

p-trifluoromethylacetophenone (Columbia Organic) were further purified by trap-to-trap distillation under vacuum immediately before use.

Kinetic Studies. A general description of the lifetime apparatus has already been given.¹⁵ The measurements were carried out over a temperature range using the brass block thermostat already described.¹⁸ Above ambient temperatures were reached by means of heating coils imbedded in the block, while low temperatures were obtained by passing cold nitrogen through a series of channels cut in the block. Because of the large heat capacity of the block, temperatures accurate to 0.05 °C could easily be obtained. A small section of the emission cell protruded from the block and this volume was kept a few degrees warmer than the block temperature to minimize any distillation. The filter system for all three ketones was the same, i.e., excitation 7–54, emission 3–72 and 4–96 in series (Corning).

Emission Spectra and Quantum Yields. Spectra and quantum yield data were obtained using a Hitachi MPF-4 spectrofluorimeter and quinine bisulfate as a quantum yield standard.¹⁹ Radiative lifetimes were determined by measuring both the lifetimes and the quantum yields of emission of the samples ($\tau_{\text{rad}} = \tau/\varphi_{\text{em}}$).

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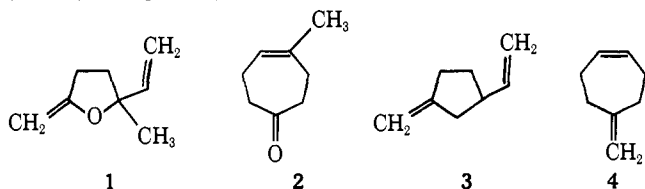
Interconversion of 1-Methylene-3-vinylcyclopentane and 5-Methylenecycloheptene. A Cope Rearrangement^{1,2}

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Abstract: 1-Methylene-3-vinylcyclopentane (**3**) and 5-methylenecycloheptene (**4**) undergo first-order interconversion in the temperature range 260–300 °C with $\Delta H_{287}^{\ddagger} = 35.5 \pm 1.0$ kcal/mol for the reactions $3 \rightarrow 4$ and $4 \rightarrow 3$ and $\Delta S_{287}^{\ddagger} = -16.6 \pm 3.0$ eu for the reaction $3 \rightarrow 4$ and -12.7 ± 3.0 eu for the reaction $4 \rightarrow 3$. A study of the conversion of **4**, labeled with deuterium at the *exo*-methylene group, to **3**, labeled exclusively in the five-membered ring, establishes the reaction as a concerted [3,3]-sigmatropic process.

In an earlier study we reported the thermal conversion of 2-methyl-2-vinyl-5-methylenetetrahydrofuran (**1**) to 4-methyl-4-cycloheptenone (**2**).³ Although the unidirectional nature of the rearrangement and the characteristic activation quantities seemed to safely place the reaction in the category of concerted [3,3]-sigmatropic processes (an aliphatic Claisen rearrangement), a vestige of uncertainty remained. Conceivably, a diradical or a sequence of two [1,3]-sigmatropic shifts could have intervened and the single product observed was simply a result of thermodynamic control. Accordingly, we undertook a study of an analogous "Cope" system in which the thermodynamic bias for the formation of a carbonyl compound would be absent. In this paper we report on the Cope isomerization of 1-methylene-3-vinylcyclopentane (**3**) and 5-methylenecycloheptene (**4**).



Results

Preparation of 3 and 4. The requisite 1,5-dienes, **3** and **4**, were prepared as outlined in Schemes I and II. Dieckmann cyclization of diethyl β -vinyl adipate (**5**)⁴ produced a mixture of β -keto esters which upon hydrolysis and decarboxylation

