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Charge-Transfer Structures of Bicumene EDA Complexes with Nitrosonium. Common Pathways for Spontaneous Thermal and Photochemical C–C Bond Cleavages

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Introduction

The cleavage of carbon–carbon bonds has been systematically examined in variously substituted 1,2-diphenylethanes,[1,2] in which the weakening or elongation of the central (benzylic) bonds can result from "through bond" (π) orbital interactions.[3,4] The latter may also be manifested in the ease of thermal[5,6] and photoinduced[7,8] oxidations of different diphenylethane-type donors such as bibenzyl,[9,10] bicumene,[11] benzpinacol,[8,12] etc., to the corresponding cation radicals that are ipso facto more susceptible to mesolytic cleavage.[13,14] In order to determine experimentally the effects of electron removal on the bond elongation (and thermal lability) of these aromatic donors (D), we sought an electron acceptor (A) which will form electron donor–acceptor or EDA complexes with high degrees of charge transfer in the ground state—conveniently described in qualitative valence-bond terms as

$$\psi_{GS} = \frac{1}{N}[a\phi_0 + b\phi_1 + ...] \qquad (1)$$

where the ground-state wave function ψ_{GS} mainly contains contributions from ϕ_0 and ϕ_1 representing the weak van der Waals or no-bond interaction of [D,A] and the dative or charge-transfer component $[D^{\bullet+}A^{\bullet}]$, respectively, and N is the normalization factor.[15,16] Since we recently found the nitrosonium cation to form aromatic EDA complexes that can exhibit high degrees of charge transfer[17] (i.e., $b \gg a$ in eq 1), we focus in this study on the isolation and X-ray crystallographic study of the nitrosonium EDA complex with bicumene (BC) serving as the prototypical (diphenylethane) donor. The chemical consequences of the high degree of charge transfer in these EDA complexes are also examined in the accompanying thermal and photochemical activation of bicumene and related diphenylethane-type donors in Chart I by the NO^+ acceptor.

Results

I. Charge-Transfer Complexes of Bicumene with Nitrosonium in Solution. The solution of bicumene in acetonitrile turned bright orange immediately upon the addition of nitrosonium tetrafluoroborate under an argon atmosphere. The color change was accompanied by the simultaneous growth of a new absorption band (Figure 1) with λ_{max} = 340 nm which persisted for prolonged periods upon standing in the dark. For comparative purposes, Figure 1 also shows the charge-transfer spectrum of NO^+ and *tert*-butylbenzene at three representative concentrations. Similar spectra were observed in dichloromethane and nitromethane solutions. The 4,4′-dimethyl analogue of bicumene produced with NO^+ an orange solution that was bleached within an hour, and the charge-transfer (CT) complex from 4,4′-dimethoxybicumene was observed only as a fleeting red-orange color.

The binding energies of the electron donor–acceptor complexes were evaluated spectrophotometrically in acetonitrile solution by the intensification of the charge-transfer bands attendant upon the successive addition of bicumene (BC). Thus the concentration dependence of the charge-transfer absorption is given by the Benesi–Hildebrand relationship[18]

$$\frac{[NO^+BF_4^-]}{A_{CT}} = \frac{1}{\epsilon_{CT}} + \frac{1}{K\epsilon_{CT}[BC]} \qquad (2)$$

where A_{CT} and ϵ_{CT} are the absorbance and extinction coefficient, respectively, at the spectral maxima under conditions in which bicumene was present in excess. The values of the formation constants $K = 11\ M^{-1}$ and the extinction coefficient $\epsilon_{CT} = 295\ M^{-1}\ cm^{-1}$ were obtained from the slopes and intercepts, respectively, of the plots (eq 2) for the 1:1 complexes, i.e.[17]

$$BC + NO^+BF_4^- \overset{K_{EDA}}{\rightleftharpoons} [BC, NO^+BF_4^-] \qquad (3)$$

For the corresponding *tert*-butylbenzene complex, $K = 7\ M^{-1}\ cm^{-1}$ and $\epsilon_{CT} = 350\ M^{-1}\ cm^{-1}$ under the same experimental conditions.

The vibrational spectrum of the bicumene EDA complex with $NO^+PF_6^-$ showed a single (stretching) band at ν_{NO} = 2014 cm^{-1} with a bandwidth (fwhm) of 110 cm^{-1} in nitromethane. The corresponding EDA complex of *tert*-butylbenzene exhibited the stretching frequency of the nitrosonium acceptor at ν_{NO} = 2010 cm^{-1} (90 cm^{-1}). Both nitrosyl bands were significantly displaced from that of the uncomplexed nitrosonium cation (either as $NO^+BF_4^-$,

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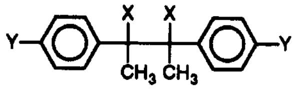
Chart I



$X = CH_3, CH_3O, (CH_3)_3SiO$
$Y = H, CH_3\ CH_3O$

$NO^+PF_6^-$, or $NO^+SbCl_6^-$), in which the nitrogen-oxygen stretching band occurred at $\nu_{NO} = 2280 \pm 10$ cm^{-1} (44 cm^{-1}) in nitromethane solution. Indeed, the red-shifted values of ν_{NO} for the nitrosonium moiety in the EDA complexes approached that of $\nu_{NO} = 1876$ cm^{-1} in the completely reduced form (nitric oxide).[19]

II. Isolation and X-ray Crystallography of the Bicumene EDA Complex with Nitrosonium. When a dilute solution of bicumene in dichloromethane was slurried with $NO^+SbCl_6^-$, the nitrosonium salt gradually dissolved with an increasing red coloration of the solution. Upon standing in the dark at −20 °C, reddish brown crystals slowly separated from solution in the monoclinic space group $P2_1/m$ with $a = 8.098$ (3) Å, $b = 16.350$ (4) Å, and $c = 9.035$ (2) Å, $\beta = 101.85$ (2)°.[20] The X-ray diffraction data were collected at −50 °C owing to the labile nature of the bicumene EDA complex with $NO^+SbCl_6^-$ (vide infra).

