Stereochemical Study of 1,2,3,4,5,6-Hexakis(methoxycarbonyl)cyclohexanes

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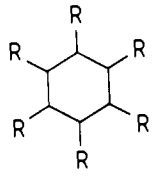
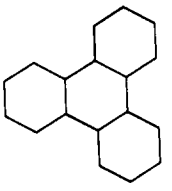
Abstract: The stereoisomers cis, epi, myo, muco, chiro, and scyllo of the title compound were prepared directly from bicyclooctene precursors or by epimerization, their structure being ascertained by NMR analysis and, in some cases, by X-ray analysis; the NMR spectra of the cis and muco compounds are temperature-dependent. The stereochemical pathway of alkaline epimerization was found to be cis → epi ⇄ muco ⇄ chiro ⇄ myo ⇄ scyllo. A seventh compound, detected by GC after a long reaction time, was tentatively identified as neo. The most abundant isomer in the equilibrium mixture at 25 °C is myo; however, if one considers the difference in symmetry, the order of stability in terms of conformational energy is scyllo > myo > chiro > muco. An interesting regioselective phenomenon was observed during ozonolysis of a bicyclooctene precursor and was attributed to the different stereochemical environment of the two saturated atoms involved in the reaction.

Substituted cyclohexanes bearing six equivalent groups (**1**) represent a classic topic of organic stereochemistry. Although the number of effective examples known in the literature does not exceed a dozen, the variety of the structures, the subtle problems regarding nomenclature and the presence among them of the simplest chiral homosubstituted cyclic compound, have attracted much interest to these compounds for a long time.

The first studies on inositols (**1a**) began in the middle of the last century, but the identification of all eight isomers was made only in the 1950s.[1-3] ^{1}H NMR spectra of the corresponding





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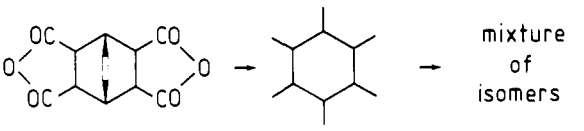
1a R = OH
b R = $OCOCH_3$
c R = Cl
d R = CH_3
e R = C_2H_5
f R = CH_2COOH
g R = $COC(CH_3)_3$
h R = $COOCH_3$
i R = COOH

hexaacetates (**1b**) were discussed by Brownstein.[4] Although the reported numerical data contained errors,[5] their study demonstrated that three of the isomers (cis, allo, and muco) are endowed with conformational mobility and that the spectrum of the cis isomer at room temperature corresponds to that predicted for slow exchange conditions.

Angyal thoroughly investigated the above compounds, including their ^{13}C NMR spectra[6] and epimerization pathway in acidic conditions,[7] in his studies on the conformation of carbohydrates and their analogues.

The hexachlorocyclohexanes (**1c**) have become very important since the discovery of the insecticidal power of the γ isomer (or muco). Structural studies on the α (chiro), β (scyllo), δ (myo), and ϵ (neo) isomers were carried out by means of X-ray[8] and NMR[9] techniques.

Scheme I



11 3i 3h-10h

Only recently have studies on the stereochemistry of hexamethylcyclohexanes (**1d**) been carried out. Berman, Zakharenko, and Petrov have recognized at least four isomers (cis, chiro, muco, and scyllo) and have studied their equilibium on Pt/C at 250 °C. In their turn Mann, Werner et al. identified the cis[11,12] and epi[13] isomers by using NMR and, in the former case, they studied the ring inversion.