Scheme I

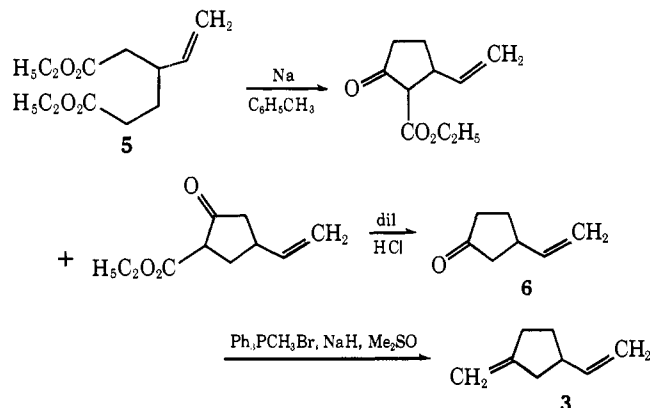
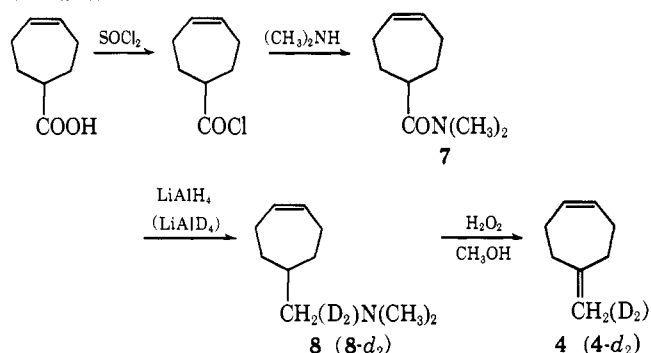


Table I. Rate Data and Activation Parameters for the Interconversion of **4** and **3**

temp, °C	$(k_1 + k_2) \times 10^5 \text{ s}^{-1} \text{ }^a$	$k_1 \times 10^5 \text{ s}^{-1}$	$k_2 \times 10^5 \text{ s}^{-1}$
304	34.0 ± 0.6	30.3	3.74
287	13.2 ± 0.3	11.7	1.45
261	2.50 ± 0.06	2.22	0.28

temp, °C	reaction	ΔH^\ddagger , kcal/mol ^b	ΔS^\ddagger , eu ^b
287	4 → 3	35.3 ± 1.0	-12.7 ± 3.0
	3 → 4	35.5 ± 1.0	-16.6 ± 3.0

^a Uncertainties of the rate constants reflect standard deviations of the first-order plots. Since the value of K_{eq} over the temperature range examined remained constant at 8.1 ± 0.1 , this value was used throughout for the determination of k_{eq} and the evaluation of k_1 and k_2 . ^b Uncertainties are statistical errors calculated by the method of E. L. Purlee, R. W. Taft, Jr., and C. A. Defazio, *J. Am. Chem. Soc.*, **77**, 837 (1955).

Scheme II

yielded 3-vinylcyclopentanone (**6**). A Wittig reaction of the latter with methylene triphenylphosphorane led to **3**. The starting material for the cycloheptene derivative, **4**, was 4-cycloheptenecarboxylic acid.⁵ Conversion of the carboxy function to an exocyclic methylene group was accomplished by the sequence of reactions shown in Scheme II, following the general method of Conia and Gore.⁶ Substitution of lithium aluminum deuteride for the hydride in the reduction step of the sequence furnished 5-dideuteriomethylenecycloheptene (**4-d₂**), labeled completely and exclusively at the exo position.⁷ The structures of **3**, **4**, and **4-d₂** follow from their mode of synthesis and are fully supported by their spectral properties, detailed in the Experimental Section. Of particular importance to the solution of the problem at hand are the NMR characteristic absorptions of the vinylic protons of **3**, **4**, and **4-d₂**. The protons of the exomethylene group in **4** appear as a singlet at δ 4.62, well separated from those of the endo double bond of **4** at 5.75 and from the various vinylic proton signals of **3** which are found farther downfield (centered at \sim 4.86 and 5.76). The NMR spectrum of **4-d₂** is simplified to a set of two signals, that of the endo vinylic protons at δ 5.75 and that of the allylic protons of the ring at 2.19 in a ratio of 1:4.

