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 Ketones[1])

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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 reactions[3]).

***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*).

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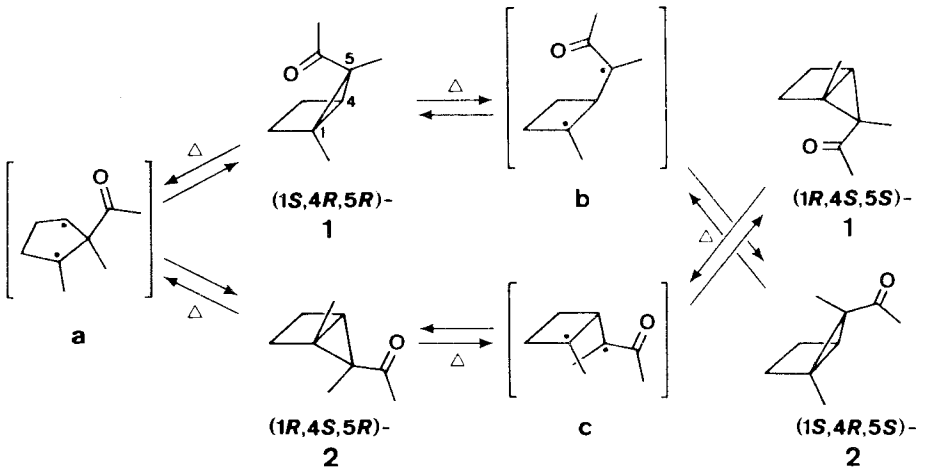
1) Taken in part from the Doctoral Theses by *Gonzenbach* (ETH Zürich, 1973) and *Grosclaude* (Université de Genève, 1976). For preliminary communications see [1].

2) Address correspondence to Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung, Stiftstrasse 34–36, D–4330 Mülheim/Ruhr.

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 photorearrangement 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 $\Delta\varepsilon_{max}^{+20°} = -7.40$ at 299 nm in the circular dichroism of (–)-**3** and its temperature gradient, I_{-195}^{+20} (299 nm) = –33.3%[5]).

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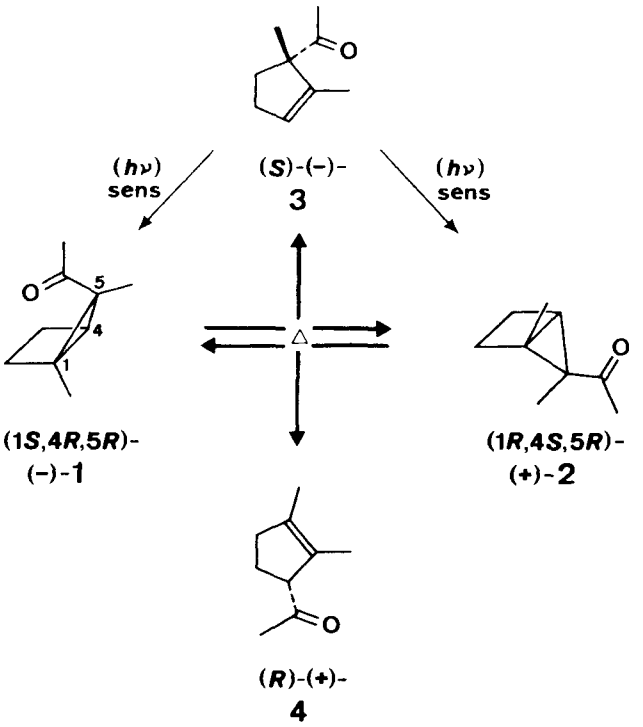
4) In a subsequent paper [5] it will be shown that a photolytic *endo-exo* stereomutation **1** $\rightleftarrows$ **2** does not occur at room temperature. As a possible reason for this failure, inhibition of rotation around the 4,5-bond in biradical intermediates such as **b** and **c** by nonbonding 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* (1S,4R,5R)-(−)-**1** *and* (1R,4S,5R)-(+)-**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 $Pr(HFC)_3$, experimental error $\pm$ 3%.

[b]) In 0.2 M acetone solution +254 nm at room temperature.

