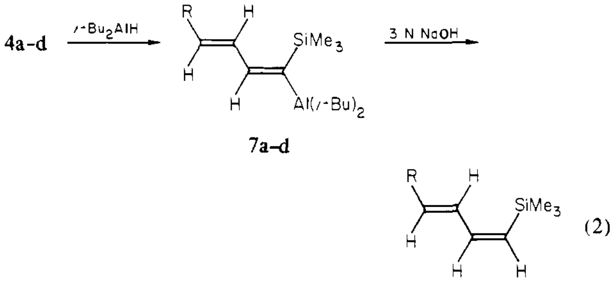
From a practical point of view, it is important to note that the now readily available 1-(trimethylsilyl)-*trans*-3-en-1-ynes **4** contain the easily manipulable (trimethysilyl)ethynyl group and hence are themselves of considerable value as synthetic intermediates. Thus, treatment of crude 1-(trimethylsilyl)-*trans*-3-decen-1-yne (**4a**) with KF·2H$_2$O in DMF[7] resulted in quantitative desilylation to afford the terminal enyne, *trans*-3-decen-1-yne, in 93% yield on the basis of the silyldiyne precursor **1a**. This novel methodology has been successfully applied to the synthesis of the insect pheromone Bombykol **6**[8] in an 81% yield based on **5**[5] (Scheme I).

Another attractive synthetic use of the 1-(trimethylsilyl)-*trans*-3-en-1-ynes **4** was their reduction to the corresponding trimethylsilylated butadienes **8**, which are valuable substrates for cycloaddition reactions.[11] Thus, treatment of **4** with diisobutylaluminum hydride produced the dienylalanes **7**.[12] Hydrolysis of **7**[14] afforded the 1-(trimethylsilyl)-(1*Z*,3*E*)-dienes **8** (eq 2) in high yields (Table I).



7a–d

8a–d

To establish the regiochemistry for hydroalumination of **4a**, the dienylalane **7a** was treated at 0 °C with deuterium oxide. Examination of the resultant deuterated dienylsilane by ^{1}H NMR revealed that at least 95% of one deuterium was incorporated at the C-1 carbon. Therefore, the hydroalumination of **4a** with diisobutylaluminum hydride must involve a cis addition of the Al–H bond to the (trimethylsilyl)ethynyl group with aluminum being attached nearly exclusively at the silicon-bearing carbon.[15]

Typical procedures for the preparation of **4a** and **8a** are as follows. To a solution of diisobutylaluminum hydride (1.0 mL, 5.5 mmol) in DME (7 mL) was added at 0 °C a 2.4 M solution of *n*-butyllithium (2.3 mL, 5.5 mmol) in hexane. The mixture was stirred at 0 °C for 15 min, treated with **1a**[5] (1.0 g, 5.5 mmol), stirred at 0 °C for 15 min, then warmed to room temperature, and stirred for an additional hour. The resultant solution was slowly poured into stirred, ice-cold 3 N HCl (10 mL). After extraction with hexane, the combined organic phases were washed successively with 3 N HCl, saturated aqueous NaHCO$_3$, and saturated aqueous NaCl and dried over MgSO$_4$. Distillation (Kugelrohr) yielded 0.99 g (95%) of **4a**: bp 95 °C (2 torr); $n^{25}{}_\mathrm{D}$ 1.4681.

1-(Trimethylsilyl)-*trans*-3-decen-1-yne (**4a**) was reduced as follows. To a solution of **4a** (0.42 g, 2.0 mmol) in ether (2 mL) at 25 °C was added neat diisobutylaluminum hydride (0.4 mL, 2.2 mmol). The mixture was heated at 40 °C for 4 h, then cooled to room temperature, and slowly poured into stirred, ice-cold 3 N NaOH (10 mL). After extraction with hexane, the combined organic phases were successively washed with 3 N NaOH and saturated aqueous NaCl and then were dried (MgSO$_4$). Distillation (Kugelrohr) afforded 0.41 g (97%) of **8a**: bp 65 °C (0.01 torr); $n^{25}{}_\mathrm{D}$ 1.4667.