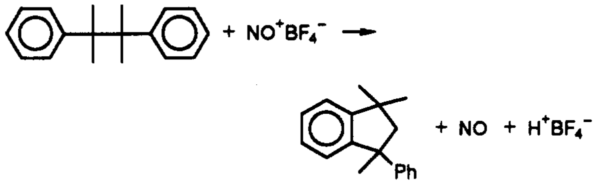
The ORTEP diagram of the 1:1 EDA complex in Figure 2 shows the bicumene donor to exist in the staggered conformation with anti phenyl groups that are mutually coplanar. The relevant charge-transfer absorption arises from the nitrosonium cation poised over the centroid of the phenyl group (with a slight tilt favoring nitrogen) at a nonbonded distance of closest approach to an aromatic carbon atom of 2.63 Å. The monoclinic crystal is thus comprised of heterosoric stacks of infinite (quasi) chains consisting of alternating 2:1 charge-transfer interactions, as illustrated (dashed lines) by the stereoscopic view in Figure 3.

Most notable is the N–O separation of 1.09 Å in the nitrosonium moiety of the bicumene complex (Table I). Indeed, this bond distance is significantly longer than that extant in the uncomplexed nitrosonium cation itself (e.g., 0.95 Å in $NO^+SbCl_6^-$),[21] and it approaches the bond length (1.15 Å) in the completely reduced form, viz., nitric oxide.[19] Such a lengthening of N–O bond distance was thus consistent with the red-shift of ν_{NO} noted above in the IR spectrum—both being symptomatic of a (partial) one-electron reduction of the nitrosonium moiety in the EDA complex. In the context of the Mulliken formulation in eq 1, it must be accompanied by a charge transfer that is tantamount to the one-electron oxidation of the bicumene acceptor, i.e.

$$[BC, NO^+] \rightarrow [BC^{\bullet +}, NO] \qquad (4)$$

The carbon separation of the central C(7)–C(7′) bond in the bicumene moiety of the EDA complex is 1.60 Å (Table I), which is significantly longer than the usual bond distance of 1.54 Å between (sp^3 hybridized) carbon atoms. In order to establish whether such a bond elongation in bicumene is unique to its EDA complex, we grew a single crystal (by controlled sublimation in vacuo) of pure bicumene in the orthorhombic space group *Pbca* with $a = 11.607$ (3) Å, $b = 6.734$ (1) Å, and $c = 18.252$ (3) Å. The crystal structure was solved by direct methods (see the Experimental Section), and bicumene was found to exist in the same anti (staggered) conformation shown for the bicumene donor in the EDA complex in Figure 2. Most importantly, the C(7)–C(7′) separation of 1.59 Å in the central bond is experimentally indistinguishable (within 1σ) from that found in the EDA complex. Moreover, the significantly compressed methyl–C(7)–methyl bond angle of 105° is the same in both,[21] so that the bicumene structures are virtually superimposable.

III. Thermal Decomposition of Bicumene EDA Complexes with Nitrosonium. Upon standing in the dark at room temperature, the orange solution of bicumene and $NO^+BF_4^-$ in nitromethane slowly bleached. Aqueous workup of the reaction mixture after 4 days yielded 1-phenyl-1,3,3-trimethylindan as the principal organic product, i.e.



(5)

together with minor amounts of cumene, cumyl alcohol, and an unidentified biaryl (see the Experimental Section). The trimethylindan in eq 5 was isolated as a colorless crystal (showing three characteristic methyl singlets at δ 1.03, 1.35, and 1.69 and a pair of methylene doublets at 2.19 and 2.42 in the ^{1}H NMR spectrum) and found to be identical with an authentic sample prepared by the acid-catalyzed dimerization of α-methylstyrene.[22,23]

The thermal decomposition of the charge-transfer complex of 4,4′-dimethylbicumene and $NO^+BF_4^-$ under the same experimental conditions was monitored by following the changes in the ^{1}H NMR spectrum (at δ 1.26, s, 12 H) with ethylene dichloride as the internal standard. Within a few minutes, the trimethylindan analogue to that in eq 5 was formed (75%), as judged by the growth of the three diagnostic methyl singlets at δ 1.03, 1.32, and 1.64 (9 H) and the methylene multiplet at δ 2.30 (2 H).[22] Workup of the reaction mixture after 30 min, followed by GC analysis indicated a 25% conversion of 4,4′-dimethylbicumene. By contrast, the charge-transfer complex of 4,4′-dimethoxybicumene and $NO^+BF_4^-$ in acetonitrile was completely converted within 1 h (in the dark) at room temperature to yield a complex mixture that contained 4-methoxycumene, 4-methoxyisopropenylbenzene, and 4-methoxyacetophenone, among other cleavage products (see the Experimental Section). However, our inability to detect the diagnostic methyl resonances (vide supra) in the ^{1}H NMR spectrum suggested that (dimethoxy)trimethylindan (analogous to that in eq 5) was not an important product. Similarly, 2,3-dimethoxy-2,3-diphenylbutane in acetonitrile was completely converted within 5 min by the addition of $NO^+BF_4^-$ to a complex mixture