The crystalline structure of the *scyllo*-hexaethylcyclohexane (**1e**), a molecule with a curious spiderlike conformation, was determined by Immirzi and Torti.[14]

Hill and Ladner synthesized the *scyllo*-cyclohexaneacetic acid (**1f**)[15] while Charpentier-Morize and Sansoulet reported the conversion of *tert*-butyl methyl ketone into a mixture of two stereoisomers of hexapivalocyclohexane (**1g**).[16]

Our interest in this stereochemical system goes back to many years ago when we proposed the cyclic compounds as configurational models for high molecular weight polymers.[17] A particular study was made of the stereochemistry of the perhydrotriphenylene (**2**), where a hexasubstituted cyclohexane is situated at the center of a tetracyclic system.[18-20] In these papers, we have made a comparison—regarding the number of stereoisomers and their symmetry—between these tetracyclic compounds and the cyclohexanes carrying simple substituents. We then turned our attention to both chiral and achiral high-symmetry compunds,[21-25]

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Table I. Nomenclature and Physical Properties of Stereoisomeric Hexaesters

form	prefix	syst name	molec sym and spect mult: rigid body	molec sym and spect mult: av	GC retent time, min	mp, °C
3	cis	1,2,3,4,5,6/0-	C_{3v} (3:3)	C_{6v} (6)	13.38	235[b]
4	epi	1,2,3,4,5/6-	C_s (1:2:2:1)		11.85	170
5	allo	1,2,3,4/5,6-	C_1 (1:1:1:1:1:1)	C_s (2:2:2)		
6	myo	1,2,3,5/4,6-	C_s (1:2:2:1)		9.32	120
7	muco	1,2,4,5/3,6-	C_s (1:2:2:1)	C_{2v} (2:4)	9.55	122
8	neo	1,2,3/4,5,6-	C_{2h} (2:4)		8.81	n.d.
9	chiro	1,2,4/3,5,6-	C_2 (2:2:2)		9.10	128
10	scyllo	1,3,5/2,4,6-	D_{3d} (6)		9.92	200

[a] OV-1 25-m capillary column, 225 °C isothermal, 2 mL/min H_2. [b] Enantiotropic solid–solid transition at 166 °C.

generally hydrocarbons, and more recently we have dealt with more reactive compounds, e.g., organic[26] and inorganic[27] esters.

Following this line of research, we found the series of hexamethyl esters of cyclohexanehexacarboxylic acid or 1,2,3,4,5,6-hexakis(methoxycarbonyl)cyclohexanes (**1h**) to be particularly suitable for systematic study. Cyclohexanehexacarboxylic acid (**1i**), a compound closely related to the above, is known in patent literature. The cis isomer, the result of the oxidation of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid 2,3:5,6-dianhydride, is transformed under suitable conditions into the scyllo, the chiro, or a mixture of the epi and muco isomers.[28,29]

In this article, we discuss the structure of six of the eight possible isomers and the most significant points of the synthesis and epimerization of the hexamethyl esters **1h** and of analogous compounds.

Some preliminary accounts of this work have already been given[26-30] as well as reports on the crystalline structure of cis and myo,[31,32] on the dynamic NMR spectra of cis and muco,[33,34] and on EI and CI mass spectra of all six isomers.[35,36]

Experimental Section

GC analyses were performed on a Dani 3800 GC instrument equipped with 25-m capillary columns and OV-17.01, OV-1, and SE-52 as stationary phases. Melting points were recorded on Mettler TA-2000 DTA. ^1H and ^{13}C NMR spectra were recorded on Varian XL-100 and XL-200 and Brucker SY-80 and SY-400 spectrometers (10% solutions, $CDCl_3$ as solvent, TMS as internal standard). Preparative chromatography was performed on Jobin-Yvon Cromatospac Prep instrument.

1,2,3,4,5,6-Cyclohexanehexacarboxylic Acid (3i). **3i** was prepared according to ref 28 (see Scheme I). Fifty grams of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic 2,3:5,6-dianhydride (**11**) was added slowly to 100 mL of 70% HNO_3 containing 0.5 g of NH_4VO_3 at 50 °C. The reaction temperature was kept for 15 h at 55–60 °C. The reaction mixture was then cooled to 0 °C and filtered. The product was washed 2 times with cold methanol.

