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## References and Notes

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- (15) These two diastereomes **13** were prepared analogously to **6**, i.e., from the respective *cis* and *trans* isomers of the bicyclic thiazolidine.

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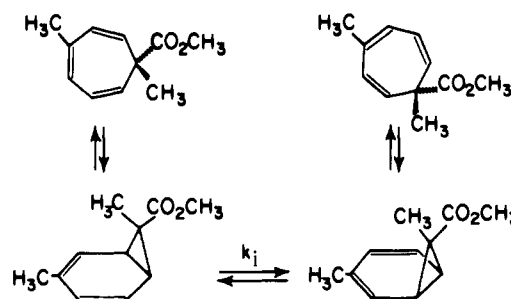
## Kinetics of the Stereomutations of (+)-2-Deuterio-3,7-dimethyl-7-methoxymethylcyclohepta-1,3,5-triene: One-Centered Epimerization at C(7) and [1,5] Carbon Migration with Retention of Configuration in a Norcaradiene

Sir:

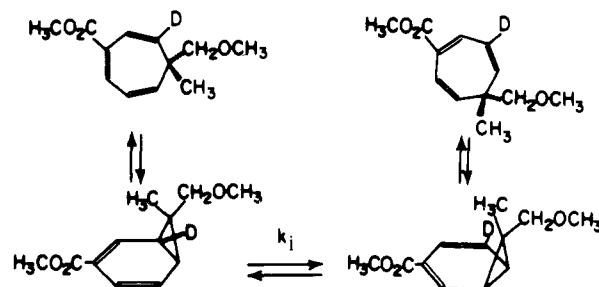
The ring-walk interconversions of the *n*,7,7-trimethyltropolidenes discovered by Berson and Willcott in 1965<sup>1</sup> involve tropilidene-norcaradiene valence isomerizations and [1,5] carbon migrations. The stereochemical features of such [1,5] shifts are the concern of this communication.

Optically active 3,7-dimethyl-7-methoxycarbonylcycloheptatriene has been shown to undergo thermal racemization as well as isomerization to 2,7-dimethyl-7-methoxycarbonylcycloheptatriene<sup>2</sup> (Scheme I), an observation taken as evidence for [1,5] carbon migrations with highly stereoselective inversion stereochemistry. This finding diametrically opposed to expectations based on orbital symmetry theory<sup>3</sup> has been validated through molecular orbital calculations: the [1,5] "forbidden" shift with inversion was held to be favored over the [1,5] "allowed" shift with retention of configuration by

Scheme I



Scheme II



some 1.4 kcal/mol, thanks to subjacent orbital effects.<sup>4</sup>

Very recent work, which came to our attention just as our own experimental efforts were nearly completed,<sup>5</sup> supported the conclusion that the [1,5] shift involves inversion of stereochemistry. Hansen found that optically active 1-deuterio-3-methoxycarbonyl-7-methyl-7-methoxymethylcycloheptatriene racemized thermally at approximately the same rate as its degenerate deuterium-scrambling isomerization took place (Scheme II).

Our approach was based on synthesis of optically active (+)-2-deuterio-3,7-dimethyl-7-methoxymethylcycloheptatriene and determination of its kinetics of degenerate rearrangement, with cognizance of the possible intrusion of one-centered epimerization at C(7) of the norcaradiene form of the substrate.<sup>6</sup> We sought experimental measures of the rate constants  $k_e$ ,  $k_i$ , and  $k_r$  defined in Scheme III.

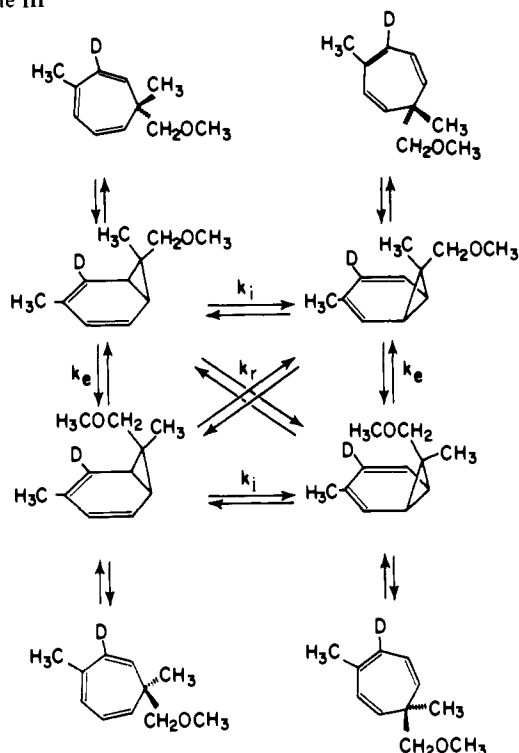
The required synthesis began with selective epoxidation of carvone with *m*-chloroperbenzoic acid; the keto epoxide<sup>7</sup> was isomerized with lithium diisopropylamide to provide 2,6-dimethyl-6-hydroxymethylcyclohepta-2,4-dien-1-one. Its hemiphthalate was resolved through recrystallizations of the related (-)- $\alpha$ -methylbenzylamine salt from ether-chloroform; the amine salt had mp 132–133 °C,  $[\alpha]_{\text{CHCl}_3}^{\text{D}} +60.2^\circ$ . Reduction of the resolved hemiphthalate with sodium borodeuteride, followed by dehydration catalyzed by *p*-toluenesulfonic acid in methylene chloride at reflux, gave the hemiphthalate of one antipode of 2-deuterio-3,7-dimethyl-7-hydroxymethylcycloheptatriene. Hydrolysis with 3 N sodium hydroxide, followed by methylation using *n*-butyllithium and methyl iodide in  $\text{Me}_2\text{SO}$ , gave the desired compound 96.4% optically pure (according to NMR analysis in the presence of an optically active shift reagent) and containing 94% of one deuterium at C(2).

