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]

References and Notes

(1) E. F. Kiefer, T. J. Levek, and T. T. Bopp, *J. Am. Chem. Soc.*, **94**, 4751–4753 (1972).

(2) T. Ottersen, L. W. Jelinski, E. F. Kiefer, and K. Seff, *Acta Crystallogr., Sec. B*, **30**, 960–965 (1974).

(3) D. S. Bomse and T. H. Morton, *Tetrahedron Lett.*, 3491–3494 (1974).

(4) D. J. Pasto and W. R. Scheidt, *J. Org. Chem.*, **40**, 1444–1447 (1975).

(5) A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *Tetrahedron Lett.*, 2153–2156 (1974), and references cited therein.

(6) D. J. Pasto and J. K. Borchardt, *J. Am. Chem. Soc.*, **96**, 6220–6221, 6937–6943, 6944–6948 (1974).

(7) M. Rösner and G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **13**, 741–742 (1974).

(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)).

(10) The diastereotopic *gem*-dimethyl groups in **5b** are equivalent in ^{1}H NMR in a variety of solvents, in the presence of the shift reagent $Eu(fod)_3$, and in ^{13}C NMR.

(11) J. B. Lambert, C. E. Mixan, and D. H. Johnson, *J. Am. Chem. Soc.*, **95**, 4634–4639 (1973).

(12) E. L. Eliel, R. L. Willer, A. T. McPhail, and K. D. Onan, *J. Am. Chem. Soc.*, **96**, 3021–3022 (1974).

(13) J. E. Anderson, *J. Am. Chem. Soc.*, **91**, 6374–6380 (1969), and references cited therein.

(14) R. E. Carter and P. Berntsson, *Acta Chem. Scand.*, **22**, 1047–1050 (1968).

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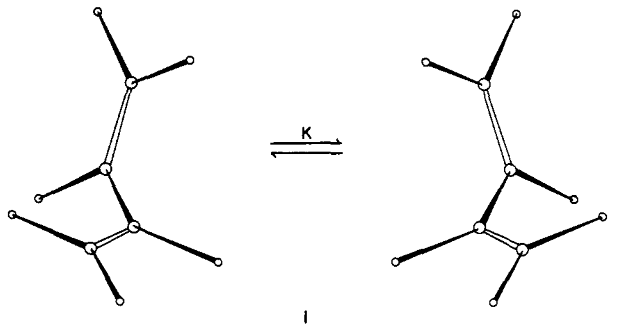
Dissymmetric 1,3-Dienes. IV.[1] Syntheses and Enantiomerization Barriers of Some Acyclic *vic*-Dialkylidene Compounds

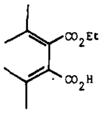
Sir:

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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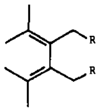


3 R = OH, $\Delta G_{138}^{\ddagger}$ = 20.4 kcal/mol

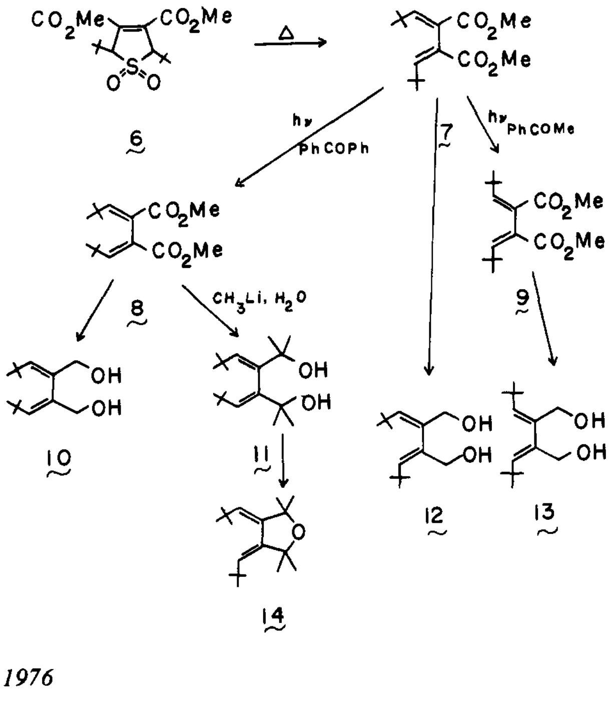
4 R = Br, $\Delta G_{109}^{\ddagger}$ = 19.0 kcal/mol

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



Although inaccessible via the double Stobbe condensation with pival aldehyde, the diester (**7**) could be obtained in high yield by pyrolysis of the known sulfone **6**.[5] Selective photosensitized isomerization[9] of **7** does not proceed quantitatively, but a photostationary state can be achieved consisting of 25% of isomer **8**,[5] which is separable by preparative TLC on silica gel. Whereas reduction of esters **7** and **9** with diisobutylaluminum hydride occurs cleanly to produce alcohols **12** and **13**, respectively, similar reduction of **8** is accompanied by extensive rearrangement.