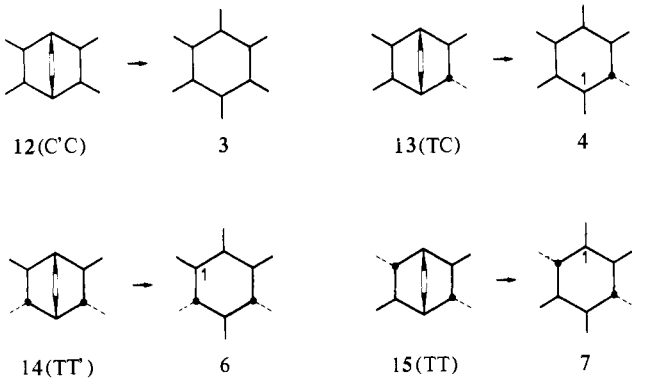
1,2,3,4,5,6-Hexakis(methoxycarbonyl)cyclohexane (3a). The esterification of **3i** was performed by two methods. For analytical purposes, 100 mg of **3i** was suspended in 10 mL of anhydrous ether and treated with an ethereal solution of CH_2N_2. For preparative purposes, 20 g of **3i** was dissolved in 200 mL of MeOH with a catalytic amount of H_2SO_4, and it was kept at boiling temperature overnight. **3a** was obtained by crystallization from MeOH (30% yield). Some other isomers were obtained by preparative chromatography on Lichroprep Si-60 and as eluent a benzene–ethyl acetate mixture (2:1 v/v).

Ozonization. The starting bicyclooctene (see Scheme II) was dissolved in CCl_4 and treated with ozone at 0 °C to persistent blue color. The solvent was eliminated with care, the ozonide was treated with H_2O_2 (6% v/v). Decomposition of the excess of H_2O_2 was carried out by Pd/C. The acid was dried and esterified with an ethereal solution of CH_2N_2.

Kinetic Experiments. To a stirred solution of 1 g of **3a** in 20 mL of dry MeOH, 2 mL of MeONa (0.51 M solution in MeOH) was quickly added. The solution was kept at 25 ± 0.1 °C. Samples were quenched with AcOH. The equilibrium composition was determined starting from different stereoisomeric mixtures.

Analogous experiments were carried out in MeOD.

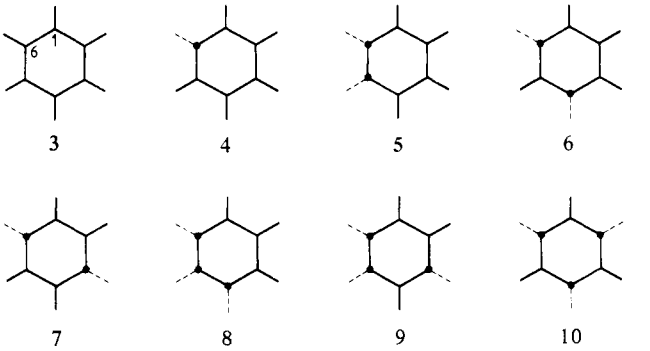
Scheme II



Synthesis and Structural Assignments

In the course of this research, we were able to isolate and characterize six of the eight predicted stereoisomers, and a seventh was identified in the reaction mixture. For their representation, we have followed the IUPAC recommendations for inositols,[37] and formulas and nomenclature are reported in **3–10** and Table I.

The cis isomer **3** was obtained by oxidation of the bicyclooctene precursor **11** followed by esterification (Scheme I).[28] The same isomer **3** and isomers **4** (epi), **6** (myo), and **7** (muco) were obtained



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Scheme III

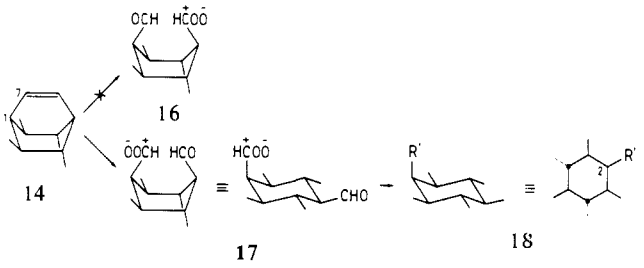


Table II. ^{13}C NMR Spectra of Six Stereoisomers (ppm from TMS)

