient picosecond as well as nanosecond laser-flash spectroscopy. Thus, the laser pulse at λ_{exc} = 532 nm (corresponding to the second harmonic of a Q-switched Nd^{3+}: YAG laser) was well suited for the selective excitation of the charge-transfer bands derived from various enol silyl ethers and tetranitromethane (see Figure 3). The transient absorption spectrum in Figure 6a represents the spectral transient obtained upon the application of a 25-ps laser pulse at λ_{exc} = 532 nm to the red solution of β-tetralone enol silyl ether **7** and TNM in dichloromethane at −78 °C. The transient absorption band with a maximum at 530 nm did not change over a period of 4 ns after laser excitation. In order to inquire into the fate of the spectral transient with time, we excited the same sample with a longer 10-ns laser pulse. Indeed, the 532-nm excitation with a 10-ns laser pulse produced the same transient (see inset), which followed second-order decay kinetics on the microsecond time scale with k_{DEC} = 1.9 × 10^5 s^{-1} in dichloromethane.

Identification of the transient absorption spectrum shown in Figure 6a was independently carried out by the method of Gschwind and Hasselbach[37] in which triplet chloranil (^{3}CA) was used to effect electron transfer from

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[35] See Bockman *et al.* in ref 33b.

[36] For example, see Wei, C.-H.; Bockman, T. M.; Kochi, J. K. *J. Organomet. Chem.* **1992**, *428*, 85.

[37] Gschwind, R.; Hasselbach, E. *Helv. Chim. Acta* **1979**, *62*, 941 see also Kawai, K.; Yamamoto, N.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 369.

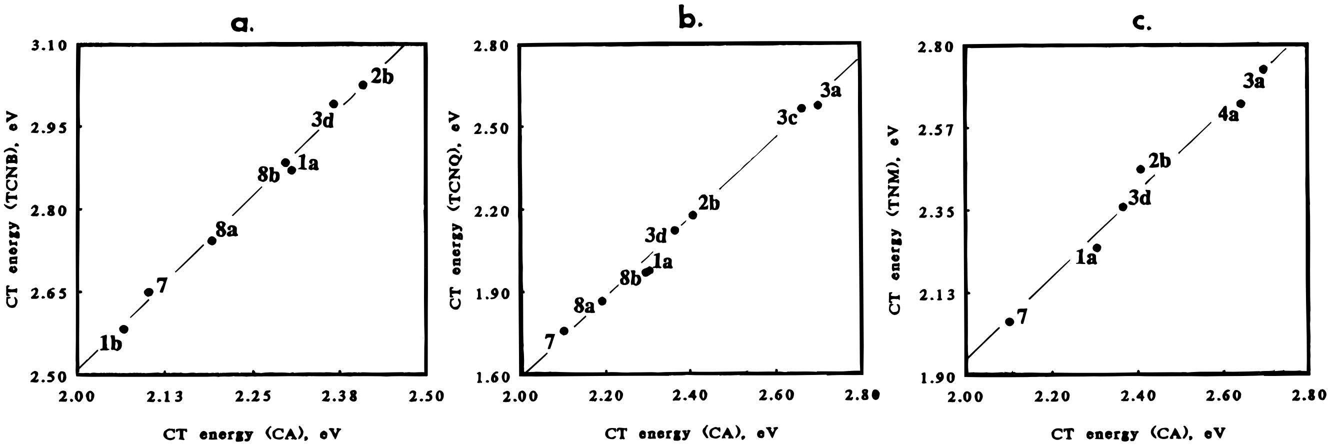
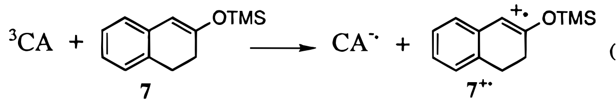


Figure 5. Correlations of the charge-transfer energies ($h\nu_{CT}$) of the enol silyl ether complexes of chloranil with those of (a) tetracyanobenzene, (b) tetracyanoquinodimethane, and (c) tetranitromethane with the same series of enol silyl ethers (identified by numbers in Table 1).

enol silyl ether **7**, *i.e.*



(8)

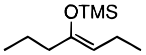
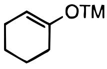
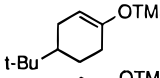
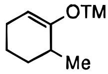
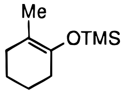
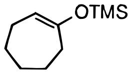
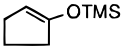
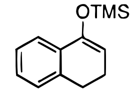
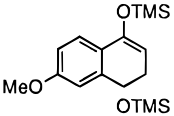
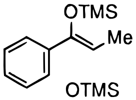
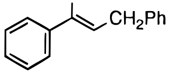
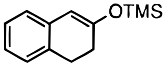
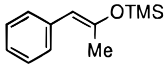
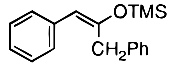
The transient spectrum of the enol silyl ether cation radical $\mathbf{7}^{\bullet+}$ is shown in Figure 6b by the absorption band at 520–30 nm[38] together with that of chloranil anion radical at 440–450 nm.[37] We estimate the extinction coefficient of $\mathbf{7}^{\bullet+}$ to be ~5000 M^{-1} cm^{-1} based on the value of $\epsilon = 9600$ M^{-1} cm^{-1} for chloranil anion radical.[39]

The 25-ps laser pulse at $\lambda_{exc} = 532$ nm was also used in the photoexcitation of the EDA complexes of tetranitromethane with the enol silyl ethers of α-tetralone and cyclohexanone. Even under optimum conditions, however, we were able to observe at best only a weak, nondescript absorbance in the spectral region from 460–600 nm. Clearly, the lifetimes of the spectral transients derived from these enol silyl ethers were shorter than the 25-ps pulsewidth of the laser.

Discussion

The facile nitration of ketones with tetranitromethane (TNM) in Tables 1 and 2 is illustrative of the synthetic utility of enol silyl ethers in facilitating the α-substitution of carbonyl derivatives.[40] Moreover, the simple experimental procedures, the mild reaction conditions, and the trivial workup enable this to be the method of choice for α-nitro ketone isolation. The fact that various enol silyl ethers (**1a**, **2b**, **3a**, **3b**) can be nitrated with tetranitromethane in the dark at room temperature (see Table 1) or equally well with the aid of actinic promotion at very low temperatures (see Table 2) is unique, and particularly noteworthy from a mechanistic viewpoint. The striking parallel between the thermal and photo-

Table 3. EDA Complex Formation with Enol Silyl Ethers and Various Electron Acceptors in Dichloromethane at 25 °C

No.	Enol Silyl Ether	IP[a]	TCNB	λ_{CT} (nm) CA	TCNQ
4a		8.3	b	469	480
3a		8.4	b	460	482
3b		8.3	b	466	500
3c		8.4	b	466	484
3d		7.9	415	524	585
3e		8.3	b	468	486
3f		8.3	b	466	489
1a		7.8	432	538	628
1b		7.5	480	600	c
2b		8.0	410	515	570
2e		7.9	b	472[d]	550
7		7.5	468	590	705
8a		7.7	452	566	665
8b		7.8	430	540	630

[a] From ref. 33a. [b] No new charge-transfer band observed in UV-vis absorption spectrum. [c] Not measured. [d] Solution not stable.

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(38) (a) A similar spectral transient was observed when either tetracyanobenzene or maleic anhydride excited singlet was quenched with enol silyl ether **7** (unpublished results, S. Hubig). (b) Compare also the spectral transient produced from diphenylacetaldehyde enol methyl ether: Mattay, J.; Vondenhof, M. *Topics Curr. Chem.* **1991**, *159*, 221.