Acknowledgment. We thank the National Science Foundation for support of this investigation.

Supplementary Material Available: Data supporting the purity and assignment of the products **4**, **6**, and **8** (3 pages). Ordering information is given on any current masthead page.

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(6) For syntheses of 1-(trimethylsily)-*trans*-3-en-1-ynes via the Wittig reaction, see: Corey, E. J.; Ruden, R. A. *Tetrahedron Lett.* **1973**, 1495. Corey, E. J., Fleet, G. W. J.; Koto, M. *Ibid.* **1973**, 3963. Hann, M. M.; Sammes, P. G.; Kennewell, P. D.; Taylor, J. B. *J. Chem. Soc., Chem. Commun.* **1980**, 234. For syntheses of 1-(trimethylsilyl)-*cis*-3-en-1-ynes, see: Holmes, A. B.; Raphael, R. A.; Wellard, N. K. *Tetrahedron Lett.* **1976**, 1539. Yamakado, Y.; Ishiguro, M.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 5568. Corey, E. J.; Rücker, C. *Tetrahedron Lett.* **1982**, 719; Jones, G. E.; Holmes, A. B. *Ibid.* **1982**, *23*, 3203.

(7) Corey, E. J.; Ruden, R. A. *Tetrahedron Lett.* **1973**, 1495.

(8) Eiter, K. Fortschr. *Chem. Forsch.* **1970**, *28*, 204. Negishi, E.; Lew, G.; Yoshida, T. *J. Chem. Soc., Chem. Commun.* **1973**, 874. Normant, J. F.; Commercon, A.; Villieras, J. *Tetrahedron Lett.* **1975**, 1465.

(9) Zweifel, G.; Clark, G. M.; Polston, N. L. *J. Am. Chem. Soc.* **1971**, *93*, 3395.

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(11) For a recent summary of Diels–Alder reactions of trimethylsilylated butadienes, see: Koreeda, M.; Ciufolini, M. A. *J. Am. Chem. Soc.* **1982**, *104*, 2308.

(12) It is noteworthy that replacement of the trimethylsilyl group in **4** by an alkyl group results in a reversal of the direction of addition of the Al–H bond to the enyne, placing the aluminum preferentially at the alkenyl-substituted carbon of the triple bond.[13]

(13) Knox, I.; Chang, S. C.; Andrist, A. M. *J. Org. Chem.* **1977**, *42*, 3981.

(14) Hydrolysis of the dienylalane **7a** with 3 N hydrochloric acid afforded a 9:1 mixture of the (1*Z*,3*E*)- and (1*E*,3*E*)-silyldienes.

(15) For stereoselective monohydroaluminations of (1-alkynyl)trimethylsilanes see: Eisch, J. J. Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. Eisch, J. J.; Damasevitz, G. A. *Ibid.* **1976**, *41*, 2214. Uchida, K.; Utimoto, K.; Nozaki, H. *Ibid.* **1976**, *41*, 2215. Zweifel, G.; Lewis, W. *Ibid.* **1978**, *43*, 2739.

(16) For syntheses of (1*E*,3*E*)-bis(trimethylsilyl)-1,3-butadiene, see: Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1978**, *144*, 1. Carter, M. J.; Fleming, I.; Percival, A. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2415.

An Unprecedented Bis(carbyne) Cluster Rearrangement Involving Simultaneous Coupling and Decoupling of Carbyne Fragments: A New Homogeneous Model for C–C Bond Forming and Bond Breaking on Surfaces

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Carbyne complexes are of considerable current interest because of their intrinsic novelty[1] and their potential as homogeneous analogues of surface carbynes, postulated to occur as crucial intermediates in hydrocarbon rearrangements[2] and synthesis via the reduction of carbon monoxide (Fischer–Tropsch synthesis).[3] Carbyne–carbyne coupling[4a] could constitute an alternative to the currently accepted mechanisms of carbon chain buildup in these

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(1) See N. M. Kostić and R. F. Fenske, *J. Am. Chem. Soc.*, **103**, 4677 (1981), and references therein.

