J. Am. Chem. Soc. 1981, 103, 5935–5937

ditions, which include solvent and temperature changes, as well as addition of quenchers such as cyclohexane (vide infra). These observations provide conclusive proof that the 400 and 500-nm transients are products resulting from reactions of the 470-nm species.

When the above experiment is repeated in the presence of diethyl fumarate (0.025 M) or oxygen, the same two bands are formed, but each decays with different kinetics (see Figure 1, where the ratio of lifetimes for the two bands is 10) and hence cannot be assigned to the same species. In the presence of diethyl fumarate the transient at 400 nm decays more rapidly, suggesting that the assignment of ^{3}Fl is correct, while in the presence of oxygen the converse is true. This suggests that the 500-nm transient may be due to the 9-fluorenyl radical. Indeed, it is the only transient formed from ^{1}Fl decay if the photolysis is carried out in cyclohexane which serves as a good hydrogen donor.

The assignment of the 500-nm peak (and its characteristic 470-nm shoulder band) was confirmed by generating the 9-fluorenyl radical independently. Thus, photolysis of di-*tert*-butyl peroxide in a benzene solution containing fluorene using either laser flash photolysis or modulation spectroscopy[12,13] for detection gives the same spectrum in the 500-nm region as is observed in the photolysis of DAF (Figure 2).

When DAF is photolyzed in CD_3CN at 27 °C, the lifetime of ^{1}Fl is 37 ns as compared with 27 ns for CH_3CN as solvent, an effect which we believe is due to a deuterium isotope effect on the abstraction process. If we assume that the isotope effect is infinitely large, we can obtain a *lower* limit of 27% for the extent to which ^{1}Fl is converted to the fluorenyl radical in acetonitrile. Hence, hydrogen abstraction by ^{1}Fl is an important reaction pathway even in a fairly inert solvent.

A rough estimate of the importance of hydrogen abstraction in acetonitrile can also be obtained by using the signals in cyclohexane as a relative actinometer. If we assume that under these conditions abstraction is quantitative (no other transient detected), then, by comparing the optical densities due to fluorenyl radical in both solvents, we estimate that abstraction accounts for 20–35% of the ^{1}Fl decay in acetonitrile. When small amounts of cyclohexane were added to a solution of DAF in CD_3CN, we observe a gradual increase in the yield of the 500-nm transient relative to that of ^{3}Fl (which remained long lived), as well as a decrease of the lifetimes associated with the processes at 400, 470, and 500 nm. The lifetimes measured (e.g., 14 ns for 0.46 M cyclohexane at 30 °C) were wavelength independent, as expected, and thus rule out the possibility that the radical could be formed in this time scale from the long-lived ^{3}Fl or a short-lived excited-state precursor. From a plot of the reciprocal of the ^{1}Fl lifetime vs. cyclohexane concentration, we estimate k(cyclohexane) = 8.3×10^{-7} M^{-1} s^{-1} at 30 °C.[14]

Further, evidence for the radical like behavior of ^{1}Fl was obtained by photolyzing DAF (8×10^{-4} M) in carbon tetrachloride at 27 °C. The transient absorption spectrum due to ^{3}Fl could not be detected but a sharp peak at 490 nm with a shape virtually identical with that recorded for the fluorenyl radical was formed, which is assigned to the 9-chlorofluorenyl radical. As support for this assignment, we and others[15] have isolated 9,9′-dichloro-9,9′-bifluorenyl in ca. 50% yield. Moreover, typical carbene scavengers such as diethyl fumarate have little or no effect on the lifetime of this transient.

An important consequence of the role of hydrogen abstraction by ^{1}Fl is that its lifetime cannot be regarded as a measure of the rate constant for intersystem crossing.[8] The observed rate constants for singlet decay represent a composite due to intersystem crossing and hydrogen abstraction.