(39) (a) Andre, J. J.; Weill, G. *Mol. Phys.* **1968**, *15*, 97. (b) Kobashi, H.; Funabashi, M.; Kondo, T.; Morita, T.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3557. (c) Iida, Y. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 2772. (d) Bonneau, R.; Carmichael, I.; Hug, G. L. *Pure Appl. Chem.* **1991**, *63*, 289.

(40) The method is also potentially applicable to other carbonyl compounds such as aldehydes, esters, *etc.* For example, see Fukuzumi *et al.* in ref 25.

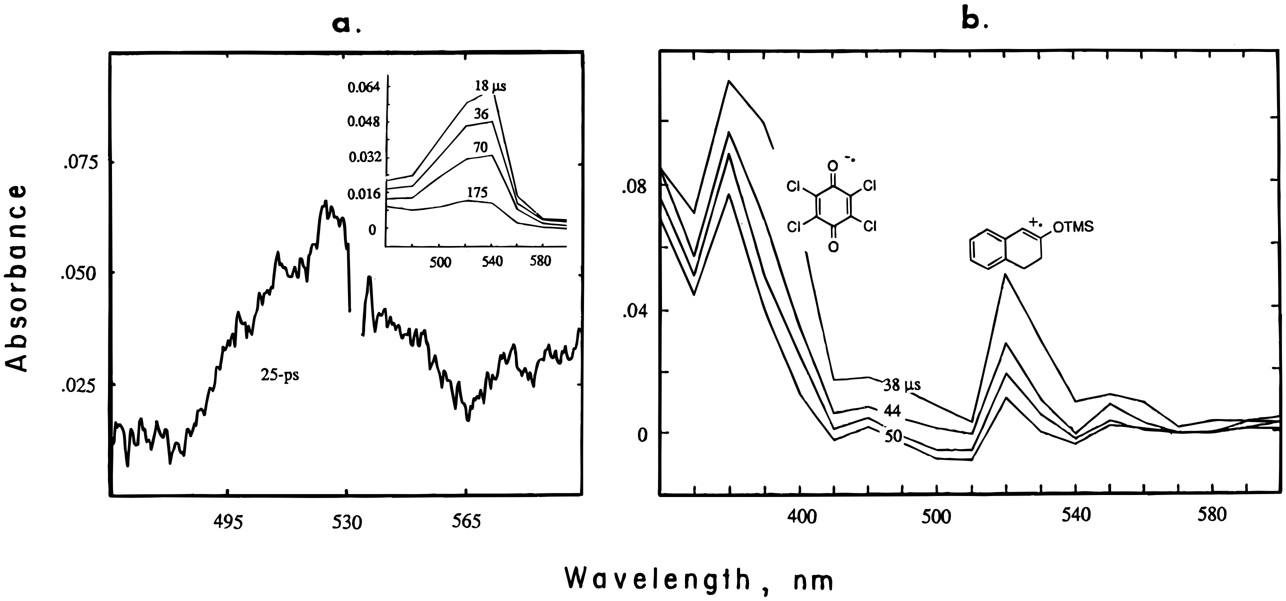

Figure 6. (a) Spectral transient obtained at 25-ps following the 532-nm excitation of the EDA complex from 0.1 M β-tetralone enol silyl ether **7** and 0.1 M TNM in dichloromethane (at −78 °C). Inset: Temporal evolution of the same spectral transient (from the sample above) measured at the indicated times following the 532-nm excitation with a 10-ns laser pulse. (b) Transient absorption spectrum of the cation radical of β-tetralone enol silyl ether ($\mathbf{7}^{\bullet+}$) and the chloranil anion radical ($CA^{\bullet-}$) obtained from the photoexcitation of the chloranil complex of **7** with a 10-ns laser pulse at 532 nm according to the method of Gschwind and Hasselbach.[37]

chemical nitrations extends to the isomeric enol silyl ethers of tetralone, in which the α-isomer is quite reactive and yields α-nitrotetralone in essentially quantitative yields in both procedures, whereas the β-isomer is unreactive and/or yields a complex mixture of products in which β-nitrotetralone is absent. Since the dramatic color changes accompanying the treatment of enol silyl ethers with TNM is an unmistakable feature of the nitrations, let us first consider how they bear critically on all mechanistic questions in the following way.

Pre-Equilibrium Formation of Charge-Transfer Complexes. The development of a strong (orange to dark red) coloration immediately upon the mixing of enol silyl ethers with tetranitromethane (TNM) invariably precedes the actual production of the α-nitro ketones. Spectroscopic studies reveal the transient colors to be due to new broad charge-transfer absorption bands (Figure 3) resulting from the instantaneous formation of electron donor−acceptor (EDA) complexes between the enol silyl ethers and TNM according to eq 6. The correlations in Figure 5 show that the colored EDA complexes of various enol silyl ethers with tetranitromethane (as the common electron acceptor) are similar to those formed with other well-known electron acceptors, such as chloranil (CA), tetracyanobenzene (TCNB), and tetracyanoquinodimethane (TCNQ).[41] All of these complexes are typical of intermolecular associations of the type described by Mulliken for aromatic electron donors.[42] Indeed, the linear variation of the charge-transfer energies ($h\nu_{CT}$) for the EDA complexes with the ionization potentials of the enol silyl ethers (see IP in Table 3) confirms the Mulliken prediction[42] that $h\nu_{CT} = IP - EA - \omega$, under conditions in which the electron affinity (EA) of the acceptor and the electrostatic interaction term (ω) of the charge-transfer ion pair in eq 7 are invariant when a related series of EDA complexes are considered. The linear correlations obtained between the energies of the charge-transfer bands ($h\nu_{CT}$) of chloranil complexes with those of the corresponding tetracyanobenzene and tetracyanoquinodimethane complexes (see Figure 5, parts a and b, respectively) show that enol silyl ethers form a family of analogous 1:1 electron donor−acceptor complexes with various π-acceptors. Furthermore, the distinctive colors associated with charge-transfer transitions ($h\nu_{CT}$) provide the quantitative guide for assessing the electron donor properties of enol silyl ethers (see Table 3).[33a] Since charge-transfer energies of chloranil complexes are linearly correlated ($r = 0.99$) with those of the corresponding tetranitromethane complexes with a slope close to unity (as shown in Figure 5c), those factors relevant to the charge-transfer interactions of both acceptors with the enol silyl ethers are more or less equivalent—despite the marked difference in the LUMOs of chloranil and tetranitromethane.[43]

Charge-Transfer Photonitration of Enol Silyl Ether. According to Mulliken theory,[42] the direct photoactivation of intermolecular EDA complexes by the selective irradiation of the charge-transfer band ($h\nu_{CT}$) leads to a photoinduced electron transfer.[44] As applied to the EDA complexes of enol silyl ethers and TNM examined in this study, such a photoactivation is tantamount to the spontaneous formation of the ion−radical pair in Scheme 1.[45]

The experimental results of the photochemical nitration of enol silyl ethers with TNM indeed coincide with the mechanistic formulation in Scheme 1. Thus, Figure

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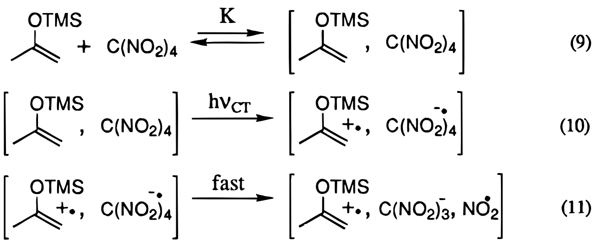
[41] Foster, R. F. *Organic Charge-Transfer Complexes*; Academic: New York, 1969.

[42] (a) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811. (b) Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley: New York, 1969.

