

311. The Thermal Isomerizations of Bicyclo[2.1.0]pent-5-yl Methyl Ketones: *endo-exo* Stereomutation and Cyclopropyl-Allylic Rearrangement to Cyclopent-2-enyl Methyl Ketones¹⁾

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Summary. Bicyclo[2.1.0]pent-5-yl methyl ketones undergo two thermal isomerization reactions. The *endo-exo* stereomutation follows the ring-flip path in better than 90%, with inversion of the configuration of the angular carbon atoms by cleavage and reclosure of the central bond. Stereomutation and cyclopropyl-allylic rearrangement to cyclopent-2-enyl methyl ketone do not involve a common intermediate and proceed on separate potential energy surfaces. The activation parameters of the rearrangement suggest an allowed concerted cycloreversion process.

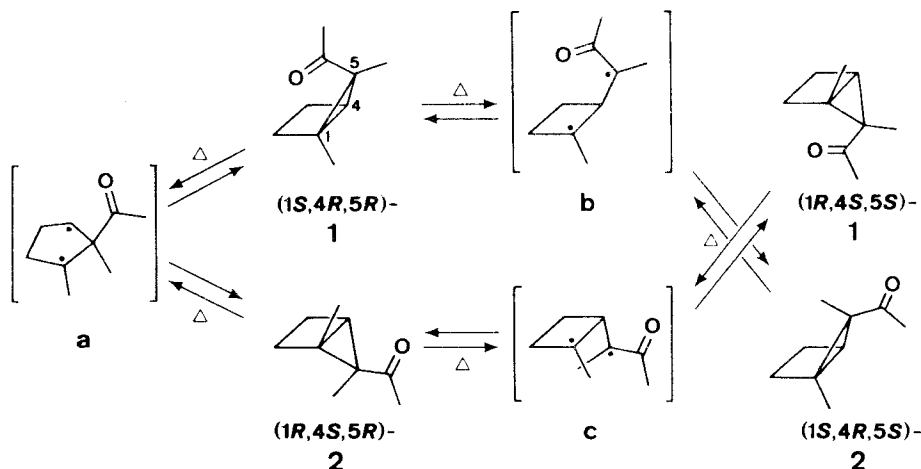
Bicyclo[2.1.0]pent-5-yl methyl ketones undergo *endo-exo* stereomutation and cyclopropyl-allylic rearrangement to cyclopent-2-enyl methyl ketones at temperatures above *ca.* 130° in inert solvents. These isomerizations are not accompanied by any other detectable thermal processes. The stereomutation has been described first by Jorgenson & Thacher [2] for the (1,5-dimethylbicyclopent-5-yl) methyl ketones, and the rearrangement was encountered simultaneously by these authors with the same compounds and by ourselves [3] with the 1,4,5-trimethyl homologs. We now report the results of a study designed to elucidate the mechanistic paths followed by the two thermal reactions³⁾.

***Endo-exo* Stereomutation of the (1, 5-dimethylbicyclo[2.1.0]pent-5-yl) methyl ketones 1 and 2. Chiroptical study.** – For the quantitative evaluation of the two possible pathways of stereomutation in bicyclopent-5-yl methyl ketones – by way of cleavage of the central or of a lateral cyclopropane bond – the chiroptical study of the asymmetrically substituted and optically active methyl homologs (1*S*, 4*R*, 5*R*)-1 and (1*R*, 4*S*, 5*R*)-2 were chosen. *Endo-exo* interconversion of these two compounds can, if at all, only occur *via* the cyclopentane 1,3-biradical **a**, *i.e.*, with inversion of configuration at the angular positions C(1) and C(4) and with retention at the apical carbon atom C(5) (Scheme 1).

¹⁾ Taken in part from the Doctoral Theses by Gonzenbach (ETH Zürich, 1973) and Grosclaude (Université de Genève, 1976). For preliminary communications see [1].

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³⁾ An intended joint effort in the pursuit of our initial independent entries into this field with Prof. Margaret J. Jorgenson, Boston University, was prevented by her death in March 1970 before we had occasion to plan the project. Our own subsequent work profited at the beginning from a sample of ethyl *endo*- and *exo-rac*-1,5-dimethylbicyclo[2.1.0]pentane-5-carboxylate prepared by the Jorgenson group [4].

Scheme 1. Possible mechanisms of *endo-exo* stereomutation of the dimethylbicyclopent-5-yl methyl ketones **1** and **2**

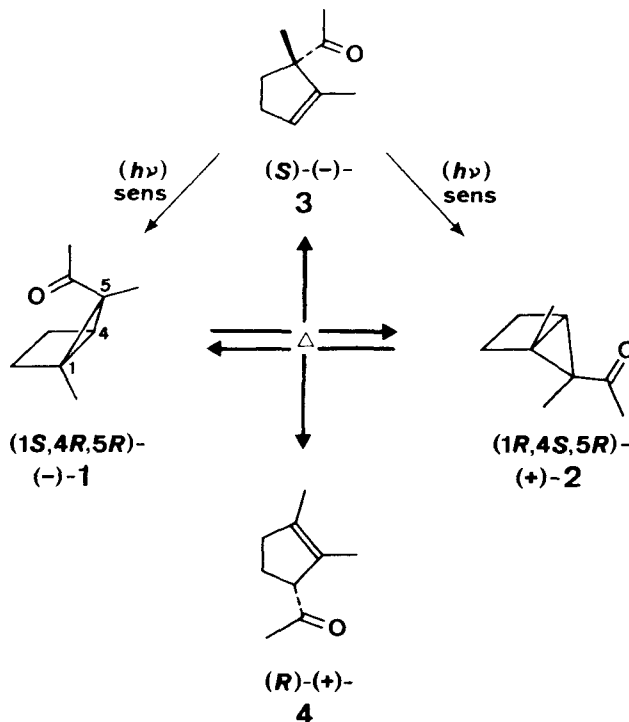
Alternatively, cleavage of a lateral cyclopropane bond, *e.g.*, to intermediates **b** and **c**⁴⁾, would reverse the configurational outcome of the reaction, and the resulting products would be the enantiomers of those formed in the ring flip mode *via a*.