Measurements of the rate constants over the temperature range −40 to +60 °C in CH_3CN and CD_3CN can be represented, respectively, by the expressions 1 and 2, where $\theta = 2.3RT$ kcal

$$\log k/\mathrm{s}^{-1} = 9.64 \pm 0.10 - (2.85 \pm 0.13)/\theta \tag{1}$$

$$\log k/\mathrm{s}^{-1} = 9.23 \pm 0.25 - (2.47 \pm 0.29)/\theta \tag{2}$$

mol^{-1} and the errors correspond to 95% confidence limits. These expressions do not yield Arrhenius parameters directly since they cannot be assigned to elementary steps in the decay of ^{1}Fl. However, since in CH_3CN the ratio[17] of the signals at 400 and 500 nm changes from 7.1 at 57 °C to 9.1 at −40 °C, we can conclude[18] that 2.85 kcal mol^{-1} represents a lower limit for the activation energy of hydrogen abstraction and an upper limit to that for intersystem crossing.

Finally, it should be noted that hydrogen abstraction from the solvent by ^{1}Fl does not affect the conclusions regarding the kinetics of the reactions of ^{1}Fl with olefins. Our values for the activation energies and log A values for reaction of ^{1}Fl with two olefins based on direct, time-resolved experiments in CD_3CN are in good agreement with those published for other olefins.[18] For diethyl fumarate and 2,3-dimethylbutene, we obtained activation energies of 0.29 and 1.93 kcal mol^{-1} and log A/M^{-1} s^{-1} values of 9.37 and 10.23, respectively.[19]

Acknowledgment. Thanks are due to S. E. Sugamori for his technical assistance and also to Dr. C. Huggenberger and Professor H. Fischer for generously sharing the design for their modulation spectrometer.

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[12] Huggenberger, C.; Lipscher, J.; Fischer, H. *J. Phys. Chem.* **1980**, *84*, 3467–3474. Huggenberger, C.; Fischer, H. *Helv. Chim. Acta*, in press.

[13] The modulation spectrometer used in this work was substantially the same as that designed by Huggenberger and Fischer.[12]

[14] We are grateful to the referees for suggesting this experiment.

[15] Murahashi, S.; Moritani, I.; Nagai, T., *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1655–1660.

[16] The activation energy for deuterium abstraction can be expected to be higher than for hydrogen; however, the apparent activation energy is smaller in acetonitrile-d_3 because the relative importance of abstraction decreases (with a concurrent increase in intersystem crossing which tends to decrease E_a).

[17] This ratio cannot be used directly to determine the difference in activation energy between the two processes because of the possibility of some underlying absorption by ^{3}Fl.

[18] A value of 1.9 kcal mol^{-1} was previously obtained as the apparent activation energy for singlet decay,[8] from measurements over a smaller temperature range. This lower value was incorporated in competition studies into activation energies for quenching of ^{1}Fl by olefins and led to negative activation energies for the latter reactions.[8]

[19] The experimental data obtained in this work were corrected to allow for the increase in concentrations which occurs as the solutions contract on cooling.

Carbenes and the O–H Bond: Cyclopentadienylidene and Cycloheptatrienylidene

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Received June 1, 1981

A variety of carbenes react with alcohols to give ethers.[1] The mechanism of these "O–H insertions" has not received much attention. At least three plausible reaction paths are conceivable: (a) One-step insertion into the O–H bond (comparable to the C–H insertion of singlet carbenes), (b) electrophilic attack of the carbene at oxygen, followed by proton transfer, and (c) protonation of the carbene to give a carbocation (or ion pair) (Scheme I). The electrophilic vs. nucleophilic character of the carbene should play a major role in selecting the proper mechanism. Cyclo-

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[1] For reviews of older work, see: Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23. Kirmse, W. "Carbene Chemistry"; Academic Press: New York, 1970; pp 423–425. For some recent leading references, see: Kang, U. G.; Shechter, H. *J. Am. Chem. Soc.* **1978**, *100*, 651. Hoffmann, R. V.; Shechter, H. *Ibid.* **1978**, *100*, 7934. Tomioka, H.; Griffin, G. W.; Nishiyama, K. *Ibid.* **1979**, *101*, 6009. Padwa, A.; Blacklock, T. J.; Loza, R.; Polniaszek, R. *J. Org. Chem.* **1980**, *45*, 2181. Tomioka, H.; Okuno, H.; Izawa, Y. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1636. *J. Org. Chem.* **1980**, *45*, 5278.

