6334 J. Org. Chem. 1990, 55, 6334-6347

Photochemically Generated Ion and Radical Pairs. Self-Destructive Charge-Transfer Complexes

Przemyslaw Maslak* and William H. Chapman, Jr.

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 12, 1990

Irradiation of CT complexes between 4-methoxy-4′-X-bicumenes, **1a–e** (X = H, **a**; OMe, **b**; Me, **c**, CF_3, **d**, CN, **e**) and tetranitromethane (**2**) results in efficient generation of radical and ion pairs ($\Phi \approx 0.20$). The identity of the final products depends on the dynamics of these pairs, which in turn is dramatically influenced by substitution and solvent. In all cases, $\mathbf{2}^{\bullet-}$ dissociates rapidly (<3 ps) into $(NO_2)_3C^-$ ($\mathbf{4}^-$) and $NO_2^\bullet$. In CH_2Cl_2, $\mathbf{1a}^{\bullet+}$ reacts with $\mathbf{4}^-$ (aromatic trinitromethylation) and undergoes C–C bond fragmentation before diffusional separation of fragments can occur. Thus, a tetrad of reactive intermediates (cumyl radical, $NO_2^\bullet$, *p*-methoxycumyl cation and $\mathbf{4}^-$) are produced in a single solvent cage. The cumyl radical is oxidized by **2**, and both cumyl cations undergo α-trinitromethylation. The cumyl cations undergo trinitromethylation in the original solvent cage which is kinetically equivalent to a contact ion pair (CIP). In CH_3CN the fragmentation is accompanied by aromatic nitration (radical collapse). In this solvent, the *p*-methoxycumyl cations produced by cleavage reaction undergo trinitromethylation at the CIP stage, but cumyl cations produced by thermal oxidation of the cumyl radicals are trapped by $\mathbf{4}^-$ at the solvent-separated ion pair stage. In CH_2Cl_2, $\mathbf{1b–c}^{\bullet+}$ undergo exclusively fragmentation, completely within the solvent cage. The cleavage of $\mathbf{1d–e}^{\bullet+}$ is much slower, and the radical cations undergo instead aromatic trinitromethylation. The observed substituent effect on the rate of cleavage ($\rho^+ = -2.2$) indicates significant charge transfer across the scissile bond in the transition state for this process. The products of these reactions are predominantly derived from ion annihilation. The radical coupling processes are limited to radical cation/radical collapse that lead to nitrated products.

Photoinduced electron transfer between neutral molecules leads to formation of ion pairs.[1-10] Dynamics of these ions determines the efficiency and final outcome of many photoprocesses.[1-10] The efficiency of the reaction, expressed as the fraction of ions that yields products, is largely dependent on relative rates of back-electron transfer (BET) and follow-up chemical reaction or diffusional separation of ions produced. Moreover, the dynamics of these processes may influence the identity of final products. All these processes are critically dependent on the solvation status of ions produced. The solvation determines energetics of BET and distance between the ions, which in turn control the rate of BET. Ease of diffusional separation or chemical reaction of the ions produced are also influenced by the solvation.

Most commonly, photogeneration of radical ions involves deposition of excitation energy in either acceptor or donor molecules.[1-4] An alternative approach is based on irradiation of charge-transfer (CT) bands of properly selected donor–acceptor pairs.[1,5-10] The two methods differ in the initial solvation status of the ions produced. It is believed that in polar media the first method usually leads to solvent-separated ion pairs[1,4] (SSIP) but contact ion pairs (CIP) are formed[1,6] when the second method is used. Thus, the classical Winstein formulation[12] is commonly applied to describe radical ion pair dynamics, with or without explicit inclusion of spin interactions between the odd-electron species.

We would like to describe a system designed to probe ion solvation status that is based on rapid fragmentation of photogenerated radical ions converting them to closed-shell ion pairs and radical pairs. In turn, reactivity of these ions can be explored within the classical framework of ion pairing. Our experiments (Scheme I) were based on the elegant work of Kochi et al.[7-9] and involved CT complexes, $[\mathbf{1a–e}\cdots\mathbf{2}]_{CT}$, between a series of substituted bicumenes (**1a–e**) and tetranitromethane (**2**). According to Mulliken theory,[13] irradiation of charge-transfer bands of such complexes leads to formation of ion pairs (in our case: $\mathbf{1}^{\bullet+}\ \mathbf{2}^{\bullet+}$), in all likelihood as contact ion pairs. Both components of our experimental system were selected to

---

[1] For an excellent review, see: Fox, A. M., Chanon, M. Eds. *Photoinduced Electron Transfer*, Elsevier: Amsterdam, 1988.

[2] (a) Davidson, R. S. In *Advances in Physical Organic Chemistry*, Gold, V., Bethell, D., Eds.; Academic Press: London, 1983; Vol. 19, p 1. (b) Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917. (c) Fox, M. A. In *Advances in Photochemistry*; Volman, D. H., Gollnick, K., Hammond, G. S., Eds.; Wiley: New York, 1986; Vol. 13, p 237.

[3] (a) Mattay, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 825. (b) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (c) Mattes, S. L.; Farid S. In *Organic Photochemistry*; Padwa, A. Ed.; Marcel Dekker: New York, 1983; Vol. 6, p 233.

[4] (a) Gould, I. R.; Moser, J. E.; Ege, D.; Farid, S. *J. Am. Chem. Soc.*) **1988**, *110*, 1991. (b) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

[5] Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

[6] Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.

[7] (a) Fukuzumi, S.; Kochi, J. K. *J. Org. Chem.* **1981**, *46*, 4116. (b) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 1126 and references therein. (c) Hilinski, E. F.; Milton, S. V.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 5193 and references therein. (d) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167. (e) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071. (f) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7880. (g) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Phys. Chem.* **1985**, *89*, 5387. (e) Masnovi, J. M.; Kochi, J. K. *J. Phys. Chem.* **1987**, *91*, 1878.

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

[9] (a) Takahashi, Y.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 2954. (b) Wallis, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 8270.

[10] (a) Jones, G. II; Becker, W. G. *J. Am. Chem. Soc.* **1983**, *105*, 1276. (b) Peacock, N. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 3632. (c) Jones, G. II; Hanley, W. A.; Phan, X. T. *J. Am. Chem. Soc.* **1988**, *110*, 1922.

[11] For example, see: (a) Miyashi, T.; Kamata, M.; Mukai, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1577. (b) Tsujimoto, K.; Fujimori, T.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1986**, 304. (c) Penn, J. H.; Deng, D.-L.; Aleshire, S. K. *J. Org. Chem.* **1988**, *53*, 3572. (d) Hasegawa, E.; Xu, W.; Mariano, P. S.; Yoon, U.-C.; Kim, J.-U. *J. Am. Chem. Soc.* **1988**, *110*, 8099.

[12] For a review, see: Raber, D. J.; Harris, J. M.; Schleyer P. v. R. In *Ions and Pairs in* Organic *Reactions*; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2.

[13] (a) Mulliken, R. S.; Pearson, W. B. In *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

0022-3263/90/1955-6334$02.50/0

Table I. Product Yields for Irradiation of CT Complexes of *p*-Methoxybicumenes and Tetranitromethane

			yields,[a] %					
X	1	solvent	**5b**	**5**	**6**	**7b**	**7**	**8**
H	**a**	CH_2Cl_2	50	56	32	–	–	–
	a	CH_3CN	45	38	–	–	–	20
	a	c-C_6H_{12}	*d*	*d*	85	–	–	–
	a	CH_2Cl_2/MeOH[b]	35	35	–	24	35	10
	a	CH_3CN/MeOH[c]	54	20	–	36	72	7
MeO	**b**	CH_2Cl_2	80	–	–	–	–	–
	b	c-C_6H_{12}	28	–	60	–	–	–
	b	CH_2Cl_2/MeOH[b]	45	–	–	41	–	–
Me	**c**	CH_2Cl_2	77	90	<5	–	–	–
	c	c-C_6H_{12}	–	–	97	–	–	–
	c	CH_3CN/MeOH[c]	44	24		45	67	–
CF_3	**d**	CH_2Cl_2	*d*	*d*	68	–	–	–
	d	CH_2Cl_2/MeOH[b,e]	16	8	30	9	23	–
	d	CH_3CN/MeOH[c]	50	23	–	41	71	–
CN	**e**	CH_2Cl_2	*d*	*d*	93	–	–	–
	e	CH_2Cl_2/MeOH[b,e]	16	8	38	16	23	4

[a] The yields of products obtained from irradiation of deoxygenated solution of **1a–e** (0.08 M) and **2** (0.4 M) through a cut-off filter (420 nm). The yields (estimated error is ca. 10%) were determined at ca. 50–60% conversion of starting materials to minimize secondary reactions. [b] [MeOH] = 0.5 M (2% v/v). [c] [MeOH] = 0.74 M (3% v/v). [d] Trace: <3%. [e] These reactions also gave aromatic dinitromethylation: 4-methoxy-3-(dinitromethyl)-4′-(trifluoromethyl)bicumene in 21% yield from **1d** and 4-methoxy-3-(dinitromethyl)-4′-cyanobicumene 25% yield from **1e**.

Table II. Effect of Added MeOH and 4^- on Product Ratios[a]

		additive (M)		observed ratio		
experimental system	solvent	[MeOH]	$[4^-]$	**7b/5b**	**7x/5x**	other compd
cumyl bromide	CH_2Cl_2	0.25	0.41	–	>8.3	
cumyl bromide	CH_3CN	0.25	0.41	–	>5.0	
irradiation of $[\mathbf{1a}\cdots\mathbf{2}]_{CT}$	CH_2Cl_2	0.25	–	0.2	0.4	*b*
		0.50	–	0.7	1.0	*c*
		0.75	–	0.8	1.1	*c*
		1.25	–	1.4	1.8	*c*
		2.50	–	3.3	3.4	*c*
		0.25	0.30	0.5	0.6	
irradiation of $[\mathbf{1a}\cdots\mathbf{2}]_{CT}$	CH_3CN	0.25	–	0.2	2.5	*d*
		0.75	–	0.7	3.4	*d*
		1.25	–	1.0	5.1	*d*
		2.50	–	3.8	7.2	*d*
		0.25	0.30	0.1	1.1	
irradiation of $[\mathbf{1e}\cdots\mathbf{2}]_{CT}$	CH_2Cl_2	0.50	–	1.0	3.3	*e*
		1.25	–	1.1	5.0	*e*
		2.50	–	1.2	7.1	*e*

[a] Reaction carried out to less than 30% conversion (typically 20–30%). The concentration of **2** was 0.25–0.40 M, the concentration of bicumenes was 0.06–0.08 M. Some data are averages of two or three determinations. Estimated errors are ±0.1. The products listed accounted for at least 90% of the consumed bicumenes. Other compounds (*b*) **6a** 8%, **8a** 4%; (*c*) **6a** <3%, **8a** 8–10%; (*d*) **8a** 7–14%; (*e*) **6e** 20–30%, 4-methoxy-3-(dinitromethyl)-4′-(trifluoromethyl)bicumene ca. 30%.

be highly activated toward fragmentation.[8,14] Such self-destructive CT complexes provide a convenient mechanistic tool to probe ion and radical pair dynamics in considerable detail.

Results

Charge-Transfer Complexes and Quantum Yield Measurements. In CH_2Cl_2, **1a–e** formed yellow CT complexes with **2**. The absorption spectra and formation constants measured at 480 and 500 nm by the Benesi–Hildebrand technique[15] indicated that these complexes are very similar to each other and to that formed by 4-methylanisole[8] (see the Experimental Section).

Irradiation of $[\mathbf{1a\text{–}e}\cdots\mathbf{2}]_{CT}$ complexes led to efficient consumption of the starting materials. The quantum yields for disappearance of **1a–e** measured at 450 ± 10 and 520 ± 10 nm in CH_2Cl_2 were similar for all the compounds ($\Phi = 0.2 \pm 0.05$) and essentially identical to that measured[8] by Kochi et al. for *p*-methylanisole ($\Phi = 0.19$ at 520 nm).

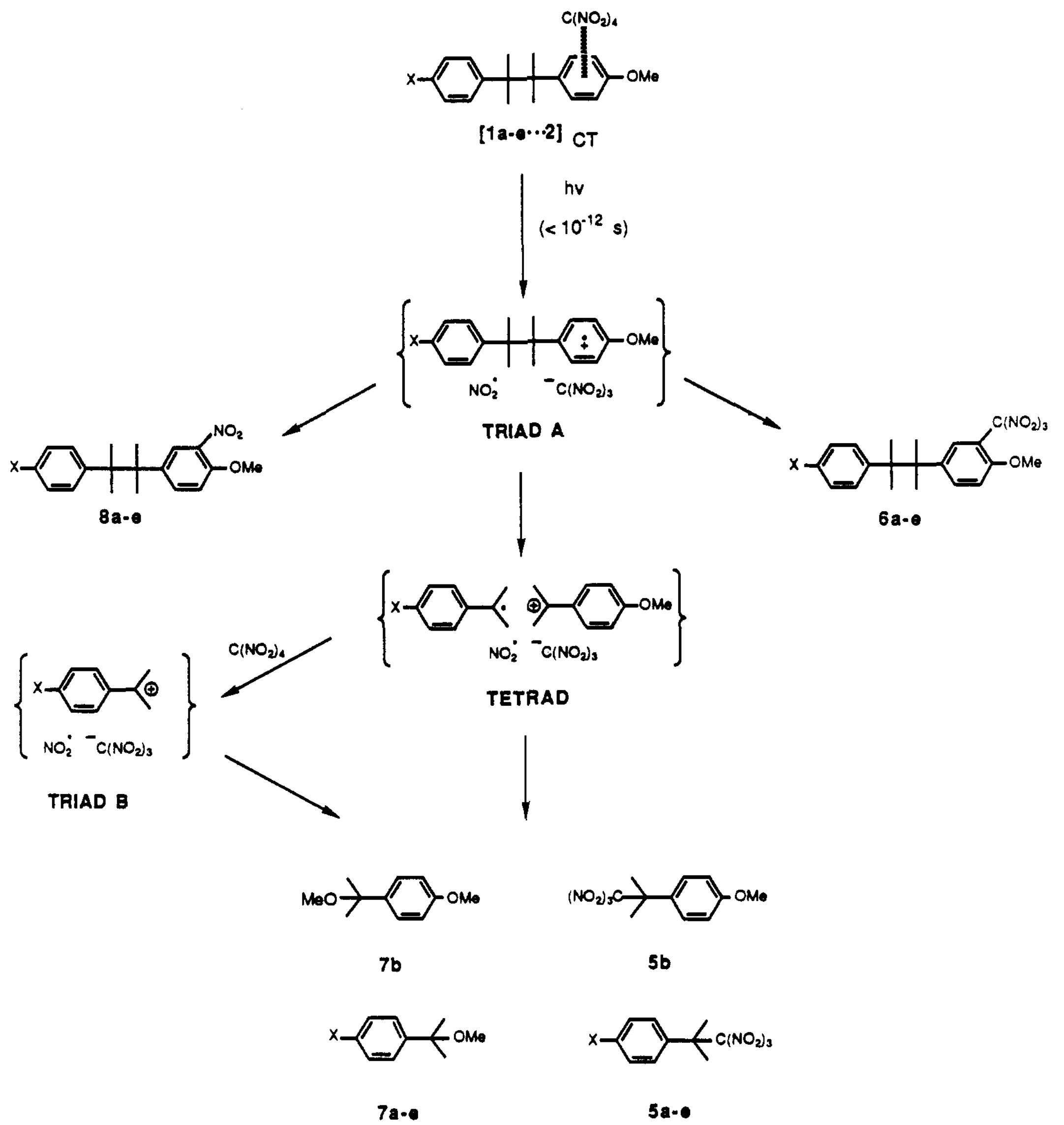
Product Studies. For product studies, deoxygenated solutions of **1a–e** (0.02–0.08 M) and **2** (0.10–0.38 M) were irradiated through a 420-nm cut-off filter. The products were isolated and identified by comparison with authentic samples or by spectral analysis (see the Experimental Section). The yields of **5–8** (Table I, Scheme I) were determined in deuterated solvents at ca. 50–60% conversion of starting bicumenes to minimize secondary reactions, since it was determined that **5b** is slowly consumed under