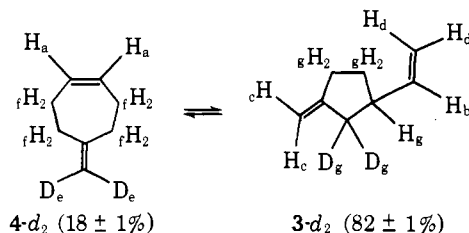
Rate Studies of the Isomerization of **3 and **4**.** The interconversion of **3** and **4** occurs clearly in the gas phase in the temperature range of 260–300 °C by first-order processes to give an equilibrium mixture in which the five-membered-ring compound, **3**, strongly dominates (\sim 89%). The same equilibrium composition was found when approached from either side; the gathering of rate data was limited to the seven-membered-ring compound as starting material. Kinetic and equilibrium data for the system

**Table II.** Thermal Isomerization of 5-Dideuteriomethylenecycloheptene (**4-d₂**) at 325 °C

group(s)	protons	relative area ^a	number of protons	
			exptl	calcd ^b
A	a + b	1.00 ± 0.02	1.14 ± 0.03	1.18
B	c + d	2.76 ± 0.07	3.15 ± 0.09	2.46
C	f + g	5.00 ± 0.12	5.71 ± 0.17	6.18
D	e	0	0	0

Ratios			
B/A		2.76 ± 0.10	2.77
C/B		1.81 ± 0.07	1.69
C/A		5.00 ± 0.20	4.69
A/D		∞	∞

^a Mean value of 10 determinations. ^b The method of calculation is described in the Experimental Section.

Scheme III

were measured at three temperatures and the rate constants for the forward and reverse reactions evaluated from the relationship

$$\ln \% (4 - 4_{\text{eq}}) = -(k_1 + k_2)t + \ln \% (4_0 - 4_{\text{eq}})$$

for reversible first-order processes and the independently determined equilibrium constant.⁹ These data together with the corresponding activation parameters are collected in Table I.

Isomerization of 5-Dideuteriomethylenecycloheptene (4-d₂**).** A sample of **4-d₂** held at 325 °C for 25 min produced a mixture composed of 82% **3-d₂** and 18% **4-d₂** as revealed by GLC analysis. For purposes of comparison, the 100-MHz NMR spectra of an equilibrated sample of nondeuterated isomers and the mixture of deuterated isomers obtained in this experiment are displayed in Figures 1 and 2. It will be noted that the signal of the *exo*-methylene protons, e of **4** stands out clearly at δ 4.62 in the spectrum of the nondeuterated mixture but is totally absent in the spectrum of the mixture of deuterated compounds. Moreover, in the latter spectrum there is an obvious diminution of the relative areas of the group of signals produced by the nonvinylic protons, f and g, due to the incorporation of two deuterons in the five-membered-ring component of the mixture. Further evidence that the mixture consists solely of **4-d₂** and **3-d₂** is provided by comparison of the areas of integratable groups of protons (Table II). Group A consists of protons a and b, group B of protons c and d, group C of protons f and g, and group D of any protons e which would appear on the *exo*-methylene group of the cycloheptene derivative (see Scheme III). After correction for the mixture composition, values for the number of protons expected in each group were calculated for both a randomized "diradical" process (or its indistinguishable alternative of possible [1,3] shifts) and a concerted one-step [3,3]-sigmatropic process. These values as well as the experimental and calculated ratios of the various groups of protons are set forth in Table II.

Discussion

Comparison of the activation quantities for the interconversion of **4** and **3** with data available for unconstrained acyclic