isomer	CH	OCH_3	COO
3 cis (room temp)	39.01 (3)	51.80 (3)	169.80 (3)
	46.94 (3)	51.89 (3)	169.90 (3)
4 epi	39.32 (1)	52.02 (2)	170.28 (2)
	40.76 (2)	52.22 (4)	170.47 (2)
	45.34 (1)		170.58 (1)
	47.26 (2)		174.70 (1)
6 myo	42.60 (3)	52.31 (6)	170.29 (1)
	44.85 (2)		170.83 (3)
	49.19 (1)		172.80 (2)
7 muco (room temp)	41.29 (2)	52.34 (4)	171.43[a]
	42.27 (4)	52.67 (2)	173.67[a]
7 muco (−64 °C)	38.97 (1)	52.70 (1)	171.11 (1)
	40.15 (2)	52.82 (2)	171.35 (2)
	42.91 (1)	52.94 (2)	171.72 (2)
	43.38 (2)	53.80 (1)	176.31 (1)
9 chiro	41.60 (2)	52.15 (2)	170.90 (2)
	43.10 (2)	52.31 (2)	171.38 (2)
	43.87 (2)	52.78 (2)	173.03 (2)
10 scyllo	43.23	52.42	171.26

[a] Ill-defined intensity.

by ozonolysis, followed by oxidation and esterification, of the stereoisomers C′C, TC, TT′, and TT (**12**–**15**) of 2,3,5,6-tetrakis(methoxycarbonyl)bicyclo[2.2.2]oct-7-ene, the stereochemistry of which had already been studied by us[26] (Scheme II).

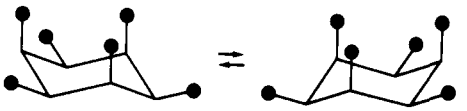
Isomers **4**, **6**, **7**, **9** (chiro), and **10** (scyllo) were obtained from **3** by epimerization under alkaline conditions. The best conditions for their isolation on a preparative scale can be deduced from the reaction scheme reported later.

As for the ozonolysis of the bicyclooctene derivatives, there is a point worthy of note. When the reaction takes place in $CHCl_3$ containing small amounts of EtOH as stabilizer, the isomer TT′ is converted into a mixture of two products: one corresponds to **6** (hexaester myo), which is the only product obtained when purified $CHCl_3$ or CCl_4 is used (see Scheme II), while the second contains a COOEt group. Using a $CHCl_3$–EtOH mixture in different ratios, we always obtained a single monoethyl-substituted compound. This indicates a high regiospecificity in the evolution of the ozonide, linked to a different steric environment of the two carbon atoms involved. X-ray analysis[32] of the compound was used to determine which of the two possible positional isomers is formed. The COOEt (R′) group was found in an axial conformation (position 2),[38] corresponding to the carbon originally numbered as 7, i.e., flanked by two endo substituents (Scheme III).

The regioselectivity, in agreement with Criegee's mechanism for ozonolysis in the presence of participating solvents, was attributed to the step of cleavage of the ozonide into an aldehyde and a carbonyloxide; of the two possible intermediates, **16** ought to be less stable due to the electron-withdrawing effect on to the carbonium ion by the two trans axial methoxycarbonyl groups. The attack of the solvent on the preferred compound **17**, followed by oxidation and esterification, affords **18**.

The structure of the stereoisomers was deduced by synthesis and by analysis of the NMR spectra and their variation with temperature and, in some cases, was confirmed by X-ray analysis.[31,32] Table II shows the ^{13}C NMR spectra recorded at room temperature, which are in agreement with those predicted by rigid body symmetry, with the exception of **7** where a rapid conformational exchange was observed; for this compound, even the spectrum at low temperature is reported.