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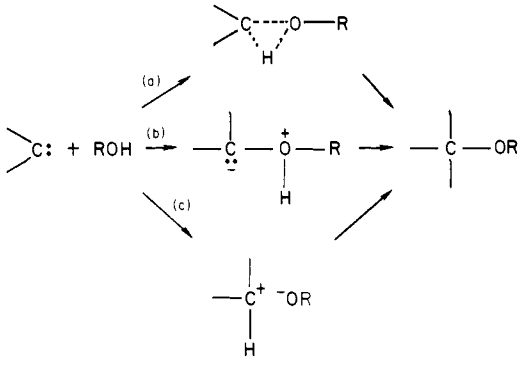
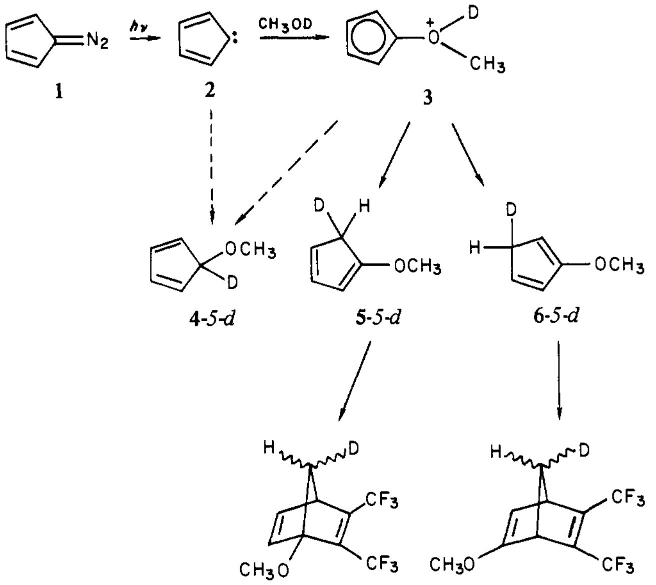
Scheme I



Scheme II

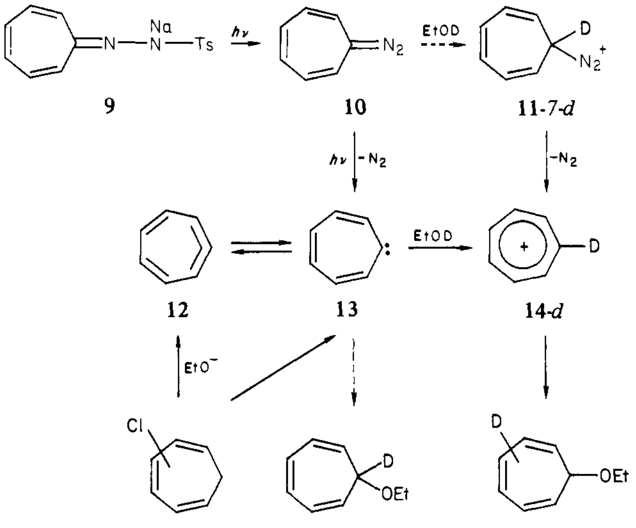


1 **2** **3** **4**-*5-d* **5**-*5-d* **6**-*5-d* **7**-*7-d* **8**-*7-d*

pentadienylidene is likely to follow path b whereas cycloheptatrienylidene might be protonated with formation of the stable tropylium ion. We report experimental evidence which confirms these expectations.