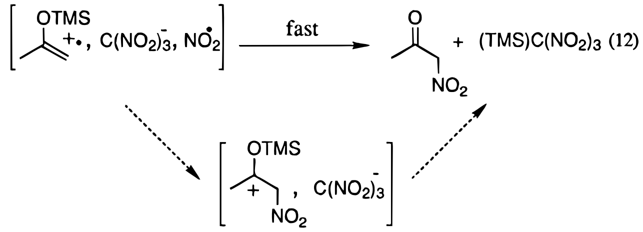
[43] Chloranil is an extensively delocalized planar π-acceptor, whereas tetranitromethane is a rather localized tetrahedral acceptor in which only one NO_2 group is (presumably) involved in the charge-transfer interaction. An X-ray crystallographic determination of a TNM charge-transfer complex would establish this point.

[44] Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071.

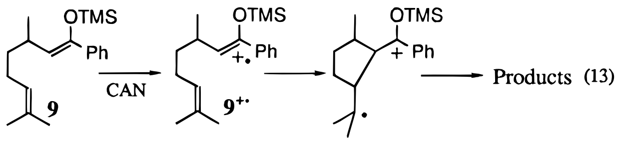
Scheme 1



3 shows that the exposure of enol silyl ether to TNM leads immediately to the colored EDA complex in eq 9. The photoactivation of the EDA complex by the specific irradiation of the charge-transfer band (under the conditions where thermal reaction is too slow to compete) results in the photoinduced electron transfer in eq 10. The rapid fragmentation of the tetranitromethane anion radical leads to the ion radical triad shown in eq 11.[46] As such, this mechanistic formulation is related to previous studies of the photoinduced electron transfer of tetranitromethane with arene donors (ArH), in which the corresponding radical ion triad [$ArH^{\bullet+}$, $C(NO_2)_3^-$, $NO_2^\bullet$] was directly produced in the course of charge-transfer activation.[47] The observation of the enol silyl ether radical cation by time-resolved spectroscopy in Figure 6 thus confirms the formulation in Scheme 1. Furthermore, the excellent material balance obtained in charge-transfer nitrations (Table 2) demands that the radical ion triad in eq 11 proceeds quantitatively to the nitration products by the following stoichiometry



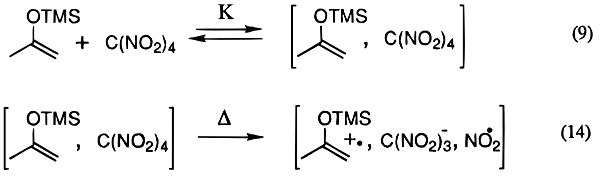
The short life time of less than 3 ps for $C(NO_2)_4^{\bullet-}$,[32,44] indicates that the triad in eq 11 is initially trapped within the solvent cage, since this time scale precludes any competition from diffusional separation.[47] Thus, a fast homolytic coupling of radical cation of enol silyl ether with $NO_2^\bullet$, followed by the loss of the cationic trimethylsilyl moiety accounts for the α-nitro ketone formed in eq 12 (see the pathway indicated by the dashed arrows).[48] The failure to spectrally observe the radical cations of the reactive α-tetralone and cyclohexanone derivatives **1a** and **3a**, respectively, in marked contrast to the unreactive β-tetralone enol silyl ether **7**, strongly suggests that the radical pair annihilation in eq 12 is fast and it effectively supersedes cage escape.[49] Indeed, the homolytic coupling of an enol silyl ether radical cation with $NO_2^\bullet$ is so rapid that it even precludes competition from the facile intramolecular capture of the radical cation by a tethered olefinic group in the citronellal derivative $\mathbf{9}^{\bullet+}$, as previously identified by Snider and Kwon,[30b] *i.e.*



The absence of cyclized products in the photochemical nitration of enol silyl ether **9** (see Table 2) is thus consistent with the time-resolved spectroscopic results, which establish short lifetimes of the enol silyl ether cation radicals of generally less than 10^{-7} s. Only the most stable cation radical such as the highly conjugated $\mathbf{7}^{\bullet+}$ is sufficiently persistent to record its transient spectrum on the ps/ns timescale (see Figure 6).

Comments on the Thermal Nitration of Enol Silyl Ethers with Tetranitromethane. As useful as time-resolved spectroscopy is for the detection and identification of highly reactive intermediates in establishing the mechanism of the photochemical nitration according to Scheme 1, no comparable technique is available to probe the same types of intermediates in the corresponding thermal nitration described in Table 1.[50] Let us therefore resort to an indirect (inferential) approach to relate the mechanism of the photochemical nitration in Scheme 1 to the corresponding thermal process. First, the strikingly similar color changes that accompanying the photochemical and thermal nitration of enol silyl ethers with tetranitromethane indicates that the pre-equilibrium formation of the EDA complex described in eq 9 is common to both processes. Next, it is singularly noteworthy that the thermal nitration (in the dark) at 25 °C and photonitration at −40 °C leads to the same α-nitro ketones in Tables 1 and 2, respectively. One can conclude from these observations that intermediates leading to thermal nitration are similar to, if not the same as, those derived by photonitration. Accordingly, the differences in the qualitative rates of thermal nitration are best reconciled on the basis of donor strength of enol silyl ethers toward TNM as a weak oxidant[27] in a thermal electron transfer (Δ), as described in Scheme 2, eq 14.

Scheme 2



According to Scheme 2, the pre-equilibrium formation of the EDA complex of the enol silyl ether and TNM (eq 9) is followed by the rate-limiting electron transfer to afford the ion radical triad in eq 14.[51] As such, the reactivity of the various enol silyl ethers in thermal nitrations is directly related to their donor strengths. For example, the tetralone derivatives, being among the best

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[45] (a) Compare Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. N. *J. Am. Chem. Soc.* **1986**, *108*, 1126. (b) Note that the direct photoexcitation of the EDA complex by irradiation of the charge-transfer band allows the nitration in high yields of such relatively poor donors as the enol silyl ethers **3a**, **3b**, and **4a** even at low temperatures.

[46] (a) Rabani, J.; Mulac, W. A.; Matheson, M. S. *J. Phys. Chem.* **1965**, *69*, 53. (b) Chaudhri, S. A., Asmus, K.-D. *Ibid.* **1972**, *76*, 26.

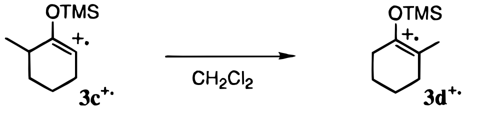
[47] See Bockman, T. M.; Kochi, J. K. *J. Phys. Org. Chem.* **1994**, *7*, 325.

[48] (a) Compare the TMS transfer in the related (chloranil) charge-transfer process, as described by Bockman, T. M. *et al.* in ref 33b. (b) Although the alternative sequence (involving TMS transfer in the ion pair, followed by homolytic coupling) cannot be rigorously discounted, it is disfavored since it does not readily account for the difference in nitro ketone yield between the isomeric **1a** and **7**.

[49] The analogous kinetic behavior of $NO_2^\bullet$ toward reactive aromatic radical cations is described in ref 47.