---

[14] For examples of photogenerated radical cations undergoing C–C bond scission, see: (a) Okamato, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175 and references therein. (b) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. N. *Can. J. Chem.* **1984**, *62*, 424. (c) Davis, H. L.; Das, P. K.; Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968. (d) Eaton, D. F. *Pure Appl. Chem.* **1984**, *56* 1191. (e) Masnovi, J. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 6781. (f) Ci, X.; Whitten, D. G. *J. Am. Chem. Soc.* **1987**, *109*, 7215; **1989**, *111*, 3459 and references therein. (g) Albini, A.; Mella, M. *Tetrahedron* **1986**, *42*, 6219. (h) Sankararaman, S.; Perrier, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 6448. (i) Popielarz, R.; Arnold, D. R. *J. Am. Chem. Soc.* **1990**, *112*, 3068.

[15] Benesi, H. G.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.

Scheme I



the reaction conditions (see the Experimental Section). A careful integration of well-separated signals of various products and internal standard (methyl *tert*-butyl ether) provided data necessary for calculation of absolute yields.

Similar methodology was used to study the effect of various additives on product distribution and to obtain information on cumyl bromide and cumyl alcohol solvolyses (see below). To assure accurate ratios of products, these reactions were carried out to 20–30% conversion of the starting materials (ca. 5-min irradiation time), and the NMR spectra were recorded immediately after irradiation. Under these conditions the ratios of ethers to α-(trinitromethyl)cumenes (**7**/**5**) were reproducible and independent of the degree of conversion. Data from these experiments are presented in Table II.

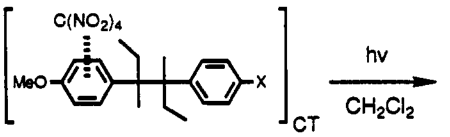
Product Stability and Model Solvolyses. In the reaction mixtures derived from **1a**, ether **7a** and α-trinitromethyl derivative **5a** were stable over a period of a few hours, but the **7b**/**5b** ratios changed slowly over time. For example, in CH_2Cl_2/MeOH (1% v/v) **7b** was slowly converted to **5b** (the **7b**/**5b** ratio changed ca. 25% in 30 min). In CH_3CN/MeOH (1% v/v), ether **7b** decomposed slowly (ca. 5% change in the **7b**/**5b** ratio in 1 h) to the corresponding styrene which dimerized and/or oligomerized under the reaction conditions. The changes in product ratios with time were smaller in solutions containing a higher proportion of MeOH. It has to be stressed that these slow processes *do not significantly* affect the ratios measured immediately after the irradiation (Table II). Samples of **5b** and **5a** were thermally stable in both solvents over a period of hours, even in the presence of nitroform. Similarly, the samples of **7b** and **7a** were stable in CH_3CN containing potassium trinitromethide (K^+ 4^-). The instability of **7b** in the medium of photochemical reactions was apparently caused by nitroform produced in situ.

Irradiation of $[\mathbf{1a}\text{–}\mathbf{e}\cdots\mathbf{2}]_{CT}$ in CH_2Cl_2/MeOH produced nitroform in amounts equivalent to **7** formed in these reactions, as expected from the stoichiometry of the process. Nevertheless, the total concentration of nitroform under the conditions of our studies (Table II) was quite small and did not exceed 8×10^{-3} M. The cumyl ethers **7a,b** (see above) and the corresponding alcohols (see below) reacted with nitroform only very slowly under these conditions. In pure CH_2Cl_2 and at higher concentrations, nitroform was used to independently prepare samples of **5a,b** from the cumyl alcohols (see the Experimental Section).

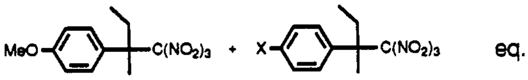
To compare nucleophilicity of MeOH and 4^- under conditions similar to the photochemical experiments, control solvolyses were performed. Thus, treatment of the cumyl alcohol with nitroform (ca. 0.046 M) in CH_2Cl_2/MeOH (1% v/v) gave the **7a**/**5a** ratio >20. In the corresponding experiments with *p*-methoxycumyl alcohol and nitroform (ca. 0.014 M) the **7b**/**5b** ratio was a function of time and changed from 4.3 (immediately after mixing, 27% alcohol conversion) to 2.2 (1 h after mixing, 47% alcohol conversion) to 1.32 (2 h after mixing, 74% alcohol conversion) to 0.96 (after 3 h, 86% alcohol conversion). Under these conditions, **7b** is slowly transformed to **5b**. Importantly, in both experiments the **7x**/**5x** ratios were *significantly larger* than those observed in the photochemical reactions despite the fact that in these experiments the nitroform concentrations were at least two times higher than those produced in photochemical reactions.

The second solvolysis experiment involved cumyl bromide. This source of the cumyl cation was allowed to react with a mixture of 4^- (tetraethylammonium or potassium salts) and MeOH in CH_2Cl_2 or CH_3CN and the ratio of **7a**/**5a** was determined at low degree of conversion of the bromide (Table II). Methanolysis of the cumyl bromide produces protons which may neutralize 4^-. Consequently, the nitroform anion was used in excess over methanol in these experiments. Since **5a** was produced only in small quantities, the obtained ratios represent a lower limit of the relative reactivity of the two competing nucleophiles.

Reversibility of the C–C Bond Cleavage. The reversibility of fragmentation of radical cations was probed in CH_2Cl_2 using diastereochemically pure *erythro*-3,4-dimethyl-3-(4-methoxyphenyl)-4-phenylhexane (**9**) and *meso*-3,4-dimethyl-3,4-bis(4′-methoxyphenyl)hexane (**10**). Irradiation of CT complexes of these compounds resulted only in cleavage products (α-trinitromethyl derivatives, see the Experimental Section). No aromatic alkylation or nitration was observed. Samples of **9** and **10** recovered after ca. 50% conversion of the starting materials showed no isomerization (<1%).



9-erythro (X = H)
10-meso (X = MeO)

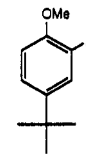


X = H, MeO

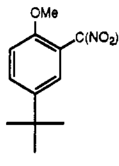
Additional testing of reversibility was carried out with **1a** using various concentrations of **2** in CH_2Cl_2. The ratio of **5b**/**6b** *increased* very slightly with decreasing concentration of **2**, from 1.5 at 1.5 M of **2** to 1.8 at 0.08 M of **2**.

Model Nitration Experiments. Treatment of **1a** or **1e** with $NO_2^\bullet$ in CH_2Cl_2/MeOH *did not* result in any nitro derivatives of **1a**,**e**. Under these conditions, only fragmentation products were observed (see the Experimental Section) yielding α-nitrocumenes (**11a**,**e**) and *p*-nitroanisole (**12**) among other products. Under identical conditions, *p*-*tert*-butylanisole yielded **12** and 2-nitro-4-*tert*-butylanisole (**13**). Irradiation of the CT complex of *p*-*tert*-butylanisole and **2** in CH_2Cl_2/MeOH resulted in ortho-trinitromethylation (**14**, 46%) and ortho-dinitromethylation (**15**, 36%). Only small amounts of **13** (13%) and *p*-nitroanisole (**12**, 4%) were detected.

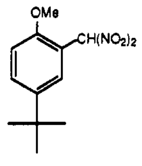
Aromatic Dinitromethylation. As indicated above, irradiation of the [*p*-*tert*-butylanisole···**2**]$_{CT}$ complex in CH_2Cl_2/MeOH produced a significant amount of 2-(dinitromethyl)-4-*tert*-butylanisole (**15**). The identical reaction was observed for *p*-methylanisole, and analogous products were detected for **1d**,**e** (Table I, footnote *e*). No such products were observed in other solvents used in this study. The **14**/**15** ratio was independent of MeOH concentration in the 0.25–5 M range, and similar results were obtained in pure MeOH. This ratio was also unaffected by addition of O_2 or nitroform to the reaction mixture.



13



14



15

The dinitromethyl derivative **15** could be independently prepared by irradiation of the [4-*tert*-butylanisole···nitroform]$_{CT}$ complex through Pyrex glass or uranium glass filters, but with a 420-nm cut-off filter this pathway of production of **15** was totaly inefficient. Although, during the irradiation of the CT complexes between *p*-*tert*-butylanisole and **2** in CH_2Cl_2 or CH_2Cl_2/MeOH, nitroform was produced in amounts equivalent to **13** formed (ca. 13–16%), the [4-*tert*-butylanisole···nitroform]$_{CT}$ complex did not absorb significantly above 420 nm. The dinitromethyl derivative *was not* produced from **14**. Irradiation of CH_2Cl_2/MeOH solution containing **14** using the 420-nm cut-off filter did not yield **15**. Similarly, irradiation of the [4-methylanisole···**2**]$_{CT}$ complex in the presence of **14** gave no **15**, although dinitromethyl derivative of *p*-methylanisole was produced in high yield.

Nanosecond Flash Experiments. Irradiation of [*p*-methylanisole···**2**]$_{CT}$ complex in CH_2Cl_2 and CH_3CN with a 8-ns 532-nm pulse from a YAG laser gave a broad absorption band with a λ_{max} at ca. 450 nm which was assigned to the radical cation of *p*-methylanisole in analogy to one observed by Kochi.[8] With an identical irradiation dose, the absorbance measured 10–50 ns after the pulse was ca. 10 times more intense in CH_3CN than in CH_2Cl_2. Irradiation of [**1a**,**d**···**3**]$_{CT}$ complexes under identical conditions gave no peak in the 450-nm region. In independent photoionization experiments (λ = 266 nm) carried out with **1a**–**e**, both the *p*-methoxycumyl cation and *p*-X-substituted cumyl radicals (but not the radical cations) were directly observed on a nanosecond time scale.[16,17]

Discussion

Electronic Similarity of the Donor Molecules. The irradiation of charge transfer complexes results in essentially instantaneous promotion of an electron within the CT complex and formation of $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet-}$, presumably as a CIP. This process was directly observed by Kochi et al. for various anisole derivatives,[8] including 4-methylanisole (**3**) and confirmed by us for 4-methylanisole. Rapid fragmentation (τ < 3 ps) of $\mathbf{2}^{\bullet-}$ to form nitroform anion (4^-) and $NO_2^\bullet$ competes with back-electron transfer (BET)

---

(16) (a) Prof. S. Steenken, private communication. (b) We have indepependently confirmed these observations. Thus, on the nanosecond time scale *p*-*tert*-butylanisole produced a "stable" radical cation, while in case of **1a**–**e** only fragments were observed. Picosecond time scale experiments are in progress.

(17) Thermodynamic considerations predict that in all cases the *p*-methoxycumyl cation and para-X-substituted cumyl radical should be the most stable fragments. Thus, oxidation potentials of cumyl radicals of importance to this work are (in V vs SCE, in CH_3CN): *p*-OMe –0.14, H, 0.16, *p*-CN 0.46. These redox potentials were obtained by D. D. M. Wayner (for the technique see: Wayner, D. D. M.; McPhee, D. J.; Griller D. *J. Am. Chem. Soc.* **1988**, *110*, 132). We are indebted to Dr. Wayner for these data. Compare also ref 14j.

within the ion pair.[8] This competition determines the quantum yield of the overall process. Since this step is common to all compounds studied (and **3**), the uniform quantum yields indicate that rates of BET are essentially the same for all pairs, implying that all radical cations are electronically very similar.

Also, similar CT formation constants for **1a–e** and **3** imply that the interaction between **2** and the *p*-methoxy ring of **1** is the major contributor to the complex formation. Additional confirmation of similarity of the electronic reservoir in all donor compounds comes from the observation that all donors under study, including **3** and 4-*tert*-butylanisole, have similar $h\nu_{CT}$ values in complexes with chloranil.[18]

Initial Photoinduced Processes. Photoinduced ET between the components of the CT complex leads to rapid (3 ps or less) formation of two ions (**1**$^{\bullet+}$ and **4**$^-$) and a radical ($NO_2^\bullet$) in a solvent cage.[8] This triad (A) is an intermediate common to all bicumenes (and **3**) studied. The fate of this triad and consequently the fate of **1**$^{\bullet+}$ depends strongly on substituent and solvent. (Scheme I).

Primary Reactions of Radical Cations. In CH_2Cl_2, **1a**$^{\bullet+}$ fragments to the *p*-methoxycumyl cation and cumyl radical[17] yielding a tetrad of reactive intermediates. In photoionization experiments, both the cation and radical were directly observed on a nanosecond time scale.[16] The radical cations must therefore fragment with rates faster than 5×10^8 s^{-1}. In the presence of **2**, the radical is rapidly oxidized[19] to another cumyl cation. This oxidation yields triad B of reactive intermediates that is similar to triad A and the tetrad. Both cumyl cations react with **4**$^-$ yielding **5a** and **5b**. In a competing process **1a**$^{\bullet+}$ undergoes trinitromethylation of the *p*-methoxy ring giving **6a**. Exclusive methylation of the anisole moiety requires that the unpaired electron in the reacting radical cation be localized on the methoxy-substituted half of the molecule in agreement with selective excitation of the CT band.

