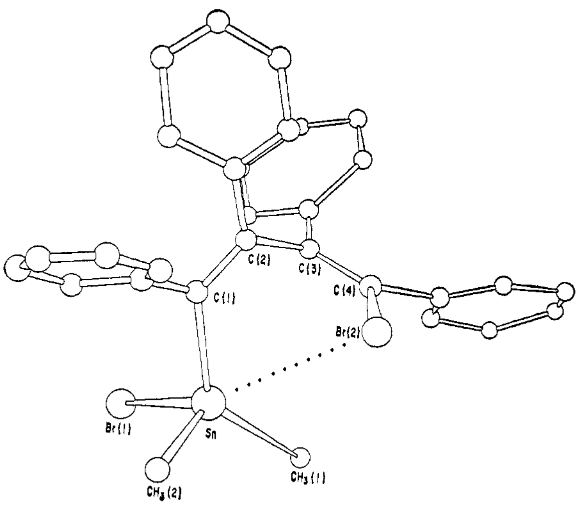

Figure 1. Molecular conformation of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (I). The intramolecular Sn–Br(2) interaction is shown by the dotted line.

mains as the most likely possibility. The magnetic nonequivalence of similar nuclei in an asymmetric environment has been well established,[4] and in this study magnetic nonequivalence arising from a preferred dissymmetric diene conformation is analogous to the nonequivalence observed in the dissymmetric biphenyls.[5]

To explain the absence of rotation about the C(2)–C(3) bond in I–III, we speculated that an internal tin-halogen bond served to stablize an unusual cisoid-skew conformation[6] at lower temperatures in nonbasic solvents. Diene rotation and methyl equivalence could be restored by breaking this weak bond, and this has been experimentally accomplished by (1) warming the sample, (2) adding a base to compete with Br for coordination to Sn, or (3) replacing the 4-halogen of I–III by H, as in IV.

The predicted molecular conformation of I has now been confirmed by a single-crystal X-ray diffraction study. The parameters of the monoclinic cell, a = 14.82, b = 18.65, c = 13.60 A, and β = 131.2°, give a calculated density of 1.562 g cm^{-3} with four molecules per unit cell. Absence of 0k0 reflections with k odd and $h0l$ with l odd indicates the centrosymmetric space group $P2_1/c$. The intensities of 1137 independent reflections were measured with Cu Kα radiation on the Picker automatic diffractometer using the 2θ scan technique. After the Sn and Br atoms had been located in the Patterson function, the C atoms were identified in an electron density map calculated using the heavy-atom phases. Refinement of the structure was terminated after four cycles of full-matrix least-squares variation of the positions and isotropic temperature factors of the Sn, Br, and C atoms, giving a value of R = 0.147. Additional X-ray intensity data are presently being collected, and further refinement is contemplated.

The structure (Figure 1) confirms the presence of a weak bond between Sn and Br(2) of length 3.769 ± 0.007 A, approximately 0.4 A less than the sum of the van der Waals radii.[7] To provide room for this interaction, the angle C(1)–Sn–CH$_3$(1) has opened to 130.3° from the normal tetrahedral value of 109.5°. Further evidence for pentacoordinate bonding is given by the increases in the lengths of the bonds at Sn from their normal values and an apparent lengthening of the C(4)–Br(2) bond. Observed and "normal" distances (parentheses)[8] for these bonds are (in angstroms): Sn–Br(1), 2.507 ± 0.007 (2.46); Sn–Cl(1), 2.19 ± 0.04 (2.14); Sn–CH$_3$(1) = Sn–CH$_3$(2), 2.24 ± 0.04 (2.18); and C(4)–Br(2), 2.01 ± 0.04 (1.89).