Two compounds present no assignment problems: the isomers *scyllo*-**10** and *cis*-**3**. The former shows single signals for CH and for OCH_3 groups, both in the proton and the carbon spectra; the latter, at room temperature, shows a spectrum corresponding to a rigid chair conformation: in the proton spectrum, two triplets of equal intensity (CH) centered at δ 2.74 and 3.80 (the latter being partially masked) and two singlets (OCH_3) at δ 3.65 and 3.74; in the carbon spectrum two signals of equal intensity for CH, two for OCH_3, and two for the COO groups (Table II). At higher temperatures, the spectra broaden and tend to coalesce because of the chair–chair conformation inversion (**19**). A



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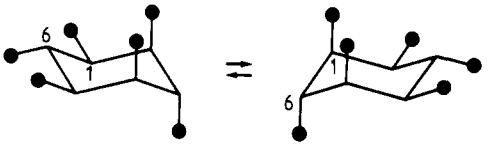
line-shape analysis on the ^{13}C NMR has led to the determination of an inversion barrier equal to 69.8 kJ mol^{-1} ($\Delta G^{\ddagger}_{ch\text{-}hb}$ at 25 °C),[33] one of the highest values observed, until now, in monocyclic cyclohexane compounds.

Compounds **3** is dimorphic with a solid–solid enantiotropic transition at 166 °C and a melting point at 235 °C. The crystalline form, stable at room temperature, has two independent molecules in the elemental cell.[31] Their conformation is very similar for the cyclohexane moiety but different for the orientation of the $COOCH_3$ groups. A deformation in the molecular geometry mainly localized in the bond angles inside the ring (three are more than 115°) permits the axial substituents to move as far as 3.3–3.4 Å.

A temperature dependence of the NMR spectrum, this time toward low temperatures, was also observed for another compound. In principle one could opt for the structures muco (**7**) and allo (**5**); both can undergo conformational inversion with barrier energies lower than those observed for the compounds cis.[34] The choice of the structure muco (**7**) appears unequivocal. In the room-temperature carbon spectrum, both the OCH_3 and CH subspectra appear as doublets of signals in the ratio 2:4 as predicted for **7** (see **20**) and not as 2:2:2 triplets as expected for **5**.



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A chance coincidence is quite improbable as the phenomenon happens also in the proton spectrum, though less clearly for the lower resolution. At −64 °C, a splitting of all signals occurs with the intensity ratio as predicted for compound **7** in rigid conformation.

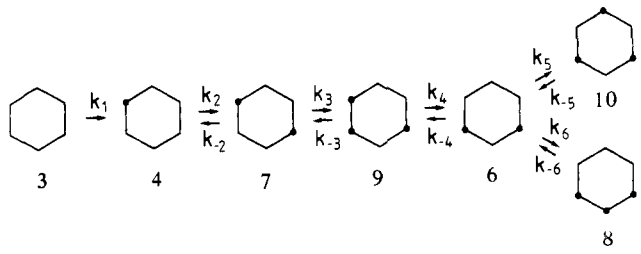
The method of synthesis shown in Scheme II indicates that our conclusion is correct. It could be questioned only if one could change the structural assignment of the precursor from TT to CC. In a former paper,[26] such as assignment was made on the basis of kinetic and thermodynamic considerations. We can now add that the ^1H NMR spectrum of the bicyclooctene precursor shows for the hydrogens in position 2, 3, 5, and 6 two doublets of doublets compatible only with the structure TT and not with CC, which

(38) For the sake of clarity we use this numeration although inappropriate. In ref 32 the substituent is correctly indicated in position 1.

(39) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1, p 111.

(40) The mass spectrum of the nondeuterated cyclohexane hexaesters does not show the molecular peak (*m/e* 432). The largest fragments are 401 [M − OCH_3]$^+$ and 400 [M − CH_3OH]$^{+\cdot}$, this last being absent only in the cis isomer; for this reason the analysis of the deuterium content can be conducted with accuracy only in this case. For the other isomers, a loss of deuterium can occur even in the first fragmentation.

Scheme IV



would have only two doublets. The conformational mobility of the muco isomer ($\Delta G^{\ddagger}_{ch-hb}$ = 50.8 kJ mol^{-1} at 25 °C) allows us to exclude any possible confusion with the isomer neo (**8**) not convertible into a isoenergetic form.