The optically active bicyclopentyl ketones **1** and **2** were prepared as follows: (–)-1,2-dimethyl-2-cyclopentenecarboxylic acid was obtained by fractional crystallization of the salt formed by the (±)-acid with (–)-dehydroabietylamine. The (–)-acid was converted into (–)-methyl ketone **3** with methyl lithium, and acetone-sensitized rearrangement [5] of (–)-**3** at room temperature afforded (–)-**1** and (+)-**2** (Scheme 2). The enantiomeric purity of **1–3**, as determined by NMR. spectroscopy using optically active Pr(HFC)₃ as a shift reagent, was over 90% in each case, and no loss of enantiomeric purity of recovered starting material and products had occurred in the photochemical reaction (see Table 1).

The $\alpha \rightarrow \beta$ acyl shift, an integral feature of the oxadi- π -methane photocycloisomerization of β, γ -unsaturated ketones irrespective of the mechanistic details [1c] [5] [6], is assumed to proceed in **3** on the side of the initial acetyl attachment on the cyclopentene, resulting in *endo*-**1** and *exo*-**2** possessing *identical* absolute configurations at C(5). This assumption is quite plausible and it is determinant for the mechanistic conclusions to be drawn later from the results of the thermal isomerization of (–)-**1** and (+)-**2**. The assignment of the absolute configuration, not essential to this conclusion, is based on the negative Cotton effect of $\Delta\epsilon_{\max}^{+20} = -7.40$ at 299 nm in the circular dichroism of (–)-**3** and its temperature gradient, $I_{-195}^{+20}(299 \text{ nm}) = -33.3\%$ ⁵⁾.

4) In a subsequent paper [5] it will be shown that a photolytic *endo-exo* stereomutation $\mathbf{1} \rightleftharpoons \mathbf{2}$ does not occur at room temperature. As a possible reason for this failure, inhibition of rotation around the 4, 5-bond in biradical intermediates such as **b** and **c** by nonbonding steric interaction with the *cis*-methylene hydrogen atoms are considered. This does not necessarily rule out *a priori* these intermediates in the thermal isomerization at temperatures above 130°.

5) We thank Prof. G. Snatzke, Ruhr-Universität Bochum, for the CD. measurement. For the relationship between Cotton effect and absolute configuration of cyclopent-2-enyl methyl ketones and the definition of the CD. temperature gradient $I_{T_2}^{T_1}$ see [7].

Scheme 2. Results of the thermal isomerization of (1*S*,4*R*,5*R*)-(–)-**1** and (1*R*,4*S*,5*R*)-(+)-**2**

The thermolyses of (–)-**1** and (+)-**2** were carried out separately in benzene solutions at 200° and interrupted at conversions of *ca.* 80% and 40% starting material, respectively. Each mixture consisted of the same components, (–)-**1**, (+)-**2**, (–)-**3**, and (+)-**4** (*cf.* Table 1). The enantiomeric purities of **1**, **2**, and **3** were determined as described above. They were the same as that of the starting ketone in each run. The NMR. signals of compound **4** could not be sufficiently resolved with the aid of shift reagents to allow a determination of the enantiomeric purity, but the positive specific rotation is in accord with the formation of the (*R*)-enantiomer as expected in analogy to the rearrangement to (*S*)-**3**.

These results establish that the endo-exo stereomutation of the bicyclopentyl methyl ketones 1 and 2 proceeds, within the experimental error, entirely with inversion at the angular carbon atoms through cleavage and restitution of the central bond as indicated in Scheme 1 utilizing a as a formal illustration. However, our experiments do not specify any further the particulars of the reaction coordinate. Intervention of a biradical intermediate corresponding to a, which would occupy an energy minimum, is possible. Yet the species may just as well represent any other point on the potential energy surface, or a transition state with incomplete rupture of the central bond may intervene instead.

Discussion. – The two cleavage processes which are proposed in Scheme 1 as *a priori* possible mechanisms for the stereoequilibration of **1** and **2** [4], have been

Table 1. Triplet rearrangement of (–)-**3** and thermal isomerization of (–)-**1** and (+)-**2**: Sign of specific rotation and enantiomeric purity of products^{a)}

Starting ketone (enantiomeric purity, %)	Enantiomeric purity of products, %			
	(–)- 1	(+)- 2	(–)- 3	(+)- 4
(–)- 3 (95) ^{b)}	93	94	95 ^{c)}	–
(–)- 1 (93) ^{d)}	94 ^{c)}	93	92	^{e)}
(+)- 2 (94) ^{d)}	92	94 ^{c)}	91	^{e)}

^{a)} $[\alpha]_D^{20}$, $c \sim 0.1$ – 2.2 in CHCl_3 ; enantiomeric purity by NMR. with $\text{Pr}(\text{HFC})_3$, experimental error $\pm 3\%$.