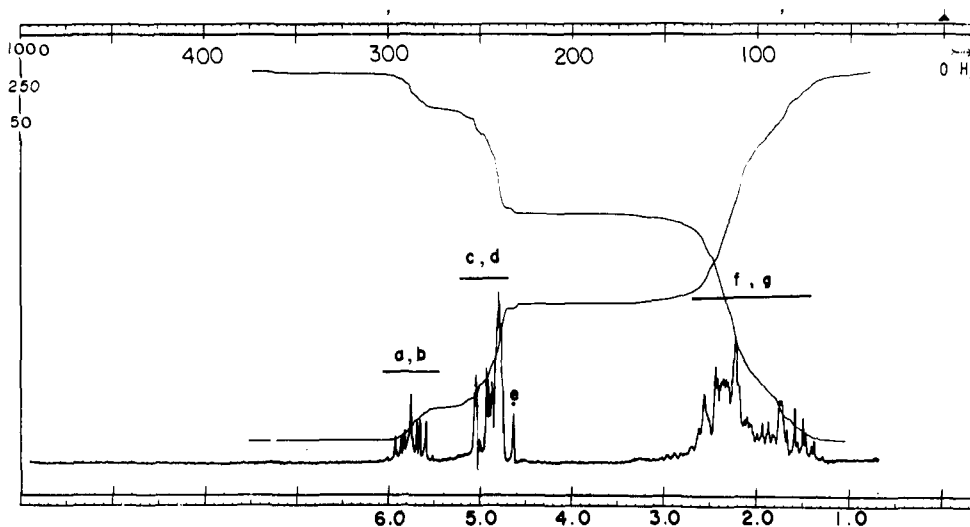


Figure 1. The 100-MHz ^1H NMR spectrum of a 11:89 mixture of 4 and 3 equilibrated at 325 °C. The signals of protons a–g correspond to the positions shown in Scheme III.

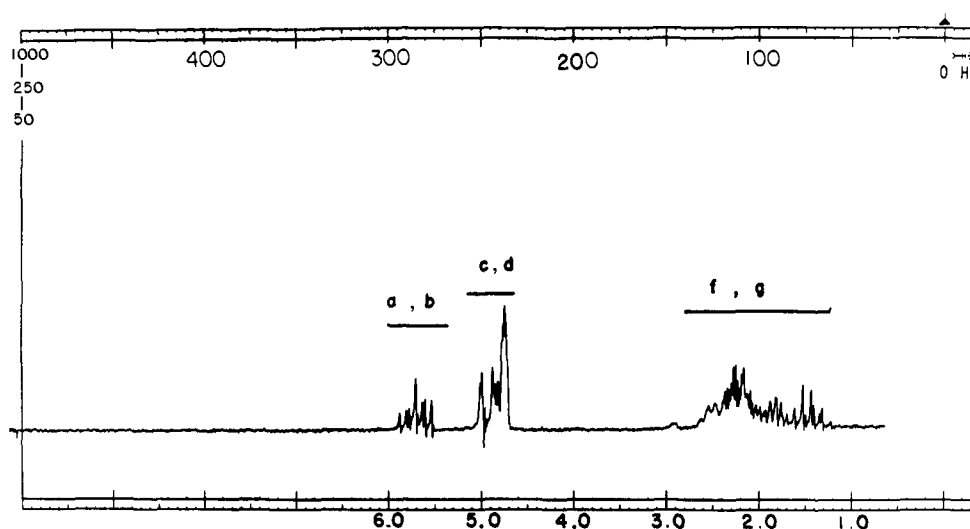
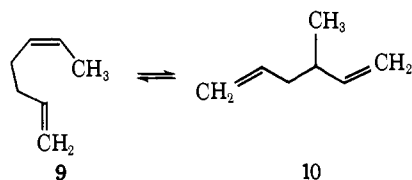
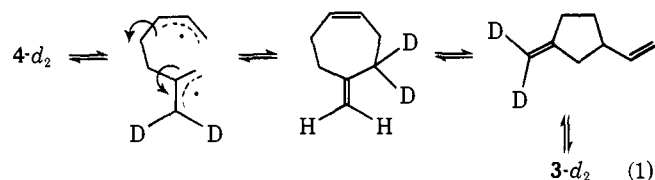


Figure 2. The 100-MHz ^1H NMR spectrum of a 18:82 mixture of 4- d_2 and 3- d_2 obtained by heating 4- d_2 at 325 °C for 25 min.

1,5-dienes¹⁰ reveals a close correspondence, which in itself seems to place this system securely in the concerted category. For example, for the structurally similar system, *cis*-1,5-heptadiene (9) which equilibrates with 3-methyl-1,5-hexadiene (10), Frey and Solly¹¹ reported values of ΔH^\ddagger and ΔS^\ddagger of 35.6 kcal/mol and -13.0 eu (calculated for 287 °C) for the forward reaction $9 \rightarrow 10$, whereas the reverse reaction $10 \rightarrow 9$ shows ΔH^\ddagger of 34.6 kcal/mol and ΔS^\ddagger of -13.6 eu.