Two of the compounds we isolated display ^{13}C NMR spectra with four signals in the CH zone with intensities 1:2:2:1, compatible with a rigid C_s structure (by a chance coincidence, one of the spectra has a 1:2:3 distribution which in no way alters our conclusions). These signals were assigned to the epi (**4**) and myo (**6**) isomers on the basis of the method of synthesis (Scheme II), on kinetic and thermodynamic criteria, and on spectral considerations. Isomer epi represents the first stage of epimerization of the cis isomer and should therefore be present after a short reaction time; the myo isomer has a more favorable arrangement of substituents (five equatorial and only one axial), and it should therefore be present in a noteworthy amount in the equilibrium mixture.

The proton spectra of the two compounds are very similar. The most significant difference concerns the coupling constants of a triplet of area 2, of the order of 12 Hz in one compound and of 5 Hz in the other. The first structure is characteristic of the myo isomer: here two axial isochronous hydrogens each present two trans axial relationships with the neighboring hydrogens. The second structure is assigned to the epi isomer where the two equatorial isochronous hydrogens have only gauche interactions. These assignments were later confirmed by X-ray analysis of the myo isomer.[32]

The sixth compound shows a pattern for CH carbons having three signals of equal intensity (2:2:2). This could correspond to the chiro (**9**, point group C_2) or the allo (**5**) isomer if examined under fast-exchange conditions; however, the substantial temperature independence of proton and carbon spectra (−60 to +30 °C) suggest a chiro structure, which is also favored considering the stability and the position of this compound in the epimerization path. Its proton spectrum has been interpreted as a AA′BB′XX′ system. Excellent agreement between the experimental and the calculated spectra was obtained by using coupling constant values compatible only with a chiro structure. In particular, a value of J equal to 12 Hz can be explained by a rigid axial arrangement of at least three neighboring hydrogens, but not by a situation averaged between an axial–axial and an equatorial–equatorial arrangement.

Lastly, we must mention that in the epimerization runs conducted for a long period of time near the equilibrium state, a seventh isomer, which we were unable to isolate, was detected; the neo (**8**) structure was assigned in preference to the allo (**5**) because it fits better into the sequence of products of epimerization of which, however, it represents a nonessential element.

Steric Course of Alkaline Epimerization

Epimerization experiments of the cis isomer were carried out at the beginning of the research in order to find a synthetic method for the preparation of the scyllo hexaester. This compound represented the primary object of our research because of its high symmetry (D_{3d}) and its stereochemical correspondence with the trans, anti, trans, anti-trans isomer of perhydrotriphenylene, already exhaustively studied.[18-20] The complexity of the reaction prompted us to study it in detail, as we had already done for the epimerization of the previously mentioned bicyclooctenes.[26] The reaction was carried out in the presence of MeONa, in MeOH, or in MeOD. As a starting material, we used both the cis isomer

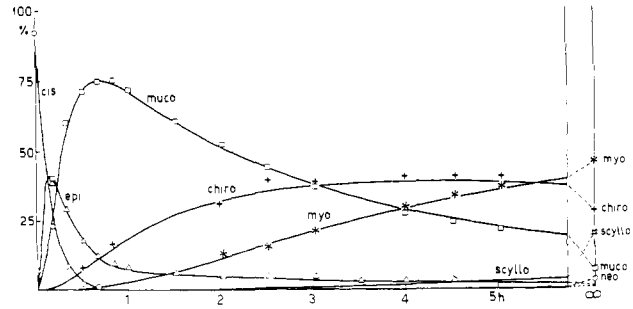


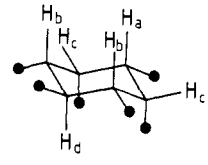
Figure 1. Kinetics of epimerization. Curves are calculated according to Scheme IV with the following relative values of rate constants: k_1 = 1; k_2 = 0.9; k_{-2} = 0.08; k_3 = 0.06; k_{-3} = 0.012; k_4 = 0.06; k_{-4} = 0.037; k_5 = 0.006; k_{-5} = 0.015; k_6 = 0.0001; k_{-6} = 0.0016.

and, to better understand a few intermediate steps, the *muco* isomer. The general reaction path is shown in Scheme IV. Such a process is different from that determined by Angyal for the epimerization of the inositols in acidic medium,[7] where two independent series of reactions were observed: the first (epi ⇄ allo ⇄ neo) was not noted for our compounds, while the second (muco ⇄ chiro ⇄ myo) coincides with part of our scheme.

