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**.

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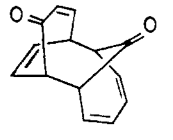
The Novel Double [6 + 4] Cycloaddition of Tropone to Dimethylfulvene

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 ($\lambda_{max}^{cyclohexane}$ 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.

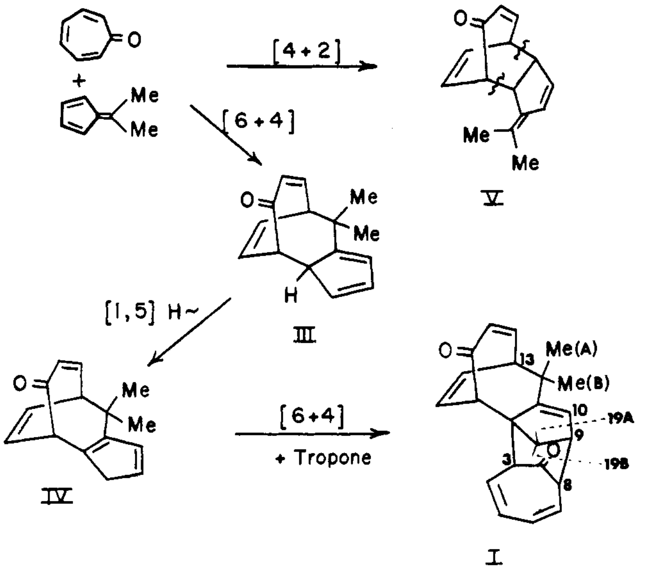
(8) A. S. Kende, *J. Amer. Chem. Soc.*, **88**, 5026 (1966); A. S. Kende and J. E. Lancaster, *ibid.*, **89**, 5283 (1967).

(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).

of tropone (4π) across the termini of the fulvene (6π) to give III was followed by a [1,5] sigmatropic hydrogen shift to give the thermodynamically more stable cyclopentadiene IV, which subsequently underwent a second [6 + 4] cycloaddition with tropone to form I.

Of the 16 possible isomers formed by syn or anti [6 + 4] cycloaddition of dimethylfulvene to tropone, one or three [1,5] sigmatropic hydrogen shifts in the resulting cyclopentadiene moiety, and exo or endo [6 + 4] cycloaddition of tropone to the "top" or "bottom" of the cyclopentadiene ring, only one of these structures (I) was compatible with the following nmr evidence. Irradiation of the higher field methyl (A) resulted in enhanced intensity of 15% in the resonances due to H-13 (proving the initial [6 + 4] cycloaddition was anti) and H-10 (proving a single [1,5] sigmatropic hydrogen shift precedes the second addition). The coupling constants in the cyclohexanone ring ($J_{19\text{A}-19\text{B}}$ = 12.0, $J_{19\text{A}-9}$ = 5.0, $J_{19\text{A}-3}$ = 2.0, $J_{19\text{A}-8}$ = 1.0, $J_{19\text{B}-10}$ = 1.5, $J_{19\text{B}-9}$ = 0.8) are compatible with a chair rather than a boat cyclohexanone, and thus with exo [6 + 4] cycloaddition of the second tropone. Finally, irradiation of the lower field methyl resonance (B) resulted in a 13% enhancement of the intensity of the H-3 resonance. The proximity of Me-B and H-3 and the low-field position of Me-B are most compatible with addition of the second tropone to the "bottom" of the cyclopentadiene ring.[9]

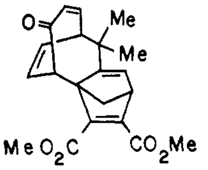


Reaction of equimolar amounts of dimethylfulvene and tropone in ether at room temperature for 3 weeks and separation of adducts by plc gave two oily 1:1 adducts IV (22%) and V (4%) along with the 2:1 adduct I (66% based on tropone).

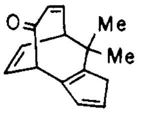
The [4 + 2] nature of adduct V[7b] was revealed by the ir (CCl_4, 5.98 μ) and the methyl resonances (δ 1.75, 1.80) and six olefinic protons in the nmr ($CDCl_3$). While the exact structure of V must await complete analysis of the nmr spectrum of the pure adduct, one of the four Diels–Alder structures represented by V is proposed for this product.

Although adduct IV[7b] could not be purified completely and underwent slow isomerization (*vida infra*) and decomposition, samples suitable for spectral analysis were obtained by plc. The presence of an α,β-unsaturated ketone (ir, CCl_4, 5.96, 6.08 μ), methyls at a saturated carbon ($CDCl_3$ δ 1.21, 1.28), and six olefinic protons in the nmr suggested that IV was the product of [6 + 4] cycloaddition followed by a [1,5] sigmatropic hydrogen shift.

