tion of the most stable anion ($ArSO_3^-$) compensate for the breaking of the C–O bond.

The new compounds I, III, and IV were characterized by elemental analyses and ir, nmr, and mass spectra. Since dialkyl alkoximidocarbonates had not been reported, IIIa, IIIc, and IIId were prepared independently from the corresponding hydroximidocarbonates and the appropriate alkyl iodides.

Acknowledgment. We are greatly indebted to the National Science Foundation for support of this work under Grant No. GP27951X.

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Received August 18, 1972

Reversible Intramolecular Photocycloaddition of Naphthalene to Anthracene

Sir:

The technique of attaching two potentially interacting groups to a chain of methylene groups has proven to be of considerable value in the study of molecular interactions in dilute solution.[1,2] Separation of the interacting groups by three saturated carbon atoms offers the best geometrical relationship for the observation of excited-state interactions. This was the origin of our interest in 1-(9-anthryl)-3-(1-naphthyl)-propane (ANP). We have found that it readily undergoes intramolecular photochemical cycloaddition of the naphthalene and anthracene moieties.

The absorption spectrum of ANP shows no evidence for intramolecular interaction at either 77 or 298°K. Its fluorescence was originally studied by Schnepp and Levy[3] who demonstrated complete intramolecular transfer of energy from naphthalene to anthracene. The fluorescence spectrum is unfortunately rather unexciting; it displays no significant exciplex interaction under conditions (-80 to $+50°$) where the two symmetrical dinaphthylpropanes exhibit substantial intramolecular excimer formation.[1] The fluorescence intensity is decreased by increasing temperature; the activation energy is similar to that found for 9-methylanthracene.[4]

ANP undergoes two photochemical transformations on irradiation with light of $\lambda > 350$ nm. Both can be observed easily by absorption spectroscopy. At concentrations above 10^{-3} *M*, in deaerated solution, bimolecular photodimerization of the anthracene occurs. The absorption spectrum of the product has no bands attributable to anthracene but the absorption of the naphthalene moiety is still present.

In contrast to this finding, the irradiation of much more dilute (*ca.* 2×10^5 *M*) solutions of ANP in methylcyclohexane results in the simultaneous disappearance of both naphthalene (*ca.* 280 nm) and anthracene (260, 330–380 nm) absorption, resulting in the formation of a species whose absorption spectrum (Figure 1) is similar to that of dianthracene. Irradiation of the solution with 254-nm light restores the original spectrum to 70% of its original intensity. The new species must be the result of intramolecular addition of anthracene to naphthalene, an unexpected reaction, and the only structure in accord with the absorption spectrum is I.

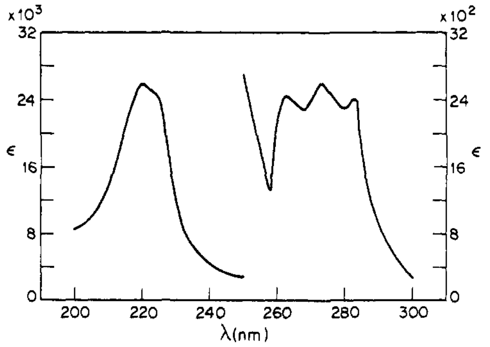
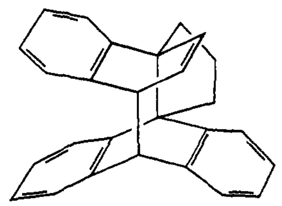


Figure 1. The absorption spectrum of the intramolecular adduct obtained on irradiation of 1-(9-anthryl)-3-(1-naphthyl)propane (2×10^{-5} *M* in methylcyclohexane).



I

The new compound is unaffected by heating at 75° several hours [*cf.* the facile rearrangement of the intramolecular dimer of 1,3-bis(1-naphthyl)propane][5] but can be broken to ANP by heating at 165°. This experiment was not entirely satisfactory because of the competing decomposition of ANP, attributed to residual oxygen, at the low concentrations employed; more concentrated solutions show no decomposition. We have not attempted to isolate the photoisomer because of the obvious difficulties involved but we feel that the structural assignment is unambiguous.