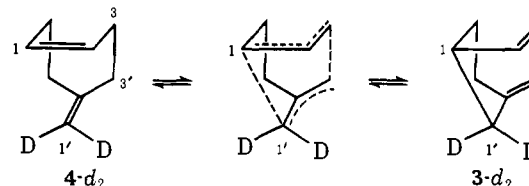


The outcome of the experiment with the deuterated isomer, 4- d_2 , leaves no doubt that the isomerization belongs to the class of concerted [3,3]-sigmatropic processes. As set forth in Table II, only the concerted [3,3] process is compatible with the



deuterium distribution found in the isomerized mixture. A freely rotating bisallylic diradical (or combinations of [1,3]-sigmatropic shifts) would lead to scrambling of the deuterium labels between the *exo*-methylene groups and adjacent ring carbons of both isomers, i.e., eq 1.

It must be concluded that the isomerization occurs exclusively by way of the concerted [3,3] process in which bond-making and -breaking processes are closely synchronized. The transition state visualized for this reorganization, as in the analogous Claisen rearrangement,³ resembles the preferred "four-centered" array.¹²



Experimental Section

General. Infrared spectra were obtained as thin films between sodium chloride plates with a Perkin-Elmer Model 621 spectrophotometer. A Varian Associates HA-100 instrument was used to obtain NMR spectra employing carbon tetrachloride as the solvent and Me_4Si as an internal standard. Mass spectral data were recorded with a Varian-Mat CH-5 instrument at 70 eV; peak heights are reported

as percent of the base peak. Gas-liquid chromatographic (GLC) analyses and preparative separations were carried out with a variety of column materials and conditions detailed under individual experiments. Helium was the carrier gas in all cases. Elemental analyses were performed by the Galbraith Laboratories, Knoxville, Tenn.

Diethyl β -Vinyladipate (5). A solution of 25.0 g (0.145 mol) of β -vinyladipic acid⁵ in 25 mL of absolute ethanol and 26 mL of toluene containing 5 drops of concentrated sulfuric acid was heated to boiling and the water-toluene-ethanol azeotrope slowly distilled out over a period of 4 h. Addition of toluene and ethanol followed by azeotropic distillation for 1 h was repeated three times and the reaction mixture was finally distilled under reduced pressure to give 27.9 g (84%) of product: bp 150–152 °C (20 mm); GLC analysis (6 ft \times 1/4 in. 10% Carbowax 1500 on Gas-Chrom P at 175 °C) indicated a purity of >99%; IR 1732 (s), 1633 (w), 1175 (s), 1140 (s), 990 (m), 910 (m) cm^{-1} ; NMR δ 5.5 (m, 1), 5.0 (m, 2), 4.0 (q, 4), 2.6–2.1 (m's, 5), 1.65 (m, 2), 1.2 (t, 6).

Dieckmann Cyclization of 5. To a slurry of sodium sand (2.9 g, 0.12 mol) in 40 mL of toluene at 110–115 °C under a nitrogen atmosphere and with vigorous stirring was added 27.5 g (0.12 mol) of **5** in 100 mL of toluene over a period of 1 h. The reaction mixture was maintained at 110–115 °C for an additional 3.5 h and then cooled and poured into 100 mL of 10% acetic acid. The organic phase was separated and washed successively with water, aqueous Na_2CO_3 solution, and water. Distillation of the toluene extract afforded 10.9 g (49.8%) of a mixture of β -keto esters, bp 87–88 °C (2 mm). The IR spectrum of the mixture was consistent with the structures of the expected products: 1750 (s), 1720 (s), 1638 (w), 990 (m), 910 (m) cm^{-1} .

3-Vinylcyclopentanone (6). The mixture of β -keto esters obtained in the Dieckmann cyclization of **5** was heated with 30 mL of 6 N HCl for 0.75 h to effect hydrolysis and decarboxylation. After cooling, the reaction mixture was extracted with ether and the ether extract washed successively with aqueous NaHCO_3 and water and finally dried over anhydrous MgSO_4 . Distillation of the concentrate yielded 3.0 g of product, bp 68–75 °C (0.2 mm), containing a single major component (80%) contaminated by higher boiling materials as revealed by GLC analysis (6 ft \times 1/4 in. 10% Carbowax 1500 at 100 °C). The IR spectrum of the major component was consistent with the structure of **6**: 1743 (s, C=O of cyclopentanone), 1640 (m, C=CH₂), 990 (m), 910 (m, C=CH₂) cm^{-1} . Further purification was not attempted and the crude ketone was directly converted to **3**.