^{b)} In 0.2M acetone solution $+254\text{ nm}$ at room temperature.

^{c)} Recovered starting material

^{d)} In 0.36M benzene solution at 200° ; conversions 80% in the run with **1**, 60% in the run with **2**.

^{e)} Not determined.

discussed and tested previously for the parent hydrocarbon and its derivatives [8]. Breaking of the central bond and intervention of a cyclopropane 1,3-biradical intermediate corresponding to **a** has been demonstrated repeatedly [8b] [9]⁶⁾ 7). The same reaction path might have been anticipated also as the preferred variant for **1** and **2** on purely thermochemical grounds [12]. However, the system $\mathbf{1} \rightleftharpoons \mathbf{2}$ constitutes the first example of such *endo-exo* interconversion in which bicyclo[2.1.0]pentanes with a π -acceptor group on C(5) are involved. Apical π -donating substituents are known to lower the isomerization barrier appreciably [13], and cleavage of the central bond has been demonstrated experimentally in one such case, 5-benzoyloxybicyclo[2.1.0]pentane [14]⁸⁾. This effect is ascribed to two cooperative factors introduced by a π -donor on C(5). Overlap with the Walsh LUMO enhances the antibonding character of all three cyclopropane bonds [15]. At the same time, the destabilizing interaction of the biradical orbital of S-type symmetry with an electronegative substituent should be smaller than with a methylene group, which lowers this orbital below the A-type HOMO of 1,3-cyclopentadiyl [16]. Accordingly, and in agreement with extended Hückel calculations, the symmetry-imposed barrier to converting bicyclo[2.1.0]pentane to 1,3-cyclopentadiyl should presumably be eliminated and the disrotatory opening become an allowed process.

In the presence of a π -acceptor group these conditions are not fulfilled. Its interaction with the Walsh HOMO decreases the antibonding properties of, and hence fortifies, the central bond and still weakens the lateral cyclopropane bonds by lowering their bonding character, which introduces in **1** and **2** factors in favor of the reaction path involving cleavage to **b** and **c**. The experimental result shows that these electronic factors are qualitatively not determinant. In fact, the barrier to isomeri-

⁶⁾ Cf. also Turner *et al.* [10] for a thermodynamic argument in favor of the existence of 1,3-cyclopentadiyl as an intermediate in the ring flip isomerization of bicyclo[2.1.0]pentane in the gas phase.

⁷⁾ Matrix-isolated 1,3-cyclopentadiyl has been recently detected directly by ESR. spectroscopy upon UV. irradiation of 2,3-diazabicyclo[2.2.1]heptene-2 at 5.5 K [11].

⁸⁾ Added in proof: Arnold & Morchat have shown recently that a 1,4,5-triphenylbicyclo[2.1.0]pentane *exo* $\rightarrow$ *endo* isomerizes with an activation energy of 12 kcal/mol less than 2-methylbicyclopentane, presumably so also *via* the ring-flipping process. – We thank Prof. D. R. Arnold for the communication of this result prior to publication.

zation is found to be even *ca.* 4 kcal/mol less (*vide infra*, Table 3) than the activation energy of 38.9 kcal/mol reported by Chesick [9] for 2-methylbicyclo[2.1.0]pentane.

Endo-exo stereomutation and cyclopropyl-allylic rearrangement of the (5-methylbicyclo[2.1.0]pent-5-yl) methyl ketones 5 and 6. Kinetic analysis. – When the reaction path of $1 \rightleftharpoons 2$ had been established, intervention of a biradical intermediate **a** common to both the *endo-exo* interconversion and the rearrangements $1/2 \rightarrow 3 + 4$ appeared to be an economic mechanistic rationale, even though we are

Scheme 3. Results of the kinetic analysis of the thermolysis of **5** and **6**

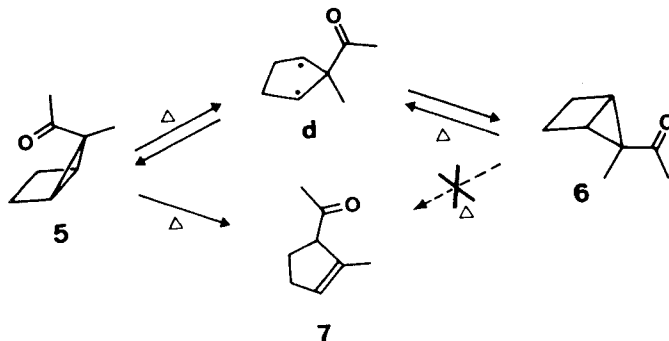


Table 2. First-order rate constants of stereoisomerizations and cyclopropyl-allylic rearrangement of the bicyclopentyl methyl ketones **1**, **2**, **5** and **6** in benzene

