induced nuclear spin polarization. One may inquire how the results compare with predictions of theory. If one assumes, for the reaction of methyl iodide with a sodium mirror, that ethane is formed in geminate combinations of methyl radicals generated in steps analogous to (3), and if one applies the CKO model, extended to include t_1–s interactions, one reaches the prediction that the ethane formed should exhibit enhanced absorption, not the observed emission.[7b] This conclusion is predicated on the assumption of an electronic *singlet* initial state for the critical radical pairs. In order to obtain a prediction of emission from the extended CKO model, one would have to assume initially *triplet* radical pairs, the formation of a substantial portion of the ethane in nongeminate encounters, or an effective J value for the critical pairs corresponding to a lower lying triplet than singlet. Alternatively, the extended CKO model used may be at fault for its neglect of dipolar nuclear-electron coupling terms in the Hamiltonian employed.[7b,13]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(13) S. H. Glarum has treated the anisotropic nuclear-electron coupling with the finding that for polarization arising from t_1–s interactions the contribution from this term is in the opposite direction from the contribution due to isotropic coupling: personal communication from S. H. Glarum.

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Stereoselective Synthesis and Stereochemistry of Optically Active Isopropyl Methylphosphinothionate

Sir:

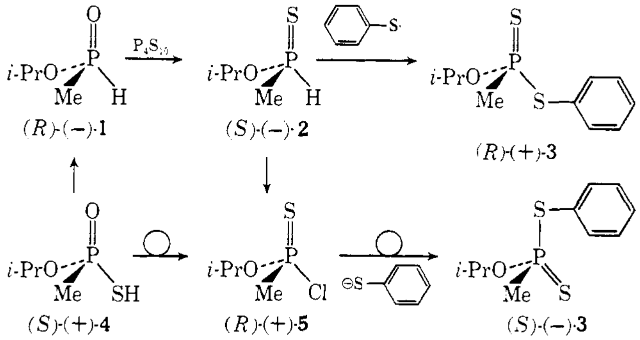
We wish to report the first example of an optically active hydrogen phosphinothionate (2), and offer a preliminary account of our studies of the stereochemistry of this synthetically versatile compound, in comparison to its phosphinate analog (1).[1]

Treatment of 4.1 mmol of (*R*)-(−)-isopropyl methylphosphinate[1] (1), [α]D −29.9° (EtOH), with 0.47 mmol of P_4S_{10} in benzene, essentially according to Schrader's procedure[2] for the synthesis of ethyl ethylphosphinothionate, gave after vacuum distillation at room temperature 1.4 mmol of (*S*)-(−)-isopropyl methylphosphinothionate (2), readily distinguishable from 1 by its ir spectrum (no $\nu_{P=O}$; $\nu_{PH}^{CCl_4}$ 2312 cm^{-1}) and longer glpc retention time on a 10-ft, 10% SE-30 column. This product had [α]D −16.2° (benzene), −17.4° (CCl_4), and −20.4° (ethanol). It is believed to be 68% optically pure, and was formed (see below) with predominant retention of configuration. The reaction thus represents a new addition to a small but growing number of displacements in acyclic systems that are known to proceed with retention of configuration at the phosphorus atom.[3] In this case, apparently, a four-membered ring is formed as the reaction intermediate.[4]

The stereochemical stability of (−)-**2** is similar to that of (−)-**1**. Thus, (−)-**2** has been stored for 6 weeks under nitrogen in the refrigerator, or refluxed for 15 min in benzene solution, with no racemization. It showed no racemization after 8 days in benzene solution containing either isopropyl methylphosphonothioic acid (racemic **4**, 0.5 equiv) or triethylamine (0.7 equiv), or for 17 hr in 95% methanolic 0.05 *M* HCl. However, it was instantaneously racemized by 0.15 equiv of 0.06 *M* sodium methoxide in methanol solution, presumably *via* the phosphinothioyl anion [Me(*i*-PrO)P(S)]$^-$. In MeOD, it exchanged the P–H for a P–D bond (followed by pmr spectra), with little or no change in specific rotation, hence with total retention of configuration.

