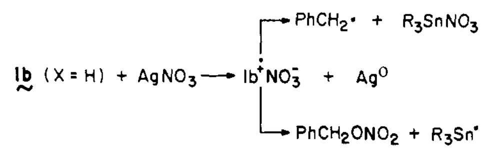
Scheme II



(**5**, 36%), and tri(n-butyl)tin nitrate (**11**, 36%).[10] Analysis of the product mixture according to Scheme II indicates that the partition ratio of 4a:4b (cf. eq 4) is 52:48. Kinetically free benzyl and (n-Bu)$_3$Sn radicals are implicated since bibenzyl and **5** are isolated.[11] However, products derived from formal cationic intermediates appear to be formed via in-cage processes: when the **1b**-Ag$^+$ reaction is carried out in CH$_3$CN-CHCl$_3$-CH$_3$OH, benzylmethyl ether is *not* present (GC analysis) at early stages after reaction, but appears only after methanolysis of the primary product benzyl nitrate.

We conclude that charge transfer induced radical ion formation in the systems **1**-TCNE or **1**-Ag$^+$ proceeds via tight radical ion-ion caged partners, and that in-cage ion recombination at either a benzyl or a tin center displaces a tin-centered radical or a benzyl radical, respectively. The initial ion recombination site appears to be determined by both the nucleophilicity of the counterion (or ion radical in the case of TCNE$^-$·) and the relative electrophilic character of the benzylic and tin centers in 1$^+$· as modulated by substituents.

References and Notes

(1) Gardner, H. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1975,** *97*, 5026; **1976,** *98*, 558, 2460, 6150, and references therein.
(2) Moore, C. J., et al. *J. Organomet. Chem.* **1973,** *59*, 225.
(3) Traylor, T. G.; Berwin, H. J.; Jercunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972,** *30*, 599.
(4) Yields 78% (CH$_2$Cl$_2$), 59% (CH$_3$CN); mp 190–200 °C dec; NMR (DMSO-d_6–Me$_4$Si) δ 7.6–7.1 (m, 5 H), 6.20 (S, 1 H), 0.55 (S, 9 H); IR (KBr) 2207 (conjd CN), 2145 (C=C=N), 1190 (Sn—C), 690 cm^{-1}; UV (acetone), λ_{max} (ϵ), 408 (22 100 M^{-1} cm^{-1}). Anal. (C, H, N, Sn) and high resolution MS (calcd M$^+$, 357.0288; found, 357.0246). Raman spectrum showed no unconjugated nitrile.
(5) NMR (CDCl$_3$–2% CH$_2$Cl$_2$) δ 7.4 (m, 5 H), 3.33 (S, 2 H), 0.41 (S, 9 H). During the preparation of this manuscript, Reutov and co-workers (Reutov, O. A.; Rozenberg, V. I.; Gavrilova, G. V.; Nikanorov, V. A. *J. Orgmet. Chem.* **1979,** *177*, 101) reported the **1a**-TCNE reaction to afford a product whose properties closely match those of **3**. These workers concluded that the adduct would have the structure resulting from 1,2-oxidative addition rather than that of the 1,4-addition product that we propose for **3**. We prefer the structure shown for **3** based on its conversion into **2** but cannot rule out the 1,2-addition structure conclusively.
(6) (a) Products were isolated by silica gel chromatography and compared with authentic samples (**4** and **5**); compounds **6** were characterized by UV/vis and NMR spectroscopy. (b) Isolated yields of **6** were 10–28%.
(7) Reutov[5] obtained **6** (X = H) and Me$_3$SnCN as the ultimate products from reaction of 1a and TCNE, and proposed a thermal elimination of Me$_3$SnCN from **3** as an explanation for the formation of **6** (X = H). We have not observed decomposition of **3** to **6** (X = H). Reutov further showed facile HCl cleavage of **3** to Me$_3$SnCl and 1,1,2,2-tetracyanopropylbenzene (**12**). We have eliminated an acid cleavage route to **5** in the present work based on our failure to observe **12** and on the systematic change in the **5**:**4** ratio obtained as a function of substituent.
(8) We do not imply that true bipartite fragmentation of **1**$^+$· occurs. The triple cage species C-1 and C-2 are valence-bond representations of intermediates which we believe to be required to rationalize the nature of the products and the substituent dependence of their ratio.
(9) Yields are expressed in terms of total benzyl fragment or tin fragment yield. All compounds were isolated, except the tin nitrate (cf. note 10), by chromatography and compared with authentic samples. Silver metal was identified by atomic absorption spectroscopy.
(10) Not isolated. An authentic sample was prepared from **5** and AgNO$_3$ and its presence in the reaction mixture proved by IR. Analysis was performed by determining **5** by GC and then adding fluoride ion to precipitate all ionic tin (**5** and **11**), which was weighed; **11** was determined by difference.
(11) Alternate mechanisms involving PhCH$_2$Ag or Bu$_3$SnAg species cannot be eliminated at this time.