Ketone	Reaction	Temperature, °C	<i>k</i> , sec ⁻¹
1	1 → 2	170	$(6.50 \pm 0.14) \cdot 10^{-2}$
	2 → 1	170	$(3.41 \pm 0.06) \cdot 10^{-2}$
	1 → 3	170	$(1.70 \pm 0.21) \cdot 10^{-3}$
	1 → 4	170	$(0.80 \pm 0.21) \cdot 10^{-3}$
	2 → 3 + 4	170	$< 2.96 \cdot 10^{-7 \text{ a}}$
5	5 → 6	160	$(3.27 \pm 0.13) \cdot 10^{-3}$
		180	$(2.51 \pm 0.38) \cdot 10^{-2}$
		200	$(9.30 \pm 0.22) \cdot 10^{-2}$
		220	$(4.61 \pm 0.13) \cdot 10^{-1}$
	6 → 5	160	$(8.65 \pm 3.65) \cdot 10^{-4}$
		180	$(6.87 \pm 0.69) \cdot 10^{-3}$
		200	$(2.42 \pm 0.15) \cdot 10^{-2}$
		220	$(1.34 \pm 0.09) \cdot 10^{-1}$
	5 → 7	160	$(1.68 \pm 0.26) \cdot 10^{-4}$
		180	$(1.29 \pm 0.44) \cdot 10^{-3}$
		200	$(1.96 \pm 0.22) \cdot 10^{-3}$
		220	$(5.37 \pm 0.72) \cdot 10^{-3}$
6	6 → 7	160–220	$< 2.96 \cdot 10^{-7 \text{ a}}$
	5 → 6	180	$(3.65 \pm 0.38) \cdot 10^{-2}$
	6 → 5	180	$(5.74 \pm 0.65) \cdot 10^{-3}$
	5 → 7	180	$(2.03 \pm 0.28) \cdot 10^{-3}$
	6 → 7	180	$(8.20 \pm 0.78) \cdot 10^{-6}$

^{a)} For *k*₂₃₄ and *k*₆₇ see footnote 8.

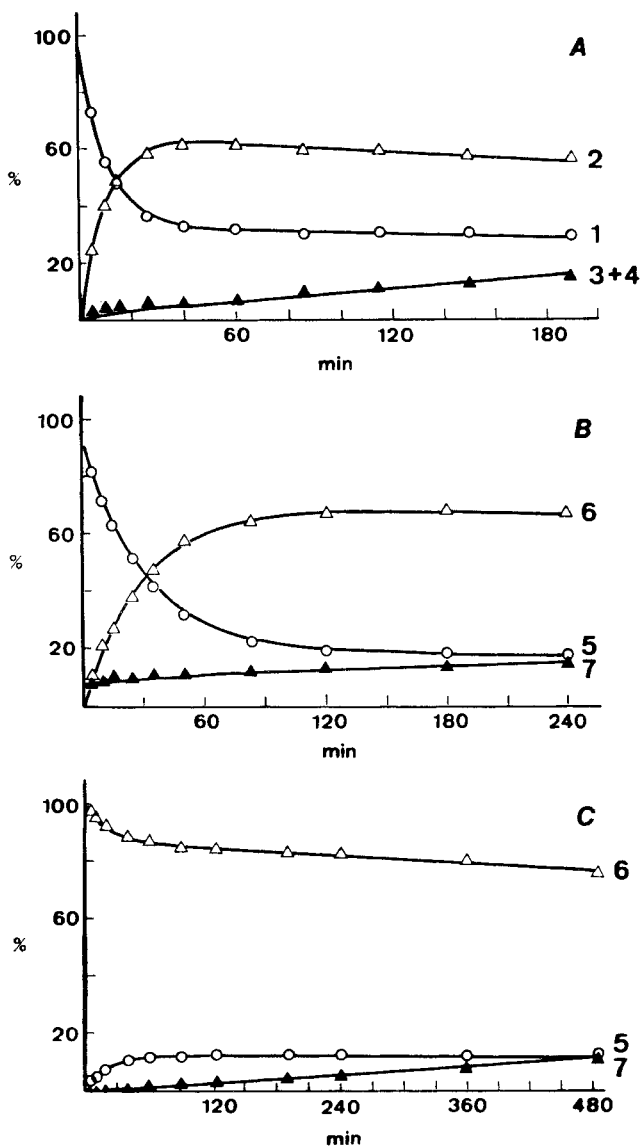


Fig. 1. Thermolyses of **1** (at 170°: A), **5** (at 180°: B), and **6** (at 180°: C): experimental and calculated plots of percentage product composition vs. reaction time

not aware of an adequate precedent for the 1,2-acetyl migration which would then be required in the latter process. We therefore turned to a kinetic study of the two fundamental isomerization processes. The 5-methylbicyclopent-5-yl methyl ketones **5** and **6** [5] were chosen first as they are somewhat more thermostable than the 1-methyl homologs and therefore better suited for quantitative capillary GC. analysis.

When a 3% solution of 31.9% **5**, 58.9% **6** and 9.2% **7** in benzene was thermolysed for 22 h at 220°, the resulting composition was 3.5% **5**, 4.2% **6** and 92.3% **7** with no other products detectable by GC. The kinetic runs with benzene solutions of **5** and **6** were carried out in the temperature range 160–220°, the rearrangement product **7** remaining unchanged under these conditions. Best-fit rate constants were then calculated using programs designed to handle up to four components linked by equilibria [17], and these data are given in Table 2. The experimental results are in good agreement with simulated curves for percentage product composition *vs.* reaction time using the calculated rate constants (for examples see Fig. 1). The rate constants remained the same within experimental error when *ca.* 3% pyridine were added to a solution of **5** at 200°. Catalysis of the isomerization by traces of acid is therefore excluded. The rate constant of the cyclopropyl-allylic rearrangement is smaller for the *exo*-bicyclopentane (k_{67}) than for the *endo*-isomer (k_{57}) by a factor of $> 10^3$ and may be neglected altogether⁹). The result of a kinetic experiment with ketone **1** at 170° shows (Table 2)⁹) that the orders in rate constants are quite similar in the two homologous series, *i.e.*, $k_{endo \rightarrow exo} > k_{exo \rightarrow endo} > k_{endo \text{ rearr}} \gg k_{exo \text{ rearr}} \sim 0$. A combinatory interpretation of the analytical results in both series, *i.e.* the chiroptical (of **1** $\rightarrow$ **2**) and kinetic studies (of **6** $\rightleftharpoons$ **5** $\rightarrow$ **7**), appears therefore acceptable.