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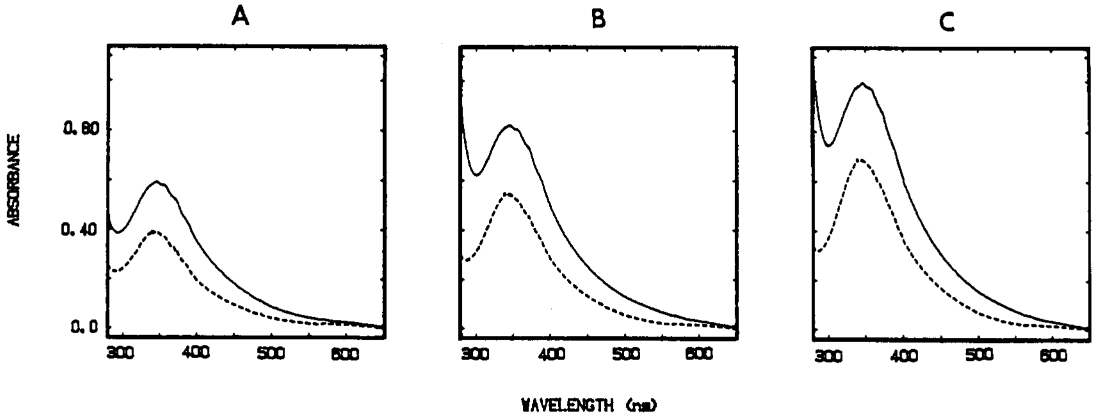


Figure 1. Charge-transfer spectra from 9.6 mM $NO^+BF_4^-$ and (A) 26 mM, (B) 40 mM, and (C) 54 mM bicumene (—) or *tert*-butylbenzene (- - -) in acetonitrile at 23 °C.

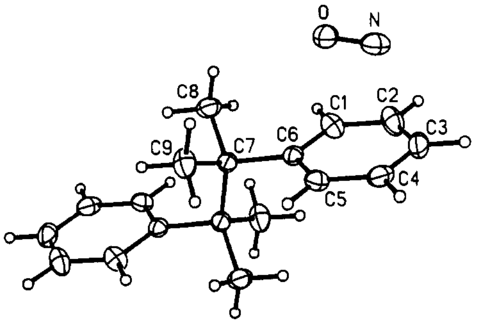


Figure 2. ORTEP diagram of the 1:1 bicumene EDA complex with nitrosonium cation.

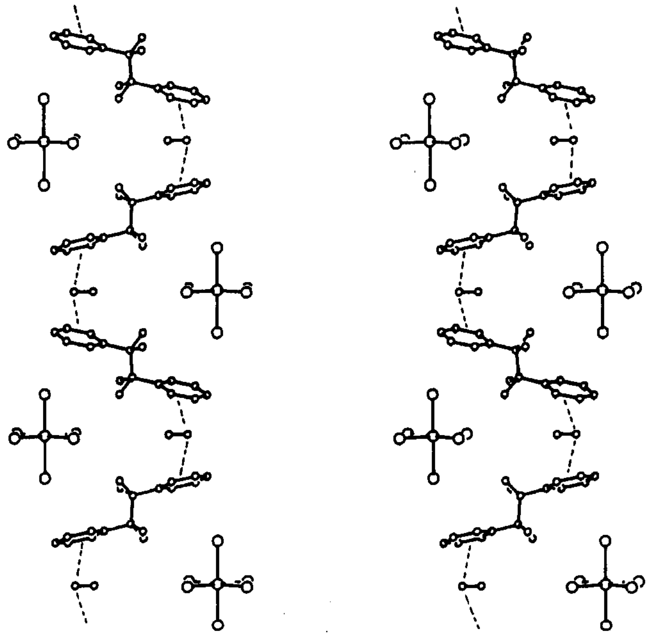


Figure 3. Stereoscopic view of the extended charge-transfer interactions of bicumene and NO^+ in the EDA complex.

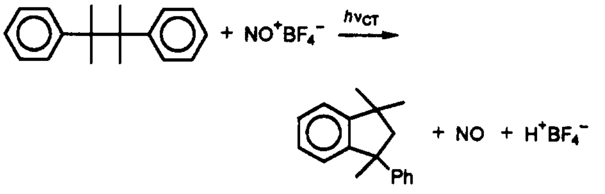
Table I. Selected Bond Distances (Å) and Bond Angles (deg)[a]

distance/angle	[bicumene, NO^+]	bicumene
O–N	1.092 (6)	
C(1)–C(2)	1.387 (5)	1.379 (4)
C(1)–C(6)	1.392 (4)	1.396 (4)
C(2)–C(3)	1.371 (5)	1.377 (5)
C(6)–C(7)	1.540 (5)	1.557 (3)
C(7)–C(8)	1.533 (4)	1.530 (3)
C(7)–C(9)	1.538 (4)	1.540 (3)
C(7)–C(7′)	1.597 (5)	1.594 (5)
C(6)–C(7)–C(9)	110.0 (2)	109.6 (2)
C(6)–C(7)–C(7′)	109.1 (3)	107.9 (2)
C(6)–C(7)–C(8)	110.0 (2)	110.2 (2)
C(8)–C(7)–C(9)	105.3 (3)	105.8 (2)

[a] See Figure 2 for numbering scheme.

which was tentatively identified by ^1H NMR and GC–MS analysis to include 3,3-diphenylbutanone and variously substituted indenes and indans (see the Experimental Section). The siloxy analogue 2,3-bis(trimethylsiloxy)-2,3-diphenylbutane also underwent a facile reaction with $NO^+BF_4^-$ in acetonitrile at room temperature. Within 5 min, the ^1H NMR spectrum of the reaction mixture indicated the presence of acetophenone (10%) and 3,3′-diphenylbutanone (40%), the amounts of which were quantified by the subsequent aqueous workup of the reaction mixture, followed by GC–MS analysis (see the Experimental Section).