The reaction series studied in the scheme can be divided into two parts: in the first (**3** → **4** ⇄ **7**), reactions are fast and practically irreversible; in the second, the rate is low and the system proceeds toward the thermodynamic equilibrium. This is clearly seen from Figure 1 where the continuous lines represent the behavior predicted on the basis of Scheme IV and obtained by numerical simulation.

The two most important facts—the high rate of the cis-to-epi and epi-to-muco reactions and the selectivity of the evolution of epi into muco and not into allo—can be related to a single factor, viz., to the stereoelectronic relation between the hydrogen atoms and the adjacent carboxylic groups.

Looking at the formula of the epi isomer (**21**) different types of hydrogen atoms can be distinguished: axial hydrogens adjacent to COOR transaxial groups (H_a), axial hydrogens adjacent to a



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single axial COOR group (H_b), equatorial hydrogens (H_c), and axial hydrogens (H_d) without transaxial relationships with the adjacent COOR groups. If the rate of attack of the base on the hydrogen atoms is a function on their relative acidity, the predicted order of reactivity is $H_a > H_b > H_c$ and H_d. This sequence fits perfectly with the observed facts.

The epi isomer has a H_a in position 3 and two H_b in positions 1 and 5. The preferred reaction on H_a affords muco, that on H_b allo. Supposing that this latter could form, it would be very reactive: by reaction on H_a, it would rapidly transform into chiro and on H_b (position 5 or 1) into neo. As a consequence, either allo does not form or, if it does, it would always have a very low concentration in the reaction mixture; its contribution, if any, to the formation of chiro and neo occurs unobserved, due to the presence of more efficient parallel reactions. As there is no significant experimental evidence of the presence of allo at any stage of the reaction, its formation will not be further considered.

Once the muco isomer is formed, highly reactive positions (H_a) cease to exist and the reaction rate decreases by 1 order of magnitude. Due to the conformational inversion **20**, the four hydrogens 1, 2, 4, and 5 in the muco isomer have the same reactivity; further epimerization results in the formation of chiro (existing as an enantiomeric mixture). The twofold symmetry of this last isomer renders all the reaction pathways to myo equivalent.

Table III. Equilibrium Composition at 24.6 °C and Order of Stability

isomer	mol %	$\Delta G°$[a]	ΔH[b]
myo	44.7		2.30
chiro	28.2	1.14	3.44
scyllo	18.8	2.14	
muco	5.7	5.10	7.40
(neo)	2.6	not calcd	not calcd

[a] Referred to myo. [b] Calculated from $\Delta G°$, taking into account entropic contributions from symmetry number and mixing of enantiomers. Values referred to scyllo.

The high reactivity of the cis isomer calls for two last observations. The conformational inversion **19** makes the hydrogens equivalent, and all can assume the highly reactive axial position (H_a); furthermore the accessibility of the reagents to the carbon atoms of the ring is very easy and attack on the face carrying axial hydrogens is favored. This fact greatly influences the reactivity of the cis compound, e.g., in H/D exchange.