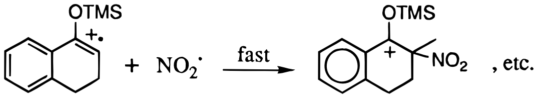
[50] With thermal activations, the steady-state concentrations of reactive intermediates are generally so low as to make their detection experimentally difficult to observe.

electron donors, do indeed react the fastest with TNM (see Table 1) in comparison to the acyclic derivatives (**4a**,**b**), which are poor electron donors and react the slowest. The alternative electrophilic mechanism for the thermal nitration of enol silyl ethers with TNM requires the intimate approach of the nucleophilic enol silyl ether to a NO_2 group on the quaternary carbon center of TNM, which is sterically very demanding and thus does not readily account for the observed reactivity. Furthermore, the observed lack of regioselectivity in the nitration of the isomeric enol silyl ethers (**3c** and **3d**) of 2-methylcyclohexanone with TNM that leads to the same 2-nitro-2-methylcyclohexanone in eq 2 is not readily reconciled with an electrophilic mechanism. On the other hand, the cation radical of the kinetic enol silyl ether **3c**$^{\bullet+}$ is readily converted to the cation radical of the thermodynamic isomer **3d**$^{\bullet+}$ by a 1,3-prototropic shift in the course of the photoinduced electron transfer with chloranil,[52] *i.e.*

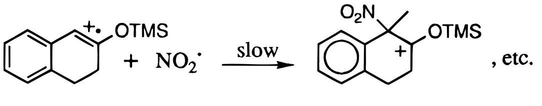


(15)

Such an efficient photoisomerization of the cation radical **3c**$^{\bullet+}$ to **3d**$^{\bullet+}$ accounts for the isomerization of enol silyl ethers **3c** to **3d** in the course of the thermal nitration with TNM, and it explains the lack of regioselectivity in eq 2 (*vide supra*). Other evidence that the cation radicals are critical intermediates in the thermal nitration of enol silyl ethers can be deduced from the distinctive behavior of the α- and *β*-tetralone derivatives **1a** and **7**. Thus, the cation radical of *β*-tetralone enol silyl ether (**7**$^{\bullet+}$) is stabilized owing to extensive *π*-delocalization, which accords with its unusually long lifetime in the time-resolved spectroscopic experiments (Figure 6a) in marked contrast to the short lifetime of the cross conjugated and more reactive α-isomer (**1a**$^{\bullet+}$).[53] We thus attribute the disparate yields of the respective nitrotetralones (Table 1) to derive from the relative rate difference in homolytic coupling in eq 12, *i.e.*



(16)



(17)

It is noteworthy that a similar disparate behavior of α- and *β*-tetralone enol silyl ethers has been recently noted in their charge-transfer α-arylations with cationic aromatic diazonium acceptors.[18]

Experimental Section

Materials. Tetrachloro-*p*-benzoquinone (chloranil), 2,6-dichloro-*p*-benzoquinone, 1,2,4,5-tetracyanobenzene (TCNB), and tetracyanoquinodimethane (TCNQ) were commercially available (Aldrich), and they were purified by recrystallization prior to use. Chlorotrimethylsilane (TMSCl, Aldrich), sodium iodide (Aldrich), cyclohexanone, cyclopentanone, cycloheptanone, 2-methylcyclohexanone, propiophenone, α-tetralone, *β*-tetralone, diphenylacetone, 3-heptanone, pinacolone, norbornanone, and camphor (Aldrich) were used as received. Dihydrochalcone was prepared according to the procedure in *Organic Syntheses*.[54] Dichloromethane (Mallinckrodt analytical reagent) was repeatedly stirred with fresh aliquots of concd sulfuric acid (~20% by volume) until the acid layer remained clear. After separation, the dichloromethane was washed successively with water, aqueous sodium bicarbonate, water, and aqueous sodium chloride, and it was then dried over anhydrous calcium chloride. The dichloromethane was distilled twice from P_2O_5 under an argon atmosphere and stored in a Schlenk tube equipped with a Teflon valve fitted with Viton O-rings. Acetonitrile (Fischer) was stirred with $KMnO_4$ for 24 h, and the mixture was refluxed until the liquid was colorless. The MnO_2 was removed by filtration. The acetonitrile was distilled from P_2O_5 under an argon atmosphere and then refluxed over CaH_2 for 6 h. After distillation from the CaH_2, the acetonitrile was stored in a Schlenk flask under an argon atmosphere. The *n*-pentane was distilled twice from P_2O_5 and stored in a Schlenk flask under an argon atmosphere. Tetranitromethane was prepared as described in *Organic Syntheses*[55] and purified by steam distillation.

Instrumentation. The time-resolved spectra were obtained with a flash photolysis apparatus described earlier.[32] The steady-state photolyses were carried out with the focussed beam from a 500-W high pressure mercury lamp. The beam was passed through a water filter and the appropriate glass cutoff filter (Corning CS series) to remove infrared and ultraviolet light.

Preparation of Enol Silyl Ethers. The enol silyl ethers used in this study were prepared from commercially available ketones using the procedure of Cazeau et al.,[56] in which a mixture of the ketone (25 mmol) and pre-dried sodium iodide (4.50 g, 30 mmol) in dry acetonitrile (30 mL) was stirred under an argon atmosphere. To the resulting solution, triethylamine (3.04 g, 30 mmol) was added, followed by chlorotrimethylsilane (3.26 g, 30 mmol). The reaction mixture was stirred for 0.5 h, and it was successively treated with prechilled (~0 °C) pentane (50 mL) and saturated aqueous ammonium chloride (50 mL). The aqueous phase was further extracted with pentane (2 × 25 mL). The combined pentane extract was washed with ice−water (2 × 50 mL), followed by saturated ammonium chloride (50 mL), and then dried over anhydrous magnesium sulfate. Removal of solvent *in vacuo* afforded the crude enol silyl ether as a colorless oil, which was further purified by fractional distillation under reduced pressure. The various enol silyl

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(51) (a) The thermal electron-transfer step (eq 14) is presented as a *dissociative* electron attachment to tetranitromethane. The alternative *stepwise* electron transfer (*i.e.* eq 10 followed by eq 11) is expected to be too slow owing to a driving force that is estimated to be endergonic by at least $+\Delta G_{ET} = 25-34$ kcal mol^{-1}, based on the reduction potential for TNM of $E°_{red} \leq 0.0$ V vs SCE[27b] and oxidation potentials for various enol silyl ethers of $E°_{ox} \geq 1.1 - 1.5$ V vs SCE (calculated from the values of the irreversible anodic (CV) peak potentials E_p in ref 33a plus the correction according to: Andrieux, C. P.; LeGorande, A.; Savéant, J.-M. *J. Am. Chem. Soc.* **1992**, *114*, 6892). (b) On the other hand, the *dissociative* electron attachment as presented in eq 14 is more favorable than the *stepwise* mechanism, since it will lead to an enhancement in the driving force for electron transfer ($-\Delta G_{ET}$) owing to the simultaneous (concerted) formation of the stable fragments $C(NO_2)_3^-$ and $NO_2^\bullet$. [For a discussion of this important point, see Savéant, J.-M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.]

(52) (a) See the Experimental Section for the photochemical generation of **3c**$^{\bullet+}$ and its rearrangement to the isomeric **3d**$^{\bullet+}$ by the procedure of Gschwind and Hasselbach in ref 37. (b) The facile 1,3-hydrogen shift in the prototypical propene radical cation has been predicted by Clark, T. *J. Am. Chem. Soc.* **1987**, *109*, 6838. For the analogous conversion of 1-butene radical cation to the 2-butene isomer, see Roth, H. D. *Topics Curr. Chem.* **1992**, *163*, 168.

(53) The unusually long lifetime of **7**$^{\bullet+}$ allows sufficient time for the diffusive separation of the ion radical triad in Scheme 1; and it accounts for the observed second-order decay kinetics (compare Figure 6a). Otherwise the formulation in eq 12 predicts first-order decay kinetics of the spectral transients in the photochemical nitrations with TNM.

(54) Adams, R.; Kern, J. W.; Shriner, R. L. *Org. Synth.* **1941**, *1*, 101.

(55) Available from Aldrich Chemical Co. or readily prepared according to Liang, P. *Org. Synth.* **1955**, *3*, 803. **Warning**: Although we have never encountered difficulties, TNM is potentially hazardous.