IV. Charge-Transfer Activation of the Bicumene EDA Complex with Nitrosonium. When the orange solution of the bicumene EDA complex with NO^+ in acetonitrile was deliberately irradiated with filtered light ($\lambda_{exc} > 400$ nm), it liberated nitric oxide ($\nu_{NO} = 1876$ cm^{-1}) as the color bleached. Analysis of the photolysate after 4 h indicated that bicumene (20%) was converted principally to 1-phenyl-1,3,3-trimethylindan, i.e.



(6)

together with minor amounts of cumyl alcohol and acetophenone. Significantly higher yields of the trimethylindan (90%) were obtained when the bicumene EDA complex with $NO^+SbCl_6^-$ was irradiated ($\lambda_{exc} > 480$ nm) in dichloromethane solution for 12 h (see the Experimental Section). The quantum efficiency for the photoinduced oxidative rearrangement (eq 6) was measured by the absorbance change in the charge-transfer band relative to the Reineckate actinometer[24] as $\Phi = 0.2 \pm 0.1$ in nitromethane, dichloromethane, or acetonitrile.

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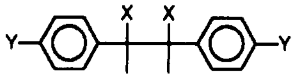
Table II. Thermal and Photochemical (CT) Reactivity of Diphenylethane-Type Donors with Nitrosonium



Y	X	(μmol)	NO^+ (μmol)	solvent[a]	product(s) (μmol)	rec[b] (μmol)	conv[c] (%)	temp/time (°C/h)
H	CH_3	(72)[d]	270	NM	6[g,h]	56	22	25/84
H	CH_3	(327)[e]	660	NM	57[g,i]	258	21	23/4.5
H	CH_3	(64)[f]	64	DCM	55[g,i]	14	78	23/12
CH_3	CH_3	(27)[d]	50	NM	6[j]	19	25	23/0.5
CH_3O	CH_3	(25)[d]	50	AN	19[k]	0	100	23/1
H	OCH_3	(200)[d]	430	AN	m	0	100	23/0.1
H	$OSiMe_3$	(200)[d]	140	AN	12[n,p]	80	86	23/0.01

[a] NM = nitromethane, AN = acetonitrile, DCM = dichloromethane. [b] Recovered donor. [c] Conversion based on donor recovered. [d] Thermal reaction (in the dark). [e] CT reaction with $\lambda_{exc} > 425$ nm. [f] CT reaction with $\lambda_{exc} > 480$ nm. [g] 1-Phenyl-1,3,3-trimethylindan. [h] Cumene and cumyl alcohol also present. [i] Acetophenone present. [j] 1-*p*-Tolyl-1,3,3,5-tetramethylindan. [k] Mixture of *p*-methoxy-α-methylstyrene, *p*-methoxycumene, etc. (see the Experimental Section). [m] See text. [n] Acetophenone. [p] 3,3-Diphenyl-2-butanone (50 μmol).

Discussion

Charge-Transfer Structure of the Bicumene EDA Complex with Nitrosonium Cation. The importance of ground-state charge transfer in the EDA complex of bicumene and NO^+ is observed in the ORTEP diagram (Figure 2) by the marked change in the nitrosonium moiety upon its complexation according to eq 3. Thus X-ray crystallography analysis establishes the significant lengthening of the N–O distance that occurs concomitantly with the vibrational (infrared) decrease in the stretching frequency (ν_{NO}) to approach that of nitric oxide. Both of these experimental manifestations of the significant alteration of the nitrosonium moiety within the bicumene EDA complex relate to the general theory of the structural changes due to charge-transfer as evaluated by the parameter *Z*.[25] As a reflection of the degree of charge transfer, *Z* is well accommodated in nitrosonium complexes in which the variations in the vibrational frequencies of the simple diatomic acceptor are rather unambiguous measures of the structural change developed by Friederich and Person,[2629] i.e.

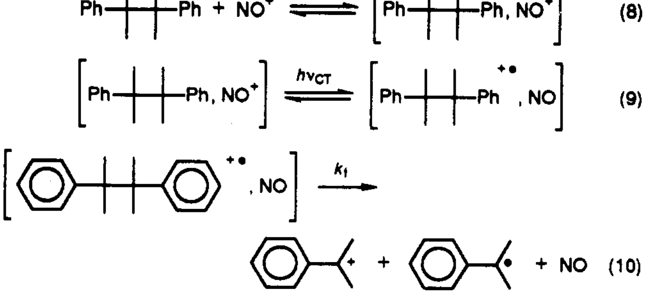
$$Z = (\nu_{NO^+}{}^2 - \nu_c{}^2)/(\nu_{NO^+}{}^2 - \nu_{NO}{}^2) \qquad (7)$$

where ν_{NO^+}, ν_c, and ν_{NO} refer to the N–O frequencies of the free nitrosonium cation, the EDA complex, and nitric oxide, respectively.[17] The value of $Z = 0.7$ evaluated in this way indicates the bicumene EDA complex to exist in the ground state with a rather large degree of charge transfer.

The extent to which charge transfer is relevant to the alteration of the nitrosonium moiety within the EDA complex to that of nitric oxide, as described above, must coincide with the bicumene moiety taking on an equal measure of cationic character (compare eq 4)—the exothermic energetics of ~18 kcal mol^{-1} for $[BC,NO^+] < [BC^{\bullet+},NO]$ being underscored by the lower ionization potential of bicumene (8.47 eV)[27] relative to that of nitric oxide (9.26 eV).[28] Nonetheless the X-ray structure (Table I) shows that such an electronic contribution is not manifested in the bicumene moiety by an accompanying elongation of the central C(7)–C(7′) bond to a degree that is experimentally significant.[29] However, evidence for such a weakening of the central bond may be deduced from the thermal and photochemical lability of the bicumene EDA complex with NO^+ in the following way.