During the epimerization of **3** in the presence of MeOD/MeONa, almost complete deuteration occurs before epimerization. GC–MS analysis of a mixture 45:35:20 of the cis, epi, and muco isomers (obtained after a short reaction time) shows that the starting compound cis contains about 70% d_6 and 30% d_5 molecules. We interpreted the phenomenon as an attack of the base onto a hydrogen H_a from the less-hindered side, further reaction with the solvent, and incorporation of H or D from the same side. All the steps of this process are very rapid. This stereochemical result is in contrast with our observations of the epimerization of the bicyclooctene esters **12–15**,[26] where deuterium incorporation coincides with epimerization. The difference between the two systems is in the lower reactivity of the bicyclooctenes, where no axial relationships exist between the hydrogen atoms and the adjacent COOR groups and in the lower difference in steric hindrance. Thus, a concerted mechanism is operating in which the addition of H^+ or D^+ occurs on the side opposite that undergoing attack of the base, with contemporary inversion of the configuration of the carbon.

During the heating of *cis*-cyclohexanehexacarboxylic acid (**3i**) in D_2O, we observed the same effect in the course of the NMR study of the chair inversion.[33] Around coalescence temperature, the cis acid signals broaden until they disappear. Under such conditions, the progressive appearance of a new compound could be detected. Its methine protons give rise to a five spin spectrum (a doublet of area 2 and two triplets of areas 1 and 2) that was attributed to the formation of the epi acid **4i** monodeuterated in position 6. When cooled, to room temperature, the spectrum of the nonepimerized cis acid **3i** shows no evidence of deuteration. Deuteration and epimerization come at the same stage of the reaction as was found for the bicyclooctenes. The contrast with alkaline epimerization discussed earlier prompted us to examine the epimerization of the **3h** ester under acid conditions. Studies are in progress and will be reported in the future.

The composition of the equilibrium mixture and the $\Delta G°$ values of the various isomers are reported in Table III. The most abundant isomer is myo with an axial substituent and not scyllo which is fully equatorial. Although rather strange at first sight, this datum is not unexpected, having been already observed for the hexamethylcyclohexanes.[10]

Taking into account the strong entropic destabilization of scyllo, owing to its high symmetry, and making the corresponding correction on $\Delta G°$, the order of stability is scyllo, myo, chiro, muco, expressed as increasing values of the conformation energy.

The same conclusion can be reached from the data obtained in the epimerization of the hexamethylcyclohexanes on Pt/C at 250 °C. The equilibrium composition myo chiro scyllo is equal to 54:21:18 (plus other isomers). The value of $\Delta G°$ with reference to myo is 4.1 kJ mol^{-1} for chiro and 4.8 kJ for scyllo. Correction with the symmetry factor gives a value for scyllo of −3.0 kJ mol^{-1}, in excellent agreement with that found in this paper.

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Registry No. 3h, 77117-51-2; **3l**, 2216-84-4; **4h**, 94054-00-9; **6h**, 83861-33-0; **7h**, 83238-59-9; **9h**, 94054-01-0; **10h**, 94054-02-1; **11**, 1719-83-1; **12**, 56745-93-8; **13**, 56782-33-3; **14**, 56782-36-6; **15**, 56782-35-5.

Long Range Photoinduced Electron Transfer in a Rigid Polymer

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Abstract: Electron (hole) tunnelling reactions are studied in a rigid polymer medium by following the reductive quenching of a series of $Ru(LL)_3^{2+*}$ homologues by a series of aromatic amines. Tunnelling distances up to 12 Å (edge to edge) are observed. The experimental data include a determination of the exponential damping factor α in the electronic term (H_{ab}). The data are consistent with a weak dependence of α on binding energy. Such a weak dependence is more consistent with a superexchange description than with a barrier tunnelling description of electron (hole) transfer. These reactions are shown to be essentially temperature independent between 298 K and 359 K, but are significantly slower at 77 K.

Although long distance electron transfer is central to biological systems[1a] and to attempts to mimic such systems,[1b] understanding of the parameters which control long distance (nonadiabatic) electron transer is incomplete at best. Recently, data have become available from pulse radiolysis.[2] and photochemical studies[3] which may provide tests of the theoretical models[1] for long distance electron transfer.

In previous papers from this lab, reactions of $Ru(LL_3^{2+}$ with MV^{2+} (methyl viologen) in glycerol were described.[3a,b,4] Two

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