Photolysis of diazocyclopentadiene (**1**)[2] in methanol at room temperature afforded an equilibrium mixture of 1- and 2-methoxycyclopentadiene (**5**/**6** = 3:1 by NMR spectroscopy) (Scheme II).[3] The same mixture was obtained from an independent synthesis.[4] Diels–Alder reaction of **5** + **6** with hexafluoro-2-butyne produced the adducts **7** and **8** in a 3:1 ratio.[5] The equilibration of the methoxycyclopentadienes at room temperature does not allow any mechanistic conclusions. Therefore **1** was photolyzed in MeOD at −70 °C and the photolysate treated with hexafluoro-2-butyne for 24 h at the same temperature to achieve complete conversion of **5** and **6**. The adducts **7** and **8** were thus obtained in a 4:1 ratio and were shown by ^{1}H and ^{2}H NMR spectroscopy to carry deuterium only at C-7. No adduct derived from 5-methoxycyclopentadiene (**4**) was found. Although a 1,5-D shift might convert **4**-*5-d* to **5**-*5-d*, further 1,5 shifts cannot produce **6**-*5-d* exclusively. The deuterium distribution in **8** excludes direct O–H insertion (**2** → **4** → **5** → **6**) but is consistent with electrophilic attack of cyclopentadienylidene at the oxygen of methanol (**2** → **3** → **5** + **6**).

Scheme III



9 **10** **11**-*7-d* **12** **13** **14**-*d* **15** **16**-*7-d* **16**-*d*

Cycloheptatrienylidene (**13**) is most conveniently generated by photolysis of tropone tosylhydrazone sodium salt (**9**) (Scheme III).[6] When we photolyzed **9** in EtOD, we obtained 7-ethoxycycloheptatriene (**16**) with random distribution of the deuterium among all positions of the cycloheptatriene (by ^{2}H NMR spectroscopy).[7] The intermediacy of the tropylium ion **14**-*d* is obvious, but its origin is equivocal: rather than from cycloheptatrienylidene (**13**) the tropylium ion might arise via the diazonium ion **11**-*7-d*. Another approach to **13** is elimination of hydrogen chloride from chlorocycloheptatriene (**15**, mixture of the 1-, 2-, and 3-chloro isomers).[8,9] When we treated **15** with 3 M EtONa/EtOD (24 h, 80 °C, 58% conversion), **16**-*d* with random distribution of the deuterium was isolated in 50% yield.[10,11] In this case we see no alternative to a reaction path which involves protonation of cycloheptatrienylidene (**15** → **13** → **14** → **16**). The role of cycloheptatetraene (**12**) is an open problem in cycloheptatrienylidene chemistry. Many transformations are in accordance with the carbene structure, but some are indicative of a strained cyclic allene.[12] The formation of tropyl ether **16** belongs to the former

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(2) Doering, W. v. E.; DePuy, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 5955. Regitz, M., Liedhegener, A. *Tetrahedron* **1967**, *23*, 2701.

(3) The methoxycyclopentadienes are fairly stable in dilute solution but rapidly polymerize as a neat liquid. ^{1}H NMR (CD$_3$COCD$_3$) 2.85 (m, 5-H), 3.58 (s, OCH$_3$), 5.05 (t, J = 2 Hz, 1-H of **6**), 5.25 (m, 2-H of **5**), 5.55 (dq, J = 6, 1.5 Hz, 4-H of **5**), 6.2–6.3 (m, 3-H of **5**, 3, 4-H of **6**). On most GC columns the mixture gave a single peak; two peaks were seen at 20 °C on a 160-m capillary column coated with heptaglycol isononylphenyl ether (retention time ca. 3 h).

(4) Kirmse, W., Loosen, K., *Chem. Ber.* **1981**, *114*, 400.

(5) Adducts **7** and **8** were obtained in nearly quantitative yield and were readily separated by preparative GC (1-m column, 10% heptaglycol isononyl phenyl ether on chromosorb P, 70 °C). **7**: ^{1}H NMR (CCl$_4$) 2.32 (7-H), 3.36 (OCH$_3$), 3.75 (4-H), 6.73 (5-,6-H). **8**: ^{1}H NMR (CCl$_4$) 2.26 (7-H), 3.55 (OCH$_3$), 3.5–3.75 (1-, 4-H) 5.12 (6-H). The signals of syn and anti-7-H coincide in narrow multiplets.

(6) (a) Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391. (b) Mayor, C.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4498. (c) Duell, B. L.; Jones, W. M. *J. Org. Chem.* **1978**, *43*, 4901.

(7) Dilute solutions (ca. 0.01 M) and long wavelengths (≥355 nm, bismuth trichloride filter) gave acceptable yields (ca. 25%) of **16**. Shorter wavelengths led to the known photoproducts of **16** (Borden, G. W.; Chapman, O. L.; Swindell, R.; Tezuka, T. *J. Am. Chem. Soc.* **1967**, *89*, 2979); concentrated solutions produced amorphous solids.