Charge-Transfer Activation of the Bicumene EDA Complex with Nitrosonium. The photoinduced transformation of bicumene in eq 6 relates directly to the direct, prior activation of the EDA complex. Thus the inspection of Figure 1 shows that the use of filtered light with $\lambda_{exc} > 400$ nm selectively excites only the charge-transfer absorption band of the bicumene EDA complex with NO^+; the possibility of the adventitious excitation of either the uncomplexed bicumene or nitrosonium cation is thus precluded. Time-resolved spectroscopic studies previously established[30] that such a charge-transfer activation of an aromatic donor is tantamount to its photoinduced oxidation to the cation radical. As applied to the bicumene donor, the photochemical process for charge-transfer activation ($h\nu_{CT}$) includes bimolecular association (K_{EDA}) and unimolecular fragmentation (k_f) as the preequilibrium and followup processes, respectively, i.e.

Scheme I



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(26) (a) Friedrich, H. B.; Person, W. B. *J. Chem. Phys.* **1966**, *44*, 2161. (b) The evaluation of the degree of charge transfer by IR changes in the diatomic NO^+ is straightforward in comparison to most polyatomic acceptors in which the rigorous normal coordinate analysis of the complex vibrations is difficult. [Compare: Chappell, J. S.; Bloch, A. N.; Bryden, W. A.; Maxfield, M.; Poehler, T. O.; Cowan, D. O. *J. Am. Chem. Soc.* **1981**, *103*, 2442. Kampar, V. E.; Valtere, S. P.; Neilands, O. Ya. *Theor. Exp. Chem.* **1978**, *14*, 288.]

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(29) For a discussion of the elongation of the central bond in bibenzyl strutures, see ref 4. For an unusually long central bond, see: Littke, W.; Drück, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 406.

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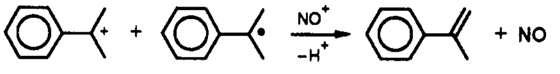
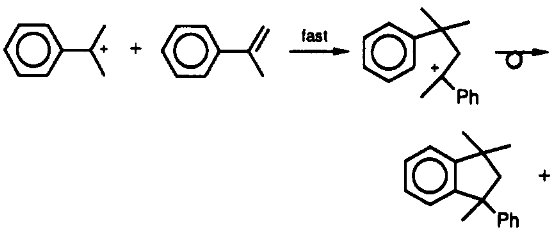
Since the rapid fragmentation of the labile bicumene cation radical occurs with an estimated rate constant[11] $k_f > 10^8\ s^{-1}$, the overall quantum yield of $\Phi \sim 0.2$ from eq 6 indicates that the back electron transfer from the radical ion pair in eq 9 is $k_{-1} > 4 \times 10^8\ s^{-1}$. The cumyl radical and cation that are coproduced from the fragmentation in eq 10 are responsible for the photoproducts derived from bicumene. Thus the oxidation of cumyl radical[11,31] and proton loss from the cumyl cation to afford α-methylstyrene[32] are facile, as is the subsequent head-to-tail recombination of the fragments to the dimeric 1-phenyl-1,3,3-trimethylindan,[23] i.e.



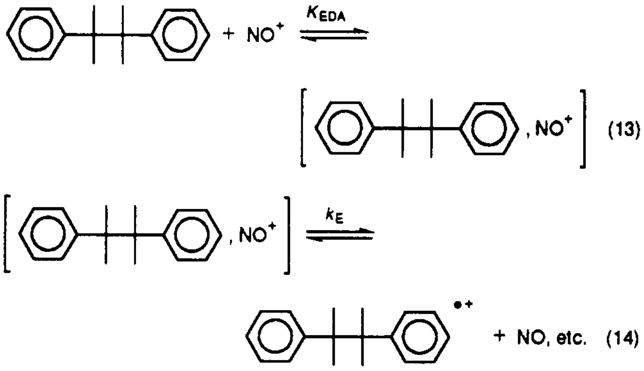
(11)



(12)

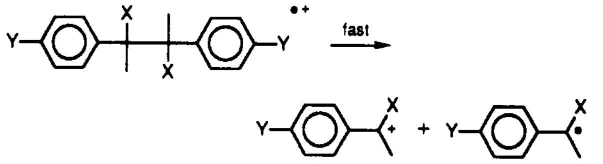
Electron Transfer in the Thermal Activation of Bicumene by Nitrosonium. The thermal and photochemical activations of bicumene according to eqs 5 and 6, respectively, share in common the rapid, preequilibrium formation of the EDA complex in eq 3. Moreover both methods yield the same unique oxidative dimer, namely, 1-phenyl-1,3,3-trimethylindan as the principal product. Since time-resolved spectroscopy identifies the bicumene cation radical as the critical intermediate in the photochemical ($h\nu_{CT}$) activation according to Scheme I, the most direct formulation of the thermal process invokes the production of the same intermediate, e.g.

Scheme II



Since the electron transfer in eq 14 represents the adiabatic counterpart to the photochemical process, the bicumene cation radical should be equivalent to that formed in eq 9, and its spontaneous fragmentation would lead to the same cumyl cation/radical pair (eq 10) that are precursors to 1-phenyl-1,3,3-trimethylindan as presented in eqs 11 and 12.