Reversibility of Bond Scission. To assure unambiguous interpretation of the results, the question of reversibility of C–C bond scission has been addressed using standard stereochemical probes. Within the limits of this technique, *erythro*-**9** and *meso*-**10** recovered from the reaction mixture showed no detectable loss of stereochemical integrity, thus excluding recombination of any (even slightly) separated fragments. These tests would not be able, however, to eliminate very rapid radical–cation recombinations that do not involve any separation of fragments.

The separate test carried out in the presence of varied amounts of **2** was designed to probe for the possibility that the oxidation of the radical formed by fragmentation is kinetically significant. Hypothetically, the cleavage reaction of **1a**$^{\bullet+}$ may lead to detectable products only when **2** oxidizes the cumyl radical, removing it from the equilibrium between the fragments and **1a**$^{\bullet+}$. Under such circumstances, lowering the concentration of **2** should increase the **6a**/**5b** ratio. Such effect was not observed, and the slight trend opposite to the one predicted may be due to changes in medium polarity (**2** ($\epsilon = 2.52$) is less polar than CH_2Cl_2 ($\epsilon = 9.1$)) or to electron hopping between neighboring molecules of **2**. Such a process would increase the probability of generation of products ions (i.e. cumyl and **4**$^-$) as solvent separated pairs or free ions. This mechanism would tend to increase the amount of **5b** produced over that of **6a**. The results of these tests practically exclude the possibility of reversible C–C bond scission influencing the product distribution.

Reactions of Geminate Ion Pairs. (a) Methylene Chloride. Both aromatic trinitromethylation and fragmentation occur at the geminate ion pair stage. The measured rates of reaction of **3**$^{\bullet+}$ and radical cations of other substituted anisoles with **4**$^-$ are near-diffusion limited in CH_2Cl_2.[8] In fact, a comparison of intensities of the published[8] transient spectra of **3**$^{\bullet+}$ obtained in CH_2Cl_2 and CH_3CN suggests that most of the reaction in CH_2Cl_2 occurs on the picosecond time scale. The optical density of **3**$^{\bullet+}$ in methylene chloride is ca. 10 times smaller than that in CH_3CN although the quantum yields of reactions in both solvents are similar.[8] The published data do not specify the irradiation dose employed; however, our measurements with the [*p*-methylanisole···**2**]$_{CT}$ complexes confirm that difference in optical density. These data imply that in CH_2Cl_2 most of **3**$^{\bullet+}$ and the radical cation of *p*-methylanisole reacted with **4**$^-$ before direct observation was possible. Thus, the second-order decays[8] correspond to annihilation of a small number of ions that escaped in-cage reactions, most likely by a mechanism involving an electron-transfer reaction with neighboring anisole or tetranitromethane molecules (as discussed above). In the latter case, high concentration of **2** used in these experiments (0.4–0.8 M) make such an electron jump quite plausible.

(b) Methylene Chloride/Methanol. Independent evidence for the geminate origin of **5b** and **6a** was obtained in our investigation by product studies performed in CH_2Cl_2/MeOH mixtures. For example with 2% (v/v) of MeOH, **1a** yields mostly cleavage products **5a**,**b** and **7a**,**b**. The presence of methanol slows down the rate of aromatic trinitromethylation, perhaps due to hydrogen bonding of **4**$^-$. On the other hand, judging by our experiments with radical cations of (*N*,*N*-dimethylamino)bicumenes,[20] methanol has rather small effect on rates of C–C bond scission. Importantly for our argument, methanol also competes with **4**$^-$ by trapping some of the cumyl cations and yielding ethers. Almost all of **5b** must be derived, however, from the geminate ion annihilation, due to the fact that the bulk concentration of MeOH is at least 100 times higher than that of **4**$^-$ and methanol reacts faster with cumyl cation than does **4**$^-$ (see below). It is important to note than in all reactions of **1a**$^{\bullet+}$ in CH_2Cl_2/MeOH the fragments (**5a**,**b** and **7a**,**b**) accounted for ca. 90% of the bicumene consumed. Under such circumstances the **7x**/**5x** is a sensitive and accurate reflection of the relative reactivity of the ion pairs involved.

When tetra-*n*-butylammonium **4**$^-$ and MeOH were allowed to compete for cumyl bromide in CH_2Cl_2 under conditions similar to those used in photochemical experiments the ratio of **7a** to **5a** was found to be very different from that observed upon irradiation of the CT complexes (Table II). This experiment illustrates that at comparable bulk concentrations of both competing nucleophiles, methanol is at least 14 times more effective than **4**$^-$ in trapping the cumyl cation. It is expected that *p*-methoxycumyl cation is at least as selective. It has to be

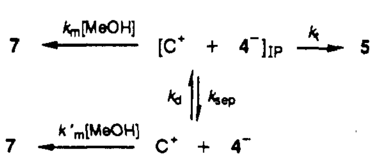
---

[18] Maslak, P.; Chapman, W. H., Jr. *J. Chem. Soc., Chem. Commun.* **1989**, 1809.

[19] Irreversible reduction potential (E_p in cyclic voltammetry) of **2** is −0.15 in CH_2Cl_2 vs SCE. However, **2** oxides *N*,*N*-dimethyl-*p*-*tert*-butylaniline ($E_{1/2}$ = 0.68 vs SCE) upon mixing. The hardest to oxidize radical, 4-cyanocumyl radical, has $E_{1/2}$ = 0.45 vs SCE (ref 17). The ability of **2** to oxidize cumyl radicals was independently confirmed in an experiment involving generation of these radicals in the presence of **2**. Thus, a 0.2 M the solution of di-*tert*-butyl peroxyoxalate in deoxygenated cumene kept at 55 °C for 40 min gave 70% yield of bicumene (based on the perester). Similar reaction carried out in the presence of 0.14 M **2** gave **5a** in ca. 50% yield. No bicumene was detected in this reaction. Cumene and **2**, without the perester, gave no reaction.

[20] Maslak, P.; Asel, S. L. *J. Am. Chem. Soc.* **1988**, *110*, 8260.

Scheme II



stressed that the addition of tetra-*n*-butylammonium salts (4^- or ClO_4^-) to the photochemical reaction medium had no effect on the **7x**/**5x** ratio (see below).

The presence of salts in the above experiments should favor formation of solvent separated ion pairs or free ions. The observed selectivity should be characteristic of such species. However, even under conditions similar to those of the photochemical experiments, MeOH was found to be a more effective nucleophile than 4^-. Thus, nitroform-induced (i.e. acid-catalyzed) solvolysis of cumyl alcohols produced **7x**/**5x** ratios much higher than those found in photochemical reaction. The observed differences between the cumyl and *p*-methoxycumyl alcohols also fit the geminate ion reactivity patterns. Thus, the protonated cumyl alcohol (or ether **7a**) dissociates slowly enough to allow 4^- to escape the cage. As a result, very little **5a** forms in this case. More reactive (in their protonated forms) *p*-methoxycumyl alcohol and ether **7b** fragment rapidly while still ion paired with 4^-, resulting in production of **5b**. All these solvolysis experiments strongly suggest that 4^- is a competent nucleophile only in contact ion pairs; solvation by MeOH diminishes its reactivity significantly. Thus, the in-cage ion annihilation is necessary to account for the low **7x**/**5x** ratios in the photochemical system.

Under such conditions, the kinetic scheme for generation of **5x** and **7x** is relatively simple (Scheme II: C^+ = any cumyl cation, IP = any geminate ion pair). According to this model the geminate ion annihilation within the ion pair (in this case equivalent to the tetrad) competes with methanol trapping of that pair. This model predicts a linear correlation of the **7x**/**5x** ratio with MeOH concentration. Systematic studies of this system with various amounts of methanol added to the reaction mixture (Figure 1) confirm this model. The observed linear correlation with a characteristic zero intercept is consistent with involvement of contact ion pairs.[21] The slope of of the line in Figure 1 corresponds to k_m/k_t, where k_m is the rate constant for reaction with methanol and k_t is the rate constant for in-cage α-trinitromethylation.[21]

All these results require that C–C bond fragmentation is faster than ion separation in this medium. Additional support for this interpretation is obtained from an experimental involving addition of tetra-*n*-butylammonium 4^- to the reaction mixture. Added 4^- leads to a small *increase* of the **7b**/**5b** ratio. A similar effect is caused by addition of tetra-*n*-butylammonium perchlorate. Based on classical interpretation of ion pair reactivity in solvolysis reactions,[12] this result clearly implies that the ion pair of Scheme II corresponds to the contact ion pair. Thus, the tetrad, and consequently triad A, must also represent CIP.

Analysis of analogous data for **7a**/**5a** (Figure 1) obtained in these experiments indicates that a similar ion pair is involved in the case of cumyl cation as well. Thus, rapid fragmentation of $2^{\bullet-}$ (produced from oxidation of the cumyl radical) yields triad B, which is kinetically equivalent to the tetrad. It has to be noted that this ion pair is produced by collisional ET between cumyl radical and **2**. Despite the fact that the solvent reorganization necessary to accomplish the charge transfer should be advanced in the transition state, the outcome of this ET process is also a contact ion pair. In agreement with this interpretation, addition of salts of 4^- does not decrease the **7a**/**5a** ratio.

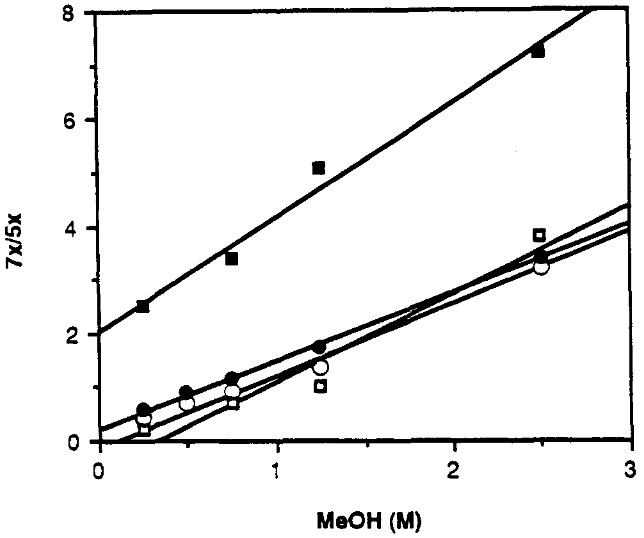


Figure 1. The ratio of methyl esters to α-trinitromethylation product (**7x**/**5x**) obtained by irradiation of $[1a\cdots2]_{CT}$ in solution containing varying amounts of MeOH. Open circles, **7b**/**5b** in CH_2Cl_2, filled circles, **7a**/**5a** in CH_2Cl_2; open squares, **7b**/**5b** in CH_3/CN; filled squares, **7a**/**5a** in CH_3CN.

(c) Acetonitrile and Acetonitrile/Methanol. In a polar medium (CH_3CN), where reactivity of 4^- is diminished, aromatic *nitration* (radical collapse) competes with the fragmentation of $1a^{\bullet+}$. In the latter case, as indicated by the effect of added MeOH, the cleavage still takes place at the geminate ion pair stage. Measurable quantities of **5a,b** are observed despite the large excess of MeOH over 4^- in this reaction mixture. Moreover, as found in experiments with cumyl bromide (Table II), MeOH traps the cumyl cations more efficiently than 4^- in this solvent system.

A more detailed study of the effect of added methanol is summarized in Figure 1. The **7b**/**5b** ratio is a function of the added methanol with zero intercept. This ratio is unaffected by added 4^-. The similarity of this function to one observed in CH_2Cl_2 and the undetectable effect of the added common ion (4^-) suggest that in this case CIP are again involved, i.e. the tetrad corresponds to a contact ion pair.

A dramatically different situation is found for the **7a**/**5a** ratios. As discussed above, these products are the results of a thermal ET reaction between cumyl radical and **2**. The observed correlation is significantly shifted as compared to the other lines, and a non-zero intercept[21] is observed (Figure 1). Additionally the **7a**/**5a** ratio is affected by added 4^- (Table II). These results indicate that the ions in this case (triad B) must react, at least parialy, at the SSIP stage. Ion pairs rather than free ions are required to explain the different **7a**/**5a** ratio in this system as compared to one wherein cumyl cation competes for similar bulk concentrations of MeOH and 4^-.

Substituent Effects. In CH_2Cl_2, for bicumenes with electron-donating substituents ($1b,c^{\bullet+}$), the C–C cleavage is the dominant process observed, for compounds bearing electron-withdrawing substituents ($1d,e^{\bullet+}$) only aromatic alkylation is detected (**6d,e**). Since all the radical cations are expected to have similar diffusive properties and the

---

(21) Using a steady-state assumption for IP and free ions, taking into account that under the reaction conditions k_m[MeOH] ≫ k_d[4^-], the 7/5 ratio can be expressed as follows: $7/5 = (k_m/k_t)[\mathrm{MeOH}] + k_{sep}/k_t$. Explicit inclusion of two ion pairs gives a more complex expression, but a zero intercept is possible only if the competition between **2** and MeOH takes place at the CIP stage.

rate of aromatic trinitromethylation should not depend on substituion on the other ring,[22] the observed changes must be attributed mainly to different rates of fragmentation. To account for the almost exclusive formation of fragments, electron donating groups (*p*-Me, *p*-MeO) have to facilitate the cleavage by a factor of at least 10, indicating that the scission is taking place completely in the original solvent cage. On the other hand, *p*-CN and *p*-CF_3 groups slow down the fragmentation more than ten fold.

Similar effects are observed in other solvents. In a nonpolar solvent such as cyclohexane, where reactivity of 4^- is at its highest, the aromatic trinitromethylation of $\mathbf{1a}^{\bullet+}$ (ion annihilation) is faster than its cleavage (Table I). Similarly, no fragmentation products are detected in the case of $\mathbf{1c}^{\bullet+}$, but cleavage of $\mathbf{1b}^{\bullet+}$ can still successfully compete with aromatic trinitromethylation. These data indicate that the *p*-methoxy substituent accelerates the rate of C–C bond scission at least 10-fold compared to the methyl group if equal rates of aromatic trinitromethylation for $\mathbf{1b}^{\bullet+}$ and $\mathbf{1c}^{\bullet+}$ are assumed.[22] In more polar media (CH_2Cl_2/MeOH) where reactivity of 4^- is diminished, even the "slow" fragmentation of $\mathbf{1d}^{\bullet+}$ and $\mathbf{1e}^{\bullet+}$ has a chance to ocur at the expense of aromatic trinitromethylation, dinitromethylation, or nitration. In these cases (**1d,e**) the ratio of cleavage rates cannot be easily estimated from the available data due to the fact that diffusional ion separation influences the ratio of products (see below). An additional complication is caused by the fact that the aromatic dinitromethylation most likely takes place at a different ion pairing stage than the aromatic trinitromethylation (see below).

