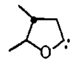
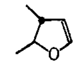
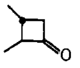
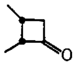
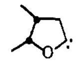
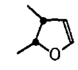
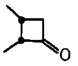
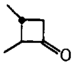
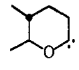
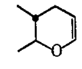
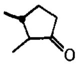
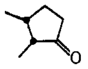
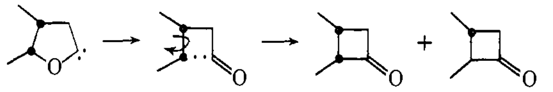
Table I. Pyrolysis Products from **1d–3d**

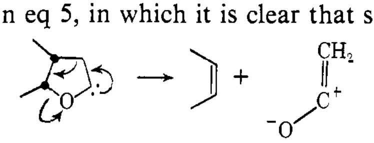
		Products, % yield						
	Presumed carbene	Enol ether	Ketone (ret)	Ketone (inv)	Alkene (ret)	Alkene (inv)	Cyclopropane (ret)	Cyclopropane (inv)
1		 24	 15	 1.3	 32	 <1	 3.6	 2.3
2		 17	 11	 11	 42	 3	 2.5	 0.5
3		 6	 41	 8				

previous experience,[2] while the remaining compounds were identified by comparison with authentic samples.[9] Table I presents a summary of the results, and we wish to draw particular attention to several of these findings. First, there is appreciable loss of stereochemical integrity in the ring contraction leading to ketone. The amount of inversion varies considerably in the three examples, but in series **2** it amounts to 50%, and in series **3** it has gone well past the reported equilibrium trans:cis ratio of 19:1.[10] The results are inconsistent with contraction solely by a concerted pathway (eq 2) or by any mechanism leading to the equilibrium distribution of isomers, and they suggest that part or all of the reaction proceeds through a biradical intermediate which may lose stereochemical integrity (eq 4). Both


(4)

concerted and biradical pathways have been discussed[4] for the reverse photochemical conversion of cyclobutanones to oxycarbenes, and in that case a biradical intermediate was favored.

The second result of interest is that, in contrast to ring contraction, the fragmentation leading from **1d** and **2d** to 2-butenes (and presumably ketene) is highly stereospecific. This fragmentation thus appears to involve intermediates other than the biradicals implicated in ring contraction (eq 4), and we suggest that a concerted, symmetry-allowed [4 + 2] cycloreversion[11] can account for the stereospecificity observed. This is depicted in eq 5, in which it is clear that such a process


(5)

is tantamount to a reverse 1,3-dipolar cycloaddition with ketene functioning uniquely as a 1,3 dipole.[12] The process of eq 5 is of course unknown in the opposite direction; it not only would be highly endothermic but also would necessarily compete with the facile [2 + 2] cycloaddition of olefin to ketene. In this connection it is noteworthy that recent extensive study[5] of the gas-phase photolysis of the 2,3-dimethylcyclobutanones has also demonstrated fragmentation to the 2-butenes with retention of stereochemistry. To account for their results the investigators were led to postulate[5] two distinguishable biradical intermediates, one which maintained stereochemistry and went on to 2-butene, and another which gave other products with loss of stereochemistry. Concerning the postulated biradical which maintains its steric configuration these authors noted further that "it is conceivable that it is correlated with" an oxycarbene intermediate. Our present findings provide evidence that an oxycarbene intermediate can indeed fragment stereospecifically to olefin, as this suggestion requires.

Finally a brief comment concerning the cyclopropanes should be made. The yields are too low to permit rigorous conclusions, but there is clearly greater loss of stereochemistry in the trans (**1**) series than in the isomeric cis (**2**) series. This is reminiscent of the unexplained observation that gas-phase pyrolysis of both *cis*- and *trans*-2,3-dimethylcyclobutanone yields 1,2-dimethylcyclopropane chiefly as the cis isomer.[6]

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Received November 13, 1972

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[9] The authentic 2,3-dimethylcyclobutanones were generously provided by Professor N. J. Turro and Dr. P. Lechtken, Columbia University (see ref 10).

[10] D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1662 (1965). The ratio for the 2,3-dimethylcyclobutanones is 3.26:1 [N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970)].