[c]) Recovered starting material

[d]) In 0.36 M 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 **1** $\rightleftarrows$ **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[2.10]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* → *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** ⇄ **2** had been established, intervention of a biradical intermediate **a** common to both the *endo-exo* interconversion and the rearrangements **1**/**2** → **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**

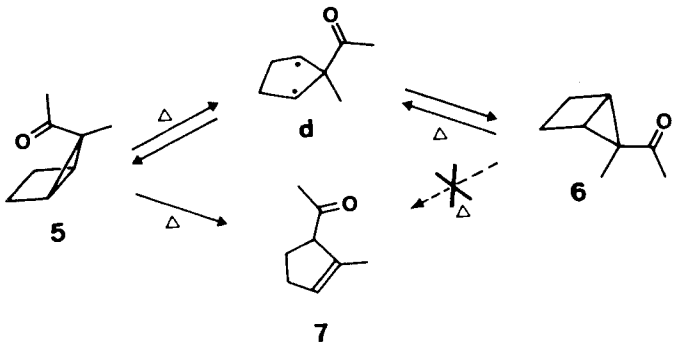


Table 2. *First-order rate constants of stereoisomerizations and cyclopropyl-allylic rearrangement of the bicyclopentyl methyl ketones* **1**, **2**, **5** *and* **6** *in benzene*

Ketone	Reaction	Temperature, °C	k, 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	$< 2.96 \cdot 10^{-7}$ [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 → **7**	160–220	$< 2.96 \cdot 10^{-7}$ [a]
6	**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.

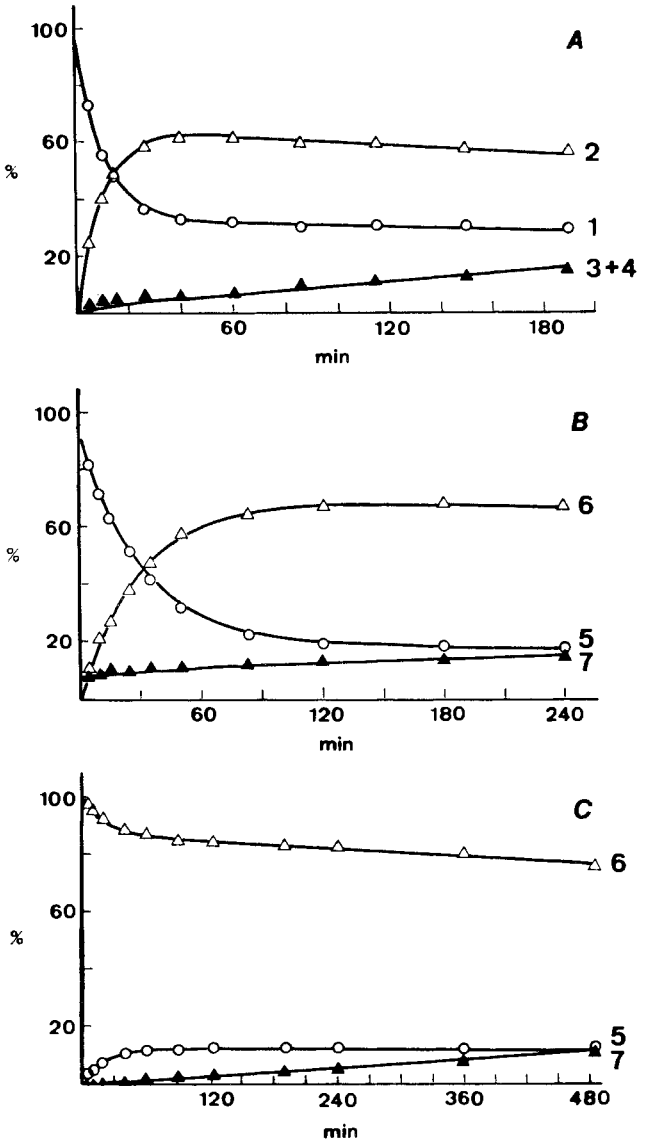


Fig. 1. *Thermolyses of* **1** *(at 170°*: A), **5** *(at 180°*: B), *and* **6** *(at 180°*: C): *experimental and calculated plots of percentage product composition* vs. *reaction time*

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 altogether[9]). 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** → **2**) and kinetic studies (of **6** ⇄ **5** → **7**), appears therefore acceptable.