According to Scheme II, the fragmentation rate (k_f) must be sufficiently rapid to drive the highly endergonic electron-transfer equilibrium in eq 14 with a value of $\Delta G_E > 20$ kcal mol^{-1} based on an estimated oxidation potential $E_{ox}° \sim 2.1$ for bicumene.[33,34] Such a conclusion is consistent with the persistence of *tert*-butylbenzene under the same conditions, despite the comparable degree of charge transfer in the ground-state EDA complex with NO^+ (vide supra). Methyl and methoxy substituents on the para positions of bicumeme facilitate the oxidative cleavage of the central C(7)–C(7′) bond, as shown by the rapid reduction of NO^+ to nitric oxide and the concomitant formation of cleavage products (trimethylindans, cumenes, α-methylstyrenes, etc.) in high conversions, i.e.



(15)

especially when X = CH_3O and $(CH_3)_3SiO$ and Y = CH_3O. The increased (mesolytic) lability of the bicumene cation radicals with 4,4′-dimethyl and -dimethoxy substituents accords with earlier conclusions based on the photoinduced cleavage of bicumenes with tetranitromethane.[11] Even more dramatic is the oxidative labilization of the central bond when a pair of α-methyl groups in bicumene is replaced with either methoxy or trimethylsiloxy groups.

Experimental Section

Materials. $NOBF_4$ (Pfaltz and Bauer) was recrystallized from acetonitrile at -20 °C, followed by filtration in a drybox, and vacuum drying yielded a colorless crystalline powder. $NOPF_6$ (Pfaltz and Bauer) was used without purification. $NOSbCl_6$ was synthesized from NOCl[35] and $SbCl_5$ in dichloromethane at -20 °C under an argon atmosphere. Cumene, *p*-cymene, isopropylanisole, acetophenone, 4-methylacetophenone, 4-methoxyacetophenone, and α-methylstyrene from Aldrich were used directly as received. Bicumene, 4,4′-dimethylbicumene, and 4,4′-dimethoxybicumene were synthesized according to the method described in the literature.[11] Thus equimolar amounts of the appropriately substituted cumene and di-*tert*-butyl peroxide were combined under an argon atmosphere and the mixture refluxed for 6 h. Every 6 h, an equivalent of di-*tert*-butyl peroxide was added to the reaction mixture, until a total of 4 equiv of di-*tert*-butyl peroxide was used. Crude 4,4′-dimethylbicumene was isolated from the mixture upon cooling to room temperature followed by filtration. Recrystallization from ethanol afforded colorless crystals (~20%). The other bicumenes were obtained by concentration in vacuo, followed by recrystallization of the residue from ethanol. Bicumene: ^1H NMR ($CDCl_3$) δ 1.27 (s, 12 H), 7.14 (s, 10 H). 4,4′-Dimethylbicumene: ^1H NMR ($CDCl_3$) δ 1.26 (s, 12 H), 2.31 (s, 6 H), 6.98 (m, 8 H). 4,4′-Dimethoxybicumene: ^1H NMR (CD_3CN) δ 1.23 (s, 12 H), 3.74 (s, 6 H), 6.76 (d, 4 H), 6.95 (d, 4 H). 2,3-Dimethoxy-2,3-diphenylbutane was synthesized from the corresponding diol.[9a] Thus, 2,3-diphenyl-2,3-butanediol (500 mg, 2.1 mmol) was added to a solution containing powdered NaOH (0.6 mg, 18 mmol) in 15 mL of DMSO. Methyl iodide (1.2 g, 8.2 mmol) was added and the mixture stirred for 30 min at 23 °C. The reaction mixture was quenched with water (10 mL), extracted three times with $CHCl_3$ (10 mL), washed with water, and dried over $MgSO_4$. Evaporation of the solvent and recrystallization from ethanol afforded colorless crystals of 2,3-dimethoxy-2,3-diphenylbutane (0.19 g): mp 109–110.5 °C (lit. mp 111.0–111.5 °C); ^1H NMR ($CDCl_3$) δ 1.63 (s, 6 H), 3.10 (s, 6 H), 7.07 (m, 4 H), 7.15 (m, 6 H); GC–MS (t = 8.78) m/z 255 (0.08), 240 (0.10), 239 (6), 136 (13), 135 (100), 105 (25), 103 (11),

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[31] Rollick, K. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 1319.

[32] See Keating, J. T.; Skell, P. S. *Carbonium Ions* **1970**, *2*, 573.

[33] From the correlation with IP[27] according to Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

[34] For $E_{red}°$ of NO^+ see: Lee, K. Y.; Kuchynka, D. J.; Kochi, J. K. *Inorg. Chem.* **1990**, *29*, 4196.

[35] Sharp, D. W. A.; Thorley, J. *J. Chem. Soc.* **1963**, 3557.

102 (2.1), 91 (9), 89 (2), 79 (2), 78 (8), 77 (40), 51 (13); IR (KBr) 3050, 3010, 2970, 2930, 2830, 1440, 1360, 1140, 1090, 1150, 880, 800, 860, 760, 760 cm^{-1}. 2,3-Bis(trimethylsiloxy)-2,3-diphenylbutane was prepared in an earlier study.[12a] Solvents were purified and dried as follows. Acetonitrile (HPLC grade, Fisher Scientific) was initially stirred over $KMnO_4$ for 12 h, and the mixture was refluxed for an additional hour. After filtration, the colorless liquid was treated with diethylenetriamine, and the mixture was refiltered. Acetonitrile was finally refractionated from P_2O_5 under an argon atmosphere. Dichloromethane (J. T. Baker) was initially stirred with concentrated sulfuric acid. The separated layer was neutralized and dried over anhydrous Na_2CO_3. It was finally distilled from anhydrous P_2O_5 under an argon atmosphere. Nitromethane (Fisher, 96%) was crystallized at −78 °C until most of it was frozen. The slightly pale yellow liquid was cannulated, and the colorless solid was recrystallized three times. The resulting nitromethane was warmed to room temperature and treated with $CaCl_2$. Distillation at reduced pressure at 150 mmHg (bp 49–50 °C) afforded colorless nitromethane that was stored under an argon atmosphere in a Schlenk flask in the dark. Nitromethane-d_3 (Aldrich, 99 atom % D, Gold label) received in a sealed ampule was opened in a drybox, stored in a Schlenk flask equipped with Teflon stopsocks. It was always used under a dry dinitrogen atmosphere.