[11] R. B. Woodward and R. Hoffmann, *Angew. Chem.*, **81**, 797 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[12] For the application of orbital symmetry considerations to 1,3-dipolar cycloadditions, see A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, **100**, 2192 (1967).

Migration of Alkoxy Groups from Carbon to Nitrogen. A Novel Rearrangement

Sir:

The migration of alkoxy groups in molecular rearrangements is not common, and alkoxy migration from carbon to nitrogen is rare.[1] We now report such a rearrangement.

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[1] Alkoxy groups migrate to a minor extent in the decomposition of certain alkoxycarbonylnitrene precursors, giving alkoxyisocyanates.[2-4]

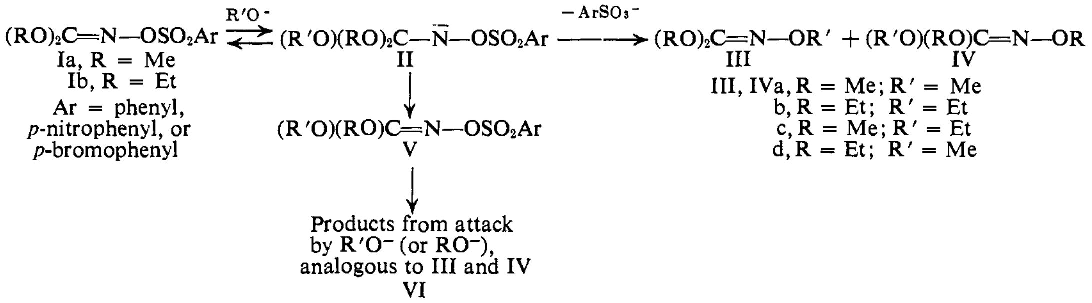
Table I. Conditions and Yields for the Reaction

$$\underset{\text{I}}{(RO)_2C{=}N{-}OSO_2C_6H_4{-}X\text{-}p} + R'O^- \longrightarrow \underset{\text{III}}{(RO)_2C{=}N{-}OR'} + \underset{\text{IV}}{(R'O)(RO)C{=}N{-}OR}$$

R	R′	X	Ratio R′O⁻/I	Solvent	Time, hr	Temp, °C	Yield, % III	IV	VI[b]	Total
Me	Me	H	1	Benzene[a]	3	75	99	Not appl		99
Me	Me	NO_2	1	Methanol	3	50	73.2	Not appl		73.2
Et	Et	H	1	Cyclohexene[a]	3	50	100	Not appl		100
Et	Me	H	1	Benzene[a]	12	23	23.6	68.2	4.7	96.5
Et	Me	H	2	Benzene[a]	12	23	20.4	68.2	10	98
Et	Me	H	1	Dimethylformamide[a]	6	23	23.2	71.7	4.7	99.6
Et	Me	Br	1	Benzene[a]	12	23	23	68	4.7	96

[a] Containing a trace of R′OH. [b] See Scheme I.

Scheme I



Dimethyl and diethyl *N*-arenesulfonyloximidocarbonates (I) were prepared from the known oximidocarbonates[5] and the appropriate arenesulfonyl chlorides. Reaction of I (Ar = phenyl, *p*-nitrophenyl, *p*-bromophenyl) with alkoxides gave dialkyl alkoximidocarbonates. Alcohols, benzene, cyclohexene, and dimethylformamide are suitable solvents and room temperature is sufficient. Examples are given in Table I. Using an alkoxide R′O different from the ester RO in I gives mixtures of two alkoximidocarbonates, $(RO)_2C{=}N{-}OR'$ (III) and $(R'O)(RO)C{=}N{-}OR$ (IV, syn and anti isomers). The yields are almost quantitative and no products arising from the solvent could be detected. Under the reaction conditions, the alkoximidocarbonates did not exchange alkoxy groups.