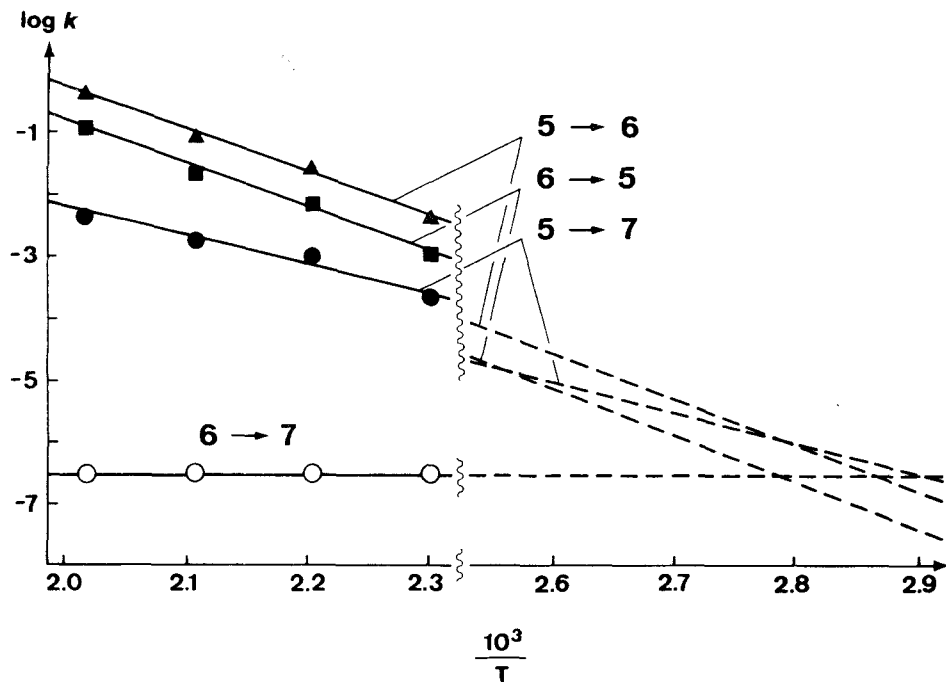


Fig. 2. Arrhenius plot of the reactions **5** $\rightarrow$ **6**, **6** $\rightarrow$ **5**, **5** $\rightarrow$ **7**, and **6** $\rightarrow$ **7**, ---- Extrapolation

⁹) The rate constants k_{234} and k_{67} (from **5** as starting material) given in Table 2 are the *maximum* values computed to comply with the other rate data.

Finally, the activation parameters associated with the rate constants k_{56} , k_{65} and k_{57} were calculated from an *Arrhenius* plot which had been optimized by linear regression (Fig. 2), and they are given in Table 3.

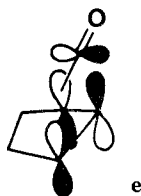
Table 3. Activation parameters of stereoisomerizations and cyclopropyl-allylic rearrangement of the bicyclopentyl methyl ketones **5** and **6** in benzene^{a)}

Reaction	E_a [kcal/mol]	$\Delta H^\ddagger$ [kcal/mol]	$\Delta S^\ddagger$ [e.u.]	$\Delta G^\ddagger$ [kcal/mol]
5 $\rightarrow$ 6	34.3 ± 0.8	33.4 ± 0.8	-1.5 ± 1.7	34.1 ± 1.6
6 $\rightarrow$ 5	34.8 ± 0.9	33.9 ± 0.9	-3.0 ± 2.0	35.3 ± 1.9
5 $\rightarrow$ 7	23.1 ± 2.2	22.2 ± 2.2	-33.0 ± 4.7	37.7 ± 4.4

^{a)} Calculated from the rate data of **5** in Table 2. Errors are standard deviations, and the correlation coefficients are 0.998 (**5** $\rightarrow$ **6**), 0.997 (**6** $\rightarrow$ **5**), and 0.996 (**5** $\rightarrow$ **7**).

Discussion. – The kinetic results provide a clear mechanistic differentiation of the *endo-exo* stereomutation and the cyclopropyl-allylic rearrangement. The order in rate constants and the significant gap in activation entropies between the stereoisomerizations **5** $\rightarrow$ **6** and **6** $\rightarrow$ **5** on the one hand and the rearrangement **5** $\rightarrow$ **7** on the other strictly preclude that the two types of reaction involve a common intermediate such as **d**, and consequently the rearrangement must occur on a separate potential energy surface.