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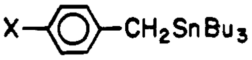
One-Electron Oxidation of Benzyltrialkylstannanes. 2. Excited-State Quenching of 9,10-Dicyanoanthracene

Sir:

Group 4a organometallics containing M-C σ bonds situated β to a neighboring π system are exceedingly electron rich as indicated by photoelectron spectroscopy,[1] facile formation of charge transfer (CT) complexes with electron-poor acceptors,[2] and reactivity toward electrophiles.[3] The one-electron oxidation of organotin compounds by electron acceptors is well established.[4] We now report that benzyltrialkylstannanes (**1**)



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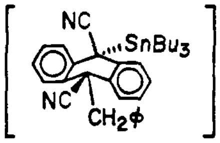
a, X = Cl; b, X = F
c, X = H, d, X = CH$_3$
e, X = OCH$_3$

are efficient quenchers of the electron-deficient singlet excited state of 9,10-dicyanoanthracene (DCA). Steady-state analysis of fluorescence quenching and photochemical product formation as a function of quencher concentration allows nearly complete dissection of the exciplex-mediated decay kinetics of the (**1**-DCA)* system and reveals several unusual facets of the processes which occur.

Observed rate constants for fluorescence quenching of singlet DCA* in benzene solutions ([DCA] ~ 10^{-4} M; [**1**] ~ 10^{-3}-10^{-1} M) are listed in Table I. Stern-Volmer rate constants $k_q{}^f$, were derived from both lifetime and intensity measurements using $\tau_f{}^0$(DCA) = 15.3 ns.[5] No new emission features (exciplex emission) were observed. A plot of log ($k_q{}^X/k_q{}^H$) vs. σ was linear with slope $\rho = -1.4$ which implicates a degree of electron transfer, in the direction (**1**$^+$·—DCA$^-$·), during the quenching act.

Photobleaching of DCA was observed on irradiation[6] of **1**-DCA solutions in degassed benzene. In a preparative experiment (Pyrex filter) with the pair **1c**-DCA, products isolated were bibenzyl (3%), hexa(n-butyl)ditin (48%, 96% based on tin), 9-benzyl-10-cyanoanthracene (28%[7]), and a material tentatively identified as 9-cyano-10-(tri-n-butyl stannyl)anthracene (1-2%[8]). We propose that the observed products result from secondary photolysis of an initial 9,10 adduct (**2**[9])



2

via preferential benzyltin homolysis. Under analytical conditions[6] (uranium glass filter), the progress of DCA photobleaching in the presence of various concentrations of **1a**–**e** can be cleanly followed spectrophotometrically to ~80% conversion of DCA. Isosbestic points in the visible spectra of DCA are retained throughout the experiments indicating that only one photoreaction occurs. Plots of the inverse of the quantum yields for DCA disappearance ($\phi_p{}^{-1}$) vs. inverse quencher concentration[10] yield a family of straight lines (Figure 1).

We adopt the kinetic scheme delineated in eq 1 in which initial, reversible, exciplex (E*) formation is followed by either

$$\begin{tikzcd} & & P \\ S_1 + Q \arrow[r, shift left, "k_1"] & E^* \arrow[l, shift left, "k_{-1}"] \arrow[ur, "k_p"] \arrow[dr, "k_r"'] & \\ & & S_0 + Q \end{tikzcd} \qquad (1)$$

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Table I. Kinetic Parameters for Quenching of DCA* by Benzylstannanes **1a–e**[a]

X	k_q^f	α	$\frac{k_1k_p}{(k_{-1}+k_r+k_p)}$	$k_q^p = \alpha k_q^f$	$k_q^r = (1-\alpha)k_q^f$
Cl	3.8	0.91 ± 0.08	3.5 ± 0.5	3.5 ± 0.3	0.3 ± 0.3
F	5.9	0.55 ± 0.05	2.5 ± 0.4	3.2 ± 0.3	3.1 ± 0.3
H	7.9	0.45 ± 0.04	2.8 ± 0.5	3.5 ± 0.4	4.8 ± 1
CH_3	10	*b*	*b*	*b*	*b*
CH_3O	21	0.11 ± 0.01	2.7 ± 0.5	2.1 ± 0.2	18 ± 1

[a] Rate constants are given in units of $M^{-1}\ s^{-1} \times 10^{-9}$. [b] Not determined.