(56) Cazeau, P.; Duboudin, F.; Moulines, F.; Babot, O.; Dunogues, J. *Tetrahedron* **1987**, *43*, 2075.

ethers were characterized by GC-MS analysis, and the NMR spectra were compared with those previously reported.[57]

Preparation of 3,7-Dimethyl-1-phenyl-6-octen-1-one (9).[30] A 500-mL flask was charged with a solution of phenylmagnesium bromide (40 mL, 3 M, Aldrich) and anhydrous diethyl ether (100 mL), and it was cooled to 0 °C. A solution of citronellal (15.4 g, 100 mmol) in ether (100 mL) was added dropwise under an argon atmosphere. The resulting mixture was stirred for 1 h at 0 °C and then for an additional 6 h at room temperature. The usual workup afforded the crude alcohol which was directly oxidized with pyridinium chlorochromate (PCC) as follows. A solution of the alcohol (20 g, 86 mmol) in dichloromethane (200 mL) was added dropwise to a stirred mixture of PCC (32 g, 150 mmol) and Celite (100 g) in dichloromethane at room temperature. The resulting suspension was stirred for 2 h, and the solvent was removed *in vacuo.* The dark solid residue was dissolved in ether (500 mL), and the ethereal solution was filtered through a short pad of silica gel. Removal of the solvent *in vacuo* and distillation afforded the desired ketone as a colorless oil (16.1 g, 70 mmol, 81%): IR (KBr) 2964, 2922, 2877, 2855, 1688 (vs), 1598, 1582, 1448, 1376, 1366, 1287, 1214, 1003, 752, 691 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.90 (d, J = 6.6 Hz, 3H), 1.17−1.42 (m, 2H), 1.53 (s, 3H), 1.61 (s, 3H), 1.97 (sym m, 2H), 2.13 (sym m, 1H), 2.67 (dd, J = 15.6, 8.1 Hz, 1H), 2.89 (dd, J = 15.6, 5.4 Hz), 5.04 (tm, J = 6.9 Hz, 1H), 7.36 (t, 2H), 7.45 (t, 1H), 7.88 (d, 2H); ^{13}C NMR (CDCl$_3$) δ 17.41, 19.68, 25.31, 25.47, 29.17, 36.92, 45.55, 124.20, 127.82, 128.25, 131.05, 132.55, 137.12, 199.82; GC-MS *m/z* 230, M$^+$, 230 calcd for $C_{16}H_{22}O$.