Several reaction mechanisms need to be considered: (a) nucleophilic displacement by $R'O^-$ on the double bonded nitrogen in I; (b) formation of the anion II and nucleophilic displacement by $R'O^-$ on the N^- in II; (c) formation of the anion II and α elimination of arenesulfonate, then rearrangement of the resulting nitrene; (d) formation of II and rearrangement concerted with loss of arenesulfonate ion. To distinguish between these mechanisms, one must know whether the reasonably expected equilibrium between starting materials and II is fast or slow, relative to the formation of III and IV. A fast equilibrium would lead to extensive exchange of alkoxy groups in I and to the appearance of the alkoxide RO^- in the reaction mixture. The equilibrium can indeed be demonstrated, but it is slow or very slow, depending on reaction conditions. Reacting I (R = Me; X = NO_2) in EtOH with 1 equiv of ethoxide, the small quantity of I left unreacted after 80 min at 50° contained 27% of exchanged I, $(MeO)(EtO)C{=}N{-}OSO_2C_6H_4NO_2$ (V). As seen in Table II, the exchange is much less important in benzene. The reaction shown in Table II demonstrates that direct attack by alkoxide on nitrogen cannot be important. All ethoxide would have to come from exchange, and even at the end of the reaction only 5% of the I has undergone exchange, while a 68% yield of N-ethoxy product IVd is found. Furthermore, the ratio IV/III remains constant during the reaction, despite the fact that only methoxide is present initially. Thus, mechanisms A and B are excluded. Mechanism C is made doubtful by the absence of products derived from the hypothetical nitrene and solvent. The solvents we used (alcohols, benzene, cyclohexene, and dimethylformamide) all react readily with other nitrenes. We favor, therefore, the concerted mechanism D, although obtaining conclusive evidence for or against it will require extensive further studies. Should mechanism C turn out to be correct, an additional step would have to be inserted into Scheme I.

Table II. Reaction of $(EtO)_2C{=}N{-}OSO_2C_6H_4Br$ with $Na^{+-}OMe$ in Benzene at 23°

Time, min	Exchange in recovd stgm,[b] % V in (I + V)	Ratio of products IVd/IIId	Products VI (from exchanged stgm[b])
0	0		
25	Not detectable	3.0	Not detected
60	<2	3.0	Trace
150[a]	3.6	3.0	3.8
205	5.2	3.0	4.5

[a] Yield of III + IV + VI about 70%, based on I, at *t* = 150 min. [b] Starting material.

Thermodynamically, mechanism D seems reasonable. Once the anion II is formed its rearrangement involves breaking and making of one N—O bond, breaking of a C—O bond, and converting a C—N single bond to a C=N double bond. The energy difference between C—N and C=N is 74 kcal/mol.[6] This and the forma-

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[2] W. Lwowski, R. DeMauriac, T. W. Mattingly, Jr., and E. Scheiffele, *Tetrahedron Lett.*, 3285 (1964).

[3] R. E. Wilde, T. K. K. Srinivasan, and W. Lwowski, *J. Amer. Chem. Soc.*, 93, 860 (1971).

[4] W. Lwowski and T. J. Maricich, unpublished results.

[5] J. Houben and E. Schmidt, *Chem. Ber.*, 46, 2447 (1913).

[6] *Cf.* C. Sandorfy in "The Chemistry of the C=N Double Bond," S. Patai, Ed., Interscience, New York, N. Y., 1970, p 5ff.

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.

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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.

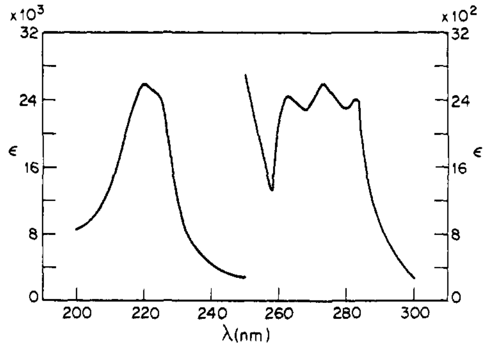
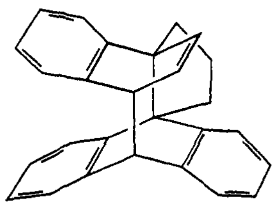


Figure 1. The absorption spectrum of the intramolecular adduct obtained on irradiation of 1-(9-anthryl)-3-(1-naphthyl)propane (2×10^{-5} *M* in methylcyclohexane).



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.

[2] E. A. Chandross and H. T. Thomas, *Chem. Phys. Lett.*, **9**, 393 (1971).

[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).

[5] E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, **92**, 703 (1970).

[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).