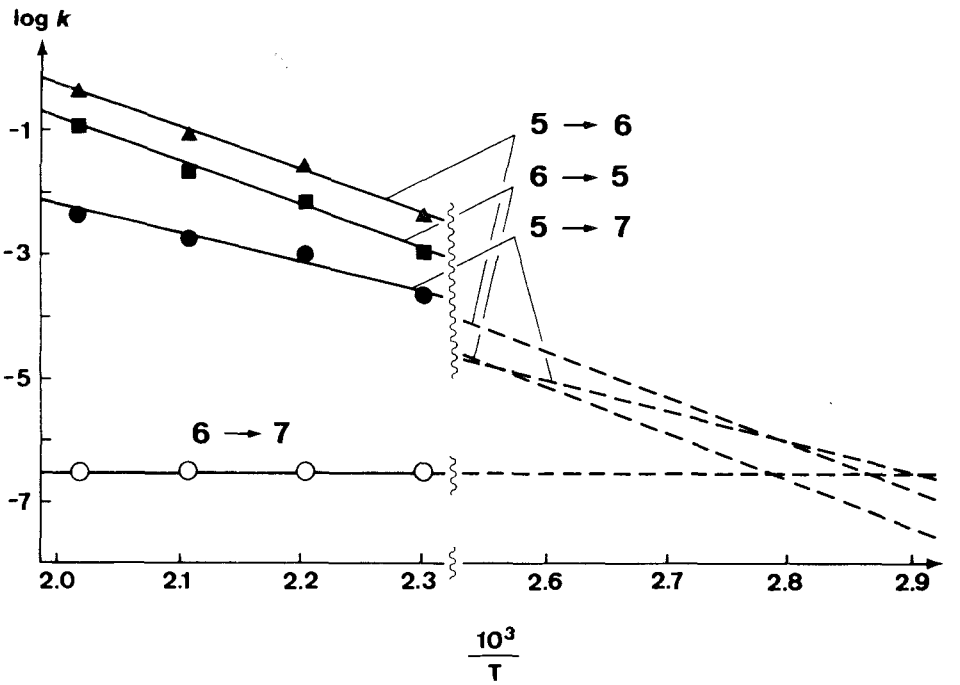


Fig. 2. *Arrhenius plot of the reactions* **5** → **6**, **6** → **5**, **5** → **7**, *and* **6** → **7**, --- Extrapolation

[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]	$\Delta H^{\neq}$ [kcal/mol]	$\Delta S^{\neq}$ [e.u.]	$\Delta G^{\neq}$ [kcal/mol]
5 → **6**	34.3 ± 0.8	33.4 ± 0.8	−1.5 ± 1.7	34.1 ± 1.6
6 → **5**	34.8 ± 0.9	33.9 ± 0.9	−3.0 ± 2.0	35.3 ± 1.9
5 → **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** → **6**), 0.997 (**6** → **5**), and 0.996 (**5** → **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** → **6** and **6** → **5** on the one hand and the rearrangement **5** → **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.

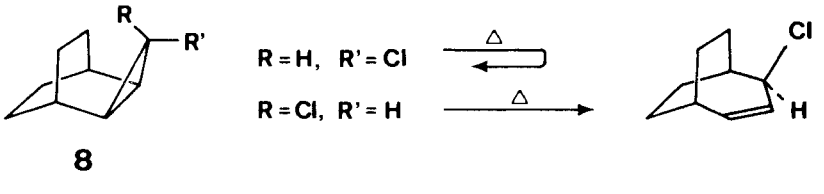
The remarkably large negative entropy of activation for **5** → **7**, $\Delta S^{\neq} = -33$ c.u., indicates that this reaction proceeds through a highly ordered transition state. A concerted electrocyclic process involving the four electrons of the internal cyclopropane and the C(5)-acetyl bonds ($_{\sigma}2_a + {}_{\sigma}2_s$) 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**,

e

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 $_{\sigma}2_a + {}_{\sigma}2_s$ 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** → **4** and **5** → **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-acetoxybicyclo[2.1.0]pentane (*cf.* **8** and **9**, respectively).



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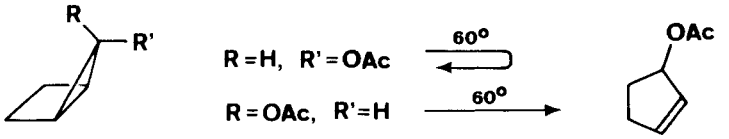

