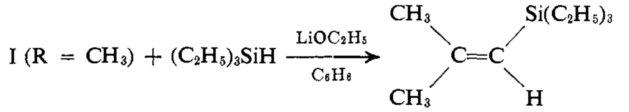
retical volume of nitrogen was collected soon after the addition of a slight excess of alkoxide and the vinyl halide isolated by distillation after a suitable work-up.

Although a bimolecular mechanism with attack of halide ion on A cannot be excluded on the basis of the experimental evidence,[4] we favor the intermediacy of the vinyl cation B which reacts with halide ion rather than the weakly nucleophilic 2-methoxyethanol.[5] The postulated vinyl cation could arise either by loss of nitrogen from A or by protonation of D.[6,7] Although trapping of B by strong nucleophiles appears likely, other reaction pathways are possible and currently under investigation.

Carbenes are reported to react by insertion with the silicon–hydrogen bond,[8,9] whereas carbonium ions generally abstract a hydride ion to yield a hydrocarbon.[10] When I was treated with lithium ethoxide in the presence of excess triethylsilane, vinylsilane V[11] was obtained in 61% yield. This result is consistent with the insertion of D into the silicon–hydrogen bond. Further work on the stereochemistry and mechanism of this insertion is in progress.



$$\mathrm{I\,(R = CH_3) + (C_2H_5)_3SiH \xrightarrow[C_6H_6]{LiOC_2H_5} (CH_3)_2C{=}C(H)Si(C_2H_5)_3}$$

V

From our experience to date apparently unsaturated carbonium ions (such as B) are involved in protic solvents whereas unsaturated carbenes (such as D) are involved in aprotic media.[12]

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(4) The possibility of the vinyl equivalent of the S_N2 reaction has been suggested in the solvolysis of vinyldiazonium ions generated by acidic treatment of triazenes: W. M. Jones and F. W. Miller, *J. Amer. Chem. Soc.*, **89**, 1960 (1967).

(5) Solvolysis of several triaryliodoethylenes in aqueous dimethylformamide have been postulated to involve intermediate vinyl cations which react preferentially with iodide ions: L. L. Miller and D. A. Kaufman, *ibid.*, 90, 7282 (1968).

(6) W. Kirmse, *Ann.*, **666**, 9 (1963).

(7) J. W. Wilt, C. A. Schneider, H. F. Dabek, J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, 31, 1543 (1966).

(8) D. Seyferth, J. M. Burlitch, H. Dertouzos, and H. D. Simmons, Jr., *J. Organometal. Chem.* (Amsterdam), 7, 405 (1967).

(9) D. Seyferth, R. Damrauer, J. Y.-P. Mui, and T. F. Jula, *J. Amer. Chem. Soc.*, 90, 2944 (1968).

(10) F. A. Carey and H. S. Tremper, *ibid.*, **91**, 2967 (1969).

(11) A. D. Petrov and G. I. Nikishin, *Zh. Obshch. Khim.*, **26**, 123 (1956).

(12) Compare with results on other systems: F. Cook, H. Shechter, J. Bayless, L. Friedman, R. L. Foltz, and R. Randall, *J. Amer. Chem. Soc.*, **88**, 3870 (1966).

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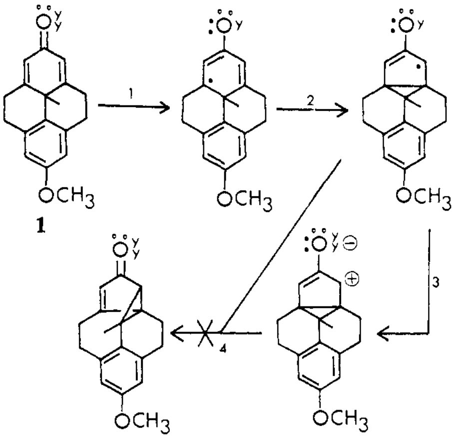
Mechanistic and Exploratory Organic Photochemistry. XLVI.[1] A Constrained 2,5-Cyclohexadienone Which Cannot Rearrange Photochemically

Sir:

The type A rearrangement of 2,5-cyclohexadienones is known[2] to be one of the most facile of photochemical transformations. We wish to report: (1) a cyclohexadienone specifically designed so that the latter stages of the type A rearrangement are geometrically impossible, (2) the actual photochemistry of this compound, (3) a marked photochemical similarity of this constrained dienone to benzophenone, (4) elucidation of the next most favored reaction which is ordinarily obscured by the facile type A rearrangement, (5) information about the nature of the zwitterionic intermediates generally postulated[2] for the type A process, and (6) an intriguing correlation between rates of excited-state reaction and radiationless decay.