The remarkable effect of the substituent on the rate of cleavage indicates a significant charge transfer to the X-substituted ring in the transition state. Assuming that the observed differences in ratios of fragmentation products to aromatic substitution products are purely due to the changes in rates of C–C bond fragmentation (a factor of 10 per substituent for $\mathbf{1a}$–$\mathbf{1d}^{\bullet+}$), the value of ρ^+ can be estimated at ca. –2.2. For comparison, the ρ^+ value measured[23,24] for solvolysis of cumyl chlorides is ca. –4.5. For the solvolysis reaction, it has been estimated[24] that 75–90% of the carbocation character is developed in the transition state. Neglecting solvent differences, this comparison suggests that up to half of the charge is transferred from the anisole moiety to the other ring in the transition state for C–C bond scission.

Ultimately, however, the X-substituted cumyl fragments end up as radicals (see above), as expected from thermodynamic considerations.[14j,17] Therefore, the electron density shift accompanying the cleavage reaction has to reverse its direction at, or after, the transition state. Such a polarization of the transition state is reminiscent of the kinetic control observed in the cleavage reaction of radical anions.[25] Thus, it seems that radical ion scission processes that do not require the reversal of charge will be more facile, i.e. fragmentations involving the charge transfer across the scissile bond are kinetically preferred. Such charge transfer assures better charge delocalization in the transition state, and this in turn suggests that the size of this kinetic effect may be influenced by solvent polarity.[18] Additionally, the comparison of the ρ^+ value estimated from these experiments (–2.2) with one measured for the radical cations of (dimethylamino)bicumenes[20] (–0.8) is now available. The latter involves relatively slow reactions (10^{-2} at 253 K) with activation energy of ca. 15 kcal/mol at 300 K, while the radical cations of methoxybicumenes undergo scission on the picosecond time scale, in a process which must have very small activation energy. This comparison suggests that the kinetic control caused by charge delocalization is more important for reactions with earlier transition states. Such an increase in selectivity for reactions with earlier transition states is an example of a violation of the reactivity–selectivity principle.

Alternatively, the substituent effect may reflect a process wherein the kinetically significant step involves a large component of the intramolecular electron transfer from the σ orbital of the scissile bond to the π-system with the unpaired electron. Such a situation would call for an unusual separation of π- and σ-networks in the system where the overlap between these networks is unhindered. Although without additional evidence such a model is difficult to accept, it has a precedent in radical anion chemistry[25d] where it has been traced to the reluctance of the system to delocalize the excess of charge across the scissile bond.

Side-chain substitution in **9** and **10** introduces extra strain along the scissile bond.[26] As expected this strain accelerates the rate of radical cation fragmentation, making it faster than the aromatic trinitromethylation. Thus, in the case of **9** only cleavage products are observed in CH_2Cl_2 (as compared to **1a** wherein both these processes have comparable rates), and in the case of **10** only fragmentation products are detected in both Ch_2Cl_2 and cyclohexane. For comparison, in cyclohexane $\mathbf{1b}^{\bullet+}$ undergoes mostly aromatic trinitromethylation (Table I).

The experiments with substituted radical cations $\mathbf{1a}$–$\mathbf{e}^{\bullet+}$ in mixed solvents provide additional support for the analysis of ion pairing of intermediates involved in these reactions. In CH_2Cl_2/MeOH the **7b**/**5b** ratios found for **1a–d** are identical, suggesting that in all cases CIP's are involved (see above). This situation changes for $\mathbf{1e}^{\bullet+}$, where the **7b**/**5b** ratio is slightly smaller, implying that the cleavage may partially take place at the SSIP stage. Interestingly, the **7x**/**5x** (**x** ≠ **b**) ratio is quite different for $\mathbf{1d,e}^{\bullet+}$ than it is for $\mathbf{1a}^{\bullet+}$. In fact, these ratios resemble those observed in CH_3CN/MeOH. We suggest that this outcome is a result of better solvation of the components in the transition state necessary to bring about the electron transfer between **2** and these tougher to oxidize cumyl radicals.[14j,17]

Reactions of Radical Pairs. Surprisingly, the final outcome of the majority of reactions is decided by ion-annihilation reactions. The plausible radical coupling processes (nitration) are detected only in a few instances in the most polar media where ion stabilization is the greatest. This observation suggests existence of some barrier to radical/radical cation coupling ($NO_2^\bullet/\mathbf{1}^{\bullet+}$) and radical/radical coupling (cumyl radical/$NO_2^\bullet$). In our system the latter process must be slower than the oxidation of the cumyl radical by **2**.

The aromatic nitration can follow at least two different mechanisms, one involving radical collapse ($\mathbf{1}^{\bullet+} + NO_2^\bullet$) and one initiated by attack of $NO_2^\bullet$ on the neutral bi-

---

[22] The electronic similarity of neutrals as expressed by $h\nu_{CT}$ (ref 18) and K of their CT complexes, as well as of their radical cations as indicated by the measured quantum yields, indicate that the remote substituent has very small effect on the *p*-methoxyphenyl moiety.

[23] Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979.

[24] Arnett, E. M.; Hofelich, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 2883 and references therein.

[25] (a) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628 and 2637. (b) Walsh, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 1511. (c) For operational convenience this kinetic control of the cleavage has been formulated[25a] as the preference for spin regioconversion. (d) Maslak, P.; Narvaez, J. N.; Kula, J.; Malinski, D. S. *J. Org. Chem.*, in press.

[26] (a) Krat, G.; Beckhaus, H.-D.; Lindner, H. J.; Rüchardt, C. *Chem. Ber.* **1983**, *116*, 3235. (b) Krat, G.; Beckhaus, H.-D.; Rüchardt, C. *Chem. Ber.* **1984**, *117*, 1748.

cumene. The independent experiments with **1a**,**e** and $NO_2^\bullet$ in CH_2Cl_2/MeOH show that **8a**,**e** are not formed under these conditions. Moreover, products characteristic of this reaction (**12** and **13**) are not present in mixtures obtained from irradiation of $[\mathbf{1a,e}\cdots\mathbf{2}]_{CT}$ complexes. We conclude, therefore, that the nitration products **8a**,**d**,**e** are the result of radical-collapse nitration. Thus, $NO_2^\bullet$ is indeed a bystander to all the cage processes described above. Its relative unreactivity with $\mathbf{1}^{\bullet+}$ may possibly be explained by the formation of a CT complex between these two species as suggested[8] by Kochi et al. However, this explanation seems inadequate to account for the absence of products derived from coupling at the benzylic position. Perhaps, $NO_2^\bullet$ is ejected (by the rapidly dissociating $\mathbf{2}^{\bullet-}$) away from the radical cation, and it is sterically screened from the reactive site by bulky $\mathbf{4}^-$.

Aromatic Dinitromethylation. In the case of *p*-methylanisole, *p*-*tert*-butylanisole, **1d** and **1e**, in addition to aromatic trinitromethylation, aromatic dinitromethylation was observed in reactions run in CH_2Cl_2/MeOH or pure methanol. These products were not detected in any other solvent system of this study. The dinitromethyl derivative was not formed by a thermal or photochemical pathway from the corresponding trinitromethyl compound as indicated by studies on **14**. Irradiation of mixtures of **14** (λ > 420 nm) with $[p\text{-methylanisole}\cdots\mathbf{2}]_{CT}$ complexes gave no detectable amount of **15**, while *p*-methylanisole underwent extensive dinitro- and trinitromethylation. The dinitromethyl derivatives could be conveniently produced by irradiation of the CT complexes between the nitroform and the anisole donors but only with shorter wavelength light. Irradiation above 420 nm was totaly ineffective. Even a hypothetical energy-transfer process from the CT complex of **2** to nitroform or its CT complex was excluded, since addition of nitroform to the reaction mixtures containing 4-*tert*-butylanisole and **2** did not increase the yield of **15**. Also, saturation of the reaction mixture with oxygen did not have any effect on the reaction, excluding participation of oxygen-scavengable, freely diffusing radicals. Finally, irradiation of mixtures containing *p*-*tert*-butylanisole and a large excess of $\mathbf{4}^-$ also gave no reaction.

It appears, therefore, that formation of radical cations of the anisole derivatives is a prerequisite to the formation of the dinitromethyl compounds. Since the reaction is only observed in CH_2Cl_2/MeOH but not in CH_3CN/MeOH it is likely that the ion annihilation and not the radical collapse yields a precursor of the dinitromethyl compound. The reaction also requires a relatively long-lived radical cation. It is only observed for the slowly fragmenting radical cations of bicumenes ($\mathbf{1d,e}^{\bullet+}$) and persistent radical cations of *p*-alkylanisoles (no rapid unimolecular reaction available). These considerations suggest that the dinitromethyl and trinitromethyl derivatives are both derived from the attack of $\mathbf{4}^-$ on the radical cation, but at different solvation stages. Thus, the geminate ion annihilation leads to aromatic trinitromethylation, after hydrogen atom abstraction by $NO_2^\bullet$ present in the cage. The dinitromethyl derivative might be formed from reencounters of the geminate ions or by collisions of nongeminate pairs. Better solvation of these ions and the absence of $NO_2^\bullet$ may enforce a different reaction pathway. For example, loss of HNO_2 followed by hydrogen abstraction by the resulting α,α-dinitrobenzyl radical might complete the reaction.

It has to be stressed that the aromatic dinitromethylation is limited only to the relatively long-lived radical cations and is observed only in CH_2Cl_2/MeOH mixtures. The conclusions of the ion pairing study performed for rapidly fragmenting $\mathbf{1a}^{\bullet+}$, and of the substituent studies carried out in solvent containing no MeOH are not affected by this side reaction. No dinitromethyl derivatives were detected in these cases.

Summary and Conclusions

Electron transfer from **1a**–**e** to **2**, initiated by irradiation of the charge-transfer complexes between the reactants, leads to efficient formation of ion and radical pairs. The rapid decomposition of $\mathbf{2}^{\bullet-}$ results in the triad of reactive intermediates (A) and sets the stage for subsequent ion and radical reactions whose relative rates are strongly dependent on substitution and solvent. In nonpolar solvent (cyclohexane) the ion annihilation ($\mathbf{1}^{\bullet+} + \mathbf{4}^-$) dominates, and only the most rapidly fragmenting radical cations ($\mathbf{1b}^{\bullet+}$ and $\mathbf{10}^{\bullet+}$) may escape the aromatic trinitromethylation. In CH_2Cl_2 the C–C bond scission is able to compete with the aromatic substitution for $\mathbf{1a\text{–}c}^{\bullet+}$, $\mathbf{9}^{\bullet+}$, and $\mathbf{10}^{\bullet+}$, but $\mathbf{1e,d}^{\bullet+}$ are trapped by $\mathbf{4}^-$ before they have a chance to undergo fragmentation. Addition of a polar component (MeOH) to the reaction mixture favors fragmentation over aromatic trinitromethylation.

The fragmentation of $\mathbf{1}^{\bullet+}$ produces *p*-methoxycumyl cations and para-X-substituted cumyl radicals. The latter are oxidized by **2** to form cumyl cations in close proximity to $\mathbf{4}^-$ and $NO_2^\bullet$. All the cumyl cations undergo α-trinitromethylation or react with added MeOH. The results of the competition between the two nucleophiles provide convincing evidence that these reactions are taking place at the CIP stage. This experimental system gives us a unique opportunity to compare the reactivity of ions formed via irradiation of the CT complexes with those produced by thermal electron transfer. In a medium of low polarity (CH_2Cl_2/MeOH) the ion pairs produced by both pathways are kinetically equivalent. In a medium of higher polarity (CH_3CN/MeOH) the fragmentation of $\mathbf{1a\text{–}d}^{\bullet+}$ still takes place at the CIP stage, but similar ion pairs (triad B) produced by thermal ET correspond to SSIP's. Only in the polar solvents, where reactivity of ions is the lowest, can products of radical reactions be observed.

The dramatic substituent effect indicates a significant charge transfer across the scissile bond in the transition state for C–C bond scission. Taking into account that the X-substituted fragment ends up as a radical, this polarization of the transition state suggests that a reversal of the charge distribution is necessary after the highest point on the potential energy surface. In analogy to radical anion cleavage,[25] this result suggests that the fragmentation of radical cations in which the charge is fully transferred across the scissile bond is kinetically advantageous over a mode of cleavage wherein the "reversal" of charge distribution is necessary to obtain the thermodynamically most stable ion and radical.[25]

The radical cations of **1a**–**e** provide us with the opportunity to use the rapid C–C bond fragmentation as a tunable probe[27] for dynamics of various ion and radical pairs involved in photoinduced ET reactions. All the radical cations cleave extremely rapidly (ca. 10^{10}–10^8 s^{-1}),[27,28] indicating tremendous activation of the central C–C bond.[20] The substituents can dramatically alter the fine balance between chemical and diffusional steps. The

---

[27] The measurements of the absolute rates of C–C bond scission in these radical cations are in progress.

[28] These rates estimates are based on our preliminary nanosecond time-scale experiments (ref 16) which agree well with extimates based on an apparently invariable rate (5×10^8 s^{-1}) of ion separation in CH_3CN (ref 4). Compare also refs 14i and 18.

results of these variations are different products whose ratios can be used as sensitive probes for ion solvation and radical reactions.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on either a Bruker WM360 or WM200 and are reported in ppm in reference to TMS. Absorption measurements were made with a HP 8450 UV/vis spectrophotometer. Gas chromatography was performed on a Varian 3700 with FI detector using either a 50 or 100 cm by $^1/_8$ in. column packed with 5% OV101 on 80/100 Supelcoport. Hexadecane or octadecane were used as internal standards. Error in all GC measurements was determined through reproducibility (four injections per sample). Mass spectra were obtained on a Kratos MS 9/50 double focusing spectrometer in electron impact (EI) mode. Peaks reporter here were either considered structurally significant or had an intensity greater than 10% of the base peak. IR spectra were recorded on a Perkin-Elmer 281B spectrophotometer. Pellets were pressed from KBr powder in a minipress and films were cast from chloroform onto NaCl plates.

All materials were purchased from Aldrich and used as received unless indicated otherwise. Solvents used for all reactions were spectrophotometric or HPLC grade. THF was distilled from potassium/benzophenone under argon. Preparative flash chromatography was carried out using Merck silica gel 60 (230–400 mesh). Preparative and analytical TLC was run on Merck precoated plates with layer thicknesses of 0.5 and 0.25 mm, respectively. Methylene chloride–hexane mixtures (listed as volume by volume ratios, *r*) were used as eluents in analytical and preparative chromatography.