Stereochemical studies of the reactions of (−)-**2** are summarized in Chart I. In this work, the (−)-**2** was first diluted with racemic **2** (prepared as above from racemic **1**), and the optical purities of the isolated products were adjusted accordingly. Thus, (*S*)-(−)-**2**, [α]D −0.26° (CCl_4), αD −0.284° (neat, 1 dm), reacted smoothly and rapidly with ice-cold CCl_4 containing tributylamine[5] to give (*R*)-(+)-*O*-isopropyl methylphosphonochloridothionate (**5**), bp 43° (4 mm), as the sole product. This product is deduced below to have been formed with predominant if not complete retention of configuration, as in the corresponding phosphinate (**1**) reaction.[1] It was 1% optically pure, in comparison to (+)-**5**, [α]D +69.9° (CCl_4), obtained (undoubtedly with inversion of configuration)[6] on treatment of optically pure (*S*)-(+)-isopropyl methylphosphonothioic acid (**4**), αD +14.00° (neat, 1 dm), with PCl_5 in ether solution. Assuming a stereospecific conversion of (+)-**4** to (+)-**5** (by analogy to the reaction of ethyl ethylphosphonothioic acid)[6] and of (−)-**2** to (+)-**5**, the specific rotation of optically pure **2** is tentatively assigned as [α]D −24° (benzene), −26° (CCl_4), and −30° (ethanol).

Chart I



(*S*)-(−)-**2** reacts with *N*-chlorosuccinimide[7] (NCS) in ice-cold CCl_4 to give a mixture, from which (*R*)-(+)-**5** was isolated, only 30% optically pure, however, in

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(1) L. P. Reiff and H. S. Aaron, *J. Amer. Chem. Soc.*, **92**, 5275 (1970).

(2) K. Sasse in "Methoden der Organischen Chemie," Vol. 12, Part 1, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1963, p 332.

(3) (a) J. Michalski, *Colloq. Nat. Cent. Nat. Rech. Sci.*, 203 (1965) [*Chem. Abstr.*, 67, 90169x (1967)]; (b) J. Michalski and R. Ratajczak, *Rocz. Chem.*, 37, 1185 (1963); (c) L. Horner and H. Winkler, *Tetrahedron Lett.*, 175 (1964); (d) W. E. McEwen, W. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, **86**, 2378 (1964).

(4) K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969).

(5) F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 660 (1945).

(6) J. Michalski and M. Mikalajczyk, *Tetrahedron*, **22**, 3055 (1966).

(7) G. W. Kenner, A. R. Todd, and F. J. Weymouth, *J. Chem. Soc.*, 3675 (1952).

comparison to that obtained from the Atherton–Openshaw–Todd reaction.[5] In contrast, the phosphinate **1** reacts with possible total stereospecificity[1] with both NCS and CCl_4–amine, although the latter reaction is extremely slow compared to the thiono analog.

(*S*)-(−)-**2** ([α]D −1.18° (benzene), 4.9% optically pure) with phenyl disulfide under uv light for 12 hr at ambient temperature undergoes a free-radical reaction to give (*R*)-(+)-*O*-isopropyl *S*-phenyl methylphosphonodithioate (**3**), bp 105° (40 μ), [α]D +3.09° (benzene). The reaction presumably proceeds with retention of configuration, by analogy to the proven stereochemical course of the corresponding phosphinate reaction.[1] The product is believed to be only 3.0% optically pure, however, from comparison of its specific rotation to that calculated for (−)-**3** ([α]D −103°, benzene). The latter was isolated from the reaction of (*R*)-(+)-**5** (20% optically pure) with sodium thiophenylate, as indicated in Chart I. Apparently, partial racemization of the radical intermediate occurred. The structure of the intermediate [Me(*i*-PrO)-P·(SH)SC_6H_5 or Me(*i*-PrO)P(S)·] is uncertain; apparently both phosphoranyl[8] and phosphoryl[1,9] radicals can react stereospecifically with retention of configuration.

Since the displacement reaction of (+)-**5** to (−)-**3** undoubtedly proceeds with predominant (if not total) inversion of configuration, (−)-**2** and (+)-**5** must have the same configuration, as shown. Thus, the known[1] configurational relationship of (−)-**1** to (+)-**4**, together with that determined above for (+)-**4** and (+)-**5**, establish that the conversion of (−)-**1** to (−)-**2** with P_4S_{10} and (−)-**2** to (+)-**5** with NCS or CCl_4–amine must all take place with predominant (total, presumably, for the CCl_4–amine reaction) retention of configuration.

Acknowledgment. We thank Mr. David I. Rossman for a sample of racemic **2**.

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(8) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).

(9) NOTE ADDED IN PROOF. See also, H. P. Benschop and D. H. J. M. Platenburg, *ibid.*, 1098 (1970).