(2) F. G. Gault and J. J. Rooney, *J. Chem. Soc., Faraday Trans. 2*, **75**, 1320 (1979); F. Weisang and F. G. Gault, *J. Chem. Soc., Chem. Commun.*, 519 (1979); L. L. Kesmodel, L. H. Dubois, and G. A. Somorjai, *J. Chem. Phys.*, **70**, 2180 (1979); J. C. Hemminger, E. L. Muetterties, and G. A. Somorjai, *J. Am. Chem. Soc.*, **101**, 62 (1979); L. H. Dubois, D. G. Castner, and G. A. Somorjai, *J. Chem. Phys.*, **72**, 5234 (1980); S. Lehwald and H. Ibach, *Surf. Sci.*, **89**, 425 (1979); J. E. Demuth, *ibid.*, **93**, 127 (1980), **93**, L82 (1980); P. Skinner, M. W. Howard, I. A. Oxton, S. F. A. Kettle, D. P. Powell, and N. Sheppard, *J. Chem. Soc., Faraday Trans. 2*, **77**, 1203 (1981); F. G. Gault, *Adv. Catal.* **30**, 1 (1981); J. H. Wengrovius, J. Sancho, and R. R. Schrock, *J. Am. Chem. Soc.*, **103**, 3932 (1981).

(3) E. L. Muetterties and J. Stein, *Chem. Rev.*, **79**, 479 (1979); C. Masters, *Adv. Organomet. Chem.*, **17**, 61 (1979); C. K. Rofer-DePoorter, *Chem. Rev.*, **81**, 447 (1981); W. A. Herrmann, *Angew. Chem.*, **94**, 118 (1982); *Angew. Chem., Int. Ed. Engl.*, **21**, 117 (1982).

(4) (a) R. Hoffmann, C. N. Wilker, and O. Eisenstein, *J. Am. Chem. Soc.*, **104**, 632 (1982); (b) R. J. Dellaca, B. R. Penfold, B. H. Robinson, W. T. Robinson, and J. L. Spencer, *Inorg. Chem.*, **9**, 2204 (1970); B. H. Robinson and J. L. Spencer, *J. Organomet. Chem.*, **30**, 267 (1971); I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, *ibid.*, **73**, 383 (1974); E. O. Fischer, A. Ruhs, P. Friedrich, and G. Huttner, *Angew. Chem.*, **89**, 481 (1977); *Angew Chem., Int. Ed. Engl.*, **16**, 465 (1977); K. M. Nicholas, M. O. Nestle, and D. Seyferth, in H. Alper, Ed., "Transition Metal Organometallics in Organic Synthesis", Vol. 2, Academic Press, New York, 1978, p 2; E. O. Fischer, D. Wittmann, D. Himmelreich, and D. Neugebauer, *Angew. Chem.*, **94**, 451 (1982); *Angew Chem., Int. Ed. Engl.*, **21**, 444 (1982); *Angew. Chem. Suppl.*, 1036 (1982).

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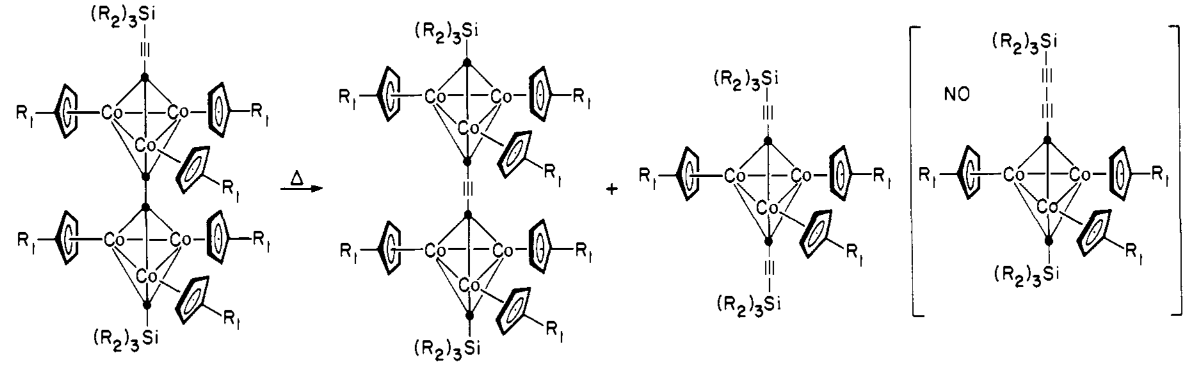
Scheme I