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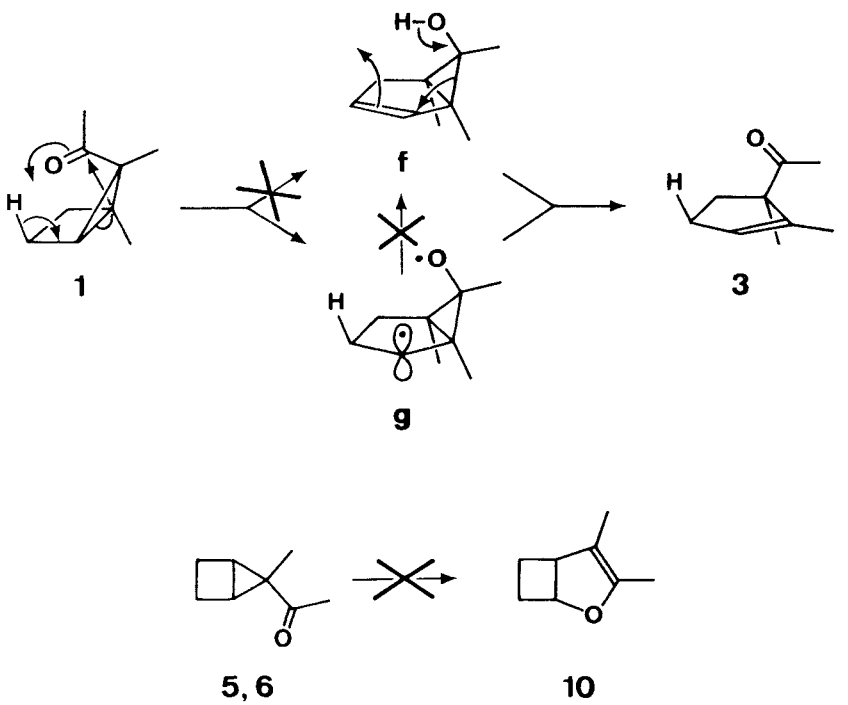
In search of alternative mechanisms which would be in accordance with our own findings, the hypothesis was tested that the rearrangement might proceed *via* the cyclopropanol intermediate **f**. Its formation could be visualized in an electrocyclic

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** → **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** → **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 SA*, 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′ × 0.01″. Packed columns: 10′ × 3/8′ and 10′ × 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, $[\alpha]_D^{20} = -22°$ (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 2N 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*; $[\alpha]_D^{20} = -152°$ (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]. – $[\alpha]_D^{20} = -402°$ (2.2)[12]). CD. (methylcyclohexane/isopentane 1:3)[5]): $\Delta\varepsilon_{max}^{+20°} = -3.33$ (318 nm), –6.33 (309), –7.40 (299), –6.33 (293), +1.83 (217); $\Delta\varepsilon_{max}^{-195°} = -5.19$ (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 0.2M solution of (–)-**3** in acetone was placed in the centre of a circular Hg low-pressure lamp (principal emission at 254 nm). The

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[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**), $[\alpha]_D^{20} = -78°$ (0.6), and (*1*R,*4*S,*5*R)-(+)-(*1,5-dimethylbicyclo*[*2.1.0*]*pent-5-yl*) *methyl ketone* (**2**), $[\alpha]_D^{20} = +43°$ (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**, $[\alpha]_D^{20} = -72°$ (0.2); 35% (+)-**2**, $[\alpha]_D^{20} = +32°$ (0.5); 18% (−)-**3**, $[\alpha]_D^{20} = -340°$ (0.4); 27% (+)-**4**, $[\alpha]_D^{20} = +288°$ (0.6).

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

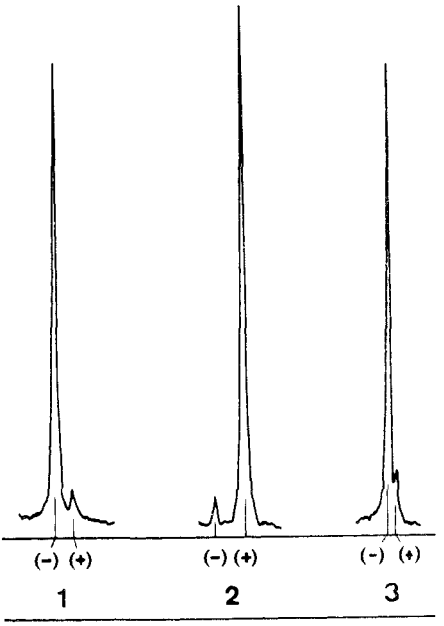

Fig. 3. *Resolved acetyl* ^{1}*H-NMR. signals of* **1**, **2** *and* **3** *in the presence of* $Pr(HFC)_3$

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 22h 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* $Pr(HFC)_3$

Ketone	Concentration of $Pr(HFC)_3$	Chemical shift differences ($\Delta\delta$) and enantiomer assignment	
0.29 M **1**	0.12 M	−3.62 (−);	−3.72 (+)
0.36 M **2**	0.07 M	−4.32 (−);	−4.45 (+)
0.24 M **3**	0.11 M	−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. 1 *B* 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. 1 *A*, 1 *C* and 2, and Table 2).

Thermolysis of **2** *in benzene/D_2O*. A 3% solution of **2** in benzene saturated with D_2O 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: ± 5%.

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