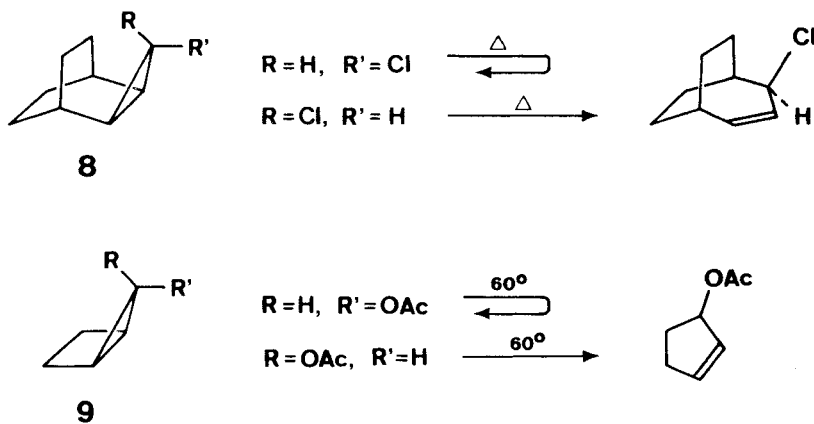
The remarkably large negative entropy of activation for **5** $\rightarrow$ **7**, $\Delta S^\ddagger = -33$ e.u., indicates that this reaction proceeds through a highly ordered transition state. A concerted electrocyclic process involving the four electrons of the internal cyclopropane and the C(5)-acetyl bonds ($\sigma_{2a} + \sigma_{2s}$) would adequately accommodate the requirements of both such a transition state and the high selectivity for *endo* starting material. Disrotatory ring opening would selectively permit the simultaneous transfer of the *endo*-acetyl substituent of **5** via a *transom* of appropriate *Möbius* topology (cf. **e**) prior to flattening of the five-membered ring with complete rupture of the central bond. An application of the concerted cycloreversion to the *exo*-ketone **6**,



although formally possible, would necessarily require this latter far-reaching geometrical change in order for the transition state to adopt an optimum geometry with near-parallel p orbitals of the allylic system, and it would thus be hardly distinguishable from species **d** (which is excluded by the kinetics)¹⁰⁾. A concerted mechanism has also

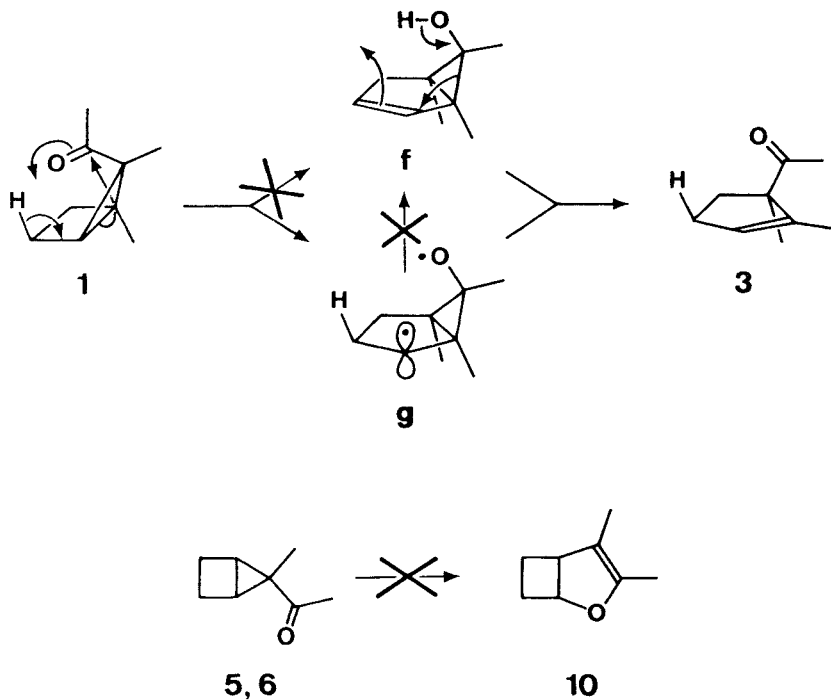
¹⁰⁾ An alternative $\sigma_{2a} + \sigma_{2s}$ cycloreversion mode which involves the 1,2- and 4,5-bonds of the bicyclo[2.1.0]pentane skeleton, would proceed with preservation of the substitution pattern and is ruled out by the transformations **1** $\rightarrow$ **4** and **5** $\rightarrow$ **7** which document the involvement of a 1,2-acetyl shift. Such a mechanism has been proposed by Baldwin [18] for the thermal isomerization of 2-methylbicyclo[2.1.0]pent-2-ene to 1-methyl-1,3-cyclopentadiene.

been tentatively considered in previous studies by *Jefford* [19] and *Tufariello* [13b] for the facile and similarly *endo*-selective cyclopropyl-allylic rearrangements of halocyclopropanes and 5-acetoxycyclo[2.1.0]pentane (*cf.* **8** and **9**, respectively).



In search of alternative mechanisms which would be in accordance with our own findings, the hypothesis was tested that the rearrangement might proceed *via* the cyclopropanol intermediate **f**. Its formation could be visualized in an electrocyclic

Scheme 4



process involving the breaking of the internal cyclopropane bond, formation of a new three-membered ring, and transfer of an *endo*-methylene hydrogen to the oxygen as summarized in **1**, *Scheme 4*. A stepwise variant of this process would include biradical **g** which is being proposed a likely intermediate in the photochemical oxadi- π -methane rearrangement **3** $\rightarrow$ **1** + **2** [5]. Evidence in favor of the existence of intermediate **f** was sought in attempting a H/D exchange between the hydroxyl and solvent. However, the result of a pyrolysis of the *endo*-ketone **2** at 200° in benzene which had been saturated with deuterium oxide was negative. After 70% conversion the mass spectra of neither the starting material (**2**) nor the major cyclopentenyl methyl ketone (**3**) exhibited any excess deuterium.