Isolation of diol **10** can be accomplished by preparative TLC;[10] however its NMR spectrum was found to consist of three singlets in $CDCl_3$, CCl_4, CS_2, benzene-d_6, and pyridine-d_5, due to accidental equivalence of the diastereotopic methylene protons.[11] Splitting of the *tert*-butyl singlet is observed in the presence of the chiral shift reagent $Eu(tfc)_3$,[12] indicating that **10** is chiral at room temperature, as expected.

An estimate of the racemization barrier in ester **8** can be made based on the temperature dependence of its NMR spectrum measured in the presence of chiral shift reagent, $Eu(tfc)_3$.[13] At 150° (the highest temperature attainable using bromobenzene-d_5 as the solvent) the peaks corresponding to the diastereomeric association complexes show incipient coalescence, placing a lower limit of ~24 kcal/mol on $\Delta G^\ddagger$ for compound **8**. In contrast, the isomeric ester **7** does not show evidence of diastereomeric complexes with $Eu(tfc)_3$ at room temperature (although large pseudo-contact shifts are observed), indicating that the energy barrier for **7** is less than ~13 kcal/mol. A closer approach to the value could not be made because of spectral broadening which occurred as the probe temperature was decreased.

The tertiary alcohol (**11**) also displays only three singlets in the NMR, and readily cyclodehydrates to the isomerized tetrahydrofuran (**14**), in which all four α-methyl groups are nonequivalent. Thermal instability of **14** precluded determination of its $\Delta G_c^\ddagger$.

Synthesis and resolution of other systems **1**, are planned.

References and Notes

(1) For part III see preceding paper in this issue.

(2) (a) D. S. Bomse and T. H. Morton, *Tetrahedron Lett.*, 3491–3494 (1974); (b) A. Mannschreck, V. Jonas, H.-O. Bödecker, H.-L. Elbe, and G. Köbrich, *ibid.*, 2153–2156 (1974); (c) H.-L. Elbe and G.Köbrich, *Chem. Ber.*, **107**, 1654–1666 (1974); (d) W. Z. M. Rhee and J. J. Zuckerman, *J. Am. Chem. Soc.*, **97**, 2291–2293 (1975).

(3) M. Rösner and G. Köbrich, *Angew Chem., Int. Ed. Engl.*, **13**, 741–742 (1974).

(4) (a) C. G. Overberger and C. W. Roberts, *J. Am. Chem. Soc.*, **71**, 3618–3621 (1949); (b) H. Stobbe, *Chem. Ber.*, **38**, 3673–3682 (1905).

(5) R. M. Kellogg and W. L. Prins, *J. Org. Chem.*, **39**, 2366–2374 (1974). We are deeply indebted to Professor Kellogg for a generous gift of the dihydrothiophene precursor of compound **6**.

(6) The crystal structure of **3** has been previously reported: T. Ottersen, L. W. Jelinski, E. F. Kiefer, and K. Seff, *Acta Crystallogr., Sect. B*, **30**, 960–965 (1974).

(7) J. P. Schaefer, J. G. Higgins, and P. K. Shenov, "Organic Syntheses", Coll. Vol., V, Wiley, New York, N.Y., 1973, pp 249–251.

(8) Spectra were recorded on Varian XL-100 or HA-100 spectrometers equipped with variable temperature units. Temperatures were calibrated against standards and are considered accurate to ±1°. All coalescence phenomena were fully reversible. $\Delta G^\ddagger$ values were calculated at the coalescence temperature from the Eyring rate equation: J. M. Lehn and J. Wagner, *Tetrahedron*, **26**, 4227–4240 (1970).

(9) V. Ramamurthy, Y. Butt, C. Yang, P. Yang, and R. S. H. Liu, *J. Org. Chem.*, **38**, 1247–1249 (1973), and references cited therein.