Thermal (Dark) Nitration of Enol Silyl Ethers with Tetranitromethane. General Procedure for the Preparation of α-Nitroketones in Dichloromethane. A 50-mL flask was charged with a solution of enol silyl ether **1a** (2.18 g, 10 mmol) in anhydrous dichloromethane (40 mL), and a solution of TNM (2.11 g, 11 mmol) in dichloromethane (10 mL) was added under an argon atmosphere at room temperature. The solution immediately developed a characteristic deep red coloration, and it was stirred at room temperature (in dark) for the specified period denoted in Table 1. The resultant yellow reaction mixture was diluted with dichloromethane (50 mL), and it was repeatedly washed with water until the washings were colorless. The dichloromethane layer was dried over anhydrous magnesium sulfate and then filtered. Removal of the solvent *in vacuo* afforded the desired 2-nitro-α-tetralone (**1a**) in essentially quantitative yields (1.88 g, 99%). **Analysis of Aqueous Layer.** The highly colored aqueous layer was transferred to a 5-L volumetric flask and diluted with distilled water. A 10-mL aliquot of the aqueous layer was further diluted to 200 mL. An aliquot was transferred to a 1-cm quartz cuvette and the UV−vis spectrum recorded. The absorbance A_{350} = 1.39 (ϵ_{350} = 14000 M^{-1} cm^{-1})[28] corresponded to a yield of 9.93 mmol (99%) of nitroform. The crude α-nitro ketones prepared from the general procedure were further purified by crystallization, distillation, or column chromatography. The spectral data for various α-nitro ketones are summarized below: **2-Nitro-α-tetralone (1a):**[7a] mp 71−72 °C (lit. mp[7a] 72−73 °C); IR (KBr) 3069, 2964, 2943, 1702 (vs), 1598, 1560 (vs), 1456, 1434, 1379, 1355, 1308, 1264, 1232, 1010, 920, 789, 764, 745, 723 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.61−2.87 (m, 2H), 3.12 (sym m, 2H), 5.43 (dd, J = 12.6, 4.8 Hz, 1H), 7.30 (sym m, 2H), 7.54 (t, 1H), 7.99 (d, 1H); ^{13}C NMR (CDCl$_3$) δ 26.53, 28.10, 89.73, 127.40, 128.15, 128.88, 130.18, 134.93, 142.75, 186.49; GC-MS *m/z* 191 M$^+$, 191 calcd for $C_{10}H_9NO_3$. **2-Nitro-6-methoxy-α-tetralone (1b):**[7a] mp 139−140 °C (lit. mp[7a] 138−139 °C); IR (KBr) 3010, 2957, 2924, 2845, 1689 (s), 1603 (vs), 1556 (vs), 1496, 1457, 1350, 1311, 1251 (vs), 1111, 1025, 919, 879, 852, 819, 746 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.63 (sym m, 1H), 2.81 (sym m, 1H), 3.08 (dd, J = 8.1, 4.5 Hz, 2H), 3.85 (s, 3H), 5.38 (dd, J = 12.0, 4.5 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 6.86 (dd, J = 8.7, 2.4 Hz, 1H), 8.01 (d, J = 8.7 Hz); ^{13}C NMR (CDCl$_3$) δ 26.92, 28.25, 55.64, 89.59, 112.68, 114.24, 123.62, 130.91, 145.32, 164.77; GC-MS *m/z* 221, M$^+$, 221 calcd for $C_{11}H_{11}NO_4$. **2-Nitro-2-methyl-α-tetralone (1c):** oil; IR (KBr) 3070, 3031, 2996, 2945, 2879, 2852, 1697 (vs), 1603, 1548 (vs), 1456, 1388, 1347, 1334, 1309, 1231, 981, 853, 806, 797, 750, 731 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.73 (s, 3H), 2.26 (sym m, 1H), 2.83−2.97 (m, 3H), 7.18 (d, J = 7.5 Hz, 1H), 7.25 (t, J = 7.5 Hz, 1H), 7.44 (td, J = 7.2, 0.9 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 20.32, 25.11, 34.38, 91.37, 127.03, 128.73, 128.08, 134.31, 142.14, 188.81; GC-MS *m/z* 205 M$^+$, 205 calcd for $C_{11}H_{11}NO_3$. Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.04; H, 5.35; N, 6.88. **α-Nitroacetophenone (2a):**[58] mp 102−103 °C (lit. mp[7a] 103−104 °C); IR (KBr) 3074, 3016, 2959, 1696 (s), 1598, 1557 (vs), 1450, 1384, 1335, 1229, 1204, 999, 761, 687, 663 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.91 (s, 2H), 7.50 (t, 2H), 7.65 (t, 1H), 7.83 (d, 2H); ^{13}C NMR (CDCl$_3$) δ 81.36, 128.14, 129.20, 132.00, 135.03, 185.92; GC-MS *m/z* 165, M$^+$, 165 calcd for $C_8H_7NO_3$. **2-Nitro-1-phenyl-1-propanone (2b):**[58] oil; IR (KBr) 3070, 3004, 2944, 1696 (vs), 1563 (vs), 1450, 1390, 1324, 1284, 1224, 1178, 1072, 1012, 965, 873, 786, 699, 660 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.74 (d, 6.9 Hz, 3H), 6.19 (q, 6.9 Hz, 1H), 7.41 (t, 2H), 7.58 (sym m, 1H), 7.87 (d, 2H); ^{13}C NMR (CDCl$_3$) δ 15.91, 84.98, 129.08, 128.66, 133.28, 134.65, 190.12; GC-MS *m/z* 179 M$^+$, 179 calcd for $C_9H_9NO_3$. **2-Nitro-1-phenyl-1-heptanone (2c):**[58] oil; IR (KBr) 2957, 2931, 2864, 1689, 1563, 1450, 1370, 1277, 1231, 972, 693 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 3H), 1.32 (sym m, 6H), 2.12 (sym m, 1H), 2.34 (sym m, 1H), 6.11 (dd, 1H), 7.38−7.56 (m, 3H), 7.95 (sym m, 2H); ^{13}C NMR (CDCl$_3$) δ 36.13.68, 22.10, 25.53, 30.43, 30.94, 89.85, 128.42, 129.06, 134.55, 137.00, 189.12; GC-MS *m/z* 235 M$^+$, 235 calcd for $C_{13}H_{17}NO_3$. **2-Nitro-1,3-diphenyl-1-propanone (2d):** oil; IR (KBr) 2969, 2951, 2832, 1697 (vs), 1560 (vs), 1494, 1455, 1370, 1259, 755, 696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.55 (dd, J = 14.7, 5.4 Hz, 1H), 3.73 (dd, J = 14.7, 9.0 Hz, 1H), 6.38 (dd, J = 9.0, 5.4 Hz, 1H), 7.25−7.42 (m, 5H), 7.57 (t, 2H), 7.72 (t, 1H), 8.01 (d, 2H); ^{13}C NMR (CDCl$_3$) δ 36.37, 90.45, 127.67, 128.86, 128.97, 129.15, 130.13, 134.48, 134.73, 188.37; GC-MS *m/z* 255 M$^+$, 255 calcd for $C_{15}H_{13}NO_3$. Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 70.23; H, 5.08; N, 5.41. **2-Nitro-1-(4-nitrophenyl)-1-ethanone (2e):**[58] mp 149−151 °C (lit. mp[58] 150−151 °C); IR (KBr) 3117, 3083, 1716 (vs), 1669, 1603, 1569, 1523 (vs), 1417, 1390, 1344, 1323, 1277, 1218, 1105, 1012, 859, 793, 719 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.62 (s, 2H),7.64 (d, J = 8.6 Hz, 2H), 8.11 (d, J = 8.6 Hz, 2H); GC-MS *m/z* 210 M$^+$, 210 calcd for $C_8H_6N_2O_5$. **2-Nitrocyclohexanone (3a):**[10a] mp 38−39 °C (lit. mp[10a] 39.5−40.5 °C); IR (KBr) 2952, 2928, 2853, 1720 (vs), 1552 (vs), 1448, 1420, 1389, 1334, 1298, 1240, 1110, 1087, 784, 648 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.48−2.56 (m, 8H), 5.19 (dd, J = 13.0, 5.2 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 22.15, 26.15, 31.30, 40.39, 91.76, 199.03; GC-MS *m/z* 143, M$^+$, 143 calcd for $C_6H_9NO_3$. **2-Nitro-4-*tert*-butylcyclohexanone (3b):**[10a] mp 86−88 °C (lit. mp[10a] 87−90 °C); IR (KBr) 2957, 2911, 2871, 1723 (vs), 1556 (vs), 1463, 1417, 1384, 1337, 1297, 1271, 1238, 1145, 1091, 786, 733, 653 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.94 (s, 9H), 1.51−2.66 (m, 7H), 5.28 (dd, J = 13.2, 5.4 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 27.52, 32.68, 33.03, 40.00, 45.06, 61.44, 92.07, 219.2; GC-MS *m/z* 199, M$^+$, 199 calcd for $C_{10}H_{17}NO_3$. **2-Nitro-2-methylcyclohexanone (3d):**[10a] mp 33−35 °C (lit. mp[10a] 34−35 °C); IR (KBr) 2951, 2877, 1731 (vs), 1645, 1612, 1550 (vs), 1453, 1431, 1388, 1356, 1337, 1294, 1266, 1125, 1088, 853, 822, 800 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.62 (s, 3H), 1.65−1.85 (m, 4H), 1.98 (sym m, 1H), 2.54 (sym m, 2H), 2.83 (sym m, 1H); ^{13}C NMR (CDCl$_3$) δ 21.52, 22.38, 26.58, 38.36, 39.20, 93.90, 200.70; GC-MS *m/z* 157, 157 calcd for $C_7H_{11}NO_3$. **2-Nitrocycloheptanone (3e):**[59] mp 37−38 °C (lit. mp[59] 38−38.5 °C); IR (KBr) 2934, 2861, 1721, 1696, 1557, 1458, 1376, 1343, 1311, 1204, 1147, 1073, 925, 843, 728 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.36 (dd, J = 3.7, 9.4 Hz, 1H), 1.28−2.55 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 23.0, 26.09, 28.56, 41.13, 43.38, 93.64, 210.44; GC-MS *m/z* 157, M$^+$, 157 calcd for $C_7H_{11}NO_3$. **3-Nitroheptan-4-one (4a):**[1a] oil; IR (KBr) 2910, 2822, 1718 (vs), 1692, 1550, 1448, 1366, 1317, 1202, 1150, 1060, 905, 809, 750 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.83

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(t, 3H), 0.90 (t, 3H), 1.42−1.51 (m, 4H), 2.30 (t, 2H), 4.99 (dd, $J = 5.4, 9.9$ H$_2$, 1H); ^{13}C NMR (CDCl$_3$) δ 13.04, 16.40, 17.79, 21.03, 41.05, 95.34, 198.98; GC-MS *m*/*z* 159, M$^+$, calcd for C$_7$H$_{13}$NO$_3$. **1-Nitro-3,3-dimethylbutan-2-one (4b):**[1a] oil; IR (KBr) 2968, 2924, 2869, 1721, 1629, 1558 (vs), 1466, 1364, 1325, 1275, 1172, 1053, 262, 683 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.98 (s, 9H), 4.82 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 22.35, 26.12, 46.90, 92.12, 201.27; GC-MS *m*/*z* 145, M$^+$, 145 calcd for C$_6$H$_{11}$NO$_3$. **3-Nitronorbornanone (5):** oil; IR (KBr) 2956, 2920, 2876, 1736 (vs), 1565 (vs), 1424, 1439, 1392, 1297, 1068, 815, 760 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.05−2.50 (m, 6H), 2.59 (br s, 1H), 3.01 (br s, 1H) 5.15 (br s, 1H) ^{13}C NMR (CDCl$_3$) δ 21.46, 24,81, 34.59, 40.70, 47.47, 89.26, 201.92; GC-MS *m*/*z* 155, m$^+$, 155 calcd for C$_7$H$_9$NO$_3$. Anal. Calcd for C$_7$H$_9$NO$_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 54.39; H, 5.89; N, 8.91. **3-Nitrocamphor (6):**[11b] mp 102−103 °C (lit. mp[11b] 103 °C); ^{1}H NMR (CDCl$_3$) δ 0.88 (s, 3H), 0.97 (s, 3H), 1.05 (s, 3H), 1.22−198 (m, 4H), 2.72 (t, $J = 4.5$ Hz, 1H), 5.04 (d, 2H); ^{13}C NMR (CDCl$_3$) δ 9.35, 18.73, 19.67, 20.74, 21.58, 29.45, 48.69, 88.95, 178.09; GC-MS *m*/*z* 197 M$^+$, 197 calcd for C$_{10}$H$_{15}$NO$_3$. **2-Nitro-3,7-dimethyl-1-phenyl-6-octen-1-one (9).** As a mixture of stereoisomers: oil; IR (KBr) 2971, 2931, 2858, 1696 (s), 1598, 1581, 1557 (vs), 1450, 1364, 1291, 1218, 680 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.95 (d, $J = 6.9$ Hz, 3H), 1.07 (d, $J = 6.6$ Hz, 3H), 1.14−1.50 (m, 2H), 1.56 (s, 3H), 1.64 (br s, 3H), 1.90−2.13 (m, 2H), 2.70 (sym m, 1H), 5.00 (sym m, 1H), 5.95 (dd, $J = 8.1, 5.7$ Hz, 1H), 7.43−7.98 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 15.34, 15.43, 17.65, 24.74, 25.12, 25.65, 32.50, 32.70, 34.51, 34.64, 93.26, 93.34, 123.06, 128.69, 128.70, 129.16, 132.56, 132.72, 134.60, 134.80, 135.02, 188.44, 188.59; GC-MS *m*/*z* 229 [M$^+$ − 46], 229 calcd for [C$_{16}$H$_{21}$NO$_3$ − NO$_2$]. Anal. Calcd for C$_{16}$H$_{21}$NO$_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.38; H, 7.46; N, 5.18.