The formation of I implies the occurrence of exciplex interaction between anthracene and naphthalene; the exciplex is presumably an intermediate in the photochemical reaction. The interaction appears to be weak, as might be expected; the irradiation of a cyclohexane solution of both anthracene (10^{-3} *M*) and naphthalene (1 *M*) gives a precipitate of dianthracene. A binding energy in the neighborhood of 3–4 kcal mol^{-1} is estimated from the emission spectrum of the anthracene–naphthalene sandwich pair at low temperature.[6] The exciplex lifetime is fairly long and this probably accounts for our failure to observe its fluorescence.

It is known that 9,10-dicyanoanthracene forms a fluorescent exciplex with naphthalene.[7] We found no evidence for photoaddition in this system, even when pure liquid 1-methylnaphthalene was used as the solvent. The irradiation of compounds II and III led

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(1) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 3586 (1970), and references cited therein.

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(3) O. Schnepp and M. Levy, *J. Amer. Chem. Soc.*, **84**, 172 (1962).

(4) E. C. Lim, J. D. Laposa, and J. M. H. Yu, *J. Mol. Spectrosc.*, **19**, 412 (1966).

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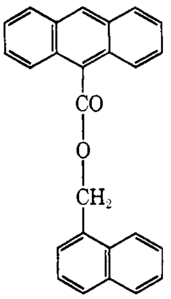
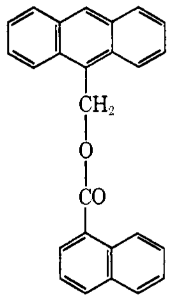
(6) E. A. Chandross and A. H. Schiebel, *ibid.*, submitted for publication.

(7) E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).



II



III

only to slow bimolecular anthracene dimerization. Thus, the intramolecular photocycloaddition which occurs in ANP appears to be somewhat unique. Its closest analog is the recent work of Bouas-Laurent and Castellan[8] who reported the photoaddition of various anthracenes to tetracene whose reactivity is vastly greater than that of naphthalene. The intramolecular addition of ethylene to benzene[9] has also been observed. It seems reasonable to expect that the mixed dimers of other polycyclic hydrocarbons could be prepared under appropriate conditions and, further, that such adducts could be of significant value in the study of molecular interactions in sandwich dimers.

[8] H. Bouas-Laurent and A. Castellan, *Chem. Commun.*, 1648 (1970).

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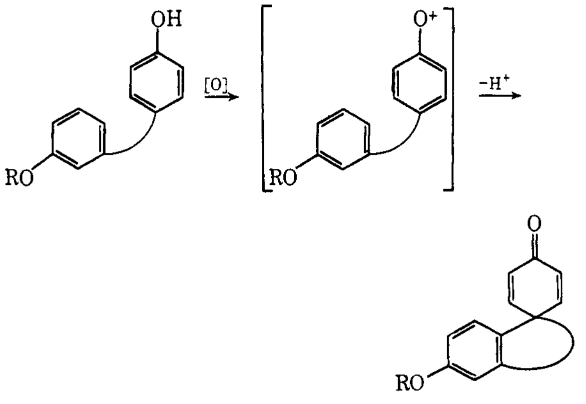
Received October 4, 1972

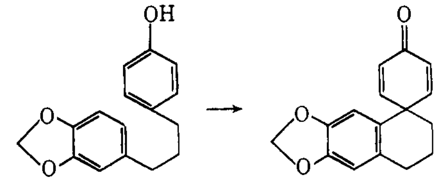
Intramolecular Oxidative Phenol Coupling. III. Two-Electron Oxidation with Thallium(III) Trifluoroacetate[1]

Sir:

In a continuing effort to develop effective intramolecular oxidative phenol coupling methods for use in alkaloid synthesis,[1a] we were interested in the possible utilization of a phenoxonium ion (or equivalent) mediated coupling, as outlined in eq 1. Although the generation of such intermediates has been investigated,[2] and an intermolecular analog of the desired transformation (eq 1) has been realized *via* anodic oxidation,[3] no example of intramolecular carbon–carbon coupling by this method has been reported. The description by Taylor and coworkers[4] of the oxidation of phenols to *p*-quinones with thallium(III) trifluoroacetate (TTFA) led us to examine the use of TTFA in the above scheme. We wish to report some success with this approach, leading to simple total syntheses of the alkaloids (±)-oxocrinine and (±)-*O*-methylandrocymbine.