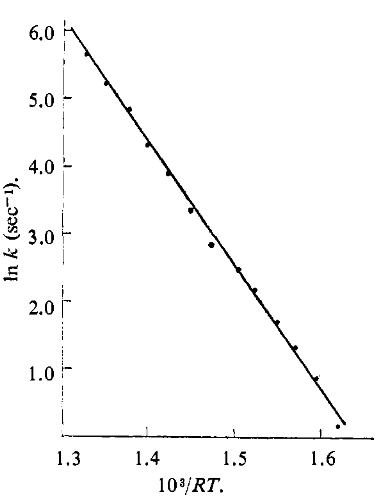

Figure 2. Temperature dependence (°K) of the rate constant (k) for methyl interchange of I in CCl$_4$.

Because of the internal bonding and the steric requirements of the bulky substituents, I suffers considerable loss of conjugation energy as shown by the unusually large skew angle between the olefinic planes (73° from cisoid coplanar) and the large angles (50–70°) between the planes of the phenyl rings and the double bonds.

Rates of rotation about the C(2)–C(3) bond of I in CCl$_4$ at various temperatures were obtained by matching computer-generated[9] curves with the experimental spectra according to Sack[10] and Gutowsky.[11] A least-squares analysis of the Arrhenius plot (Figure 2) gave E^* = 18.30 ± 0.23 kcal/mole with log A = 13.

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(4) H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2196 (1962); E. I. Snyder, *J. Am. Chem. Soc.*, **85**, 2624 (1963), and references cited therein.

(5) W. L. Meyer and R. R. Meyer, *ibid.*, **85**, 2170 (1963).

(6) The usual preferred transoid coplanar diene conformation has been found to occur even in *cis,cis*-1,2,3,4-tetraphenylbutadiene, a close, though less sterically hindered, analog of I: I. L. Karle and K. S. Dragonette, *Acta Cyst.*, **19**, 500 (1965).

(7) The radius for Br is taken as 1.95 A (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 263). The radius for Sn, 2.2 A, is estimated by extrapolating the values of neighboring elements (Sb, Te, I) on the periodic chart (see p 260), or alternatively by using the heuristic rule (p 263): r(van der Waals) = 0.8 + r(single bond).

(8) L. E. Sutton, "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, pp S10, S12, and S19. The covalent radius of the sp^2 C(1) is assumed to be about 0.04 A shorter than that of the methyl carbons.

(9) We are grateful to G. M. Whitesides for making available his EXCH 10 program.

(10) R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

(11) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, 43, 4107 (1965).

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The Ionization of Dimethyl Sulfoxide

Sir:

We wish to report the results of a study of the rates of the base-catalyzed tritiation of dimethyl sulfoxide

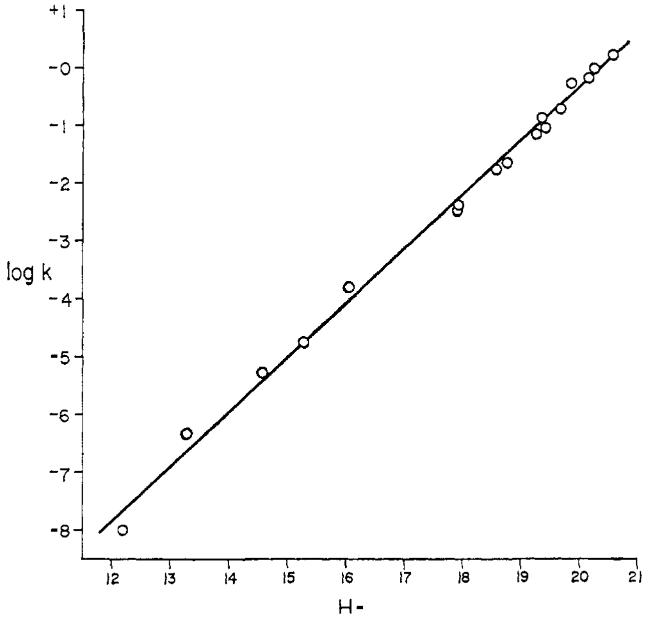

Figure 1. The logarithm of the rate of ionization of DMSO as a function of H_- of the system.