2 **3** **4** **5** $R_1 = H; R_2 = CH_3$
6 **7** **8** **9** $R_1 = R_2 = CH_3$
10 **11** **12** **13** $R_1 = H; R_2 = CH_3CH_2$

Table I. Flash Vacuum Pyrolysis Yields[a] from **2** and **3**

starting materials	temp, °C[b]	products		
		2	3	4
2	352	0.96		
	492	0.597	0.258	0.016
	550	0.0392	0.440	0.032
3	551	0.0043	0.759	0.012
	615		0.146	0.0795

[a] Yields are expressed in moles of product per mole of starting material. The sublimations of starting materials were virtually quantitative (→99%). [b] Temperature at the center of the furnace.

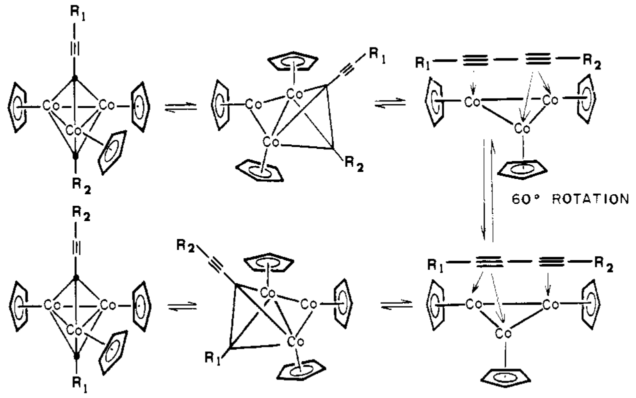
reactions. Such couplings are observed in homogenous chemistry,[4b] but examples are mechanistically ill-defined, do not occur intramolecularly, and do not involve simultaneous C–C bond making and breaking. We report here a remarkable intramolecular "deck shift" of a double-deck bis(carbyne)–cobalt cluster in which a carbyne–carbyne linkage is made at the same time as another one is broken.

In initial experiments we observed the reformation of the alkyne ligands in the flash or solution pyrolysis of $(\mu_3\text{-}\eta^1\text{-CR}_1)(\mu_3\text{-}\eta^1\text{-CR}_2)[(\eta^5\text{-C}_5H_5)Co]_3$ cluster **1** without scrambling of the individual carbyne units. For example, flash vacuum pyrolysis (FVP) of **1** ($R_1 = R_2 = C_6H_5$)[5] (668 °C, 10^{-4} torr) gave diphenylacetylene (20%) and recovered starting material.[6] More important, **1** (R_1 = Me_3Si, R_2 = H)[5] on heating in solution produced only (trimethylsilyl)ethyne (46%, in addition to **1**), with no ethyne or bis(trimethylsilyl)ethyne.

These results prompted an investigation of the double-deck system **2** (Scheme I) in which the appended alkyne unit might play a role. Fascinatingly, *FVP of* **2** *gave largely the isomer* **3** derived by a "deck shift" from the internal to the terminal position (Table I).[6] This rearrangement is reversible, since **2** resulted from the 551 °C FVP of **3** in about 1.8% yield based on 24% conversion. The fact that **3** is thermodynamically more stable than **2** could be of steric origin. The formation of the additional product **4** has as a likely intermediate (the unobserved) **5** since the ratio of **4** to **2** starting from **3** is much higher than that from **2**.