In Acetonitrile. A solution of enol silyl ether **1a** (2.18 g, 10 mmol) in dry acetonitrile (50 mL) was treated with TNM (2.16 g, 10 mmol) at 25 °C. The red solution was stirred for 15 min and diluted with 100 mL of dichloromethane. The yellow solution was washed with water (3 × 50 mL) and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded the 2-nitro-α-tetralone **1a** in essentially quantitative yield (1.90 g, 99%). UV−vis spectral analysis indicated that the aqueous layer contained 1 equiv of nitroform (∼10 mmol). **In *n*-Pentane.** Tetranitromethane (2.16 g, 11 mmol) was added to a solution of enol silyl ether **1a** (2.18 g, 10 mmol) in anhydrous *n*-pentane (50 mL) under an argon atmosphere at 25 °C. The characteristic dark-red colored solution bleached within minutes (∼10 min) as the yellow crystals of 2-nitro-α-tetralone **1a** separated. The standard aqueous workup afforded 2-nitro-α-tetralone in 98% yield (1.87 g), and the aqueous layer showed the presence of 1 equiv of nitroform. **Reaction of *β*-Tetralone Enol Silyl Ether 7 with TNM.** A dichloromethane solution of **7** (10 mL, 0.2 M) and TNM (430 mg, 2 mmol) was mixed (in the dark) at 25 °C under an argon atmosphere to produce the characteristic dark-red solution. The red solution was stirred for 12 h, but no spectral change was apparent. The solvent and TNM were removed *in vacuo*, and the crude residue was dissolved in dichloromethane (25 mL) and washed repeatedly with distilled water (3 × 50 mL). The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated *in vacuo*. The GC and GC-MS analysis showed that the enol silyl ether **7** was recovered intact (200 mg, 91%). The UV−vis spectral analysis of the aqueous layer showed the presence of traces of nitroform (0.05 mmol, 5%). The treatment of enol silyl ethers **8a** and **8b** with TNM was carried out in a similar manner. **Thermal (Dark) Nitration of Enol Silyl Ether 9.** A solution of enol silyl ether **9** (302 mg, 1 mmol) in dichloromethane (5 mL) was mixed with TNM (211 mg, 1.1 mmol) under an argon atmosphere at room temperature. The solution immediately developed a characteristic deep red coloration, and it was stirred (in dark) for 8 h at room temperature. The resultant yellow reaction mixture was diluted with dichloromethane (20 mL) and was washed with water (4 × 25 mL). The dichloromethane layer was dried over anhydrous magnesium sulfate and filtered. Removal of the solvent *in vacuo* afforded the a oily residue which upon GC and GC-MS analysis showed the presence of stereoisomeric mixture of nitro ketones **9** (*vide supra*) together with the traces of corresponding ketone and enol silyl ether. The ^{13}C NMR spectrum of the crude reaction mixture did not show a peak (∼90 ppm) for the quaternary carbon bearing a nitro group. Since this NMR resonance is characteristic of tertiary nitroalkanes, we inferred that the cyclized product **11** in eq 3 was not formed. The flash chromatography of the residue using a hexane−ether (3:1) mixture as an eluent, afforded the stereoisomeric mixture of nitro ketone **9** as a pale yellow oil (214 mg, 78%). **Thermal Nitration of 2-Methylyclohexanone Enol Silyl Ether 3c with TNM.** According to general procedure, a solution of the kinetic enol silyl ether **3c** (1.84 g, 10 mmol) in dichloromethane (50 mL) was mixed with TNM (2.11 g, 11 mmol) under an argon atmosphere at room temperature. The solution immediately developed a characteristic orange coloration, and it was stirred (in dark) for 16 h at room temperature. The resultant yellow reaction mixture was diluted with dichloromethane (20 mL), and it was washed repeatedly with water (4 × 25 mL). The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated. The GC and GC-MS analysis of the crude residue showed the presence of 2-methyl-2-nitrocyclohexanone **3d** as a major product together with the traces of the corresponding (hydrolyzed) ketone and the unreacted kinetic enol silyl ether **3c**. Distillation of the crude oil afforded the pure 2-methyl-2-nitrocyclohexanone **3d** (1.1 g, 70%). [Note that the nitro ketone **3d** obtained above from the kinetic enol silyl ether **3c** was identical to an authentic sample, prepared from the reaction of the thermodynamic enol silyl ether **3d** and TNM.] In a similar experiment, a mixture of enol silyl ether **3c** (184 mg, 1 mmol) and TNM (211 mg, 1.1 mmol) in dichloromethane was treated at room temperature. After 3 h, the solvent and excess TNM were removed under high vacuum, and the crude residue was redissolved in dichloromethane (20 mL). It was washed with distilled water (3 × 20 mL) and dried over anhydrous magnesium sulfate. The GC and GC-MS analysis (internal standard method) of the dichloromethane layer showed that the reaction mixture consisted of nitro ketone **3d** (0.12 mmol) and the unreacted enol silyl ether **3c** (0.82 mmol) together with the traces of the 2-methylcyclohexanone (<1%). [It is noteworthy that no isomerization of the kinetic enol silyl ether **3c** to the thermodynamic enol silyl ether **3d** was observed during the course of reaction, as evidenced by the recovery of only the kinetic enol silyl ether **3c**.] In another experiment, a solution of enol silyl ether **3c** (184 mg, 1 mmol) and 6-methyl-2-nitrocyclohexanone (157 mg, 1 mmol; prepared by the method of Dampawan and Zajac[11c]) in dichloromethane (5 mL) was mixed with TNM (211 mg, 1.1 mmol). The pale orange solution was stirred at room temperature for 16 h. The standard aqueous workup, as described above, afforded an oily residue. The GC and GC-MS analysis (internal standard method) showed the residue consisted of 2-methyl-2-nitrocyclohexanone (0.73 mmol) and unchanged 6-methyl-2-nitrocyclohexanone (0.96 mmol) together with a small amount of starting ketone.