1-Methylene-3-vinylcyclopentane (3). Approximately 0.03 mol of sodium hydride dispersed in mineral oil was introduced into a reaction flask protected by a nitrogen atmosphere and washed with successive portions of dry pentane to remove the mineral oil. Residual solvent was removed by evacuation and 15 mL anhydrous Me_2SO was added. The resulting mixture was heated at 85 °C for 1.25 h until evolution of hydrogen ceased. After cooling, 9.7 g (0.027 mol) of methyltriphenylphosphonium bromide in 30 mL of dry Me_2SO was added and the mixture heated at 50 °C for 20 min. Three grams of the crude 3-vinylcyclopentanone was added to the solution of phosphorane and stirring was continued for another 30 min. The reaction flask was fitted with a distilling head and the product was distilled under the vacuum of a water aspirator and trapped in a dry ice-acetone-cooled receiver. In this way 1.24 g of crude product was obtained. GLC (6 ft \times 1/4 in. 10% Carbowax on Gas-Chrom P at 60–175 °C) and IR analysis showed the distillate to be the desired product contaminated by a small amount of benzene. The crude product was purified by preparative GLC (3 m \times 1/4 in. 15% diisodecyl phthalate on Gas-Chrom P at 30 °C) to provide material of >99% purity: IR 1660 (w), 1643 (w), 990 (m) and 910 (m) cm^{-1} ; NMR δ 5.76 (m, 1, H=C=C), 5.0–4.75 (m's, 4, 2 C=CH₂), 2.7–1.4 (m, 7, ring H's). A sample of this material heated in vacuo for several hours at 325 °C equilibrated with 5-methylenecycloheptene (**4**). Preparative GLC (3 m \times 1/4 in. 15% diisodecyl phthalate on Gas-Chrom P at 60 °C) permitted the isolation of **4** which proved identical with an authentic sample (see below).

N,N-Dimethyl-4-cycloheptencarboxamide (7). 4-Cycloheptencarboxylic acid was prepared in 77% yield following the procedure of Stork and Landesman.⁵ The crude acid was converted to the acid chloride with thionyl chloride by the method of Doering et al.¹³ Distillation of the reaction mixture afforded colorless 4-cycloheptencarboxylic acid chloride in 95% yield, bp 50 °C (0.75 mm), reported bp 38 °C (0.14 mm).¹³ In an ice-cooled, three-necked flask equipped with stirrer, addition funnel, and a condenser fitted with a nitrogen inlet was placed 19 mL (0.68 mol) of liquefied anhydrous dimethylamine dissolved in 60 mL of dry benzene. A solution of 20 g (0.135

mol) of 4-cycloheptencarboxylic acid chloride in 20 mL of dry benzene was added dropwise. The resulting slurry was stirred for 16 h at room temperature and then 20 mL of water was added to dissolve the precipitate of dimethylamine hydrochloride. The layers were separated, the aqueous layer extracted with three 50-mL portions of ether, and the combined organic extracts were washed with saturated sodium chloride solution and dried over anhydrous Na_2SO_4 . After removal of solvent, the residue was distilled to yield 20 g (95%) of colorless amide: bp 83–84 °C (0.05 mm); NMR δ 5.71 (m, 2), 2.96 (d, 6), 2.5–1.7 (m's, 9). Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{NO}$: C, 71.86; H, 10.18; N, 8.38. Found: C, 71.83; H, 10.06; N, 8.14.

5,5-(N,N-Dimethylaminomethyl)cycloheptene (8). A three-necked flask, equipped with an addition funnel, stirrer, and condenser with a nitrogen inlet was dried by flaming under continuous flushing with nitrogen. To the cooled flask was added 2.4 g (0.064 mol) of lithium aluminum hydride in 150 mL of anhydrous ether followed by a solution of 10 g (0.064 mol) of **7** in 50 mL of anhydrous ether added dropwise over a period of 0.5 h. The mixture was heated under reflux for an additional hour and cautiously treated with 40 mL of 10% sulfuric acid. The solution was made strongly basic by the addition of 5 g of solid sodium hydroxide and extracted with three 50-mL portions of ether. After the mixture was dried over anhydrous MgSO_4 , the solvent was removed and the residue distilled to yield 6 g (65%) of product: bp 70–73 °C (3 mm); NMR δ 5.70 (m, 2), 2.15–1.9 (m's, 17); mass spectrum (rel intensity) m/e 153 (7, M⁺), 58 (100). Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{N}$: C, 78.43; H, 12.31; N, 9.14. Found: C, 78.69; H, 12.23; N, 8.94.