Cluster **2** sublimed unchanged (96% recovery) at 352 °C, ruling out the occurrence of a "deck shift" in the heated solid prior to entering the hot tube, indicative of a unimolecular isomerization pathway.[7,8] Although **2** gives **3** also in solution (pristane, 290 °C, 6 h, 40% yield, 15% recovery of **2**), reliable kinetics have been precluded by the partial decomposition of both clusters. A rigorous test for intramolecularity was obtained by a crossover study. Treatment of bis(timethylsilyl)hexatriyne with $(\eta^5\text{-CH}_3C_5H_4)Co(CO)_2$ (3 equiv) gave[9] complexes **6**–**8**. Similarly, reaction of bis(triethylsilyl)hexatriyne[10] with $(\eta^5\text{-C}_5H_5)Co(CO)_2$ (3 equiv) resulted[9] in the bis(triethylsilyl) analogues **10** and **12** (but not **11**). Heating a mixture of **6** and **10** (pristane, 265 °C, 59 h) gave (73% total cluster recovery) **7** and **11**, in addition to recovered **10** (33%) and *no crossover product* (field desorption mass spectroscopy). A more rigorous experiment involved **2**-d_{30} prepared[11] (95% enriched) and copyrolyzed with **10** (75% cluster recovery, 100% conversion) to again furnish products in which *no crossover* was detectable (e.g., only **3**-d_{30} and **11**). Thus, the observed "deck shift" is clearly intramolecular.

Scheme II



Among the variety of mechanisms connecting **2** with **3**, two extremes deserve particular speculative attention. The first would involve a "breathing motion" of the trinuclear cobalt core with simultaneous (concerted) slippage of the ligand through the metal

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(5) J. R. Fritch and K. P. C. Vollhardt, *Angew. Chem.*, **92**, 570 (1980); *Angew. Chem., Int. Ed. Engl.*, **19**, 559 (1980).

(6) Other products were traces of cyclopentadiene, cobaltocene, trimethylsilane, and a cobalt mirror.

(7) G. Seybold, *Angew. Chem.*, **81**, 377 (1977); *Angew. Chem., Int. Ed. Engl.*, **16**, 365 (1977).

(8) Approximate E_a = 41 kcal mol^{-1}; see J. R. Fritch and K. P. C. Vollhardt, *Organometallics*, **1**, 590 (1982), ref 56.

(9) Compound **6**: black plates, 1.2%; mp 424–426 °C dec; *m/e* 1046 (M^+, 100), 974 (4.4); ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 9 H), 1.06 (s, 9 H), 1.54 (s, 9 H), 2.08 (s, 9 H), 4.26 (AA′, m, 6 H), 4.54 (BB′, m, 6 H), 4.65 (CC′, m, 6 H), 5.06 (DD′, m, 6 H); IR (KBr) $\nu_{C \equiv C}$ 2060 cm^{-1}. **7**: black plates, 0.6%; mp 430 °C dec; *m/e* 1046 (M^+, 7.5), 217 (100); ^{1}H NMR ($CDCl_3$) δ 0.86 (s, 18 H), 1.83 (s, 18 H), 4.39 (AA′, m, 12 H), 4.63 (BB′, m, 12 H). **8**: burgundy crystals, 21%; mp 124–125 °C. **10**: bronze plates, 2.1%; mp 350 °C dec; *m/e* 1046 (M^+, 24), 320 (100); ^{1}H NMR (90 MHz; $CDCl_3$) δ 0.1–1.7 (m, 45 H), 4.60 (s, 15 H), 4.66 (s, 15 H); IR (KBr) $\nu_{C \equiv C}$ 2070 cm^{-1}. **11**: bronze crystals, 70%; mp 350 °C dec; *m/e* 1046 (M^+, 5.5), 44 (100); ^{1}H NMR ($CDCl_3$) δ 1.26–1.56 (m, 30 H), 4.64 (s, 30 H). **12**: burgundy crystals, 46%; mp 122–123 °C; *m/e* 674 (M^+, 72.8), 189 (100); ^{1}H NMR (C_6D_6) δ 0.92 (q, *J* = 8 Hz, 12 H), 1.335 (t, *J* = 8 Hz, 18 H), 4.47 (s, 15 H); IR (KBr) $\nu_{C \equiv C}$ 2060 cm^{-1}.