(8) (a) Untch, K. International Symposium on the Chemistry of Non-Benzenoid Aromatic Compounds, Sendai, Japan, 1970. (b) Mayor, C.; Jones, W. M. *Tetrahedron Lett.* **1977**, 3855.

(9) Both precursors (**9** and **15**) give the same intermediate, as judged by its reactivity toward substituted styrenes; see ref 6c.

(10) Weaker bases (e.g., MeONa/MeOH) reacted too slowly; stronger bases (e.g., *t*-BuOK/*t*-BuOH) and higher temperatures led to isomerization of **16**.

(11) Some incorporation of deuterium in the recovered chloride **15** was found. This observation does not affect our conclusions: (i) The deuterium content of recovered **15** was <0.3D whereas that of **16** was >0.9D. (ii) The deuterium in recovered **15** was predominantly at C-7. (iii) **15** did not produce **16** in the absence of strong base (e.g., by 1-, 5-H shift to give tropylium chloride). (iv) Little loss of D was found when **15**-*d* was treated with EtONa/EtOH. Consequently, treatment of **15**-*d* with EtONa/EtOD must give **16**-*d*$_2$ of which only 8% was present.

(12) Saito, K.; Omura, Y.; Mukai, T. *Chem. Lett.* **1980**, 349. See also ref 6c and 8b.

category. Strained allenes are known to produce vinyl rather than allyl ethers on reaction with $\mathrm{RO^-/ROH}$.[13]

Acknowledgment. We thank Dr. W. Dietrich for ^{2}H NMR spectra and Dr. O. Schnurr for preliminary experiments with diazocyclopentadiene.

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[13] Mohanakrishnan, P.; Toyal, S. R.; Vaidyanathaswamy, R.; Devaprabhakara, D. *Tetrahedron Lett.* **1972**, 2871. Bottini, A. T.; Anderson, B. *Ibid.* **1973**, 3321.

Catalysis of the Hydrolysis of Ethyl Benzoate by Inverted Micelles Adsorbed on Platinum

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Received February 9, 1981

In studies of electrooxidation of compounds in the presence of cationic surfactants, it was observed that the surfactant filmed the electrode, altering relative rates of electrode reactions.[1-3] The film, which was composed of a layer of anions on the platinum electrode ion paired to surfactant cations, excluded water from the surface. This allowed the obtaining of anodic voltammetric curves in aqueous solutions for many substances that normally do not give voltammetric curves in water.[3]

To obtain a better understanding of this film, a study was made of the catalysis of the hydrolysis of ethyl benzoate on the film adsorbed on platinum. The homogeneous kinetics of this system had been previously studied,[4,5] and it has been shown that the rate of hydrolysis of esters is affected by the presence of micelles.[6,7]

The kinetic runs were made in a beaker containing 100 mL of 0.0965 N sodium hydroxide, 6.8×10^{-3} mol of ethyl benzoate, and, unless otherwise stated, 2.46 mmol of the surfactant, Hyamine 2389 (predominantly (methyldodecylbenzyl)trimethylammonium chloride obtained from Rohm and Haas). The critical micelle concentration of the surfactant is 0.04% by weight of the active material.[8] (This corresponds to an approximately 1 mM solution.) The temperature was not controlled but was monitored and was 26 ± 0.5 °C. A comparison of rates determined at the two extremes of the temperature range showed that they had an average difference of only 1%.

The initial rate of disappearance of the hydroxide ion was measured by withdrawing 2.0-mL samples from the stirred solution at 10-min intervals and titrating with standard hydrochloric acid. Different area platinum foils were inserted in the solution.

The effect of potential on the rate was determined in an H cell with the compartments separated by sintered glass. The catalytic compartment contained the reaction mixture, a 9.5-cm^2 foil, and a saturated calomel reference electrode. The potentials which were controlled by an Anotrol Model 4700 potentiostat are referred to the calomel electrode. The other compartment contained a 16.5-cm^2 platinum counter electrode.