7-Methoxy-10b-methyl-4,5,9,10-tetrahydro-2(10bH)-pyrenone (**1**) was selected for study[3] since it is constrained in such a way that, although 3,5 bonding[2] should not be inhibited, the 1,4 migration[4] generally accepted as the last stage of the rearrangement is geometrically impossible (note Chart I). Additionally, we synthesized[3] for comparison 4-methyl-4-phenylcyclohexadienone (**2**) as an unconstrained but otherwise structurally similar dienone.

Chart I. Inhibition of the Type A Reaction in the Constrained Dienone[a]



[a] Step 1, excitation; 2, 3,5 bonding; 3, demotion; 4, 1,4 migration.

Indeed, the constrained dienone (**1**) proved totally unreactive (*i.e.*, $\phi < 0.005$) on irradiation[5] in benzene as well as in *t*-butyl alcohol. This contrasts with the usual near-unit efficiency of the type A rearrangement of dienones.

Photolyses of dienone **1** in isopropyl alcohol solvent did reveal a reaction, namely hydrogen abstraction. This hydrogen abstraction was followed by a methyl radical expulsion, and the methane generated was identified by mass spectral analysis. The over-all transformation is depicted in eq 1. This is in dramatic contrast to the typical type A rearrangement exhibited by 4-methyl-4-phenylcyclohexadienone (**2**) which showed no sign

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(1) For paper XLV see H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

(2) (a) H. E. Zimmerman and D. I. Schuster, *ibid.*, **83**, 4484 (1961); **84**, 4527 (1962); (b) H. E. Zimmerman, 17th National Organic Symposium, Bloomington, Ind., June 1961, Abstracts, p 31; (c) H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **89**, 906 (1967).

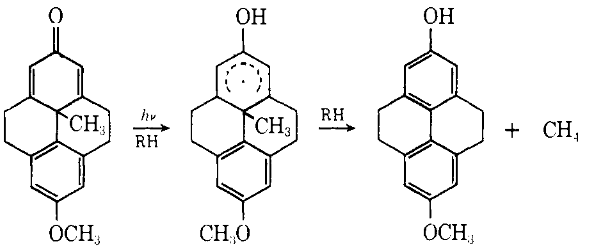
(3) The synthesis of 1, mp 132–133°, and 2, mp 53–55°, will be described in our full paper along with other details; all compounds analyzed correctly.

(4) (a) H. E. Zimmerman, D. Dopp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **88**, 5352 (1966); (b) H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); (c) H. E. Zimmerman, D. S. Crumrine, D. Dopp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(5) Photolyses were carried out in a parabolic reflector–linear beam AH6 apparatus with filter solutions, all as described by us earlier.[6]

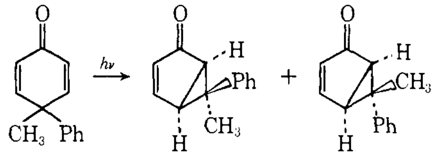
(6) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

of competitive hydrogen abstraction from isopropyl alcohol; note eq 2.



1

(1)



2

(2)

With the knowledge that constrained dienone **1** is incapable of complete type A rearrangement and with models showing that β,β bridging should not be sterically inhibited, it was of interest to try to trap an intermediate zwitterion. However, only the hydrogen abstraction reaction and no capture of zwitterion were observed when the reaction was run in n-butylamine, lithium acetate (0.54 M) in acetic acid, and lithium chloride (3.25 M) in methanol. Similarly, dimethyl acetylenedicarboxylate was ineffective in capturing zwitterion. Since hydrogen abstraction is a slow process, lack of nucleophilic pickup cannot be ascribed to exclusion by this reaction.

