[14] G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

[15] Because of the 25% excess potassium employed in these experiments, some overreduction of the protonation products did occur during the quenching process, with resultant excess weighting of the high field multiplet. A low intensity peak at *m/e* 212 was also evident in the mass spectra of samples prepared in this manner.

[16] Two *doubly* charged analogues of **2** have been reported to date: (a) the bitropylium dication (I. S. Akhrem, E. I. Fedin, B. A. Koasov, and M. E. Vol'pin, *Tetrahedron Lett.*, 5265 (1967)); (b) the bicyclononatetraenyl dianion (K. Hafner, S. Braun, T. Nakazawa, and H. Tappe, *ibid.*, 3507 (1975)). Attempts to reduce the latter species still further led to cleavage of the central bond.

[17] The authors thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous financial support. We are particularly indebted to Professor Larry Anderson and Mr. Davis Taggart for the use of their electrochemical equipment and for valuable comments and suggestions.

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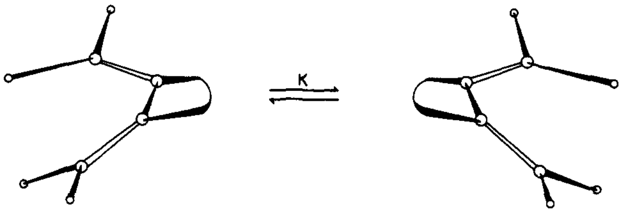
Dissymmetric 1,3-Dienes. III.[1,2] Enantiomerization Barriers in Some Cyclic *vic*-Dialkylidene Compounds

Sir:

Substitution of isopropylidene groups on adjacent carbon atoms gives rise to large energy barriers to rotation about the bond between the two carbon atoms in both cyclic[1] (**1**) and acyclic[2,3] (**2**) compounds, causing such dienes to adopt severely skewed conformations[2,4] which are dissymmetric and thus, in principle, resolvable.[5] The recent flurry of activity involving this class of compounds has included the isolation of both cyclic[6] and acyclic[7] examples in optically active form.



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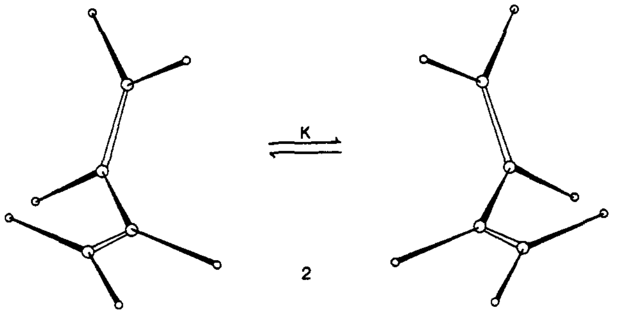

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We wish to communicate our results to date on a dynamic NMR investigation of a series of compounds related to our original model (**3**),[1] and to Pasto's alkylidenecyclopropane adducts (**4**),[6] which suggest that seemingly minor structural variations in **1** can produce large changes in the apparent enantiomerization barrier.

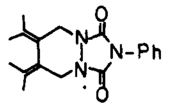
Compounds **5–7** possess temperature-dependent NMR spectra[8] enabling calculation of free energies of activation at the coalescence temperature using either complete line-shape analysis or the Eyring rate equation[9] (cf. Table I).

In contrast to Pasto's compounds (**4**) which are optically stable at room temperature[6] (thus requiring $\Delta G^\ddagger \approx 25$ kcal/mol), the similarly constituted **5b** enantiomerizes rapidly at room temperature,[10] and yields $\Delta G_c^\ddagger = 10.0$ kcal/mol at $-78°$. In order to reconcile these data one must assume either (a) that the $\Delta G^\ddagger$ value determined by NMR does not reflect the true enantiomerization process in **5b**, or (b) that apparently minor structural changes can give rise to large differences in $\Delta G^\ddagger$; i.e., that the repulsive van der Waals potential function leading to enantiomerization is very steep in this region.