Preparation of Starting Materials. 4-Methoxycumene was prepared by methylation of 4-isopropylphenol with dimethyl sulfate. 4-Cyanocumene[29] was prepared from 4-isopropylbenzaldehyde with hydroxylamine-*O*-sulfonic acid. 4-(Trifluoromethyl)cumene[30] and tetranitromethane[31] (**2**) were prepared according to the published procedures. All 4-X-cumenes were distilled to a purity greater than 98% (by GC). 4-Methoxy-4′-X-bicumenes (**1a–e**) were prepared by combining equimolar amounts of the appropriately substituted cumenes (0.066–0.075 mol each) and 1 equiv (0.066–0.075 mol) of di-*tert*-butyl peroxide. The mixtures were deoxygenated by bubbling argon and refluxed for 12–24 h. Addition of di-*tert*-butyl peroxide was continued until 40–60% of the starting materials had been consumed (GC). This usually required a total of 4 equiv of the peroxide. Crude dimethoxybicumene could be isolated from the mixture by filtering the precipitate which formed upon cooling. In case of unsymmetrical bicumenes, starting materials as well as any volatile products of the reaction were distilled off from the mixture under reduced pressure (ca. 0.01 Torr, at 100 °C), and the residue was separated by flash chromatography. Typical yields of purified (crystallized) unsymmetrical bicumenes were 15–20%. ^{13}C NMR spectra of the bicumenes are collected in Table III.

4-Methoxybicumene (1a): recrystallized twice from 95% EtOH; 99% pure by GC; mp 99–101 °C; $R_f = 0.45$ ($r = 0.25$); ^{1}H NMR ($CDCl_3$) 1.28 (s, 6 H), 1.30 (s, 6 H), 3.79 (s, 3 H), 6.71 (d, $J = 9$ Hz, 2 H), 6.96 (d, $J = 9$ Hz, 2 H), 7.04 (m, 2 H), 7.17 (m, 3 H); IR (KBr) 1610, 1500, 1280, 1230, 1170, 1010, 810 cm^{-1}; MS (relative intensity) 268 (0.3), 149 (100), 135 (25), 119 (13), 91 (19).

4,4′-Dimethoxybicumene (1b): sublimed; 98% pure by GC; mp 174–176 °C; $R_f = 0.50$ ($r = 0.67$); ^{1}H NMR ($CDCl_3$) 1.3 (s, 12 H), 3.8 (s, 6 H), 6.7 (d, $J = 9$ Hz, 4 H), 6.96 (d, $J = 9$ Hz, 4 H); IR (KBr): 1610, 1500, 1230, 1170, 1010, 810 cm^{-1}; MS (relative intensity) 298 (0.5), 149 (100), 91 (13).

4-Methoxy-4′-methylbicumene (1c): recrystallized three times from 2-propanol; 98% pure by GC; mp 102–105 °C; $R_f = 0.48$ ($r = 0.25$); ^{1}H NMR ($CDCl_3$) 1.3 (s, 12 H), 2.3 (s, 3 H), 3.8 (s, 3 H), 6.72 (d, $j = 9$ Hz, 2 H), 6.93 (m, 6 H); IR (KBr) 1600, 1500, 1230, 1170, 1020, 810 cm^{-1}.

4-Methoxy-4′-(trifluoromethyl)bicumene (1d): recrystallized twice from 95% ethanol; 99% pure by GC; mp 72–74 °C; $R_f = 0.48$ ($r = 0.25$); ^{1}H NMR ($CDCl_3$) 1.29 (s, 6 H), 1.32 (s, 6 H), 3.79 (s, 3 H), 6.72 (d, $J = 9$ Hz, 2 H), 6.93 (d, $J = 9$ Hz, 2 H), 7.12 (d, $J = 8$ Hz, 2 H), 7.41 (d, $J = 8$ Hz, 2 H); IR (KBr) 1610, 1490, 1310, 1230, 1110, 1020, 830, 810 cm^{-1}; MS (relative intensity) 187 (6), 149 (100).

4-Methoxy-4′-cyanobicumene (1e): recrystallized twice from 95% ethanol; 98% pure by GC; mp 134–135 °C; $R_f = 0.28$ ($r = 0.67$). ^{1}H NMR ($CDCl_3$) 1.29 (s, 6 H), 1.32 (s, 6 H), 3.79 (s, 3 H), 6.72 (d, $J = 9$ Hz, 2 H), 6.89 (d, $J = 9$ Hz, 2 H), 7.10 (d, $J = 9$ Hz, 2 H), 7.51 (d, $J = 9$ Hz, 2 H); IR 2180, 1600, 1500, 1230, 1170, 1020, 810 cm^{-1}.

***erythro*-3,4-Dimethyl-3-(4′-methoxyphenyl)-4-phenylhexane (9) and *meso*-3,4-Dimethyl-3,4-bis(4′-methoxyphenyl)hexane (10).** *meso*-3,4-Dimethyl-3,4-diphenylhexane[32] was dinitrated with nitric acid in acetic anhydride and purified by recrystallization from 95% ethanol: ^{1}H NMR ($CDCl_3$) 0.59 (t, $J = 7$ Hz, 6 H), 1.33 (s 6 H), 1.59 (m, 2 H), 2.21 (m, 2 H), 7.06 (d, $J = 8$ Hz, 4 H), 8.04 (d, $J = 8$ Hz, 4 H). The 4′,4″-dinitro derivative was reduced to the diamine with H_2 (4 atm) over 10% palladium on carbon in EtOAc: ^{1}H NMR ($CDCl_3$) 0.56 (t, $J = 7$ Hz, 6 H), 1.16 (s, 6 H), 1.41 (m, 2 H), 2.08 (m, 2 H), 6.50 (d, $J = 8$ Hz, 4 H), 6.73 (d, $J = 8$ Hz, 4 H). The crude diamine was diazotized[33] with boron trifluoride etherate/*tert*-butyl nitrite in a 9:1 mixture of methylene chloride and THF. The bisdiazonium tetrafluoroborate salt was precipitated in hexane, filtered, and air-dried: ^{1}H NMR (MeCN-d_3) 0.58 (t, $J = 7$ Hz, 6 H), 1.36 (s, 6 H), 1.65 (m, 2 H), 2.19 (m, 2 H), 7.41 (d, $J = 9$ Hz, 4 H), 8.29 (d, $J = 9$ Hz, 4 H). It was decomposed in refluxing methanol, and the desired products were isolated from the mixture by flash chromatography with a methylene chloride–hexane gradient.

***erythro*-3,4-Dimethyl-3-(4′-methoxyphenyl)-4-phenylhexane (9)**: recrystallized from 95% EtOH; 96% pure by GC; $R_f = 0.48$ ($r = 0.25$); ^{1}H NMR ($CDCl_3$) 0.55 (t, $J = 8$ Hz, 6 H), 1.22 (s, 3 H), 1.24 (s, 3 H), 1.50 (m, 2 H), 2.18 (m, 2 H), 3.79 (s, 3 H), 6.71 (d, $J = 9$ Hz, 2 H), 6.84 (d, $J = 9$ Hz, 2 H), 6.94 (m, 2 H), 7.16 (m, 3 H). ^{13}C NMR ($CDCl_3$) 9.2, 20.8, 20.9, 27.6, 27.7, 47.6, 48.3, 55.1, 111.7, 111.8, 125.2, 126.4, 129.9, 130.8, 135.6, 143.8, 157.1.

***meso*-3,4-Dimethyl-3,4-bis(4′-methoxyphenyl)hexane (10)**: recrystallized from 95% EtOH; 99% pure by GC; mp 83–84 °C; $R_f = 0.47$ ($r = 0.67$); ^{1}H NMR ($CDCl_3$) 0.54 (t, $J = 7$ Hz, 6 H), 1.2 (s, 6 H), 1.44 (dq, $J = 7$ Hz, $J = 7$ Hz, 2 H), 2.11 (dq, $J = 7$ Hz, $J = 7$ Hz, 2 H), 3.78 (s, 3 H), 6.7 (d, $J = 9$ Hz, 4 H), 6.8 (d, $J = 9$ Hz, 4 H).

Trinitromethane was prepared by a published procedure.[34] Tetranitromethane (20 g) was added to a solution of KOH (13 g) in 12 mL of H_2O and 28 mL of EtOH. The yellow precipitate formed was filtered, washed with absolute EtOH and anhydrous ether, and dried in vacuum (*Caution*: *the salt might be explosive*!). The potassium salt (8.2 g) was suspended in 50 mL of pentane. The yellow mixture (kept below 5 °C) was titrated with concentrated H_2SO_4, giving a colorless solution and a white solid. The liquid was decanted and cooled in the freezer overnight giving a white crystalline compound, mp <25 °C.

Formation Constants of CT Complexes and Quantum Yield Measurements. Formation constants of charge-transfer complexes were measured at 480 and 500 nm using the Benesi–Hildebrand technique.[15] Correlation coefficients for all determinations were greater than 0.98. Error was determined through reproducibility (4 runs). The values measured in CH_2Cl_2 were (K (M^{-1}), ϵ_{480} (M^{-1} cm^{-1})): **1a**, 0.17, 101; **1b**, 0.23, 146; **1e**, 0.15, 93; **3**, 0.18, 102. For comparison bicumene has $K = 0.18$ M^{-1} and $\epsilon_{480} = 4.8$ M^{-1} cm^{-1}.

Quantum yields for disappearance of **1a–e** were measured at 450 [illegible] 10 and 520 ± 10 nm using a single grating monochromator (GM100 from spectral energy) with a 1-mm slit. Light was provided by a 150-W Xe or Xe/Hg lamp. All reactions were run in 10-mm pathlength cuvettes sealed with Teflon-lined septa. The monochromator output was split into two perpendicular beams with an Oriel prism. The split ratio at the irradiation frequency

---

(29) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647.

(30) Arnold, D. R.; Nicholas, A. M. de P.; Snow, M. *Can. J. Chem.* **1985**, *63*, 1150.

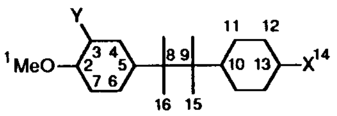
(31) Liang, P. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 803.

(32) Huang, R. L.; Kum-Tatt, L. *J. Chem. Soc.* **1954**, 2570.

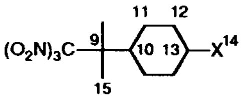
(33) Bryker, W. J.; Doyle, M. P. *J. Org. Chem.* **1979**, *44*, 1572.

(34) Homer, J.; Huck, P. J. *J. Chem. Soc. A* **1968**, 272.

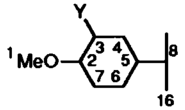
Table III. Carbon NMR Chemical Shifts of 1, 5, 6, 8, and 15



compd	Y =	X =	1	2	3	4	5	6	7	8[a]	9[a]	10	11	12	13	14	15[a]	16[a]
6e		CN	56.4	157.0	111.0	135.5	139.0	129.3	117.0	43.5	44.4	151.3	128.9	130.7	110.0	119	24.5	24.4
6d		CF_3	56.3	157.0	111.0	135.5	139.4	129.4	110.9	43.5	44.1	149.8	128.5	123.7[e]	128.4[f]	124.2[g]	24.6	24.6
6a	$(NO_2)_3C$[b]	H	56.3	156.8	110.7	135.5	140.0	129.7	110.6	43.6	43.7	145.4	126.9	128.2	126.0		24.7	24.7
6c		Me	56.3	156.7	110.6	135.3	142.3	127.3	110.6	43.4	43.7	140.1	127.3	127.6	135.8	20.7	24.7	24.7
1e		CN	55.1	157.5	112.0	129.4	137.8			43.0	44.5	152.7	129.2	130.3	109.2	119.2	25.1	24.9
1d	H	CF_3	55.1	157.5	111.9	129.5	139.5			42.9	44.1	151.2	128.9	123.4[h]	127.7[i]	124.4[j]	25.1	25.1
1a		H	55.1	157.1	111.8	128.6	139.0			43.0	43.7	146.8	126.6	129.6	125.4		25.3	25.1
1c		Me	55.1	157.2	111.8	129.6	139.0			42.9	43.3	143.9	127.3	128.5	134.7	20.8	25.3	25.2
1b		OMe	55.1	157.3	111.8	129.6	139.1			43.1		151.8					25.3	
	$(NO_2)_2HC$[c]	CN	56.1	156.2	112.5	134.1	139.1	129.1	109.8	43.3	44.4		128.6	130.7	109.6	119.0	24.9	24.7
8a	NO_2	H	56.4	150.8	138.1	125.9	139.4	134.2	111.4	43.6	43.4	145.7	126.7	128.4	125.6		25.0	24.9



compd	Y =	X =	1	2	3	4	5	6	7	8[a]	9[a]	10	11	12	13	14	15[a]	16[a]
5e		CN									47.6	142.4	129.9	132.1	113.0	117.7	26.7	
5d		CF_3									47.5	*k*	129.7	125.4[l]	*k*	*k*	26.8	
5a		H									47.7	137.3	128.5	129.1	128.9		26.7	
5c		Me									47.5	139.2	128.8	129.2	134.2	20.9	26.8	



compd	Y =	X =	1	2	3	4	5	6	7	8[a]	9[a]	10	11	12	13	14	15[a]	16[a]
14	$(NO_2)_3C$[b]		56.4	157.0	111.9	133.3	144.5	125.9	112.5	34.5								31.2
15	$(NO_2)_2HC$[d]		56.0	156.0	113.4	131.4	144.4	125.5	110.9	34.3								31.3

[a] Some assignments might be reversed: 8 ↔ 9, 15 ↔ 16. [b] Trinitromethyl carbon not observed. [c] Dinitromethyl carbon: 108.0. [d] Dinitromethyl carbon: 108.3. [e] Quartet, J_{CF} = 4.2 Hz. [f] Quartet, J_{CF} = 32 Hz. [g] Quartet, J_{CF} = 272 Hz. [h] Quartet, J_{CF} = 3.6 Hz. [i] Quartet, J_{CF} = 32 Hz. [j] Quartet, J_{CF} = 272 Hz. [k] Not observed due to small amount of sample. [l] Quaret, J_{CF} = 3.8 Hz.

was measured with ferric oxalate actinometry.[35] In a typical run, the bicumene (ca. 20 mg) and an internal standard were weighed into a 25-mL volumetric flask. This solution (2 mL) and 200 μL of 2 were transferred under argon to a cuvette. The absorbance of the sample was measured before and after the irradiation to correct for light loss due to incomplete absorption. The cuvette with the mixture was placed in one beam of light, while the actinometer solution was placed in the other. The samples were analyzed by GC after 1–5 h of irradiation, when the degree of conversion was less than 15%. Multiple measurements gave quantum yields of 0.20 ± 0.05 for all bicumenes (**1a–e**).