5-(N,N-Dimethylaminodideuteriomethyl)cycloheptene (8-d₂). The same procedure described above for the preparation of **8** was followed for the preparation of the dideuterio compound. From 6 g (0.038 mol) of the carboxamide and 1.53 g (0.038 mol) of lithium aluminum deuteride was obtained 5 g (91%) of product, bp 70–71 °C (3 mm). The NMR spectrum of the dideuterio compound showed the same signals for the two vinylic protons at δ 5.70 as did the spectrum of **8** but the remaining 15 protons appeared as a simplified group of signals centered at 2.09 ppm. The mass spectrum (rel intensity) showed m/e 155 (11, M⁺), 60 (100).

5-Methylenecycloheptene (4). A solution of 6 g (0.042 mol) of **8** in 8 mL of methanol was combined with 28 g (0.25 mol) of 30% hydrogen peroxide in a flask fitted with a condenser and stirring bar. After the solution had been stirred for 40 h at room temperature, the excess peroxide was destroyed with platinum black. The filtered solution was concentrated under reduced pressure and the concentrate decomposed by heating it at 150 °C and 10-mm pressure to yield 5-methylenecycloheptene in 50% yield. This material was identical in all respects with a sample prepared by a Wittig reaction of 4-cycloheptenone with methylenetriphenylphosphorane:¹⁴ NMR δ 5.75 (m, 2), 4.62 (s, 2), 2.19 (m's, 8); mass spectrum (rel intensity) m/e 108 (53, M⁺), 93 (65), 91 (47), 80 (94), 79 (100), 67 (35), 53 (29).

5-Dideuteriomethylenecycloheptene (4-d₂). By the same procedure described above for the preparation of **4**, **4-d₂** was prepared in 53% yield from 5.0 g (0.03 mol) of **8-d₂**: NMR δ 5.75 (m, 2), 2.19 (m, 8); mass spectrum (rel intensity) m/e 110 (63, M⁺), 95 (58), 82 (86), 81 (100), 80 (58), 67 (37), 54 (26).

Rate Studies. The thermal isomerizations were carried out in a stirred molten salt bath (50% potassium nitrate–50% sodium nitrite) heated by two immersion heaters and controlled by a Bayley precision temperature controller Model 124.¹⁵ Temperatures were measured by a secondary standard platinum-platinum + 10% rhodium thermocouple and a Rubicon Co. precision millivolt potentiometer. Temperature regulation was ± 0.02 °C at temperatures below 250 °C. The maximum deviation that could be measured above 250 °C was 0.2 °C which is the sensitivity limit of the thermocouple employed. No deviation of the thermocouple reading could be observed over a period of several days.

The starting material, **4**, for the kinetic runs was carefully purified by preparative GLC and vapor-transferred to a storage vessel. Kinetic runs were carried out in sealed tubes fashioned from 6-mm Pyrex tubing 180 mm in length which had been carefully cleaned with Alconox cleaning solution, rinsed with distilled water, soaked in concentrated ammonia solution, and flame-dried. Samples (1 μL each) of **4** were introduced into the tubes by a syringe and the tubes attached to a high vacuum line (10^{-5} mm), cooled with liquid nitrogen, and degassed by three consecutive freeze-thaw cycles. The tubes were then sealed off at the vacuum line and stored at –40 °C until used. The pressure within the tubes at 300 °C may be estimated at <0.3 atm.