Table I. Ionization Rate Coefficients (l. mole^{-1} sec^{-1}), k, for DMSO in Basic DMSO–H_2O, 25°

Mole % DMSO	k Tritiation	k Detritiation	$[OH^-]$, M	H_-[2]
2.40		1×10^{-8}[a]	0.010	12.3
11.3		4.8×10^{-7}	0.010	13.3
18.7		5.5×10^{-6}	0.020	14.6
26.5		1.9×10^{-5}	0.015	15.3
36.5		1.7×10^{-4}	0.010	16.1
50.0	0.0049[b]	0.0050[b]	0.027	17.9
51.4	0.0040		0.023	17.9
59.8	0.019		0.016	18.6
61.0	0.025		0.013	18.8
66.3	0.080		0.013	19.3
69.0	0.148		0.013	19.4
70.0	0.095		0.011	19.47[c]
72.1	0.218		0.0099	19.7
75.4	0.605		0.0076	19.9
78.4	0.81		0.0070	20.2
79.4	1.10		0.0066	20.3
82.7	2.03		0.0054	20.6

[a] Approximate value; $t_{1/2}$ at these concentrations is more than a year. [b] Essentially the same rates were found for tritiation and detritiation in agreement with the theoretical treatment of Halevi and Long.[1] [c] The H_- function of this solution was determined directly by measurements with four amine indicators[2] by Mr. A. Albagli in these laboratories. These were made on the same solution that had been used for the tracer experiment and yielded the values 19.49 (3-trifluoromethyldiphenylamine), 19.40 (3-nitrodiphenylamine), 19.50 (2,3,5,6-tetrachloroaniline), and 19.51 (3,4′-dichlorodiphenylamine).

(DMSO) and detritiation of DMSO-t which enable an estimate to be made of the acid strength, pK_{HA}, of this compound. The results also have important implications with regard to the validity of the H_- acidity scale and the correlation of reaction rates with such a scale.

Weighed amounts of DMSO and tetramethylammonium hydroxide solution containing tritiated water were mixed at 25°. Samples were withdrawn at timed intervals and injected into tubes containing 5 ml of methanol. The CH_3OT thus formed was separated from the DMSO by fractional distillation, dried, and then added to the scintillator (3.4 g l.$^{-1}$ of 2,5-diphenyloxazole in toluene) for counting. Tritiated DMSO was prepared by allowing 10 g of DMSO to equilibrate with 0.1 ml of HTO (4 mcuries ml^{-1}) containing $(CH_3)_4N^+OH^-$ (0.1 M) for 3 hr, the contents were neutralized with hydrochloric acid, and 10 ml of methanol was added. The solution was dried, the methanol was removed by distillation, and the DMSO-t was purified by vacuum distillation. The procedure for following the rates of detritiation was similar to that adopted for the tritiation. The equations used to calculate the exchange rates are $k = k_{\text{trit}} = (2.303/[OH^-]_t) \log [([MeOT]_0 - [MeOT)_\infty)/([MeOT]_0 - [MeOT]_t)]$ and $k = k_{\text{detrit}} = (2.303/[OH^-]_t \log [([MeOT]_\infty - [MeOT]_0)/([MeOT]_\infty - [MeOT]_t)]$, where k refers to the breaking of the C–T bond by hydroxyl ion.[1] The results are shown in Table I together with the H_- values of the solutions.[2] In those cases where the hydroxyl ion molarity differed from the standard value of 0.011 a correction was made using the equation $H_- = H_{-(0.011)} + \log ([OH^-]/0.011)$. In only one case did such a correction affect H_- by more than 0.3 unit.