Photonitration of Enol Silyl Ethers with TNM. General Procedure. In a typical experiment, a solution containing 0.2 M enol silyl ether and 0.22 M TNM in dichloromethane (10 mL) under an argon atmosphere was irradiated with a focussed beam that was passed through an IR water filter and a 415-nm cutoff filter from a 500-W mercury lamp. The irradiation was performed in a Pyrex tube immersed in a Dewar flask filled with a mixture of dry ice and acetonitrile (−40 °C). As the reaction progressed, the color changed from red-orange to yellow. After photolysis, the solvent and excess TNM were removed *in vacuo* at approximately −40 °C. The crude residue was redissolved in dichloromethane (20 mL) and washed with distilled water (3 × 50 mL). The dichloromethane extract was dried over anhydrous magnesium sulfate, and it was analyzed by GC, GC-MS, and NMR spectroscopy using internal standard method. The highly colored aqueous layer was transferred to a 5-L volumetric flask and diluted with distilled water. A 10-mL aliquot of the aqueous layer was further diluted to 50 mL, and an aliquot was transferred to a 1-cm quartz cuvette. UV−vis spectral analysis indicated the absorbance of $A_{350} = 1.09$ corresponded to a yield of 1.95 mmol

(97%) of nitroform. In a (dark) control experiment, an identical mixture of 0.2 M enol silyl ether and 0.22 M tetranitromethane in dichloromethane (10 mL) and kept alongside the irradiated solution (after it was tightly wrapped in aluminum foil to protect it from adventitious light.) Simultaneous workup of the photolysate and the dark control, followed by GC and GC-MS analysis, indicated that cyclohexanone enol silyl ether in the dark control was intact. (The aqueous extract was almost colorless). **Photonitration of Enol Silyl Ether 9.** According to general procedure, a solution containing 0.2 M enol silyl ether **9** and 0.22 M TNM in dichloromethane (3 mL), under an argon atmosphere, was irradiated with a focused beam from a 500-W mercury lamp at -40 °C. As the reaction proceeded, the solution changed from red-orange to yellow (0.8 h). After photolysis, the solvent and excess TNM were removed *in vacuo* and the crude residue was redissolved in dichloromethane (50 mL) and washed with distilled water (3×50 mL). The dichloromethane layer was dried over anhydrous magnesium sulfate and evaporated. The GC and GC-MS analysis of the crude residue showed the presence of stereoisomeric mixture of nitro ketones **9** (*vide supra*) together with the traces of corresponding ketone and enol silyl ether. The ^{13}C NMR spectral analysis of the crude reaction mixture as described above did not show the presence of cyclized product **11**. Chromatographic purification as above afforded the pure nitro ketone **9** (119 mg, 72%). Note that an identical mixture of 0.2 M enol silyl ether **9** and 0.22 M tetranitromethane in dichloromethane (3 mL) in dark (-40 °C) did not show any perceptible color change and GC-MS analysis indicated that enol silyl ether **9** remained unchanged.

UV−vis Spectral Measurements of EDA Complex Formation. Typically, a 0.22 M solution of tetranitromethane was placed in a 1-cm quartz cuvette (UV cell equipped with a side arm and Schlenk adapter) with the aid of a hypodermic syringe, under an argon atmosphere. The cuvette was cooled in an ice/acetone bath (-15 °C), and an aliquot of enol silyl ether (0.2 mmol) was carefully placed into the side arm with the aid of a Teflon cannula. After the cuvette was thermally equilibrated in the cooling bath, the solutions were rapidly mixed. The UV−vis absorption spectrum was then recorded immediately (see Figure 3b). All experiments were carried out in duplicate to ensure spectral reproducibility. The determination of the formation constant (K) of the EDA complex of cyclohexanone enol silyl ether **1a** and TNM was carried out as follows. A 2-mL aliquot of a 2.0 M solution of TNM in dichloromethane was placed in a cuvette, which was cooled in an ice/acetone bath (-15 °C). Enol silyl ether **1a** was added incrementally (total concentration $= 2.0 - 20.0 \times 10^{-4}$ mol) under a positive pressure of argon, and the UV−vis absorption spectra were recorded (see Figure 3a). The absorbance change was measured at $\lambda = 450$ nm, the wavelength at which both TNM and **1a** were completely transparent. From a plot of $[\mathrm{TNM}]/A_{\mathrm{CT}}$ *versus* $[\mathbf{1a}]^{-1}$, the slope was estimated as $\epsilon_{\mathrm{CT}}K_{\mathrm{EDA}}{}^{-1}$ and the intercept as $\epsilon_{\mathrm{CT}}{}^{-1}$. The average formation constant, K_{EDA}, was 0.24 M^{-1} and $\epsilon_{\mathrm{CT}} = 19$ M^{-1} cm^{-1} at 450 nm. The linear fit obtained by the least squares method generally had a correlation coefficient of >0.99.

Photoisomerization of the Kinetic Enol Silyl Ether 3c with Chloranil. A Pyrex tube containing a dichloromethane solution of enol silyl ether **3c** (0.1 M, 25 mL) and a catalytic amount of chloranil (24 mg, 0.1 mmol) under an argon atmosphere was irradiated for 2 h with a 500-W mercury lamp.[37] The solvent was evaporated *in vacuo* and the residue then treated with pentane. The colorless pentane layer was decanted, and it was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent afforded a crude residue (420 mg), which upon spectral (GC, NMR) analysis consisted of a 98:2 molar mixture of the thermodynamic enol silyl ether **3d** and the kinetic enol silyl ether **3c**. A similar isomerization of **3c** to **3d** was observed when tetracyanobenzene (TCNB) was employed as the sensitizer.

Time-Resolved Spectroscopy of the EDA Complexes of Enol Silyl Ethers with Tetranitromethane. Typically, in a 1-cm square quartz cuvette equipped with a Schlenk adapter was placed a solution of tetranitromethane with the aid of a hypodermic syringe, under an argon atmosphere. The cuvette was cooled in an dry ice/acetone bath (-78 °C), and the enol silyl ether was added. The UV−vis absorption spectrum of the enol silyl ether complex with TNM was recorded before and after laser flash photolysis to ensure that only minimal diminution of the CT absorbance occurred during the transient spectroscopic experiment. Time-resolved difference absorption spectra on the picosecond time scale were obtained by utilizing a 532 nm (second harmonic) laser pulse from a Quantel YG 501-C mode-locked Nd^{3+}: YAG laser as the excitation source.[32] This wavelength corresponded to the excitation of only the charge-transfer band of the EDA complex (see Figure 3b). The analyzing beam in the form of a white light continuum was produced by passing the 1064-nm fundamental through a solution consisting of a 1:1 mixture (v/v) of D_2O and H_2O) in a 10-cm cuvette. Temporal measurements were made by varying the optical delay between the excitation beam and the analyzing beam. The spectrograph was calibrated using a low-pressure mercury lamp. Spectra were measured at each time setting by averaging data from 300 individual pulses. Time-resolved spectra on the nanosecond time scale were obtained using the second harmonic (532 nm) of a Quantel YG 580-10 Q-switched Nd^{3+}; YAG laser with a 10-ns pulse as the excitation source. The output of a 150 W Xenon arc lamp focused on the sample at a 90° angle to the excitation beam served as the probe light. The probe beam emerging from the sample was focused on the entrance slit of an Oriel Model 77250 monochromator equipped with a Model 77298 (500 nm blaze) grating in the spectral range between 300 and 800 nm. The monochromatic light was detected by a Hamamatsu model R-928 photomultiplier tube. The timing sequence of the excitation and probing of the sample was controlled by a Kinetics Instruments sequence generator and laser controller. Data acquisition and digitization were performed with a Tektronix Model 7104 oscilloscope in conjunction with a Tektronix Model C101 video camera and DCS-01 softword. The ns-spectral decays were processed with the ASYST (2.0) scientific software package. The transient absorption spectrum of the cation radical of enol silyl ether **7** in Figure 6b was generated from a dichloromethane solution of chloranil (0.008 M) and **7** (0.03 M) under an argon atmosphere at 25 °C, using the 355-nm (10-ns) laser pulse.

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