Table III. Sample Kinetic Data for the Isomerization of 4

temp, °C	time, min	% 4	% 4 - % 4 _{eq} ^a	(k ₁ + k ₂) × 10 ⁵ s ⁻¹ ^b
261	0	100.0	89.0	2.55
	20	97.5	86.5	
	45	93.8	82.8	
	60	91.2	80.2	
	80	89.4	78.4	
	100	87.7	76.7	
	120	84.5	73.5	
287	140	82.8	71.8	13.3
	0	100.0	89.0	
	5	95.7	84.7	
	10	92.8	81.8	
	15	89.7	78.7	
	20	84.9	73.9	
	25	83.1	72.1	
	30	81.3	70.3	
304	40	76.4	65.4	33.4
	0	100.0	89.0	
	2	95.9	84.9	
	4	91.6	80.6	
	6	87.9	76.9	
	8	84.2	73.2	
	10	82.9	71.9	
	12	81.0	70.0	
14	77.5	66.5		
16	74.2	63.2		

^a % 4_{eq} was evaluated as 11% from $K_{eq} = 8.1 \pm 0.1$. ^b This value was obtained by a least-squares treatment of the data from the relationship $\ln(\% 4 - \% 4_{eq}) = -(k_1 + k_2)t + \ln(\% 4_0 - \% 4_{eq})$.

In a given kinetic run a set of samples was placed in a specially constructed stainless steel basket and lowered into the bath. At intervals a tube was removed and the reaction quenched by cooling the bottom of the tube in liquid nitrogen. The sample tube was carefully broken, 3 μ L of cyclohexane added and, after thorough mixing, aliquots of the solution were injected in the gas chromatograph. For these kinetic runs, a Varian 1200 gas chromatograph equipped with a hydrogen flame ionization detector was employed. A 2 ft \times 1/4 in. column of 10% Carbowax 1500 on Gas-Chrom P at 45 °C was used for the analysis and the peak areas of the two components were measured with a Varian Aerograph Model 477 digital integrator. The isomerizations were followed through the first 25-40% of reaction. Duplicate determinations were made for each point and at least two independent

runs were made at each temperature. Typical data are shown in Table III. Equilibrium constants were evaluated from samples which had been allowed to equilibrate over a period of 6 half-lives.

Thermal Isomerization of 4-d₂. A sample of 4-d₂ was heated in an evacuated sealed tube at 325 °C for 25 min and the composition of the mixture determined by GLC to be 82% 3-d₂ and 18% 4-d₂. The calculations of the number of protons expected in each group of integratable signals A, B, C, and D (see Table II) for the diradical process and the concerted process are based on the assumption of a randomized diradical. Diradical process: group A (H_a + H_b), 0.18(2 \times 1) + 0.82(1 \times 1) = 1.18; group B (H_c + H_d), 0.82(2 \times 0.5) + 0.82(2 \times 1) = 2.46; group C (H_f + H_g), 0.18[(8 \times 0.5) + (6 \times 0.5)] + 0.82[(7 \times 0.5) + (5 \times 0.5)] = 6.18; group D (H_e), 0.18(2 \times 0.5) = 0.18. Concerted process: group A, 0.18(2) + 0.82(1) = 1.18; group B, 0.82(4) = 3.28; group C, 0.18(8) + 0.82(5) = 5.54; group D, 0.

References and Notes

- (1) The support of this investigation under a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
- (2) Abstracted in part from the Ph.D. dissertation of J.G.K., University of Wyoming, Aug 1974. A preliminary report of this work was presented at the Rocky Mountain Regional Meeting of the American Chemical Society, Laramie, Wyo., June, 1976.
- (3) S. J. Rhoads and J. M. Watson, *J. Am. Chem. Soc.*, **93**, 5813 (1971).
- (4) Prepared by esterification of β -vinyladipic acid, a sample of which was kindly provided by the Esso Research and Engineering Co.
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- (10) For a recent compilation of data on such systems, see M. R. Willcott, R. L. Cargill, and A. B. Sears, *Prog. Phys. Org. Chem.*, **9**, 25 (1972).
- (11) H. M. Frey and R. K. Solly, *Trans. Faraday Soc.*, **64**, 1858 (1968).
- (12) After the present work was completed we became aware of a similar experiment carried out by Klumpp and coworkers, *Tetrahedron Lett.*, **12**, 1029 (1975), employing the rigid bicyclic derivative, I. Their findings parallel those reported here.
- (13) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).
- (14) J. M. Watson, unpublished experiment.
- (15) We are indebted to Professor J. A. Berson for advice on the construction of the bath and its use. A full description can be found in the Ph.D. dissertation of E. J. Walsh, University of Wisconsin, 1968.

