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DIASTEREOMERIC ASSOCIATION COMPLEXES OF CHIRAL BUTADIENES [1)]

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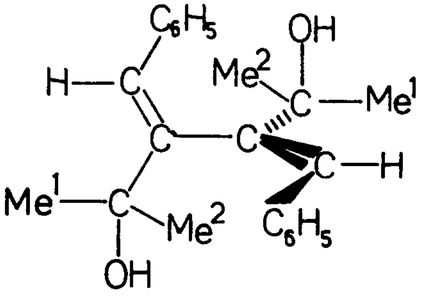
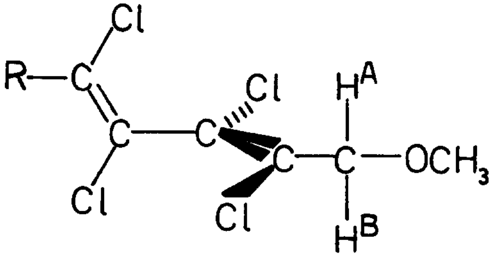
Certain 1,3-butadienes, mainly hexasubstituted ones, prefer non-planar conformations. If diastereotopic groups are present, their ^1H nmr signals may be used [4,5)] to demonstrate molecular chirality and to determine the rate of partial rotation about the C^2-C^3 single bond via a planar s-trans transition state. A second, independent method for the investigation of such butadienes is given in this communication.



(S)-**1**



(S)-**2**: R = CMe^1Me^2OH
(S)-**3**: R = H

Enantiomers may show different nmr spectra in the presence of an optically active auxiliary compound [6)]. In a number of cases [2,7)], different spectra have been detected for interconvertible enantiomers. Since a sufficiently strong association between an enantiomer and the additive is a prerequisite for these phenomena, we chose hydroxymethyl derivatives **1** and **2** as substrates and (+)-tris(3-heptafluorobutyryl-D-camphorato)europium(III), (+)-**4**, as an auxiliary compound [8)].

1 and **2** were synthesized from butadienes of know configurations at the double bonds using methods which did not affect the stereochemistry. **1**, mp 134-135°, was obtained from dimethyl (E,E)-2,3-dibenzylidene succinate 3) and excess MeLi in ether at -10°. 2, n_D^{20} = 1.5205, resulted from 3 by treatment with n-BuLi and subsequently with acetone in a Trapp mixture at -110°. 3, bp_{12} 113°, n_D^{20} = 1.5202, was obtained from (E,E)-1-methoxycarbonyl-1,2,3,4-tetrachlorbutadiene 9) by reduction with i-Bu_2AlH and etherification of the resulting alcohol, bp_{12} 120-122°, n_D^{20} = 1.5503, with CH_2N_2/BF_3 10).

A solution of 0.72 mol-% 1 in CCl_4 shows diastereotopic methyl groups at δ = 1.07 (Me^1) and 1.54 (Me^2) and the alkene protons at 6.77 (34°). Stepwise addition of 4 to this solution shifts and splits these signals (δ = 5.09 and 5.13, Me^1; 4.44 and 4.61, Me^2; 10.99 and 11.24, =CH; 0.56 mol-% (+)-4). These splittings are due to the diastereomeric association complexes (R)-1····(+)-4 and (S)-1····(+)-4; they demonstrate the chirality of 1.

2 does not show different chemical shifts for the diastereotopic methyl groups Me^1 and Me^2 in CCl_4 or C_4Cl_6, whereas in some cases, the δ-values of H^A and H^B differ slightly (table). Addition of (+)-4 shifts and splits some of the signals, depending upon solvent and temperature. The CH^AH^B absorptions were assignable to diastereotopic protons within one enantiomer, i.e. AB systems, and to two different CH_2 groups, corresponding to the (R) and (S) enantiomers of 2. In the case of the Me^1 and Me^2 signals, such assignments in the table are arbitrary; however, the appearance of up to four methyl signals signifies unequal shifts for the diastereotopic methyl groups within a given enantiomer. Addition of racemic 4 11) instead of (+)-4, results in the complete absence of all of the splittings at +34° and -12°, i.e. the three CH absorptions represent clean singlets (60 MHz), the pseudocontact shifts of which were very similar to the ones generated by (+)-4. Thus the splittings must be entirely due to the chirality of the optically active auxiliary compound 12), i.e. different pseudocontact shifts of the diastereotopic groups 13) do not contribute.