Flash Photolysis Experiments. The laser flash experiments were carried out at the Regional Laser and Biotechnology Laboratories in Philadelphia. For nanosecond experiments a YAG laser with a pulse width of 8 ns was employed for transient generation and a dual diode array system (DIDA-512, Princeton Instrument) was used for transient detection. The observed transients were averaged over 100 pulses. For irradiation of the CT complexes and for photoionization experiments, 532 and 266 nm wavelengths were used, respectively.

In irradiation of CT complexes, typical experimental conditions employed ca. 0.01 M solutions of 4-methylanisole or bicumenes **1a,d** which were 0.4 M in **2**. In case of 4-methylanisole in CH_3CN, 10–50 ns after the pulse the transient had an absorbance of ca. 0.025 at 450 nm; in CH_2Cl_2 with the identical irradition dose the absorbance was less than 0.003 (noise level). No peak in the 450-nm region was observed for the bicumenes.

For photoionization studies ca. 0.01 solution of 4-*tert*-butylanisole or bicumene, **1a–e**, in CH_2Cl_2/MeOH (50% v/v) was employed. 4-*tert*-Butylanisole gave a strong signal at 450 nm, but no absorption bands in that region were observed in the nanosecond time scale for any of the bicumenes. Similar experiments carried out in Prof. Steenken laboratory[16] showed only presence of *p*-methoxycumyl cation and X-substituted cumyl radicals.

Measurements of Product Yields. Measurement of yields of products formed during the irradiation of CT complexes between the bicumenes and tetranitromethane was performed by ^{1}H NMR. All reactions, including solvolyses and control experiments, were carried out at ambient temperature (ca. 25 °C). An NMR tube containing 5–10 mg of the bicumene and internal standard (methyl *tert*-butyl ether) was fitted with a rubber septum and flushed with argon. The appropriate deuterated solvent was injected from a freshly opened ampule. Any additives (MeOH, 4^-, etc.) were then added followed by **2** (25 μL), and a carefully integrated ^{1}H NMR spectra of the mixture was recorded. In these experiments the concentration of bicumenes was ca. 0.02–0.07 M while that of **2** was 0.1–0.38 M. The samples were irradiated at room temperature with light of wavelengths greater than 420 nm (cut-off filter) using a 450-W Hanovia Hg lamp. The lamp was placed ca. 10 cm from the filter. The sample was also 10 cm from the filter. No change in sample temperature was observed during the irradiation. Immediately after 5–30 min of irradiation, a second ^{1}H NMR spectrum was recorded. Typically, greater than 90% of all bicumene consumed could be accounted for in terms of products **5–8** if the mixture was analyzed within 2 h of photolysis and if the degree of conversion was less than 50%. For product ratio studies (Table II), the irradiation time was ca. 5 min and the conversion of the bicumenes was lower than 30%.

An illustration of the effects of prolonged irradiation was obtained with **1b** in CH_2Cl_2. Thus, yield of **5b** was 85% after 5 min of irradiation (44% conversion), 71% after 10 min (70% conversion), 33% after 30 min (100% conversion), and 17% after 45 min (100% conversion). Compound **5b** was found to be the least stable product under the reaction conditions.

Determination of Nitroform Concentration. The yield of nitroform produced in the photochemical reaction was measured using UV/visible spectroscopy.[8] For example, **1b** (23 mg) and hexadecane (20 mg, used as an internal standard) were dissolved in 2.0 mL of CH_2Cl_2/MeOH (2.5 M). After addition of **2** (120 μL), a 50-μL aliquot was withdrawn for GC analysis. After the irradiation of the sample ($\lambda > 420$ nm) another 50-μL sample was withdrawn. The degree of conversion determined by GC was 0.265 ± 0.032 and the **7b**/**5b** was 3.3. The irradiated sample (1 mL) was added to water (50 mL) and extracted with 50 mL of ether. The water layer was separated and diluted to 1000 mL. The absorption of this sample was 0.1875 (350 nm, 1 cm path). Using the known[8] extinction coefficient of 4^- (1.40×10^4 M^{-1} cm^{-1}) calculated yield of nitroform was 1.34×10^{-5} mol. Theoretically, based on the amount of **7b** formed, the yield of nitroform should be 1.57×10^{-5} mol. The extraction procedure was found to be accurate by tests with known amounts of nitroform.

A similar determination was performed for irradiation of the CT complexes of 4-*tert*-butylanisole (0.2 M) and **2** (0.7 M) in CH_2Cl_2. Under conditions where 1.3×10^{-4} mol of 4-*tert*-butylanisole was consumed 2.15×10^{-5} mol of nitroform was measured. The calculated yield of nitroform based on 16% yield of **13** formed was 2.11×10^{-5} mol.

Product Stability and Solvolysis Study. To verify the stability of products **5a,b** and **7a,b** under the reaction conditions, NMR spectra of the reaction mixture were taken at several intervals after the reaction. Thus, in CH_2Cl_2/MeOH (0.25 M) irradiation of$[\mathbf{1a}\cdots\mathbf{2}]_{CT}$ gave the following **7b**/**5b** and **7a**/**5a** ratios: immediately after irradiation (ca. 3 min) 0.24 and 0.39; after 30 min 0.18 and 0.38; after 1 h 0.12 and 0.4. Similar experiments in solution containing 2.5 M MeOH gave 3.5 and 3.6 immediately after irradiation and 2.0 and 3.5 after 1 h. Under these conditions **7b** was slowly converted by nitroform into **5b**, but both **5a** and **5b** as well as **7a** were stable. In CH_3CN containing 2.5 M MeOH, the initial ratios of **7x**/**5x** were 3.8 (**x** = **b**) and 7.2 (**x** = **a**) and they changed to 3.6 and 6.5 after 1 h. Under these conditions **7b** slowly decomposed to the corresponding α-methylstyrene which dimerized and/or oligomerized.

In an independent experiment, nitroform (3.5 mg, final concentration 0.046 M), 2-phenyl-2-propanol (2 μL, 0.029 M), and methyl *tert*-butyl ether (internal standard) were dissolved in CD_2Cl_2 containing 5 μL of CD_3OD (final concentration 0.25 M). The NMR spectrum taken immediately after mixing showed no reaction. After 12 h at room temperature 75% of the alcohol was consumed giving 83% of **7a**, ca. 1% of **5a**, and 16% of α-methylstyrene. A pure sample of **5a** showed no change in the NMR spectrum after 12 h in the CH_2Cl_2/nitroform medium similar to the reaction conditions.

A similar reaction was performed with freshly purified 2-(4-methoxyphenyl)-2-propanol (0.0135 M), nitroform (0.0137 M), and CD_3OD (0.25 M) in CD_2Cl_2 (freshly purified by passing through Al_2O_3). The spectra recorded at 1 h time intervals showed only the unreacted alcohol, **5b**, and **7b**. The time, percent conversion of the alcohol and yields of **5b** and **7b** were as follows: 3 min (immediately after mixing), 27%, 19%, 81%; 1 h, 47%, 31%, 69%; 2 h, 74%, 43%, 57%; and 3 h, 86%, 51%, 49%.

In another set of experiments, a sample of freshly prepared cumyl bromide (2 μL) was dissolved in CD_2Cl_2 (or CD_3CN) containing CD_3OD (final concentration 0.25 M)) and tetra-*n*-butylammonium (or potassium) salt of 4^- (final concentration 0.41 M). The reactions were followed by NMR. Only traces of **5a** were detected in the mixtures composed mainly of **7a** and α-methylstyrene in ca. 2:1 ratio (Table II). A pure sample of **5a** was shown to be stable under the reaction conditions.

Mechanistic Tests for Aromatic Dinitromethylation. 4-*tert*-Butylanisole (50 mg) and **2** (120 μL) were dissolved in a selected solvent (2 mL) and irradiated through a 420-nm cut-off filter. After removal of the solvent, the samples were analyzed by NMR. Several samples were run in deuterated solvents with an internal standard as described above. The yields of products were as follows: (CH_2Cl_2) **13** 17%, **14** 83%, **15** not detected (<1%); (CH_2Cl_2/MeOH (0.5 M)) **12** 4%, **13** 13%, **14** 46%, **15** 36%. Saturation of this mixture with O_2 or addition of nitroform (0.09 M) did not change the **14**/**15** ratio; (CH_2Cl_2/MeOH) (5.0 M)) **13** 12%, **14** 40%, **15** 46%; (MeOH) **13** 11%, **14** 32%, **15** 55%.

p-Methylanisole (120 mg) and **14** (49.3 mg) were dissolved in 1.6 mL of CH_2Cl_2 and 0.4 mL of MeOH. After addition of **2** (200 μL) the sample was irradiated (λ >420 nm) for 30 min. Analysis of the mixture by NMR, GC, and HPLC showed no **15**. The mixture contained unreacted **14**, 2-(trinitromethyl)-4-methylanisole (34%), 2-(dinitromethyl)-4-methylanisole (12%), 2-nitro-4-methylanisole (42%), and **12** (12%).

Irradiation of a mixture of nitroform (35 μL) and *p*-*tert*-butylanisole (18.3 mg) in 2 mL of CH_2Cl_2/MeOH (0.5 M) using the

---

[35] Parker, C. A. *Proc. R. Soc.* (*London*) **1953**, *A220*, 104.

420-nm cut-off filter for 1 h gave no reaction. Irradiation of the same mixture using Pyrex glass (λ > 300 nm) or uranium glass (λ > 350 nm) filters for 15 min gave high yields of 15 (see below).

Studies of Reversibility of C–C Bond Cleavage in Radical Cations. Irradiation of the charge-transfer complexes between 2 and *erythro*-9 or *meso*-10 was carried out on a ca. 50-mg scale in methylene chloride. The samples were irradiated for approximately 1.5 h with Pyrex-filtered light, after which time GC analysis (internal standard) showed 50–60% conversion. Only cleavage products were observed (see below). The starting materials were isolated by preparative TLC. Careful ^{1}H NMR analysis showed no isomerization (<1%) in any case. Equimolar mixtures of *erythro*/*threo*-9 and *meso*/*dl*-10 used for comparison purposes were prepared by radical coupling of the corresponding 2-arylbutanes.

Model Nitration Reactions. Reactions with $NO_2^{\bullet}$ were performed by saturating the deoxygenated solvent of choice with the $NO_2^{\bullet}$ gas (Matheson). The substrate was dissolved in the deoxygenated solvent (ca. 0.3 M) and treated with 100-μL portions of $NO_2^{\bullet}$ solution until ca. 50% of the substrate was consumed (ca. six additions over a 2-h period). The mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ (aqueous) and dried over Na_2SO_4. Under these conditions, in CH_2Cl_2 containing 0.5 M MeOH, **1a** gave (among other products[36]) **11a**[37] (15%) and **12** (55%); **1e** gave **11e**[38] (20%) and **12** (80%); 4-*tert*-butylanisole gave 2-nitro-4-*tert*-butylanisole (**13** 66%) and *p*-nitroanisole (**12**, 33%).

Product Isolation and Identification. All products were separated by chromatography on silica gel and identified by comparison with authentic samples or were characterized by spectral means. To stress their structural similarity, the ^{13}C NMR spectra for selected compounds are collected in Table III.

A typical preparative-scale reaction was carried out as follows. 4-Methoxy-4′-X-bicumene (100–140 mg) was dissolved in 5 mL of solvent (acetonitrile for isolation of α-trinitromethylation products, cyclohexane for isolation of aromatic trinitromethylation products, methylene chloride/methanol for isolation of aromatic nitration products) in a Pyrex test tube. The solution was deoxygenated by bubbling argon. Tetranitromethane (0.3 mL) was added via syringe. The dark yellow mixture was irradiated for 1 h with Pyrex-filtered light from a water-cooled Hanovia medium-pressure Hg lamp. The resulting solution was added to 50 mL of water. The aqueous solution was extracted twice with 20-mL portions of methylene chloride, and the combined organic layers were dried over sodium sulfate. After evaporation of the solvent, the yellow oils were chromatographed on silica gel with mixtures of hexane and methylene chloride.

Nitration Products. Authentic samples **8a,d,e** were generated by the action of nitric acid in acetic anhydride on **1a,d,e**.

3-Nitro-4-methoxybicumene (8a): ^{1}H NMR ($CDCl_3$) 1.31 (s, 12 H), 3.92 (s, 3 H), 6.64 (d, J = 9 Hz, 1 H), 7.01 (m, 2 H), 7.09 (dd, J = 9 Hz, J = 2.5 Hz, 1 H), 7.17 (m, 3 H), 7.45 (d, J = 2.5 Hz, 1 H); IR (film) 1610, 1520, 1490, 1330, 1000, 680 cm^{-1}.

3-Nitro-4-methoxy-4′-(trifluoromethyl)bicumene (8d): ^{1}H NMR ($CDCl_3$) 1.23 (s, 6 H), 1.25 (s, 6 H), 3.85 (s, 3 H), 6.81 (d, J = 9 Hz, 1 H), 7.02 (dd, J = 9 Hz, J = 3 Hz, 1 H), 7.06 (d, J = 8 Hz, 2 H), 7.36 (d, J = 8 Hz, 2 H), 7.42 (d, J = 3 Hz, 1 H).

3-Nitro-4-methoxy-4′-cyanobicumene (8e): ^{1}H NMR ($CDCl_3$) 1.32 (s, 6 H), 1.34 (s, 6 H), 3.95 (s, 3 H), 6.89 (d, J = 9 Hz, 1 H), 7.06 (dd, J = 9 Hz, J = 2.5 Hz, 1 H), 7.14 (d, J = 7 Hz, 2 H), 7.50 (d, J = 7 Hz, 2 H), 7.53 (d, J = 2.5 Hz, 1 H). IR (film) 2080, 1610, 1520, 1490, 1330, 1250, 1170, 1070, 1000, 820, 800 cm^{-1}.

2-Nitro-4-*tert*-butylanisole (13): ^{1}H NMR ($CDCl_3$) 1.32 (s, 9 H), 3.93 (s, 3 H), 7.02 (d, J = 9 Hz, 1 H), 7.56 (dd, J = 9 Hz, J = 2 Hz, 1 H), 7.85 (d, J = 2 Hz, 1 H).