Hydrogen abstraction by the constrained dienone **1** is similar to the photoreactivity of $n-\pi^*$ triplets, such as benzophenone, in hydrogen-donating solvent.[7] Furthermore, this parallelism with benzophenone $n-\pi^*$ triplet turned out to be more than qualitative. Stern–Volmer studies using 2,5-dimethyl-2,4-hexadiene as a quencher afforded a hydrogen abstraction rate of $k_a = 3.6 \times 10^4$ l. mol^{-1} sec^{-1}, which is not much more than an order of magnitude less than the corresponding value for benzophenone in the same solvent (*i.e.*, $k_a = 6 \times 10^5$ l. mol^{-1} sec^{-1}).[7b] The unquenched quantum yield was 0.10.

Even more striking was the rate of excited-state decay observed for the triplet of constrained dienone **1**. This rate, $k_d = 4.2 \times 10^6$ sec^{-1}, is again not far from an order of magnitude greater than the corresponding benzophenone value ($k_d = 1 \times 10^5$ sec^{-1}).[7c] This is markedly different from the rate of decay one would expect for a triplet excited state having a 2,5-cyclohexadienone π system if the rate of triplet decay were only a function of the electronics of the initial dienone triplet species prior to molecular change. Thus Stern–Volmer studies on the structurally similar 4-methyl-4-phenylcyclohexadienone (**2**) afforded a lower limit for its rate of decay $k_d > 4 \times 10^9$ sec^{-1}, a value quite similar to constants previously found for dienone excited triplets.[2c,8] Decay for the constrained dienone is therefore 10^3 times slower than might have been expected.

Hence it appears that the very rapid rate of triplet decay observed for cross-conjugated cyclohexadienones is contingent on the type A transformation itself and that, in absence of successful molecular rearrangement, only an ordinary and relatively slow decay is possible. This is reasonable if demotion occurs only during the final stage (*i.e.*, step 4, Chart I) of the type A transformation. Reversion to ground-state reactant competes with continuation to product as the beginnings of 1,4 migration facilitate intersystem crossing. Thus the evidence suggests that the dienone rearrangement is at least partially concerted and that zwitterion is formed only as it is rearranging. A second interpretation is that bridging (and rearrangement) and radiationless decay back to dienone occur competitively from a twisted species (*e.g.*, an orthogonal triplet) and that formation of this *cis-transoid* configuration is structurally inhibited in dienone **1**. In either case rearrangement and decay are coupled.

It seems likely that organic molecules in electronic excited states may fall into two classes: (1) those in which radiationless decay back to reactant and loss of excitation with rearrangement to product are molecularly related as in the present instance and (2) those in which the two processes are unrelated.[9] The latter case seems most probable where appreciable excited-state energy barriers exist.[10]

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[7] (a) G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Amer. Chem. Soc.*, **83**, 2795 (1961); (b) S. G. Cohen, D. A. Laufer, and W. V. Sherman, *ibid.*, **86**, 3060 (1964); (c) J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963); (d) A. Padwa, E. Alexander, and M. Niemcyzk, *ibid.*, **91**, 456 (1969).

[8] D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968).

[9] H. E. Zimmerman and N. Lewin, *J. Amer. Chem. Soc.*, **91**, 879 (1969).

[10] H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969).

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Halogenated Ketenes. XI. On the Stereochemistry of Aldohalo- and Methylketene Cycloadditions[1]

Sir:

There are numerous reports on the cycloaddition of ketoketenes and olefins to produce substituted cyclobutanones. However, investigations involving the cycloaddition of aldoketenes and olefins have been very limited due to the instability of these ketenes. We have recently reported the preparation and subsequent *in situ* trapping of some aldohaloketenes by 1,2 cycloaddition with cyclopentadiene.[2] This report describes the stereochemistry of these cycloaddition reactions. This is the first report to our knowledge on the stereochemistry of aldoketene–olefin cycloadditions and presents some rather novel results.[3]

The unsymmetrical nature of aldohaloketenes introduces the possibility of two stereoisomers in this 1,2-cycloaddition reaction. Both isomers were ex-

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[1] Paper X: W. T. Brady, R. Roe, Jr., E. F. Hoff, and F. H. Parry, III, *J. Amer. Chem. Soc.*, in press.

[2] W. T. Brady and E. F. Hoff, *ibid.*, **90**, 6256 (1968).

[3] The authors are aware of only one report concerning the stereochemistry of aldoketene cycloadditions which describes the addition of several aldoketenes to benzalaniline: J. L. Luche and H. B. Kagan, *Bull. Soc. Chem. Fr.*, 2450 (1968).