The weaker the acid from which a proton is abstracted by hydroxyl ion the closer will the proton be to this base in the transition state[3] and the more will the transition state resemble the products of an equilibrium ionization process. A plot of log k against H_- should, in the limit, yield a straight line of unit slope.[4] Figure 1 shows such a plot for the exchange of DMSO. The slope of this line is 0.939 ($r = 0.998$), and it can be seen that a near-linear relation exists over a remarkable range of rates—more than eight powers of ten. This provides, we feel, further indirect support for the general validity of the scale.[2] The near-unit slope corresponds in a sense to a Brønsted β coefficient of almost unity and is, as expected, higher than that found with stronger acids, *e.g.*, acetophenone.[7,8]

The rate of reaction of DMSO-t with OH^- in water, k, is 10^{-8} l. mole^{-1} sec^{-1}. The rate of reaction of DMSO under these conditions, k_1, will be greater by the amount of the isotope effect k_H/k_T (which is probably between 5 and 10),[1,7] giving a value of approximately 10^{-7} for k_1. The rate of the reverse process must

$$CH_3SOCH_3 + OH^- \rightleftharpoons CH_3SOCH_2^- + H_2O$$

be close to the limiting value of $\sim 10^{11}$ for a bimolecular process.[10] (The value of 10^8 was estimated by Long and Halevi[1] for the rate of reaction of water with $C_6H_5C{\equiv}C^-$, a much weaker base.) Assuming a value of 10^{10}

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(1) E. A. Halevi and F. A. Long, *J. Am. Chem. Soc.*, **83**, 2809 (1961).

(2) D. Dolman and R. Stewart, *Can. J. Chem.*, **45**, 912 (1967).

(3) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, pp. 164–172.

(4) This actually requires the substrate and the transition state to behave as a "Hammett acid–base pair" of the same type as the indicators used to construct the scale. Although the appropriate H_- scale would appear to be that set up with carbon acids, data in aqueous DMSO are available only for nitrogen acids (anilines and diphenylamines); this may be the best scale to use in any case.[5,6]

(5) E. C. Steiner and J. D. Starkey, *J. Am. Chem. Soc.*, **89**, 2751 (1967).

(6) D. J. Kroeger and R. Stewart, *Can. J. Chem.*, in press.

(7) J. R. Jones and R. Stewart, *J. Chem. Soc.*, in press.

(8) In one case recently reported the effect of DMSO on a reaction rate is actually much greater than its effect on the H_- function.[9] The reaction, however, did not involve a simple proton transfer.

(9) A. F. Cockerill, S. Rottschaefer, and W. A. Saunders, Jr., *J. Am. Chem. Soc.*, **89**, 901 (1967).

(10) R. P. Bell, *Quart. Rev.* (London), **13**, 169 (1959).

for k_{-1} one can calculate the acidity constant K_{HA} for the reaction $\mathrm{CH_3SOCH_3} \rightleftarrows \mathrm{H^+} + \mathrm{CH_3SOCH_2^-}$, since $K_{\mathrm{HA}} = (k_1/k_{-1})(K_w/[\mathrm{H_2O}])$, where K_w is the ion product of water.[1] This places the pK_{HA} of DMSO between 32 and 33, in close agreement with the revised value of 32.9 obtained by Steiner, *et al.*, from indicator measurements.[5,11]

Acknowledgment. The financial support of the National Research Council of Canada is gratefully acknowledged.

(11) E. C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87**, 382 (1965).

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A New Kind of Asymmetric Synthesis. The Radiation Polymerization of *trans*-1,3-Pentadiene Included in Optically Active Perhydrotriphenylene

Sir:

We wish to describe a novel example of an asymmetric synthesis in which a prochiral diene monomer, included in the crystal lattice of a chiral host compound, forms an optically active polymer on γ-ray irradiation.

We have been studying for some years the stereochemical properties of *trans,anti,trans,anti,trans*-perhydrotriphenylene (PHTP, I)[1] and its inclusion compounds with several substances having linear structure and in particular with macromolecular substances.[2] By γ irradiation of PHTP inclusion compounds with different unsaturated monomers, it is possible to obtain the corresponding high molecular weight polymers. By this method we obtained the first synthesis of an isotactic polymer in the solid state, *trans*-1,4-polypentadiene, using *trans*-1,3-pentadiene as guest monomer.[3]

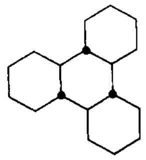
In spite of the high symmetry, PHTP does not possess any alternating axis (point group D_3) and has been recently resolved into optical antipodes.[4] Optically active PHTP forms inclusion compounds which are very similar to those of racemic PHTP: the size of the unit cell and, to a first approximation, the projection of the atoms on the *xy* plane are identical; the space group is $P6_3$, that of the racemic compound is $P6_3/m$. On principle, the channels that exist in the crystal lattice should be influenced by the lower symmetry, although an approximate examination of the channel walls shows that the differences should be rather small (<0.1 A). However, such an asymmetry is real, as we demonstrate by the asymmetric polymerization described here.