Cumyl Methyl Ethers. Authentic samples of compounds **7a–e** were generated by methanolysis of 2-bromo-2-(4′-X-phenyl)propanes. The bromides were produced by the reaction of PBr_3 with the cumyl alcohols or by action of NBS on the cumenes. The alcohols were either commercially available or were obtained from the appropriate phenyl Grignard reagent and acetone.

2-Methoxy-2-phenylpropane[39] (7a): ^{1}H NMR ($CDCl_3$) 1.53 (s, 6 H), 3.07 (s, 3 H), 7.28–7.38 (m, 5 H).

2-Methoxy-2-(4′-methoxyphenyl)propane[40] (7b): ^{1}H NMR ($CDCl_3$) 1.50 (s, 6 H), 3.03 (s, 3 H), 3.79 (s, 3 H), 6.85 (d, J = 9 Hz, 2 H), 7.31 (d, J = 9 Hz, 2 H).

2-Methoxy-2-(4′-methylphenyl)propane[41] (7c): ^{1}H NMR ($CDCl_3$) 1.50 (s, 6 H), 2.33 (s, 3 H), 3.05 (s, 3 H), 7.20 (d, J = 9 Hz, 2 H), 7.29 (d, J = 9 Hz, 2 H).

2-Methoxy-2-(4′-(trifluoromethyl)phenyl)propane[40] (7d): ^{1}H NMR ($CDCl_3$) 1.54 (s, 6 H), 3.09 (s, 3 H), 7.53 (d, J = 9 Hz, 2 H), 7.61 (d, J = 9 Hz, 2 H).

2-Methoxy-2-(4′-cyanophenyl)propane (7e): ^{1}H NMR ($CDCl_3$) 1.53 (s, 6 H), 3.09 (s, 3 H), 7.52 (d, J = 9 Hz, 2 H), 7.64 (d, J = 9 Hz, 2 H).

***α*-(Trinitromethyl)cumenes.** Authentic samples of **5a,b** were prepared by addition of nitroform to the corresponding cumyl alcohols. When dissolved in Me_2SO, **5a,b** solvolyzed to produce 4^-, which was detected by UV/vis, and the corresponding α-methylstyrenes which were detected by GC. To facilitate the structure assignment, selected peaks in the mass spectrum of **5a** are interpreted in terms of fragments lost.

A sample of **5a** was prepared from 2-phenyl-2-propanol. The alcohol (50 mg) in 3 mL of CH_2CL_2 was treated with nitroform (55 mg). The solution was allowed to stand for 4 h. Pure **5a** was separated from α-methylstyrene, the only other product of the reaction, by chromatography on silica gel. The yield was ca. 40%. In a similar way, **5b** was prepared from 2-(*p*-methoxyphenyl)-2-propanol.

2-(Trinitromethyl)-2-phenylpropane (5a): R_f = 0.54 (r = 0.25); ^{1}H NMR ($CDCl_3$) 2.02 (s, 6 H), 7.37 (m, 2 H), 7.51 (m, 3 H). IR (KBr): 1608, 1590, 1580, 1380, 1280, 830, 770, 750, 680 cm^{-1}; MS (relative intensity) 269 (P^+, 7), 223 ($P^+ - NO_2$, 2), 177 ($P^+ - 2NO_2$, 0.2), 146 (11), 131 ($P^+ - 3NO_2$, 19), 119 ($P^+ - C(NO_2)_3$, 100), 115 (12), 91 (47), 77 (13); precise molecular weight determination calculated for $C_{10}H_{11}N_3O_6$ 269.0648, found 269.0652; calculated for $[P^+ - C(NO_2)_3]$ 119.0861, found 119.0856.

In addition to the above procedure, **5b** was conveniently generated by irradiation of $[\mathbf{1b}\cdots\mathbf{2}]_{CT}$ in methylene chloride. The sample was irradiated until no starting material remained (GC). The reaction mixture was freed of nitrogen dioxide by bubbling argon.

2-(Trinitromethyl)-2-(4′-methoxyphenyl)propane (5b): ^{1}H NMR (CD_2Cl_2) 2.00 (s, 6 H), 3.83 (s, 3 H), 6.91 (d, J = 9 Hz, 2 H), 7.47 (d, J = 9 Hz, 2 H); MS (relative intensity) 299 (38), 253 (0.6), 207 (3), 161 (58), 149 (100), 146 (18), 135 (62), 133 (24), 123 (33), 121 (29), 91 (28).

2-(Trinitromethyl)-2-(4′-methylphenyl)propane (5c): R_f = 0.54 (r = 0.25); ^{1}H NMR ($CDCl_3$) 1.99 (s, 6 H), 2.34 (s, 3 H), 7.16 (d, J = 9 Hz, 2 H), 7.38 (d, J = 9 Hz, 2 H); MS (relative intensity) 283 (37), 238 (3), 191 (0.5), 145 (78), 133 (100); IR (film) 1600, 1580, 1380, 1280, 830, 770 cm^{-1}; precise molecular weight determination calculated for $C_{11}H_{13}N_3O_6$ 283.0804, found 283.0800; calculated for $[P^+ - C(NO_2)_3]$ 133.1017, found 133.1007, calculated for $[P^+ - 3NO_2]$ 145.1017, found 145.1013.

2-(Trinitromethyl)-2-(4′-(trifluoromethyl)phenyl)propane (5d): R_f = 0.54 (r = 0.25) ^{1}H NMR ($CDCl_3$) 2.05 (s, 6 H), 7.66 (m, 4 H); MS (relative intensity) 337 (0.4), 199 (16), 187 (6); IR (film) 1600, 1580, 1310, 1050, 990, 830, 820, 770, cm^{-1}; precise molecular weight determination calculated for $C_{11}H_{10}F_3N_3O_6$ 337.0522, found 337.0507; calculated for $[P^+ - C(NO_2)_3]$ 187.0734, found 187.0718, calculated for $[P^+ - F]$ 318.0538, found 318.0503.

2-(Trinitromethyl)-2-(4′-cyanophenyl)propane (5e): R_f = 0.17 (r = 0.67); ^{1}H NMR ($CDCl_3$) 2.04 (s, 6 H), 7.68 (s, 4 H); IR (film) 2195, 1590, 1570, 1380, 1280, 830, 775 cm^{-1}; precise molecular weight determination calculated for $C_{11}H_{10}N_4O_6$ 294.0601, found 283.0579; calculated for $[P^+ - C(NO_2)_3]$ 144.0813, found 144.0798, calculated for $[P^+ - 3NO_2]$ 156.0813, found 156.0802.

2-(4′-Methoxyphenyl)-2-(trinitromethyl)butane: ^{1}H NMR

---

[36] The bicumenes, **1a–e**, can serve as mechanistic probes for various nitration reactions. The results of these studies will be reported in the due course.

[37] Singh, P. R.; Khanna, P. K. *Tetrahedron Lett.* **1982**, *23*, 5355.

[38] Kornblum, N.; Cheng. L.; Kerber, R. C.; Kestner, M. M.; Newton, B. N.; Pinnick, H. W.; Smith, R. G.; Wade, P. A. *J. Org. Chem.* **1976**, *41*, 1560.

[39] Ziegler, K.; Dislich, H. *Chem. Ber.* **1957**, *90*, 1107.

[40] Okamoto, A.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2340.

[41] Sato, T.; Yoshiie, S.; Imamura, T.; Hasegawa, K.; Miyahara M.; Yamamura, S.; Ito, O. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2714.

(CD_2Cl_2) 0.78 (t, J = 8 Hz, 3 H), 1.93 (s, 3 H), 2.25 (dq, J = 7 Hz, J = 7 Hz, 1 H), 2.65 (dq, J = 7 Hz, J = Hz, J = 7 Hz, 1 H), 3.8 (s, 3 H), 6.88 (d, J = 9 Hz, 2 H), 7.35 (d, J = 9 Hz, 2 H); MS (relative intensity) 313 (1), 267 (0.3), 221 (0.2), 207 (3), 190 (1), 175 (5), 163 (100), 135 (17), 121 (30).

2-Phenyl-2-(trinitromethyl)butane: ^{1}H NMR ($CDCl_3$) 0.81 (t, J = 7 Hz, 3 H), 1.99 (s, 3 H), 2.29 (dq, J = 7 Hz, J = 7 Hz, 1 H), 2.70 (dq, J = 7 Hz, J = 7 Hz, 1 H), 7.39 (m, 3 H), 7.48 (m, 2 H). ^{13}C NMR ($CDCl_3$) 133.9, 129.7 129.0, 128.5, 52.0, 30.9, 28.7, 22.6, 8.3; MS (relative intensity) 283 (14), 238 (1), 190 (1), 160 (25), 145 (50), 135 (16), 133 (42), 117 (28), 115 (36), 105 (45), 91 (75), 86 (63), 84 (100); IR (film) 2980, 1600, 1580, 1280, 830, 780, 770, 680 cm^{-1}.

Aromatic Trinitromethyl Derivatives. The assignment of structures was based on spectral data (Table III and data below) which were analogous to those of 4-methyl-2-(trinitromethyl)anisole prepared by Kochi.[8] In addition, the trinitromethyl group in **6a** was hydrolyzed to the corresponding carboxylic acid.[8,42] The authentic sample of the acid was prepared by acetylation of **1a** followed by oxidation of the resulting ketone with NaOBr.

4-Methoxy-3-(trinitromethyl)bicumene (6a): R_f = 0.22 (r = 0.18); ^{1}H NMR ($CDCl_3$) 1.31 (s, 6 H), 1.33 (s, 6 H), 3.81 (s, 3 H), 6.42 (d, J = 2 Hz, 1 H), 6.86 (m, 2 H), 6.94 (d, J = 9 Hz, 1 H), 7.14 (m, 3 H), 7.50 (dd, J = 9 Hz, J = 2 Hz, 1 H); IR (film) 2990, 1620, 1589, 1500, 1280, 1260, 1005, 780, 682 cm^{-1}; MS (relative intensity) 417 (0.09), 371 (0.3), 326 (0.3), 298 (5), 253 (11), 252 (4), 207 (4), 191 (2), 190 (13), 176 (5), 1.49 (2), 147 (3), 119 (100), 91 (19); precise molecular weight determination calculated for $C_{11}H_{12}N_3O_7$ (4-methoxy-3-(trinitromethyl)cumyl cation) 298.0675, found 298.0658; calculated for C_9H_{11} (cumyl cation) 119.0860, found 119.0860.

The hydrolysis of **6a** (50 mg) was carried out in a mixture of 10 mL of MeOH and 10 mL of HCl_{aq}. The mixture was refluxed for 4 h. It was made basic with $NaHCO_3$ and extracted with 20 mL of ether. The water layer was acidified with HCl and extracted with CH_2Cl_2. The extract was dried over Na_2SO_4. Evaporation of the solvent gave ca. 10 mg of the carboxylic acid, which was identical (NMR, IR) with the independently prepared sample.

In an independent synthesis, 4-methoxy-3-carboxybicumene was prepared from **1a**. The bicumene (200 mg) in 10 mL of CH_2Cl_2 was added dropwise over 5 min to 10 mL of cooled CH_2Cl_2 solution (MeOH/ice bath) containing 360 mg of acetyl chloride and 100 mg of $AlCl_3$. The mixture was stirred for 4 h and then quenched by addition to 40 mL of water. The organic layer was separated, washed with water and dried over Na_2SO_4. Removal of the solvent and silica gel chromatography (hexane/ethyl acetate (20%)) gave 200 mg (86% yield) of a 4-methoxy-3-acetylbicumene.

4-Methoxy-3-acetylbicumene: ^{1}H NMR ($CDCl_3$) 1.28 (s, 6 H), 1.29 (s, 6 H), 2.57 (s, 3 H), 3.86 (s, 3 H), 6.74 (d, J = 9 Hz, 1 H), 7.03 (m, 3 H), 7.16 (m, 3 H), 7.48 (d, J = 3 Hz, 1 H).

Bromine (0.35 g) was added dropwise to 3 mL of cooled (ice/NaCl bath) H_2O solution of NaOH (0.34 g). The resulting solution was diluted with 2 mL of precooled dioxane and added to the solution of the acetyl compound (200 mg) in a mixture of 8 mL of dioxane and 2.6 mL of water immersed in an ice bath. The mixture was stirred for 4 h at low temperature and then saturated with $NaHCO_3$ and extracted with 20 mL of ether. The colorless aqueous layer was separated and acidified with concentrated HCl. Extraction with CH_2Cl_2 (20 mL) gave 163 mg (85%) of the carboxylic acid.

4-Methoxy-3-carboxybicumene: mp 145–153 °C dec; ^{1}H NMR ($CDCl_3$) 1.30 (s, 6 H), 1.32 (s, 6 H), 3.72 (s, 3 H), 6.84 (d, J = 9 Hz, 1 H), 7.05 (m, 3 H), 7.20 (m, 3 H), 8.01 (d, J = 2 Hz, 1 H); IR 2950, 1685, 1670, 1490, 1420, 1290, 1000, 795, 680 cm^{-1}.

4,4′-Dimethoxy-3-(trinitromethyl)bicumene (6b): R_f = 0.58 (r = 0.67); ^{1}H NMR ($CDCl_3$) 1.29 (s, 6 H), 1.33 (s, 6 H), 3.78 (s, 3 H), 3.81 (s, 3 H), 6.35 (d, J = 2 Hz, 1 H), 6.67 (d, J = 9 Hz, 2 H), 6.76 (d, J = 9 Hz, 2 H), 6.95 (d, J = 9 Hz, 1 H), 7.52 (dd, J = 2 Hz, J = 9 Hz, 1 H); IR (film) 2960, 1610, 1580, 1490, 1280, 1260, 1000, 800, 780 cm^{-1}; precise molecular weight determination calculated for $C_{10}H_{13}O$ (p-methoxycumyl cation) 149.0967, found 149.0942.

4-Methoxy-3-(trinitromethyl)-4′-methylbicumene (6c): R_f = 0.50 (r = 0.25); ^{1}H NMR ($CDCl_3$) 1.29 (s, 6 H), 1.33 (s, 6 H), 2.29 (s, 3 H), 3.81 (s, 3 H), 6.31 (d, J = 2 Hz, 1 H), 6.73 (d, J = 8 Hz, 2 H), 6.94 (d, J = 8 Hz, 3 H), 7.54 (dd, J = 2 Hz, J = 8 Hz, 1 H); IR (film) 1612, 1580, 1500, 1280, 1252, 1000, 800, 780, cm^{-1}; MS (relative intensity) 299 (2.5), 253 (11), 207 (11), 174 (100), 161 (4), 149 (31); precise molecular weight determination calculated for $C_{11}H_{12}N_3O_7$ (4-methoxy-3-(trinitromethyl)cumyl cation) 298.0675, found 298.0716.