Instrumentation. The UV–vis absorption spectra were measured on a Hewlett-Packard 8450A diode array spectrometer equipped with HP 89100A temperature controller. NMR spectra were recorded on a JEOL FX 90Q spectrometer operating at 90 MHz for ^1H NMR. Proton chemical shifts are reported in ppm downfield from a tetramethylsilane internal standard. Routine GC analyses were performed on a Hewlett-Packard 5790A chromatograph equipped with a flame ionization detector, using a 12.5-m SE-30 capillary column. For quantitative analyses, decane (Aldrich) was used as an internal calibrant. Such a quantification was accompanied by ^1H NMR analysis for side chain substituted products. Both GC and ^1H NMR analysis afforded the same results, within the experimental error limits. The GC-MS analyses were carried out on a Hewlett-Packard 5890 Chromatography interfaced to a HP 5970 mass spectrometer (EI, 70eV). All manipulations of the moisture-sensitive nitrosonium salts were carried out in a Vacuum Atmospheres HE-439 drybox maintained at <2 ppm water.

The light source for charge-transfer activation consisted of a 500-W Osram HB mercury lamp equipped with a parabolic reflector. The light was passed through a circulating water filter to remove IR radiation, and a fused silica biconvex lens (ϕ 4.5 cm, f 10 cm) focused the light onto the sample contained in 1.0-cm quartz cuvette. Either a sharp cutoff filter [Corning CS-3 series, no. 3387 and 3385 for $\lambda_{exc} > 425$ and 480 nm, respectively] or an interference filter (440 ± 7.5 nm) was fixed in front of the cell to ensure that only the charge-transfer band of the relevant EDA complex was irradiated.

Charge-Transfer Spectral Measurements. Typically, $NO^+BF_4^-$ was added to a 1-cm square quartz cuvette equipped with side arm and Schlenk adapter. The cell was taken out of the drybox, connected to a vacuum line, and acetonitrile was added with the aid of a hypodermic syringe. The charge-transfer absorption spectra were measured at the various concentrations of bicumene and *tert*-butylbenzene indicated in Figure 1.

Formation Constants of Arene CT Complexes with Nitrosonium. In a typical procedure, an 8-mL aliquot of a standard stock solution of nitrosonium salt in acetonitrile was transferred to a 1-cm quartz cuvette. A weighed amount of arene was added incrementally under an argon atmosphere. The absorbance changes were measured at the spectral maxima as well as at other wavelengths close to the absorption maxima. From a plot of $[NO^+](A_{CT})^{-1}$ against $(arene)^{-1}$, consisting of six data points, the slope was estimated as $(K\epsilon_{CT})^{-1}$ and the intercept as $\epsilon_{CT}{}^{-1}$.[18]

Isolation and X-ray Crystallography of the Bicumene EDA Complex with $NO^+SbCl_6^-$. Bicumene (0.31 mmol) was dissolved in 5 mL of dichloromethane (glovebox). Addition of $NOSbCl_6$ (0.30 mmol) afforded a dark-red solution and colored solid, which was removed by careful decantation. The resulting solution was chilled to −20 °C (in the dark). After 24 h, the dark red-brown crystals were collected, dried under a nitrogen stream, and then transferred to a Schlenk flask charged with purified mineral oil. A dark red block having approximate dimensions 0.60 × 0.55 × 0.45 mm was carved from a much larger block and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer, and the diffraction data collected at −50 °C. A single crystal of bicumene suitable for X-ray crystallography was obtained by slow vacuum sublimation at 23 °C. The crystallographic analysis (at −50 °C) was carried out as described above. The atomic coordinates of [bicumene, $NOSbCl_6$] and bicumene, as well as other pertinent data, have been deposited at the Cambridge Crystallographic Data Center (CCDC). They can be obtained upon request to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Infrared Spectrum of the Bicumene EDA Complex with Nitrosonium. The red-brown solution of bicumene (0.2 M) and $NOPF_6$ (0.5 M) in 1 mL of CH_3NO_2 (prepared in a glovebox) was introduced into a sealed AgCl cell (0.1-cm pathlength). The characteristic (strong) band of the N–O stretch was centered at $\nu_{NO} = 2014$ cm^{-1}. Similarly, the red-brown solution of bicumene (0.2 M) and $NOSbCl_6$ (0.2 M) in CH_3NO_2 showed $\nu_{NO} = 2017$ cm^{-1}.