(1)



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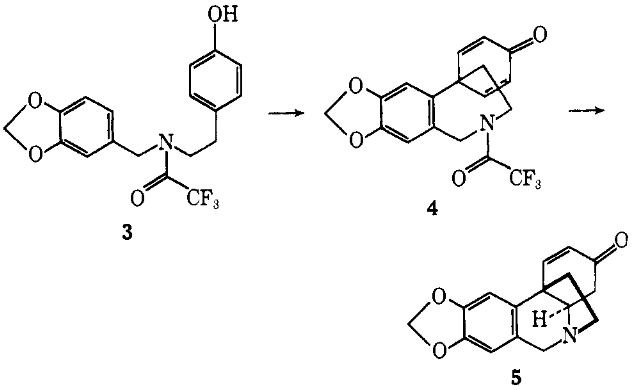

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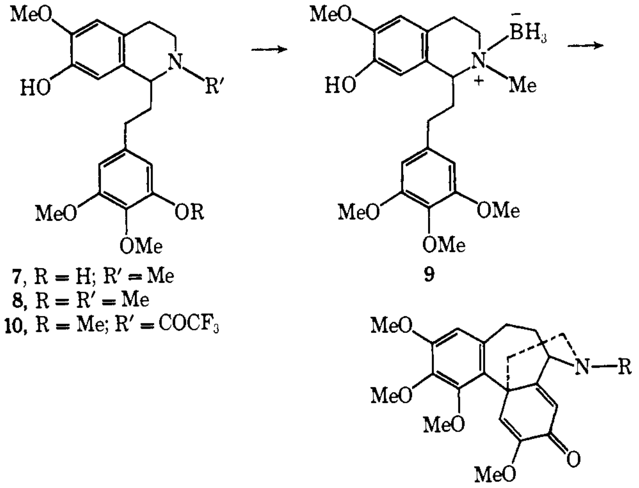

7, R = H; R′ = Me
8, R = R′ = Me
10, R = Me; R′ = COCF3
9
6, R = Me
11, R = COCF3

The potential utility of the method was demonstrated when oxidation of the diarylpropane derivative **1** (mp 73.5–74°, prepared from the corresponding chalcone) with a suspension of 1 molar equiv of TTFA in anhydrous CH_2Cl_2 (3 hr at 25°) afforded the dienone **2** in 87% yield: mp 171°; ir ($CHCl_3$) 6.03 μ; nmr ($CDCl_3$) δ 1.97 (m, 4), 2.82 (m, 2), 5.85 (s, 2), 6.23 (d, J = 10 Hz, 2), 6.40 (s, 1), 6.60 (s, 1), 6.97 (d, J = 10 Hz, 2). Extension of the method to the Amaryllidaceae alkaloid system was accomplished with ease, but with a substantial decrease in yield. The *N*-trifluoroacetyl-

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[1] (a) Previous paper in series: M. A. Schwartz and R. A. Holton, *J. Amer. Chem. Soc.*, **92**, 1090 (1970). (b) This work was supported by Public Health Service Grant CA-10136 from the National Cancer Institute.

[2] J. W. A. Findlay, P. Gupta, and J. R. Lewis, *Chem. Commun.*, 206 (1969); M. Chauhan, F. M. Dean, K. Hindley, and M. Robinson, *ibid.*, 1141 (1971); D. G. Hewitt, *J. Chem. Soc., C*, 1750 (1971).

[3] A. Ronlán, *Chem. Commun.*, 1643 (1971).

[4] A. McKillop, B. P. Swann, and E. C. Taylor, *Tetrahedron*, **26**, 4031 (1970).