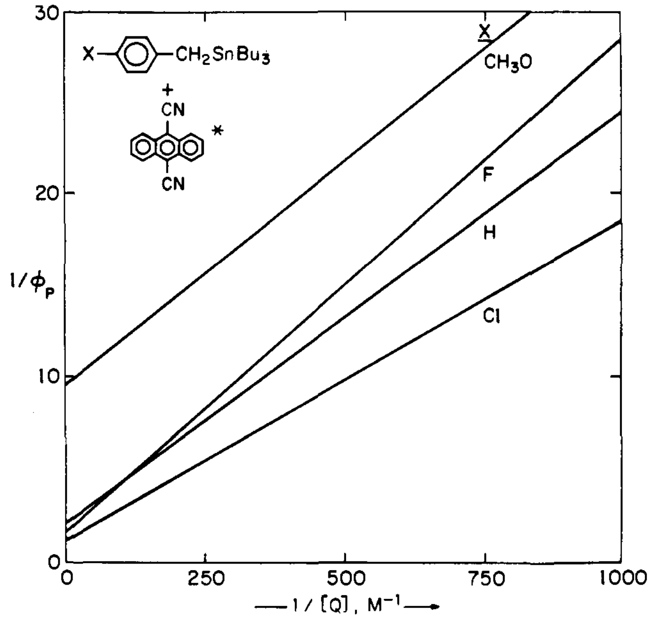

Figure 1. Plot of inverse quantum yield for DCA disappearance (ϕ_p^{-1}) vs. inverse quencher concentration ($[Q]^{-1}$) for the photoreaction DCA* + **1**.

radiationless decay to ground states (k_r) or to photoproduct(s) (k_p). Analysis according to this sequence provides the parameters listed in Table I: k_q^f derived from fluorescence quenching represents overall bimolecular exciplex decay, attenuated by exciplex reversibility, through both product-forming and non-product-forming channels; α, the efficiency of product formation at $[Q]_\infty$, and $k_1k_p/(k_1 + k_{-1} + k_p)$, the pseudo-rate constant for product-forming steps, arise from ϕ_p^{-1} vs. $[Q]^{-1}$ plots. Multiplication of k_q^f by α yields k_q^p, the overall rate constant for product-forming channels, and conversely the quantity $(1 - \alpha)k_q^f$ corresponds to radiationless but non-product-forming channels.[11]

The following trends emerge. Although the overall rate constant for deactivation (k_q^f) increases rapidly as the substituent X becomes more electron donating, the efficiency of product formation (α) simultaneously decreases, We find, quite surprisingly, that k_q^p is nearly invariant with substituent X in **1**, but that k_q^r strongly depends on the nature of X, varying by a factor of 50 from X = Cl to X = OCH_3.

A degree of insight into the peculiar behavior of the (**1**-DCA)* system is provided by assuming[12] that $k_1 = k_{dif}$ (that is, exciplex formation occurs with diffusional efficiency), in which case eq 2 and 3 obtain:

$$k_q^f/(k_{dif} - k_q^f) = (k_r + k_p)/k_{-1} \qquad (2)$$

$$\alpha(k_r + k_p)/k_{-1} = k_p/k_{-1} \qquad (3)$$

With this assumption the values in Table II are derived. These data indicate that exciplex reversibility strongly depends on the nature of the substituent X in **1**: as X becomes increasingly electron donating, exciplex reversion to S_1 and Q (k_{-1} channel) becomes increasingly unlikely, while decay via radiationless channels (k_r or k_p) becomes dominant. These results strongly implicate a charge-stabilized exciplex intermediate in the photophysical decay of the (**1**-DCA)* system and provide valuable insight into the electronic factors which contribute to various modes of exciplex decay.

Table II. Exciplex Reversibility vs. Radiationless Decay[a]

X	$(k_r + k_p)/k_{-1}$	k_p/k_{-1}
Cl	0.61	0.55
F	1.4	0.79
H	3.8	1.7
CH_3	ind[b]	*c*
CH_3O	ind[b]	ind[b]

[a] Derived from parameters in Table I assuming that $k_1 = k_{dif}$; see text. [b] For these substituents $k_q^f \sim k_{dif}$ so that application of eq 2 becomes indeterminant. The values are >5. [c] Not determined.

References and Notes

(1) (a) Brown, R. S.; Eaton, D. F., Hosomi, A.; Traylor, T. G.; Wright, J. M. *J. Organomet. Chem.* **1974,** *66*, 249. (b) Schweig, A.; Weidner, U. *Ibid.* **1974,** *67*, C4. (c) Hosomi, A.; Traylor, T. G. *J. Am. Chem. Soc.* **1975,** *97*, 3682.

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(6) Preparative irradiations were performed in an immersion well apparatus using an Hanovia 450-W medium-pressure mercury lamp. Analytical runs were done in a merry-go-round apparatus using uranium glass filters (Corning 3–74; λ >410 nm). Tin compounds **1** do not absorb in this latter region and no ground-state **1**–DCA complexes were detected by UV–visible spectroscopy.

(7) Rio, G.; Sillion, B. *Bull. Soc. Chim. Fr.* **1961,** 831.

(8) Oily yellow solid: IR 2230 cm^{-1} (CN); NMR ($CDCl_3$) δ 8.4–8.2 and 7.8–7.5 (m, 8 H), 2.0–0.8 (m, 27 H).

(9) No stereochemistry implied.

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(11) Since k_q^f and α are obtained from separate experiments, the quantities $k_q^p = \alpha k_q^l$ and $k_1k_p/(k_1 + k_{-1} + k_p)$, which are mathematically equivalent, are measured independently of one another. Their close agreement argues for the validity of our methods.

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Double-Bond Participation in Cyclopent-3-enyl Tosylate

Sir:

There has been essentially universal agreement that π participation in cyclopent-3-enyl systems is entirely absent

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