Thermal Reaction of Bicumene with Nitrosonium. The thermal reaction of bicumene (0.072 mmol) with $NOBF_4$ (0.27 mmol) in CD_3NO_2 was carried out at 23 °C in the dark.[17] Similarly, the orange solution of 4,4′-dimethylbicumene (0.027 mmol) and $NOBF_4$ (0.050 mmol) in CD_3NO_2 (0.4 mL) was kept in the dark, and the progress of the reaction was monitored by ^1H NMR analysis using 1,2-dichloroethane as an internal standard. Within 20 min, the characteristic methyl (proton) resonances of 1-phenyl-1,3,3-trimethylindan were observed at δ 1.03 (3 H, s), 1.32 (3 H, s), 1.64 (3 H, s) and methylene multiplet at 2.30. The yield of the phenylindan was 0.006 mmol (75% based on the consumed 4,4′-dimethylbicumene). The orange-red solution of 4,4′-dimethoxybicumene (0.025 mmol) and $NOBF_4$ (0.050 mmol) in 0.8 mL of acetonitrile turned deep purple within 1 h. Inspection of the ^1H NMR of the reaction mixture indicated the presence of cleavage products and 4′-methoxy-α-methylstyrene (traces). Diethyl ether was added, and the resulting yellow solution was washed with water, dried, and analyzed by GC and GC–MS to afford acetophenone (7.4%), 4′-methoxy-α-methylstyrene (1%), 4-methoxycumene (12%), 4-methoxy-*tert*-butylbenzene (7%), and 2-(4′-anisyl)-2-methoxypropane (7%). No starting material was recovered. The reaction of 2,3-dimethoxy-2,3-diphenylbutane (0.20 mmol) with $NOBF_4$ (0.43 mmol) occurred instantaneously at 25 °C in acetonitrile (4.5 mL). The ^1H NMR analysis of the reaction mixture indicated the presence of indan products (by methyl resonances at δ 1.26, 1.54, 2.10), together with other rearranged products. Reaction mixture was diluted with diethyl ether and examined by GC and GC–MS to afford 1,3-dimethyl-3-phenylindan (16%), 1,3-dimethyl-1-methoxy-3-phenylindan (21%), benzophenone (20%), 3,3-diphenyl-2-butanone (20%), and 1,3-dimethoxy-1-methyl-3-phenylindan (20%). A solution of 2,3-dimethoxy-2,3-diphenylbutane (0.2 mmol) in 0.5 mL of $CDCl_3$ was added to a solution containing $NOBF_4$ (0.085 mmol) in 0.5 mL of acetonitrile. A transient green color was observed upon mixing, and it bleached (yellow) within 10 min. The ^1H NMR analysis of the reaction mixture indicated α-methoxystyrene (25%) together with the indan derivative described above. The recovered 2,3-dimethoxy-2,3-diphenylbutane was 0.10 mmol. The reaction of 2,3-bis(trimethylsiloxy)-2,3-diphenylbutane (0.20 mmol) with $NOBF_4$ (0.14 mmol) was carried out in 0.5 mL of acetonitrile within 5 min, the ^1H NMR spectrum indicated the presence of acetophenone and 3,3-diphenyl-2-butanone. Addition of diethylether and aqueous workup afforded acetophenone (0.012 mmol), 3,3-diphenyl-2-butanone (0.050 mmol), and recovered TMS ether (0.08 mmol).

Charge-Transfer Photoactivation of Bicumene with Nitrosonium. The orange-red solution of bicumene (0.327 mmol) and $NOBF_4$ (0.66 mmol) in nitromethane (10 mL) liberated gas and bleached to a yellow solution upon exposure to a light $\lambda_{exc} > 425$ nm at 23 °C. IR analysis after 4.5 h indicated that the liberated gas consisted of nitric oxide ($\nu_{NO} = 1876$ cm). Dichloromethane was added to the photolysate, and the resultant solution was washed with water and 5% $NaHCO_3$, dried with $MgSO_4$, and subjected to GC analysis. Products were 1,1,3-trimethyl-3-phenylindan (0.030 mmol) and acetophenone (0.027

mmol), together with recovered bicumene. Similarly, the red-brown solution of bicumene (0.18 mmol) and $NOSbCl_6$ (0.064 mmol) in 6 mL of dichloromethane was irradiated with $\lambda_{exc} > 480$ nm at 23 °C. The CT color was bleached much more slowly than in the previous experiment carried out in nitromethane solution. After 12 h, aqueous workup of the photolysate afforded 0.05 mmol of 1,1,3-trimethyl-3-phenylindan (90% based on bicumene consumed) and 0.005 mmol of acetophenone (2%) together with recovered bicumene (0.125 mmol) by GC and GC–MS analysis.

Measurement of Quantum Yield. The quantum yield were carried out with an Osram 450-W high-pressure Xenon lamp that was focused through an aqueous IR filter, followed by an interference filter (10-nm bandpass). Reineckate actinometry[24] was used to calibrate the light intensity. In a typical experiment, the dicumene solution was added to a 1-cm quartz precision cuvette, which was charged with nitrosonium salt under an argon atmosphere. The solution was irradiated at 23 °C, and the bleaching of the CT band was measured periodically. The quantum yield Φ_{CT} was obtained from the following relationship: $\Phi_{CT} = M_o/\{F(t) \log T_0[\log (1 - T^{-1})/(1 - T_0^{-1})\}$[36] for the incident light flux (F) within the time interval (t) in the solution originally containing M_o moles of the limiting agent and showing the initial and final transmittance of T_0 and T, respectively. The flux was measured before and after photoreaction. Thus the orange solution of bicumene (0.005 75 M) and $NOBF_4$ (0.140 M) in acetonitrile was irradiated with $\lambda_{exc} = 440$ nm for 100 min, and the bleaching of CT band at $\lambda_{mon} = 400$, 340, and 460 nm was monitored. Similarly, the solution of bicumene (0.0055 M) and $NOBF_4$ (0.133 M) in CH_3NO_2 was irradiated with a light $\lambda_{exc} = 440$ nm, and the absorbance change was monitored at $\lambda_{mon} = 420$, 440, and 460 nm. The brown solution of bicumene (0.069 M) with $NOSbCl_6$ (0.017 M) in CH_2Cl_2 was irradiated with $\lambda_{exc} = 520$ nm, and the absorbance change was monitored at $\lambda_{mon} = 520$ nm.

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