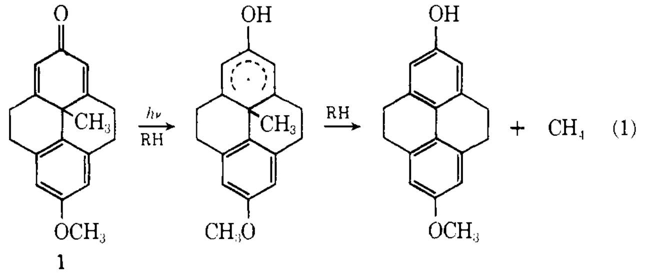
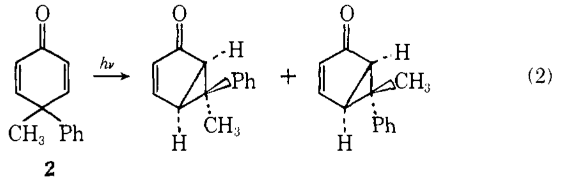
of competitive hydrogen abstraction from isopropyl alcohol; note eq 2.





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–π* triplets, such as benzophenone, in hydrogen-donating solvent.[7] Furthermore, this parallelism with benzophenone n–π* 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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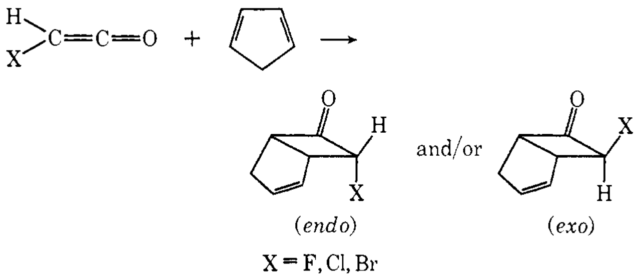
[1] Paper X: W. T. Brady, R. Roe, Jr., E. F. Hoff, and F. H. Parry, III, *J. Amer. Chem. Soc.*, in press.

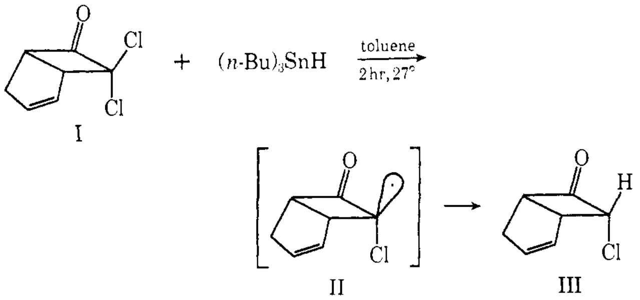
[2] W. T. Brady and E. F. Hoff, *ibid.*, **90**, 6256 (1968).

[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).

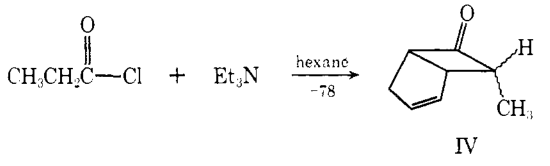


pected, but a consideration of steric factors would lead to the prediction that the *exo* isomer would predominate, particularly as the size of the substituent increases. However, vapor phase chromatography disclosed only one isomer in each of the ketene systems. In an effort to prove that the *exo* isomer was the probable isomer produced stereospecifically, the *endo*-chloro isomer III was synthesized.

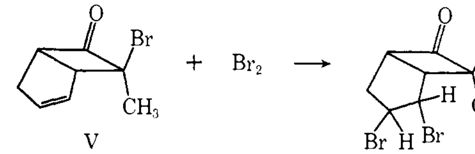
7,7-Dichlorobicyclo[3.2.0]hept-2-en-6-one[4] (I) was preferentially reduced with tri-*n*-butyltin hydride[5] to produce only the *endo* isomer III (this was possible because I was present in slight excess). A comparison of the nmr spectrum of III with the spectrum of the cycloadduct obtained by the dehydrochlorination of chloroacetyl chloride in the presence of cyclopentadiene showed the two were exactly superimposable. This result was of course very surprising. A study of the nmr spectra of the fluoro- and bromoketene cycloadducts also indicated that it was the *endo* isomer being produced.



The possibility of some peculiarity of the halogen causing the *endo* stereospecificity prompted the investigation of an aldoalkylketene system. Propionyl chloride was dehydrochlorinated in the presence of cyclopentadiene to yield the corresponding cycloadduct, IV.[6]



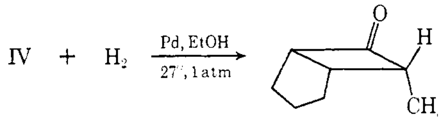
The nmr spectrum revealed the methyl resonance as a doublet centered at δ 0.99. Martin and coworkers reported that the nmr spectrum of the dimethylketene–cyclopentadiene adduct showed the methyl resonances at δ 1.28 and 0.93.[7] We have recently demonstrated in two methylhaloketene–cyclopentadiene systems that the upfield resonance was *endo*-methyl and the downfield resonance the *exo*-methyl.[8] Thus, the methyl resonance at δ 0.99 observed in this system must be due to *endo*-methyl.



$$\text{IV} + 2\text{Br}_2 \xrightarrow[0^\circ]{\text{CCl}_4} \text{VI} + \text{HBr}$$

To further demonstrate IV is the *endo* isomer, the methylketene adduct was brominated in an nmr tube and subsequently scanned. The spectrum thus obtained revealed that the product of bromination was the same as that obtained by bromination of V.[8] Compound V shows a methyl resonance at δ 1.60 which when brominated shifted to δ 1.98–1.99. The other isomer of V has a methyl resonance at δ 1.91 which when brominated shifted to δ 1.98–1.99. The methyl doublet of IV at δ 0.99 shifts to δ 1.99 upon bromination.

Furthermore, since the *endo*- and *exo*-methyl groups of IV are in different environments, hydrogenation of the residual double bond should change the environment of the *endo*-methyl and result in a shift of this doublet. This shift (~2 cps) was indeed observed upon catalytic hydrogenation, further demonstrating that IV is the *endo* isomer.



Thus, under the reaction conditions already described,[2] it appears that cycloaddition of aldoketenes, not just aldohaloketenes, with cyclopentadiene results in the stereospecific formation of the *endo* isomer. Experiments are in progress to explain this surprising phenomenon, and the results are forthcoming.

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(5) Tri-*n*-butyltin hydride reductions of bicyclic halogenated compounds are known to proceed *via* free radicals; see H. G. Kuivila, *Accounts Chem. Res.*, 1, 299 (1968). The *exo*-chloro substituent is preferentially removed, yielding the radical II which quickly abstracts a hydrogen atom. The radical does not produce an *exo* isomer (through a planar radical intermediate or inversion of the nonplanar radical) because of torsional strain; see F. R. Jensen, L. H. Gala, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968); P. von R. Schleyer, *ibid.*, **89**, 699 (1967); **89**, 701 (1967).

(6) Compound IV has been reported by J. Jaz and E. Denis, *Bull. Soc. Chem. Belges*, **75**, 845 (1966), but no mention was made of the stereochemistry involved.

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An Intermolecular Reaction of an Aryl Nitrene

Sir:

Although the minimal solvent effect on the first-order thermal decomposition of aryl azides[1,2] and the lack of