

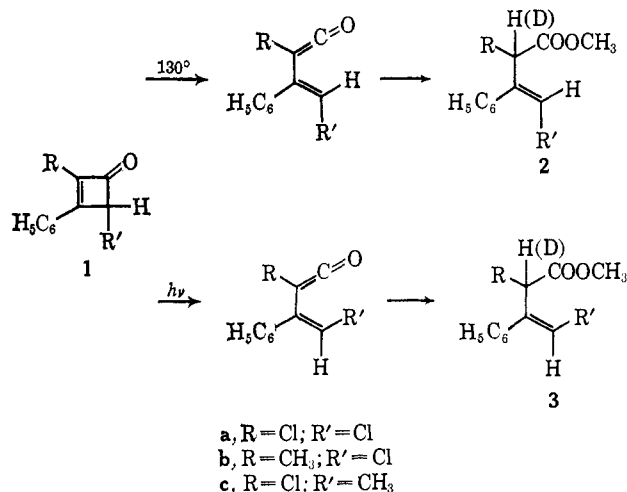
New Stereochemical Selectivities in Electrocyclic Reactions

Sir:

Those electrocyclic transformations¹ which may proceed in a conrotatory or disrotatory fashion are stereoselective,^{1,2} giving one stereochemical mode of behavior thermally and the opposite photochemically. The fundamental determinants of these stereochemical selectivities are now well recognized.¹⁻⁵

For the electrocyclic reactions of molecules like cyclobutene, the terms "conrotatory" and "disrotatory" remain meaningful, even though one could not discern experimentally the stereochemical course of these transformations without resorting to suitable deuterium-labeled analogs. But for other electrocyclic transformations, such as the conversions of cyclobutenones to the corresponding vinyl ketenes, the terms¹ "conrotatory" and "disrotatory" are meaningless. Neither current theory nor experimental precedent indicates the stereochemical characteristics of these electrocyclic reactions. We now report on three cases where they prove to be stereoselective, giving one isomer thermally and the other photochemically.

2,4-Dichloro-3-phenylcyclobutenone⁶ (**1a**) at 130° in methanol gave the β,γ -unsaturated ester **2a** having hydrogen and phenyl disposed *trans* about the carbon-carbon double bond. In O-deuteriomethanol, the α -deuterio ester was obtained. Irradiation of **1a** with a Hanovia 450-w high-pressure mercury lamp gave the *cis* isomer **3a**. 2-Methyl-3-phenyl-4-chlorocyclobutenone⁷ (**1b**) gave rise thermally to the *trans* product **2b** and photochemically to the *cis* product **3b**. Similarly, 2-chloro-3-phenyl-4-methylcyclobutenone⁷ (**1c**) gave the *trans* and *cis* isomers **2c** and **3c** thermally and photochemically, respectively. In each case, *cis-trans* isomerization of the product under the reaction



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(4) K. Fukui, *Tetrahedron Letters*, 2009 (1965).

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(7) This cyclobutenone was prepared through the addition of β -methylstyrene with 1,1-dichloro-2,2-difluoroethylene, dehydrochlorination, and hydrolysis of the *gem*-difluoro function with concentrated sulfuric acid.

Table I. Spectral Data for **1**, **2**, and **3**

Compd	Nmr absorptions ^a			J, cps	Out-of-plane bending absorption, ^b cm ⁻¹
	1H singlets	1H quartet	3H		
1a	340				
2a (H)	402, 304				701
2a (D)	412 ^c				
3a (H)	388, 352 ^d				700
3a (D)	398 ^c				
1b		330	126	1.5	
2b (D)	375		76 ^e		699
3b (D)	371		78 ^e		698.5
1c		229	82	7	
2c (D)		363	96	7	
3c (D)		354	114	7	

^a In cycles per second downfield from internal tetramethylsilane at 60 Mc/sec in carbon tetrachloride. ^b Determined on carbon tetrachloride solutions with a Beckman IR7 instrument. ^c In O-deuteriomethanol. ^d In deuteriochloroform. ^e Broad absorption.

conditions was observed to be slow relative to the rate of conversion of cyclobutenone to ester.

Assignments of stereochemistry of the three *cis-trans* pairs of olefins were based both on the observed regularities in the nmr chemical shift parameters for these compounds and on the relative energies of the out-of-plane bending absorptions in the infrared⁸ (Table I); the criterion of stereoselectivity employed for the six reactions was nmr.

The observed stereoselectivities of these reactions may be a consequence of very different geometrical constraints operative in the transition states for the thermal and photochemical processes. The stereochemistries of the electrocyclic transformations of 6,6-disubstituted cyclohexadienones and other systems for which the conrotatory-disrotatory dichotomy is irrelevant are under continuing investigation.

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(8) Cf. D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).

(9) Alfred P. Sloan Research Fellow.

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A New and Convenient Alkylation and Acylation of Pyridine N-Oxides

Sir:

Nuclear proton abstraction from substituted pyridines has only found sporadic application, this usually involving the formation of pyridyne intermediates.¹ It was expected that base-catalyzed deprotonation of pyridine N-oxides should occur much more readily than in the pyridines themselves,² and that C₂-H would be the most acidic proton, and this prediction

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