Table I

Compound	R	T_c, °C[8]	$\Delta G_c^\ddagger$, kcal/mol[9]	Method of preparation
5a	$R_1 = R_2 = R_3 = R_4 = CH_3$	48	16.0	*a*
5b	$R_1 = R_2 = CH_3$, $R_3 = Ph$, $R_4 = H$	−78	10.0	*a*
5c	$R_1 = R_2 = CH_3$, $R_3 = H$, $R_4 = Ph$	—	—	*a*
5d	$R_1 = R_2 = H$, $R_3 = R_4 = Ph$	—	—	*a*
6a	O	−109	8.0	*b*
6b	$C(CO_2Et)_2$	−46	11.1	*c*, *t*-BuOK, $CH_2(CO_2Et)_2$
6c	S	30	15.0	*c*, Na_2S
6d	SO	30	15.1	*d*
6e	SO_2	36	15.3	*d*
6f	NCH_2Ph	−95	8.7	*c*, $PhCH_2NH_2$
6g	NCH_3	<−100	<8.4	*c*, CH_3NH_2
7a	CH_2Ph	−46 131	11.0 20.4	*c*, $(PhCH_2NH-)_2$
7b	CH_3	−31 109	11.9 19.1	*c*, $(CH_3NH-)_2$

[a] Heating to ~50° the product obtained by reaction of corresponding dimethyl dialkylidenesuccinate with excess CH_3Li. [b] Reaction of 2,3-diisopropylidene-1,4-butanediol[2] with NaH and *p*-TsCl. [c] Reaction of the indicated reagent with 2,3-diisopropylidene-1,4-dibromobutane (prepared in ca. 30% yield from 2,3-diisopropylidene-1,4-butanediol[2] and Ph_3PBr_2). [d] Compound 6c plus the theoretical amount of *m*-chloroperbenzoic acid.



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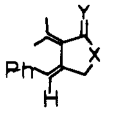
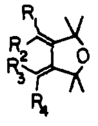


4a $X = O, Y = NSO_2Cl$

4b $X = NSO_2Cl, Y = O$



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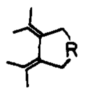

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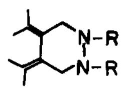

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Compound **5a** exhibits a large increase of ~8 kcal/mol caused by the saturated *gem*-dimethyl groups (termed a "buttressing effect" by Mannschreck et al.[5] in acyclic analogues) in comparison to **6a**, which again emphasizes the importance of *overall* deformational freedom in the molecular racemization process.

The substantial increase in $\Delta G^\ddagger$ as R descends the periodic table from R = O in **6a** to R = S in **6c** can be attributed to an increase in bond lengths and a decrease in the C–R–C bond angle. Both of these effects result in a closer approach of the methyl on the "inside" of the diene system in the planar transition state for enantiomerism for compound **6c**.

The decrease of $\Delta G^{\ddagger}$ within a row of the periodic table (R = C, **6b**; R = N, **6f** and **6g**; R = O, **6a**) is more subtle and may be due to a decrease in the C-R-C torsional barriers in the order $R = CR'_2 > R = NR' > R = O$.[11]

The slight increase in $\Delta G^{\ddagger}$ as the oxidation state is increased from R = S in **6c** to R = SO in **6d** and R = SO_2 in **6e** may be due both to an increase in torsional barriers[11] and to an eclipsing strain between the S=O and its neighboring C—H bonds.[12]

The cyclic hydrazines **7a** and **7b** exhibit both a low-temperature process attributable to nitrogen inversion, and a higher-energy process corresponding to ring flipping. Although predicted, this phenomenon has historically been observed in relatively few of the hydrazines investigated,[13] and serves to confirm our earlier interpretation involving urazole **3**.[1]