A thermal isomerization which *a priori* had been considered more likely than the cyclopropyl-allylic rearrangement, is a ring enlargement to a dihydrofuran, *e.g.* **5, 6** $\rightarrow$ **10** (*cf.* [4]). In none of the thermolyses of acetylbicyclopentanes the occurrence of such a product was detected.

This work was supported by the *Fonds National Suisse de la Recherche Scientifique* and by *Firmenich S.A.*, Geneva. Prof. R. W. Rozett, Fordham University, provided his computer programs (KIN1 and KIN4) and the University of Geneva allotted us free time on the CDC 3800 computer.

Experimental Part

Gas chromatography (GC.): *Perkin-Elmer* 900 and 990 chromatographs; carrier gas helium, 2 ml/min for capillary and 70–150 ml/min for packed columns; FID system. Capillary column: 150' $\times$ 0.01". Packed columns: 10' $\times$ 3/8' and 10' $\times$ 1/4'; 5% FFAP and 15% squalane, both on chromosorb W, AW/DMCS. Peak integration with an automatic digital integrator. – *Optical rotations*: *Perkin-Elmer* 141 polarimeter; 10 cm cell; CHCl_3 ; *c* added in parentheses. – *IR. spectra*: *Perkin-Elmer* 257 spectrophotometer; band positions in cm^{-1} ; *s* = strong, *m* = medium, *w* = weak, *br.* = broad. – *NMR. spectra*: *Varian* XL-100; chemical shifts in δ values, *J* in Hz; *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet of higher than first order, *br.* = broad. – *UV. spectra*: *Beckman* Acta III spectrophotometer; maxima in nm, ϵ values added in parentheses. – *Mass spectra* (MS.): *Varian* SM-113; base peak in *italics*.

Resolution of (+)-1,2-Dimethyl-2-cyclopentenecarboxylic acid [5]¹¹). Equimolar amounts of *rac*-acid and (+)-dehydroabietyl amine [prepared from the acetate (*Fluka AG*) of constant m.p. 144–145° by decomposition in aqueous 10% KOH-solution at 100°] were dissolved in CH_3OH . Evaporation of the solvent afforded a crystalline mass which by fractional crystallization in benzene gave the (–)-diastereoisomeric salt with a constant optical rotation, $[\alpha]_{\text{D}}^{20} = -22^\circ$ (0.9). This salt was dissolved in CH_2Cl_2 and decomposed by shaking with aqueous satd. NaHCO_3 solution. The aqueous layer was brought to pH 2 with 2*N* H_2SO_4 and extracted with CH_2Cl_2 . Distillation of the crude product at 75°/0.1 Torr gave (S)-(–)-1,2-dimethyl-2-cyclopentenecarboxylic acid; $[\alpha]_{\text{D}}^{20} = -152^\circ$ (0.8).

(S)-(–)-(1,2-Dimethyl-2-cyclopentenyl) methyl ketone (**3**)¹¹). The preparation from (S)-(–)-1,2-dimethyl-2-cyclopentenecarboxylic acid with CH_3Li followed the procedure employed for the racemic compounds [5]. – $[\alpha]_{\text{D}}^{20} = -402^\circ$ (2.2)¹². CD. (methylcyclohexane/isopentane 1:3)⁵): $\Delta\epsilon_{\text{max}}^{+20^\circ} = -3.33$ (318 nm), -6.33 (309), -7.40 (299), -6.33 (293), $+1.83$ (217); $\Delta\epsilon_{\text{max}}^{-195^\circ} = -5.19$ (316 nm), -10.04 (306), -11.08 (296), -9.35 (289), $+5.54$ (212); I_{-195}^{+20} (299 nm) = -33.3% .

Acetone-sensitized irradiation of (–)-3. A quartz tube with a 0.2*M* solution of (–)-**3** in acetone was placed in the centre of a circular Hg low-pressure lamp (principal emission at 254 nm). The

¹¹) For the analytical data of the racemic compounds see [5]. The spectral and chromatographic comparisons with the optically active substances were satisfactory in all cases.

¹²) Values corrected for 100% enantiomeric purity (see Table 1).

solution was purged with argon prior to and stirred magnetically during the irradiation. The photolysis was carried out at room temperature and carried to 93% conversion (monitoring by capillary GC. at 100°). Products **1** and **2** were formed in a 7:3 ratio. For analytical purposes samples of the compounds were isolated by GC. (FFAP, 100–110°): recovered (–)-**3**, (1*S*,4*R*,5*R*)-(–)-(1,5-dimethylbicyclo[2.1.0]pent-5-yl) methyl ketone (**1**), $[\alpha]_D^{20} = -78^\circ$ (0.6), and (1*R*,4*S*,5*R*)-(+)-(1,5-dimethylbicyclo[2.1.0]pent-5-yl) methyl ketone (**2**), $[\alpha]_D^{20} = +43^\circ$ (0.5)¹⁰ 11).