The reaction was found to be catalyzed by Hyamine 2389. There is a maximum in the rate at about 20 mM of Hyamine which is typical for micelle catalysis.[9]

Figure 1 shows the effect of suspending platinum foils of different areas in the solution. It can be seen that in the absence of surfactant, addition of platinum caused only small changes in rate, while in the presence of surfactant the rate increases linearly with increases in platinum area. Apparently the inverted micelle adsorbed on the platinum is a better catalyst than the normal micelle.

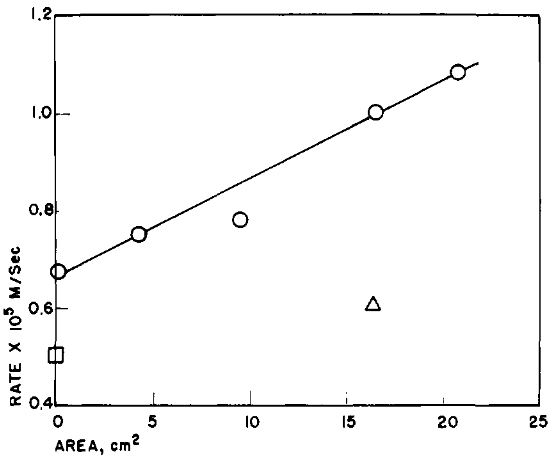

Figure 1. Effect of added platinum metal on the rate of hydrolysis of ethyl benzoate in the presence of Hyamine 2389 (4.87×10^{-2} M). (□) Rate in the absence of platinum or surfactant; (△) rate in the presence of platinum, without surfactant; (○) rate in the presence of platinum and surfactant.

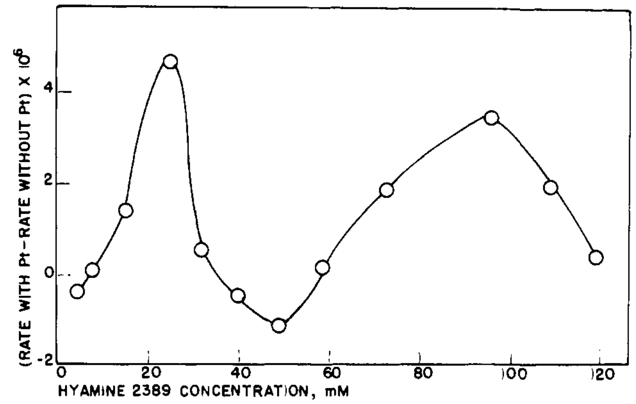

Figure 2. Effect of surfactant concentrations on the rate (×10^6 M/s) of the platinum–surfactant-film-catalyzed hydrolysis of ethyl benzoate (rate in the presence of platinum – rate in the absence of platinum).

Figure 2 shows the effect of different concentrations of surfactant on the acceleration of the rate by platinum as measured by subtracting the rate with surfactant from the rate with platinum and surfactant.

A reasonable explanation of this curve is that the first maximum in the rate occurs at the surfactant concentration that forms a monolayer which consists of an inverted micelle on the platinum surface. The decrease in rate beyond the maximum would then be caused by formation of a bilayer, with the minimum occurring on completion of the bilayer. That this explanation is correct is indicated by the fact that the concentration at the minimum is twice the concentration at the first maximum; however, this factor of 2 may be a coincidence. One would expect the third layer to be a good deal more diffuse. In agreement with this the second maximum is broader and occurs at 3.8 times the concentration of the first maximum rather than 3 times.

In the electrochemical studies[1-3] it had been observed that the Hyamine showed two oxidation waves and that this oxidation was important in the formation of the electrochemically active film. The catalysis of the hydrolysis reaction was studied on platinum potentiostatted at different potentials to determine whether Hyamine oxidation formed a film with different characteristics. No abrupt change in rate was observed, indicating that the oxidized film has essentially the same catalytic characteristics as the unoxidized film. As previously shown,[10] there is only a slight

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[7] Fendler, J. H. *Acc. Chem. Res.* **1976**, *9*, 153.

[8] Dupuy, G., personal communication, 1981.

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