Current work in this laboratory includes attempts to prepare an optically active sample of **1** or **2** which is suitable both for DNMR and polarimetric racemization studies, as it is currently suspected that discrepancies in $\Delta G^{\ddagger}$ determined by the two methods might well be noted.[14]

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(8) Spectra were recorded on either a Varian HA-100 or Varian XL-100 spectrometer equipped with a variable temperature unit. A digital temperature read-out connected directly to the probe and calibrated against the chemical shifts of methanol and ethylene glycol produced temperature readings accurate to ±1°. Spectra were recorded at ~3° intervals after temperature equilibration, and all coalescence behavior was fully reversible.
(9) In all cases the Eyring rate equation (J. M. Lehn and J. Wagner, *Tetrahedron*, **26**, 4227–4240 (1970)) produced values of $\Delta G_c^{\ddagger}$ within ±0.1 kcal/mol of those obtained by complete line-shape analysis (treatment according to R. M. Lynden-Bell, *Prog. Nucl. Magn. Reson. Spectrosc.*, **2**, 163–204 (1967)).
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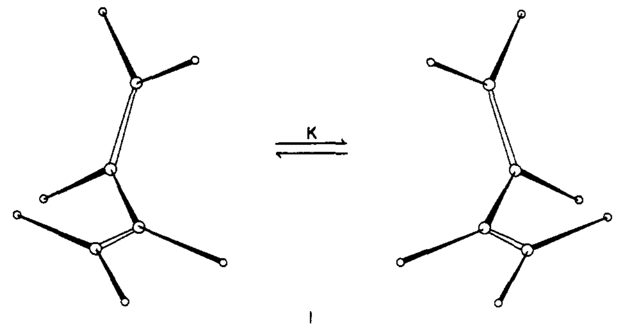
Dissymmetric 1,3-Dienes. IV.[1] Syntheses and Enantiomerization Barriers of Some Acyclic *vic*-Dialkylidene Compounds

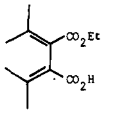
Sir:

Recent interest in the syntheses and enantiomerization rates of acyclic *vic*-dialkylidene compounds (**1**), rendered chiral by restricted rotation about the sp^2-sp^2 single bond, has led to several dynamic NMR investigations[2] and to an optical resolution yielding a polarimetric $\Delta G^{\ddagger}$.[3] We report here our initial results in a search for a molecule possessing an activation energy and spectroscopic properties suitable for both resolution and DNMR study and attempts to elucidate further the structural and steric factors influencing the enantiomerization process.



I

Entry into the desired acyclic *vic*-dialkylidene system was gained by reduction of the double Stobbe condensation product (**2**)[4] and by pyrolysis of the sulfone (**6**)[5] (Scheme I). Reduction of the half-acid ester **2** with $NaAlH_2(OCH_2CH_2OCH_3)_2$ in refluxing benzene affords diol (**3**)[6] in ca. 60% yield, which upon treatment with triphenylphosphine dibromide[7] at 0° yields 30% of pure dibromide (**4**). Compound **4** reacts with NaCN and NaN_3 to produce the corresponding dinitrile and diazide **5a** and **5b**, respectively.



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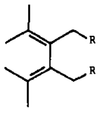

3 R = OH, $\Delta G_{138}^{\ddagger}$ = 20.4 kcal/mol
4 R = Br, $\Delta G_{109}^{\ddagger}$ = 19.0 kcal/mol
5a R = CN, $\Delta G_{109}^{\ddagger}$ = 19.0 kcal/mol
5b R = N_3, thermally unstable

The methylene resonances in the NMR spectra of compounds **3–5** appear as AB quartets at ambient temperature, coalescing to sharp singlets as the temperature is increased. The enantiomerization barriers, $\Delta G_c^{\ddagger}$, determined by DNMR,[8] indicate that although there is a substantial energy barrier associated with racemization in these *vic*-diisopropylidene compounds, it is not of the magnitude required for facile resolution. We therefore sought compound **10**.

Scheme I