All of the splittings in the spectrum of (RS)-2 in C_4Cl_6 in the presence of (+)-4 at +34° (table) are clearly discernible up to +61°. This finding puts a lower limit of 21 kcal/mol to $\Delta G_c^{\ddagger}$ for enantiomerization 14) which may be compared very roughly with $\Delta G_c^{\ddagger}$ = 12.8±0.3 kcal/mol (-20°), obtained from the CH^AH^B protons of (RS)-3 in acetone-d_6 in the absence of an auxiliary compound. The difference of approximately 8 kcal/mol between the two values indicates huge buttressing effects 4) by the CMe^1Me^2OH group. These effects increase the repulsive non-bonding interactions in the planar s-trans transition state of C^2-C^3 rotation. We shall take advantage of this finding in our attempts to resolve the enantiomers.

Mol-% (RS)-**2**	Mol-% (+)-**4**	Solvent	T [°C]	$\delta^{a,b)}$		δ	$\delta^{b)}$	
				H^A	H^B	OCH_3	Me^1	Me^2
1.29	0.00	C_4Cl_6	+34	4.23	4.23	3.28	1.54	1.54
1.22	0.8	C_4Cl_6	+34	8.51	8.51	7.19 7.22	7.10 7.15	7.07 7.07
4.07	0.00	CCl_4	+34	~4.32	~4.24	3.34	1.59	1.59
3.99	2.00	CCl_4	+34	7.53	7.41	6.18	5.57	5.50
4.03	0.00	CCl_4	-12	~4.31	~4.23	3.32	1.57	1.57
3.99	2.00	CCl_4	-12	9.81 9.40	9.30 9.40	7.79	7.21 7.36	6.94 7.06

a) $^2J_{AB}$ = 13.0 Hz
b) For assignments see text.

Thus in the presence of an optically active auxiliary compound, the demonstration of the chirality of non-planar butadienes as well as the determination of their enantiomerization barriers can be achieved without the prerequisite of diastereotopic groups in the molecule.

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5) Cf. V.Ramamurthy, T.T.Bopp, and R.S.H.Liu, Tetrahedron Lett. 1972, 3915.

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8) (+)-4 was used as obtained from commercial sources. $[\alpha]_D^{23} = +151^\circ$ ($c = 1.27$, CCl_4). The spectra obtained at $+34^\circ$ using (+)-4 as an auxiliary compound showed an additional peak between $\delta = 4.5$ and 5.2 which seems to be due to H_2O; integration indicates about 4 mol H_2O per mol (+)-4.

9) G.Köbrich and H.Büttner, Tetrahedron 25, 883 (1969).

10) Cf. H.-O.Bödecker, Diploma Thesis, Techn.Universität Hannover, 1973.

11) (±)-4 was prepared according to the method given by V.Schurig, Inorg. Chem. 11, 736 (1972) and Tetrahedron Lett. 1972, 3297, for a similar complex. However since barium bis(3-heptafluorobutyryl-DL-camphorate), mp 230-235°, is soluble in ether, the procedure had to be modified. (±)-4, dried in vacuum over P_2O_5, possesses a similar shifting ability as that of a well dried sample of (+)-4. The ^1H nmr spectra, including the water peak areas, of (±)-4 and (+)-4 resemble each other.

12) Splittings due to different environments within diastereomeric association complexes disappear in the presence of racemic auxiliary compounds because of rapid dissociation and re-association of these complexes: T.G.Burlingame and W.H.Pirkle, J.Amer.Chem.Soc. 88, 4294 (1966).

13) In suitable cases, diastereotopic groups in open-chain molecules show highly different pseudocontact shifts [2,6].

14) The measurement of rates of internal rotation due to the presence of optically active auxiliary compounds has been described [2]. Such measurements in the presence of achiral europium complexes are also known: S.R.Tanny, M.Pickering, and C.S.Springer, Jr., J.Amer.Chem.Soc. 95, 6227 (1973), and references cited therein; H.Kessler and M.Molter, Angew.Chem. 85, 1059 (1973); Angew.Chem., Int.Ed. Engl. 12 , 1011 (1973).

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