(10) That **10** is the correct geometric isomer was established by the observation of a 20% nuclear Overhauser enhancement of the vinyl proton intensity upon irradiation at the methylene frequency. The isomeric alcohol **13** shows no corresponding NOE.

(11) The same perverse spectral behavior was shown by Pasto's cyclic *vic*-dialkylidene compounds; see discussion and references in the preceding communication.

(12) $Eu(tfc)_3$ is tris(3-(trifluoromethylhydroxymethylene)-*d*-camphorato)europium(III) derivative.

(13) Determination of internal rotational rates in the presence of optically active shift reagents and solvents has been described and appears to produce values of $\Delta G^\ddagger$ ~5% greater than those determined in the absence of chiral interactions: (a) A. Mannschreck, V. Jonas, and B. Kolb, *Angew. Chem., Int. Ed. Engl.*, **12**, 909–1910 (1973); (b) L. D. Colebrook, S. Icli, and F. H. Hund, *Can. J. Chem.*, **53**, 1556–1562 (1975); (c) S. S. C. Yang and R. S. H. Liu, *Tetrahedron Lett.*, 4811–4814 (1973).

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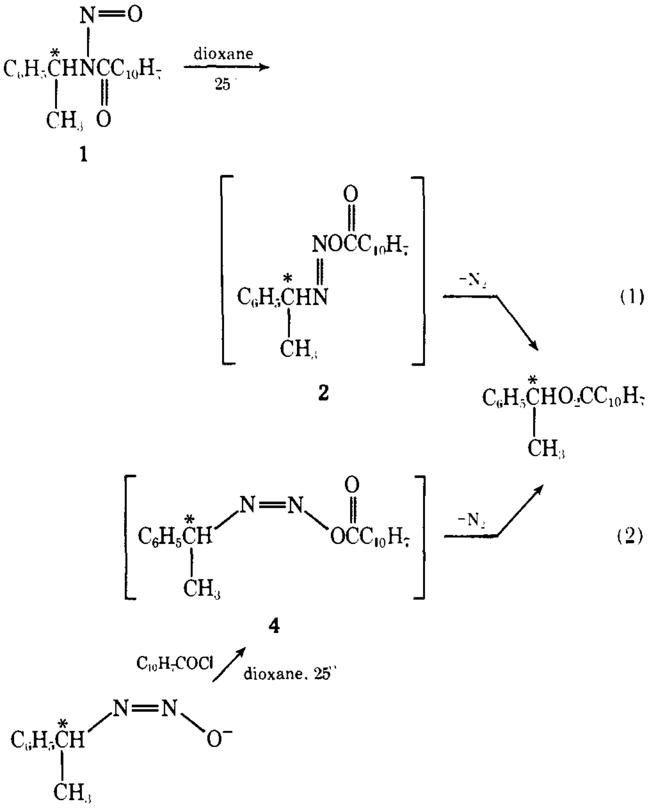
The Ethylation of *syn*- and *anti*-1-Phenylethane Diazotate. Dependence of Reaction Stereochemistry on Configuration at the Diazo Linkage[1,2]

Sir:

The thermolysis of nitrosoamide **1**, via *anti*-diazo ester **2** (eq 1), and the acylation of *syn*-1-phenylethane diazotate (**3**), via *syn*-diazo ester **4** (eq 2), yield 1-phenylethyl 2-naphthoate in similar yields, and with comparable stereochemistry (~73% overall retention).[3] It was concluded that "the stereochemistry of the diazo species is not an important variable".[3] This conclusion need not be general. The potential carboxylate counterion is large and resonance stabilized; these factors could inhibit its ability to quickly collapse with 1-phenylethyl cation, and favor geometrical equilibration of the ion pairs arising from **2** and **4**.



We now report the first *stereochemical studies* carried out *directly* on an *anti*-diazotate. Comparison of the ethylation of *anti*-1-phenylethane diazotate (**5**) (eq 4), with that of its syn isomer, **3** (eq 3), shows that the stereochemistry of the diazo species *is an important variable*.

anti-1-Phenylethane diazotate (**5**) was prepared from 1-phenylethylhydrazine,[2,4] KOC_2H_5-C_2H_5OH, and isoamyl nitrite.[3,5] Removal of volatile constituents (0.25 mmHg) afforded **5** (ir, Nujol[3]) free of alcohols, although isoamyloxide (and ethoxide) must have been present. Treatment of **5** (suspension in ether or solution in 15% HMPA-ether) with