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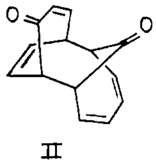
The Novel Double [6 + 4] Cycloaddition of Tropone to Dimethylfulvene

Sir:

The study of cycloaddition reactions has accelerated in intensity and sophistication since the promulgation of orbital symmetry selection rules by Woodward and Hoffmann.[1] Recent studies of the cycloadditions of polyolefins have shown that of the many concerted processes allowed by orbital symmetry considerations, only a few are ordinarily observed.[2] Cycloaddition reactions are often stereoselective[3] and regioselective,[4,5] and, in a considerable number of cases, proceed with selective formation of one of the thermally allowed adducts.[6]

We wish to report the first example of a fulvene acting as a 6π electron addend in a concerted cycloaddition and to note the remarkable selectivity of this cycloaddition. In particular, of the 50 possible 1:1 adducts, 26 of which are thermally allowed, only two are formed.

A solution of tropone and dimethylfulvene in tetrahydrofuran was heated at 50° for 2 days. Addition of ether to the cooled solution resulted in crystallization of an adduct, I, mp 177.5–178.5°, containing two tropone and one dimethylfulvene molecules, $C_{22}H_{22}O_2$.[7a,b] The ir spectrum (KBr 5.82, 5.98, 6.05 μ) and the uv spectrum ($\lambda_{\max}^{\text{cyclohexane}}$ 230 (ε 10,000) sh, 248 (ε 6000) sh, 259 (ε 5200), 270 (ε 5000), 314 nm (ε 300)) of I corresponded nearly exactly to those of the tropone [6 + 4] photodimer II,[8] consistent with the presence of cyclohepta-2,5-dienone and cyclohepta-3,5-dienone moieties in I. The 220-MHz nmr spectrum of I (C_6D_6) included sharp methyl resonances at δ 0.87 and 1.03, nine olefinic proton resonances, and a slightly broadened doublet (*J* = 12 Hz) at δ 1.92, indicative of the presence of a methylene group. Catalytic hydrogenation of I resulted in the uptake of 4 mol of hydrogen, and the resulting octahydro-I, mp 155–157°, $C_{22}H_{30}O_2$,[7a] retained one olefinic resonance in the nmr as a broad singlet at δ 5.8 (CCl_4).



II

This evidence revealed that the dimethylfulvene fragment in I contained methyls attached to a saturated carbon, one olefinic hydrogen, and a methylene group. Although several fragments with these features and a fulvene skeleton may be imagined, a reasonable mechanistic hypothesis resulted in the postulation of the gross structure of I, and this postulate, along with the subtleties of stereochemistry, were eventually proven by a complete analysis of the nmr spectrum and NOE experiments.[9] Since many cyclopentadienes undergo [1,5] sigmatropic hydrogen shifts at room temperature,[10] it was postulated that an initial [6 + 4] cycloaddition

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(1) R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046, 4388 (1965); R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(2) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143, 4145 (1970), and references therein.

(3) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(4) *E.g.*, the preferential formation of 3,4-disubstituted cyclohexenes from 1-substituted butadienes and monosubstituted ethylenes: A. Onishchenko, "Diene Synthesis," Oldbourne Press, London, 1964; A. Wassermann, "Diels-Alder Reactions," Elsevier, Amsterdam, 1965.

(5) E. W. Garbish, Jr. and R. Sprecher, *J. Amer. Chem. Soc.*, **91**, 6785 (1969); W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967).

(6) The term "perispecific" is suggested to connote a reaction proceeding through only one of the symmetry-allowed pathways available to the reactants.

(7) (a) Elemental analyses were compatible with the formula given. (b) Precise mass measurements (Varian M-66) were in agreement with the formula given.

(8) A. S. Kende, *J. Amer. Chem. Soc.*, **88**, 5026 (1966); A. S. Kende and J. E. Lancaster, *ibid.*, **89**, 5283 (1967).

(9) Details of the nmr structure proof will appear in the full paper.

(10) V. A. Mironov, E. V. Sobolev, and A. N. Elizarova, *Tetrahedron*, **19**, 1939 (1963); E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, *J. Amer. Chem. Soc.*, **90**, 5284 (1968); W. R. Roth, *Tetrahedron Lett.*, 1009 (1964); S. McLean and P. Haynes, *Tetrahedron*, **21**, 1313 (1965).