As the GC. retention times of **1** and **3** are too close for satisfactory preparative separation, the ternary mixture was taken up in acetone and **3** selectively oxidized by titration with an aqueous 2% KMnO_4 solution treated with Na_2CO_3 . After work-up the products **1** and **2** could then be isolated by GC. as above.

Preparative thermolysis of (–)-1 and (+)-2. 0.36 M solutions of each compound in benzene were heated to 200° in sealed Pyrex tubes for 1 and 2 h, respectively. After evaporation of the solvent, the products were isolated by GC. (squalane, 110°) and identified by IR., NMR. and GC. coinjection with racemic samples [5].

From (–)-**1**: 20% (–)-**1**, $[\alpha]_D^{20} = -72^\circ$ (0.2); 35% (+)-**2**, $[\alpha]_D^{20} = +32^\circ$ (0.5); 18% (–)-**3**, $[\alpha]_D^{20} = -340^\circ$ (0.4); 27% (+)-**4**, $[\alpha]_D^{20} = +288^\circ$ (0.6).

From (+)-**2**: 40% (+)-**2**, $[\alpha]_D^{20} = +38^\circ$ (0.3); 23% (–)-**1**, $[\alpha]_D^{20} = -67^\circ$ (0.13); 20% (–)-**3**, $[\alpha]_D^{20} = 311^\circ$ (0.8); 17% (+)-**4**, $[\alpha]_D^{20} = +302^\circ$ (0.9).

Determination of the enantiomeric purities of (–)-1, (+)-2, and (–)-3. The enantiomeric purities were measured by integration of the areas of the acetyl ¹H-NMR. signals of each enantiomer in the presence of the optically active shift reagent praseodymium(III)tris(3-heptafluoropropylhydroxymethylene)-*d*-camphorate. For the assignment of each signal to the enantiomer, the NMR. probes of (–)-**1**, (+)-**2** and (–)-**3** were rerun after addition of some (±)-**1**, (±)-**2**, and (+)-**3**, respectively. For the results, see Tables 1 and 4, and Figure 3.

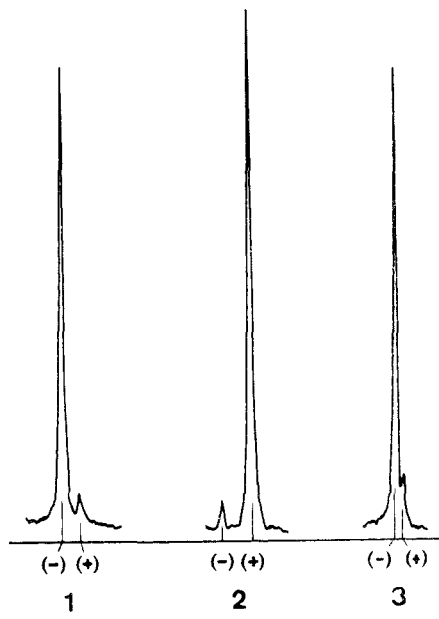


Fig. 3. Resolved acetyl ¹H-NMR. signals of **1**, **2** and **3** in the presence of $\text{Pr}(\text{HFC})_3$

Thermolysis of a mixture of endo-(5-methylbicyclo[2.1.0]pent-5-yl) methyl ketone (5), exo-(5-methylbicyclo[2.1.0]pent-5-yl) methyl ketone (6), and (2-methyl-cyclopent-2-enyl) methyl ketone (7). A 3% solution of 31.9% **5**, 58.9% **6** and 9.2% **7** in benzene was heated for 22 h to 220° in a sealed Pyrex tube. Capillary GC. (Carbowax K 1540, 110°): 3.5% **5**, 4.2% **6**, 92.3% **7**.

Table 4. Chemical shift differences of the acetyl ^1H -NMR. signals of **1**, **2** and **3** in the presence of $\text{Pr}(\text{HFC})_3$

Ketone	Concentration of $\text{Pr}(\text{HFC})_3$	Chemical shift differences ($\Delta\delta$) and enantiomer assignment	
0.29M 1	0.12M	– 3.62 (–);	– 3.72 (+)
0.36M 2	0.07M	– 4.32 (–);	– 4.45 (+)
0.24M 3	0.11M	– 4.73 (–);	– 4.81 (+)

Kinetic runs with 1, 5 and 6. a) A 2% solution of **5** in benzene was sealed in Pyrex tubes which were heated in separate batches to 160, 180, 200 and 220°. In every run, five tubes at each of several time intervals were removed and cooled in dry ice/acetone. The samples were then analysed quantitatively by capillary GC. (Carbowax K 1540, 90–100°) and the average of the five determinations were used for the determination of the rate constants (see Fig. 1B and 2, and Table 2). The plot of percentage product composition *vs.* reaction time did not vary beyond experimental error when 3% pyridine were added to a parallel run at 200°.

b) Analogous runs with **1** and **6** were carried out at 170° and 180°, respectively (see Fig. 1A, 1C and 2, and Table 2).

Thermolysis of 2 in benzene/D₂O. A 3% solution of **2** in benzene saturated with D₂O was heated in a sealed Pyrex tube for 6 h at 200°. The reaction mixture contained a 3:7 ratio of **2** and **3** which were isolated by GC. (FFAP, 120°). MS.: ($M^+ + 1$) = 30% (control sample: 27%) for **2**, 23% (control: 25%) for **3**; reference: $M^+ = 100\%$; experimental error: $\pm 5\%$.

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