(10) R. Eastmond, T. R. Johnson, and D. R. M. Walton, *Tetrahedron* **28**, 4601 (1972). This compound was prepared from hexatriynebis(magnesium bromide) and triethylchlorosilane (9.1%).

(11) This involved the preparation of $(\eta^5\text{-C}_5D_5)Co(CO)_2$ from C_5D_6: W. Grimme and W. von Eggers Doering, *Chem. Ber.*, **106**, 1765 (1973).

triangle. If one were to keep the Co–carbyne bond at its initial distance of 1.87 Å[12] during this process, the individual pairs of Co atoms would be required to separate to 3.24 Å, appreciably beyond the normal bond length.[12] A more classical mechanistic alternative is shown in Scheme II and proceeds through 16- and 18-electron metal centers. Finally, the (superficial?) similarity of the topological changes associated with the deck shifts uncovered in this work to those occurring in carboranes[13] might be mechanistically significant.

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(12) J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, and V. W. Day, *J. Am. Chem. Soc.*, **101**, 2768 (1979).

(13) See R. L. DeKock, T. P. Fehlner, C. E. Housecroft, T. V. Lubben, and K. Wade, *Inorg. Chem.*, **21**, 25 (1982), and references therein.

Photosensitized Electron-Transfer Reactions. Interception of the Geminate Radical Ion Pair

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Photosensitized electron-transfer reactions such as dimerizations, nucleophilic additions, and rearrangements are usually carried out in polar solvents, which favor the formation of separated radical ions. Indeed, most of these reactions are likely to proceed via the out-of-cage, solvated radical ions.[1] Recently, however, we showed that, in the reaction of phenylacetylene sensitized by 2,6,9,10-tetracyanoanthracene (TCA), the geminate ion pair can be intercepted by a phenylacetylene or an alkylacetylene.[2] This reaction competes with the dissociation into separated ions and the energy-wasting, reverse electron transfer within the geminate pair. Reactions via the intercepted geminate pair may extend the diversity of photochemical electron-transfer reactions because of the difference in reactivities of these intermediates and those of the separated radical ions. Interception of the radical ion pair also offers the potential for increasing the quantum yield of product formation. In this study of the kinetics of the electron-transfer-photosensitized dimerization of 1,1-diphenylethylene (D), we found that interception of the geminate pair plays a central role in this reaction.

We have found[3] that electron-transfer sensitization of D leads to 2 + 2 cyclodimerization in competition with the well-known 2 + 4 cyclodimerization, first reported by Arnold (Scheme I).[4] The product distribution of this reaction is very dependent on the concentration of D, which suggests the involvement of different intermediates. The data presented below strongly support the mechanism outlined in Scheme II, in which the interception of the geminate radical ion pair by D forms a dimeric radical cation in cage with the sensitizer radical anion, $S^{-\cdot}$. Reverse electron transfer produces the biradical $\dot{D}-\dot{D}$, which reacts differently from the dimeric radical cation, $\dot{D}-D^{+}$, formed from the separated $D^{+\cdot}$. Two sensitizers were used in this study, 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA), which have reduction potentials (in CH_3CN vs. SCE) of −0.89 and −0.45 V, respectively.