4-Methoxy-3-(trinitromethyl)-4′-(trifluoromethyl)bicumene (6d): R_f = 0.49 (r = 0.25); ^{1}H NMR ($CDCl_3$) 1.34 (s, 12 H), 3.82 (s, 3 H), 6.41 (d, J = 2 Hz, 1 H), 6.97 (d, J = 9 Hz, 3 H), 7.40 (d, J = 9 Hz, 2 H), 7.51 (dd, J = 2 Hz, J = 9 Hz, 1 H); IR (film) 1618, 1582, 1496, 1310, 1150, 1100, 1045, 990, 780 cm^{-1}; precise molecular weight determination calculated for $C_{11}H_{12}N_3O_7$ (4-methoxy-3-(trinitromethyl)cumyl cation) 298.0675, found 298.0672; calculated for $C_{10}H_{10}F_3$ (p-(trifluoromethyl)cumyl cation) 187.0735, found 187.0737.

4-Methoxy-3-(trinitromethyl)-4′-cyanobicumene (6e): R_f = 0.29 (r = 0.67); ^{1}H NMR ($CDCl_3$) 1.33 (s 6 H), 1.34 (s, 6 H), 3.83 (s, 3 H), 6.42 (d, J = 2 Hz, 1 H), 6.97 (d, J = 9 Hz, 3 H), 7.45 (d, J = 9 Hz, 2 H), 7.49 (dd, J = 2 Hz, J = 9 Hz, 1 H); IR (film) 2990, 2190, 1610, 1580, 1270, 1000, 780 cm^{-1}; MS (relative intensity) 442 (0.3), 351 (0.7), 298 (55), 253 (83), 252 (52), 207 (66), 190 (100), 176 (66), 174 (40), 149 (96), 147 (69), 145 (34), 134 (21), 116 (52); precise molecular weight determination calculated for $C_{10}H_9N$ (p-cyanocumyl cation − H) 143.0735, found 143.0692.

2-(Trimethyl)-4-*tert*-butylanisole (14): ^{1}H NMR ($CDCl_3$) 1.31 (s, 9 H), 3.82 (s, 3 H), 7.07 (d, J = 9 Hz, 1 H), 7.24 (d, J = 2 Hz, 1 H), 7.73 (dd, J = 9 Hz, J = 2 Hz, 1 H).

Aromatic Dinitromethylation. The compounds were independently prepared by irradiation of the charge-transfer complexes of the anisole donors and nitroform using an uranium glass filter (λ > 350 nm) or Pyrex glass filter (λ > 300 nm).

Nitroform (35 μL) and p-*tert*-butylanisole (18.3 mg) were dissolved in 2 mL of CH_2Cl_2 and irradiated for 15 min, giving, after evaporation of volatile components, pure **15**. Other dinitromethyl derivatives were prepared in a similar manner and purified by column chromatography.

3-(Dinitromethyl)-4-*tert*-butylanisole (15): ^{1}H NMR ($CDCl_3$) 1.30 (s, 9 H), 3.89 (s, 3 H), 6.96 (d, J = 9 Hz, 1 H), 7.39 (d, J = 2 Hz, 1 H), 7.59 (dd, J = 9 Hz, J = 2 Hz, 1 H), 7.61 (s, 1 H); precise molecular formula determination calculated for $C_{12}H_{13}N_2O_5$ 268.1059, found 268.1079; calculated for $[P^+ - CH_3]$ 253.0866, found 253.0845, calculated for $[P^+ - NO_2]$ 222.1154, found 222.1142.

The structure of **15** was confirmed by basic titration. A pure sample of **15** (5 mg) was dissolved in CD_3CN (1 mL) and treated with ca. 5 mg of DABCO. The colorless solution (λ_{max} = 288 nm) turned yellow (λ_{max} = 375 nm), and the ^{1}H NMR spectrum of anion **15**$^-$ was recorded: ^{1}H NMR 1.30 (s, 9 H), 3.75 (s, 3 H), 6.91 (d, J = 9 Hz, 1 H), 7.28 (d, J = 2 Hz, 1 H), 7.38 (dd, J = 9 Hz, J = 2 Hz, 1 H). Treatment of the mixture with a drop of concentrated HCl_{aq} quenched the yellow color and restored the original NMR spectrum.

4-Methoxy-3-(dinitromethyl)-4′-(trifluoromethyl)bicumene: ^{1}H NMR (CD_2Cl_2) 1.29 (s, 3 H), 1.31 (s, 6 H), 3.87 (s, 3 H), 6.81 (d, J = 9 Hz, 1 H), 6.94 (d, J = 2 Hz, 1 H), 6.97 (d, J = 9 Hz, 2 H), 7.16 (dd, J = 9 Hz, J = 2 Hz, 1 H), 7.40 (d, J = 9 Hz, 1 H), 7.53 (s, 1 H); IR (film) 2990, 2190, 1725, 1570, 1500, 1260, 1100 cm^{-1}; precise molecular weight determination calculated for $C_{11}H_{13}N_2O_5$ (4-methoxy-3-(dinitromethyl)cumyl cation) 253.0825, found 253.0820; calculated for $C_{10}H_{10}F_3$ (p-(trifluoromethyl)cumyl cation) 187.0735, found 187.0717.

4-Methoxy-3-(dinitromethyl)-4′-cyanobicumene: ^{1}H NMR ($CDCl_3$) 1.30 (s, 3 H), 1.32 (s, 6 H), 3.89 (s, 3 H), 6.82 (d, J = 9 Hz, 1 H), 6.93 (d, J = 2 Hz, 1 H), 7.05 (d, J = 9 Hz, 2 H), 7.16 (dd, J = 2 Hz, J = 9 Hz, 1 H), 7.47 (d, J = 9 Hz, 2 H), 7.54 (s, 1 H); IR (film) 2940, 2190, 1725, 1570, 1500, 1260, 1100 cm^{-1}.

2-(Dinitromethyl)-4-methylanisole: ^{1}H NMR ($CDCl_3$) 2.33 (s, 3 H), 3.87 (s, 3 H), 6.90 (d, J = 8.5 Hz, 1 H), 7.17 (d, J = 2.0 Hz, 1 H), 7.36 (dd, J = 8.5 Hz, J = 2.0 Hz, 1 H), 7.57 (s, 1 H).

Acknowledgment. This research was supported by grants from the NSF and the Link Foundation (Fellowship to W.H.C.). P.M. is a recipient of the Camille and Henry

---

(42) Sankararaman, S.; Kochi, J. K. *Recl. Trav. Chim., Pay-Bas* **1986**, *105*, 278.

Dreyfus Foundation New Faculty Award. The nanosecond flash-laser experiments were carried out at the Regional Laser and Biotechnology Laboratories (University of Pennsylvania) supported by a grant from the National Institutes of Health (RR 01348). We are indebted to Dr. Mark Phillips for assistance with laser experiments.

Registry No. **1a**, 127092-00-6; **1b**, 32445-98-0; **1c**, 127092-01-7; **1d**, 130379-05-4; **1e**, 129970-59-8; **2**, 509-14-8; **5a**, 130379-16-7; **5b**, 130379-17-8; **5c**, 130379-18-9; **5d**, 130379-19-0; **5e**, 130379-20-3; **6a**, 130379-23-6; **6b**, 130379-26-9; **6c**, 130379-27-0; **6d**, 130379-28-1; **6e**, 130379-29-2; **7a**, 935-67-1; **7b**, 99334-84-6; **7c**, 55708-37-7; **7d**, 99334-85-7; **7e**, 125847-22-5; **8a**, 130379-14-5; **8d**, 130405-77-5; **8e**, 130379-15-6; **9**, 130379-06-5; **10**, 127092-07-3; **11a**, 78176-20-2; **11e**, 58324-82-6; **12**, 100-17-4; **13**, 91247-60-8; **14**, 130379-11-2; 15, 130379-12-3; $[\mathbf{1a}\cdots\mathbf{2}]_{CT}$, 130379-32-7; $[\mathbf{1b}\cdots\mathbf{2}]_{CT}$, 130379-33-8; $[\mathbf{1c}\cdots\mathbf{2}]_{CT}$, 130379-34-9; $[\mathbf{1d}\cdots\mathbf{2}]_{CT}$, 130379-35-0; $[\mathbf{1e}\cdots\mathbf{2}]_{CT}$, 130379-36-1; $[\text{4-}tert\text{-Butylanisole}\cdots\mathbf{2}]_{CT}$, 130379-10-1; *meso*-3,4-dimethyl-3,4-diphenylhexane, 62678-49-3; *meso*-3,4-dimethyl-3,4-bis(4′-nitrophenyl)hexane, 83294-20-6; *meso*-3,4-dimethyl-3,4-bis(4′-aminophenyl)hexane, 130379-07-6; *meso*-3,4-dimethyl-3,4-bis(4′-diazoniophenyl)hexane ditetrafluoroborate salt, 130379-09-8; trinitromethane, 517-25-9; 2-phenyl-2-propanol, 617-94-7; 2-(4-methoxyphenyl)-2-propanol, 7428-99-1; 2-(trinitromethyl)-4-methylanisole, 108088-84-2; 2-(dinitromethyl)-4-methylanisole, 130379-13-4; 2-nitro-4-methylanisole, 119-10-8; 2-(4′-methoxyphenyl)-2-(trinitromethyl)butane, 130379-21-4; 2-phenyl-2-(trinitromethyl)butane, 130379-22-5; 4-methoxyl-3-acetylbicumene, 130379-24-7; 4-methoxy-3-carboxybicumene, 130379-25-8; 4-methoxy-3-(dinitromethyl)-4′-(trifluoromethyl)-bicumene, 130379-30-5; 4-methoxy-3-(dinitromethyl)-4′-cyano-bicumene, 130379-31-6.

Theory and Experimental Illustration of Preparative Electrochemistry Using Redox Catalysis of Electron Transfer Initiated Radical Chain Reactions. Application to the Cross-Coupling between Aryl Halides and Phenoxide Ions

N. Alam,[†] C. Amatore,[*,‡] C. Combellas,[†] A. Thiébault,[*,†] and J. N. Verpeaux[‡]

Ecole Supérieure de Physique et Chimie Industrielles, Laboratoire de Chimie et Electrochimie des Matériaux Moléculaires, URA CNRS 429. 10, rue Vauquelin, 75231 Paris, Cédex 05, France, and Ecole Normale Supérieure, Laboratoire de Chimie, URA CNRS 1110. 24, rue Lhomond, 75231 Paris, Cédex 05, France

Received April 3, 1990

A general equation predicting the yield of electron transfer initiated radical chain reaction ($S_{RN}1$ and related mechanisms) under preparative electrochemical conditions is given for situations where the electron-transfer activation of the chain is performed by means of a redox mediator. Simple tests, allowing for the choice of proper redox mediator, are given, and their origins established and discussed. The validity and application of this simple model is shown and discussed for the case of the $S_{RN}1$-like reaction involving di-*tert*-butylphenoxide as a nucleophile, to afford biaryls of interest for their properties in nonlinear optics.

Introduction

Electrochemical reduction of aromatic halides or pseudohalides is a very simple means of activating these ubiquitous molecules under perfectly controlled conditions.[1] Thus when the electrode potential is set on the reduction wave of the halide or pseudohalide, an electron is transferred to the aromatic π^* orbital to afford a frangible anion radical, $ArX^{\bullet-}$. Intramolecular (i.e. $\pi^* \rightarrow \sigma^*_{C-X}$) electron transfer[2] results then in the cleavage of the carbon–halogen or pseudohalogen bond to yield quantitatively a σ-radical, $Ar^{\bullet}$, and the halide or pseudohalide ion:

$$ArX + e \rightarrow ArX^{\bullet-} \tag{1}$$

$$ArX^{\bullet-} \xrightarrow{k_1} Ar^{\bullet} + X^- \tag{2}$$

In the absence of other reagents, the sequence of reactions (1–2) is generally followed by a second electron transfer[3-5] to the easily reducible σ-radical to give the corresponding highly basic σ-aromatic anion which affords the dehalogenated hydrocarbon.

$$Ar^{\bullet} + e \rightarrow Ar^- \tag{3a}$$

$$Ar^{\bullet} + ArX^{\bullet-} \rightarrow Ar^- + ArX \tag{3b}$$

$$Ar^- + BH \rightarrow ArH + B^- \tag{4}$$

With the exception of a few specific cases where a selective reduction is desirable, the whole sequence of reactions 1–4 presents a poor synthetic interest although its mechanistic consequences have been extensively delineated in the past decade.[1-5] However, it regains a considerable synthetic interest provided one is able to suppress the

---

[†] Ecole Supérieure de Physique et Chimie Industrielles.

[‡] Ecole Normale Supérieure.

(1) See, e.g.: (a) Feoktistov, L. G. In *Organic Electrochemistry*, 2nd ed.; Baizer, M., Lund, H., Eds.; Dekker: New York, 1983; Chapter 7, pp 259–284. (b) Savéant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (c) Savéant, J. M. *Proc. of R. A. Welch Foundation Conferences on Chem. Res. XXX. Adv. in Electrochem.*, Houston, 1986, pp 289–336.

(2) (a) Andrieux, C. P.; Savéant, J. M.; D. Zann, *New J. Chem.* **1984**, *8*, 107. (b) Savéant, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

(3) This is observed in poor H-atom-donating solvents such as liquid ammonia which is considered in this study.[4] In usual organic solvents and/or in the presence of tetraalkylammonium salts, H-atom transfer from the media (SH) is an additional mode of deactivation of $Ar^{\bullet}$,

$$Ar^{\bullet} + SH \rightarrow ArH + S^{\bullet}, \text{etc.}$$

leading to the hydrogenolysis product.[5] The electron stoichiometry may then be 1 e or 2 e depending on the ease of reduction of the $S^{\bullet}$ radical vs that of ArX.

(4) (a) Savéant, J. M.; Thiébault, A. *J. Electroanal. Chem.* **1978**, *49*, 335. (b) Teherani, T.; Bard, A. J. *Acta Chem. Scand., Ser. B* **1983**, *B37*, 419.

(5) (a) M'Halla, F.; Pinson, J.; Savéant, J. M. *J. Am. Chem. Soc.* **1980**, *102*, 4120. (b) Amatore, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 817. (c) Amatore, C.; Badoz-Lambling, J.; Bonnel-Huyghes, C.; Pinson, J.; Savéant, J. M.; Thiébault, A. *J. Am. Chem. Soc.* **1982**, *104*, 1979.

0022-3263/90/1955-6347$02.50/0