The structural properties required for the monomers to give optically active polymers were described in other papers;[5] they fully occur in *trans*-1,3 pentadiene, which had already been polymerized in an isotactic way in racemic PHTP.

A sealed vial containing 1.2 g of (−)(*R*)-PHTP (I) ($[\alpha]^{25}_{\mathrm{D}}$ −93°) and 0.4 g of *trans*-1,3 pentadiene (II) was irradiated by γ rays for 3 hr with a dose rate of 1×10^{18} ev/g min by a ^{60}Co source. After irradiation, the vial content consists of an inclusion compound of the polymer in PHTP, as revealed by the high melting point ($\simeq$190°). An analogous increase of melting point during the polymerization had already been observed for racemic PHTP.[3] After boiling acetone extraction, we obtained 64 mg of solid polymer having an infrared spectrum identical with that of isotactic *trans*-1,4-polypentadiene (III) obtained by coordination polymerization.[6] The nmr spectrum reveals a very high chemical and steric purity.

The polymer shows an unambiguous optical activity of sign opposite to that of PHTP: $[\alpha]^{25}_{\mathrm{D}}$ +2.5 ±0.3° ($\mathrm{CHCl_3}$) (Perkin-Elmer 141 polarimeter). At shorter wavelengths the rotatory power increases considerably: $[\alpha]^{25}_{436}$ +6.4°, $[\alpha]^{25}_{365}$ +9.8°.

As a checking run, pentadiene was polymerized in the presence of (+)(*S*)-PHTP with low optical purity ($[\alpha]^{25}_{\mathrm{D}}$ +35°). The polymer obtained shows a negative rotation, slightly higher than the sensitivity limit of the polarimeter.



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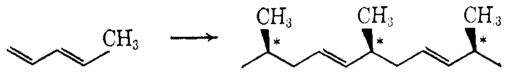

II III

Our experiments show that optical activity may be induced in simple chemical systems under rather primitive and scarcely selective conditions, like the use of ionizing radiations and the absence of complex reagents or catalysts. We are presently investigating whether the polymerization starts from asymmetric radicals or ions obtained by irradiation of PHTP, or it exclusively involves the guest molecules. In the latter hypothesis this reaction sharply differs from the other asymmetric syntheses known so far;[7] actually only weak van der Waals forces are responsible for the geometric arrangement that favors one of the sequences (*e.g.*, DDD...) with respect to the other.

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(1) M. Farina, *Tetrahedron Letters*, 2097 (1963).
(2) M. Farina, G. Allegra, and G. Natta, *J. Am. Chem. Soc.*, **86**, 516 (1964).
(3) M. Farina, G. Natta, G. Allegra, and M. Löffelholz, *J. Polymer Sci.*, Part C, in press.
(4) M. Farina and G. Audisio, *Tetrahedron Letters*, 1285 (1967).
(5) C. L. Arcus, *Progr. Stereochem.*, **3**, 264 (1962); M. Farina, *Chim. Ind.* (Milan), **46**, 761 (1964); M. Farina, M. Peraldo, and G. Natta, *Angew. Chem.*, **77**, 149 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 107 (1965).
(6) G. Natta, L. Porri, P. Corradini, G. Zanini, and F. Ciampelli, *J. Polymer Sci.*, **51**, 463 (1961).
(7) Je I. Klabunowski, "Asymmetrische Synthese," VEB Deutscher Verlag der Wissenschaften, Berlin, 1963.

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