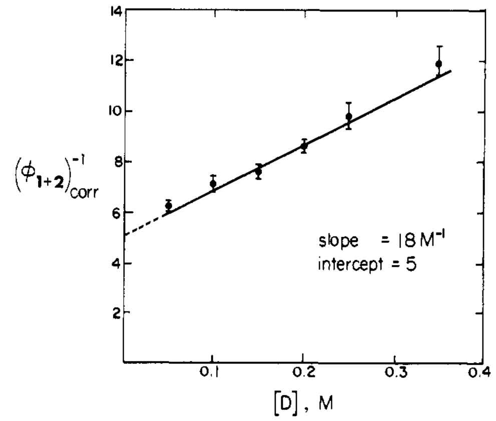
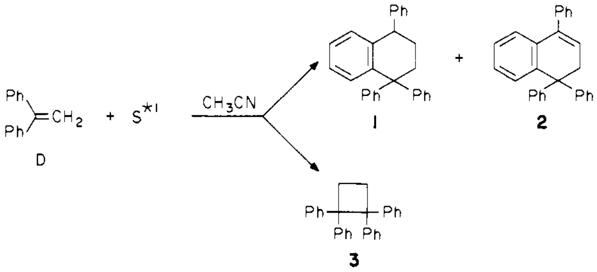
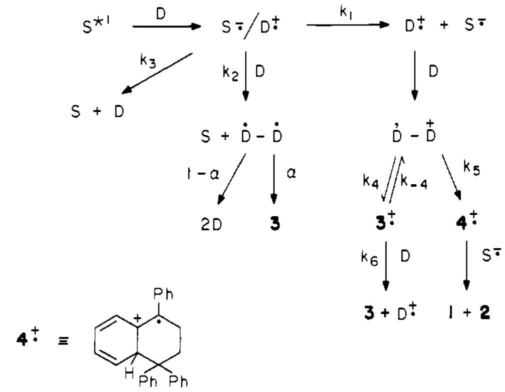


Figure 1. Plot of $(\phi_{1+2})_{corr}^{-1}$ vs. [D]. The data were obtained from irradiation (λ ≥405 nm) of saturated solutions of DCA under N_2.

Scheme I



Scheme II



According to the proposed mechanism, the quantum yield for the formation of **1** and **2**, corrected for incomplete interception of the excited sensitizer,[5] $(\phi_{1+2})_{corr}$, should decrease with increasing [D], as shown by eq 1.

$$\frac{1}{(\phi_{1+2})_{corr}} = \frac{k_1 + k_3}{k_1} + \frac{k_2}{k_1}[D] \qquad (1)$$

A plot of $1/(\phi_{1+2})_{corr}$ vs. [D], with DCA as a sensitizer, has an intercept, $(k_1 + k_3)/k_1$, of 5 and a slope, k_2/k_1, of 18 M^{-1} (Figure 1). A slight deviation from linearity at low [D] (<0.03 M) is probably due to other reactions of $D^{+\cdot}$ competing with the dimerization. With TCA as a sensitizer, the quantum yields are much lower,[6] i.e., the ratio k_3/k_1 is higher, and the dependence of $(\phi_{1+2})_{corr}$ on [D] is much less, as expected. For TCA, $(k_1 + k_3)/k_1$ is ca. 28. These values show that, at low [D], the efficiency of formation of separated radical ions from the pair $DCA^{-\cdot}/D^{+\cdot}$ is ca. 20% and from $TCA^{-\cdot}/D^{+\cdot}$ is 3–4%.

An estimate of k_2 can be obtained from the effect of quenchers on the quantum yields. Using the quencher 1,2,4-trimethoxy-

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(1) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80 and references therein.

(2) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 126.

(3) The formation of **1** or a mixture of **1** and **2** depends on the sensitizer used. With DCA as a sensitizer, **1** and **2** are formed in similar amounts. In this reaction the formation of **2**, a dehydrodimer, is accompanied by an equal yield of *cis*- and *trans*-dihydrodicyanoanthracene. The details of this reaction will be given in another publication.

(4) Neunteufel, R. A.; Arnold, D. R. *J. Am. Chem. Soc.* **1973**, *95*, 4080.

(5) The Stern–Volmer slopes for the quenching of the fluorescence of DCA and TCA by D in CH_3CN are 310 and 130 M^{-1}, respectively. The lifetimes of the singlet states of these compounds are 19.6 and 15.2 ns, respectively.

(6) The quantum yield $(\phi_{1+2})_{corr}$ at [D] = 0.1 is ca. 0.033 for TCA vs. 0.15 for DCA.

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