**Table I.** Calculated<sup>a</sup> and Observed Mole Percent Concentrations of 2- and 4-Deuterio-3,7-dimethyl-7-methoxymethylcyclohepta-1,3,5-trienes at 223.4 °C

Time, min	(+)-2-d		(-)-2-d		(+)-4-d		(-)-4-d	
	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd	Obsd
0	92.3	92.3	1.7	1.7	0	0	0	0
300	80.4	80.0	8.2	8.6	4.3	4.7	1.1	0.7
679	68.5	70.7	14.1	11.9	8.4	6.2	3.0	5.2
1500	50.9	51.2	21.6	21.3	14.0	13.7	7.5	7.8

<sup>a</sup> According to Scheme III and the rate constants  $k_e = 0.45 \times 10^{-5} \text{ s}^{-1}$ ;  $k_r = 0.29 \times 10^{-5} \text{ s}^{-1}$ ; and  $k_i = 0.05 \times 10^{-5} \text{ s}^{-1}$ .

Scheme III



The kinetic work was done at 223.4 °C using degassed solutions of substrate in toluene; after thermolysis starting material and its degenerate isomers were reisolated by preparative GLC and analyzed by polarimetry and by NMR using the optically active shift reagent tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III)<sup>8</sup> in C<sub>6</sub>D<sub>6</sub>, which shifted apart H-C(4) doublets in the (+) and (-) isomers. The extent of deuterium scrambling was determined by converting the trienes to TCNE adducts followed by NMR comparisons of the relative intensities of vinyl to adjacent bridgehead protons.

The experimental results made possible definition of the time dependence of all four isomers of Scheme III and derivation of the rate constants  $k_e$ ,  $k_i$ , and  $k_r$  using exact solutions to the required kinetic expressions. An 11-point linear plot of  $\ln$  (optical purity) vs. time gave  $2(k_e + k_i) = (1.00 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$ . An 8-point linear plot of  $\ln \{[(2-d) - (4-d)] / [(2-d) + (4-d)]\}$  against time revealed that  $2(k_i + k_r) = (0.68 \pm 0.04) \times 10^{-5} \text{ s}^{-1}$ . Finally, experimental values of  $[(+)-2-d + (+)-d_0] / [(-)-2-d + (-)-d_0]$  allowed calculation of all concentrations and  $2(k_e + k_r) = (1.48 \pm 0.15) \times 10^{-5} \text{ s}^{-1}$ . A comparison of calculated and observed mol percent concentrations is provided in Table I.

The racemization is dominated by a direct isomerization of one antipode to the other without a concomitant [1,5] carbon shift, and the [1,5] shift occurs predominantly with retention of stereochemistry at the migrating carbon.

These results demonstrate a sigmatropic [1,5] carbon shift with allowed stereochemistry in a type of molecule previously thought to isomerize according to a "forbidden" least-motion stereochemical route, and they provide an instance in which one-centered epimerization in a cyclopropane does not involve a simple diradical intermediate, for  $k_e \neq k_i$ .

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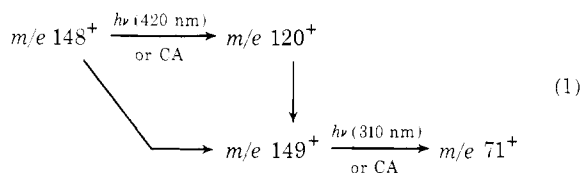
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#### Fragmentation of Butyrophenone Ions

Sir:

We have investigated the unimolecular dissociation of butyrophenone molecular ion and protonated molecular ion, using the complementary techniques of ion photodissociation in the ICR spectrometer<sup>1</sup> and collisional activation (CA) in the double focussing mass spectrometer.<sup>2</sup> Photodissociation and CA dissociation of both species were observed, and the unimolecular and ion-molecule chemistry in this system was elucidated as summarized in eq 1. This fuller understanding



of the chemistry provides a satisfactory alternative explanation for the observations which led Gooden and Brauman<sup>3</sup> to propose state-specific, noncompetitive photodissociation of butyrophenone molecular ion.

The fragmentation of polyatomic molecular ions in mass spectrometry has been a subject of theoretical and experimental investigation for a long time. In most cases, quasi-equilibrium theory<sup>4</sup> (QET) has been successfully used to explain the internal energy dependence of the relative abundances of various fragment ions formed from competing processes. It is usually assumed in application of the theory that the ions produced in excited electronic states undergo fast radiationless transition to a common electronic state, presumably the ground state, prior to decomposition. Decompositions from excited states, so-called state-specific reactions, have been observed in very few cases<sup>5</sup> in violation of this assumption.

Accordingly, instances of demonstrable noncompetitive fragmentation in ions are of some interest, and the recent report by Gooden and Brauman<sup>3</sup> of possible highly state-specific reactions in the photodissociation of butyrophenone molecular ion has received substantial attention. The chemistry shown in eq 2 was reported.

A sharp transition from dissociation path b to path a was reported to occur at a photon energy near 3.3 eV, indicating state-specific reactions. However, the failure of Kim and