Reaction of IV with dimethylacetylenedicarboxylate (room temperature, 1 hr) resulted in the formation of a single oily adduct VI,[7b] whose structure was proven by nmr and NOE.[6] In particular, the presence of a methylene group was clearly shown by the resonances at δ 1.85 and 2.22 (J = 8.5 Hz) in the nmr ($CDCl_3$). Admixture of IV and tropone in benzene solution resulted in nearly quantitative formation of I (room temperature, 3 weeks).



VI



VII

When IV was heated at 50°, partial conversion to a new isomer (33% at equilibrium) with methyl resonances at δ 0.81 and 0.96 (C_6D_6) occurred. Although the new isomer could not be separated from IV, the nmr spectra of IV and the mixture of IV and the new isomer were nearly identical except for the additional methyl resonances. It is probable that the cyclopentadiene ring in IV underwent two reversible [1.5] sigmatropic hydrogen shifts to form VII.[11]

Monitoring the reaction of tropone and dimethylfulvene by nmr revealed the presence of a rapidly formed intermediate III, with a broad singlet at δ 0.95 (C_6D_6) which never exceeded 10% of the reaction mixture. The disappearance of III was accompanied by the formation of IV and then I. Adduct V was barely detectable in these experiments and never exceeded 5% of the amount of I, indicating the initial [6 + 4] cycloaddition is at least 18 times more rapid than the [4 + 2] cycloaddition.[12]

Although other undetected thermally allowed adducts of tropone and dimethylfulvene might provide III and V by rapid [1.5] or [3,3] sigmatropic shifts,[13] the most economic rationale of these results is competition between [6 + 4] and [4 + 2] cycloadditions in which tropone behaves as the 4π component in both cycloadditions. The failure to detect intermediates in the nmr experiments, the reaction of fulvenes as 6π addends with diazomethane,[14] and the limited number of documented [1,5] sigmatropic carbon shifts[11] reinforce this conclusion.

Finally, the second tropone addition is a further example of a stereospecific exo [6 + 4] cycloaddition,

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(11) V. A. Mironov, *et al.*, *Tetrahedron Lett.*, 3997 (1968); 3347, 3985 (1969); L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, **91**, 1578 (1969); J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968); L. A. Paquette and J. C. Stowell (*Tetrahedron Lett.*, 4159 (1969)) describe an apparent [1,5] carbon shift, which could be instead a Cope rearrangement.

(12) For related competition between [6 + 4] and [4 + 2] cycloadditions, see: S. Itô, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 2873 (1970).

(13) In particular, the exo [6 + 4] adduct wherein tropone acts as the 6π addend might be expected to easily undergo Cope rearrangement to III. The failure to observe adducts of type III with fulvenes and dienes might imply the latter mechanism is operating although the distance between diene termini may be controlling: K. N. Houk and L. J. Luskus, unpublished.

(14) K. N. Houk and L. J. Luskus, *Tetrahedron Lett.*, in press.

in agreement with the mounting evidence that, in the absence of great steric demands in the transition state, secondary orbital interactions determine the stereochemistry of cycloadditions.[1,15]

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

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(15) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970).

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Book Reviews

Photomicrography: A Comprehensive Treatise. By ROGER P. LOVELAND, former Research Associate, Kodak Research Laboratories, Rochester, N. Y. John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1970. Volume I, x + 1–526 pp. Volume II, xi + 527–1039 pp. 16 × 23.5 cm. $39.50.

In his preface Roger Loveland states that the book is intended to be a text as well as a reference work, and, as he points out, the problem was to make the book useful to the neophyte as well as to the experienced photomicrographer. In this reviewer's opinion the experienced photomicrographer will find the book useful not only as a source of specific information, but as a fruitful source of ideas and suggestions for solving the many problems involved in the production of high quality photomicrographs. The neophyte, however, depending on his background, will probably find that he will frequently need to refer to works which present the fundamentals of the microscope and photography at a less sophisticated level. The author has apparently anticipated this and has included a selected bibliography arranged by topic at the end of the second volume. References useful to the advanced worker are also included in the bibliography.

The first chapter in Volume I is devoted to a discussion of optical principles, lenses and their aberrations, their use, and some information on lens design as applied to microscope objectives. An ingenious technique for the determination of the relationships between object distance, image distance, focal length, and magnification is presented that makes these troublesome calculations quite simple and should be of great aid to those who work with lenses.

The optics and use of the compound microscope make up the material in Chapter II which is presented in sufficient depth so that the experienced microscopist will profit from a careful reading. This reviewer finds the titles of the above chapters somewhat confusing; however, this is a minor criticism and the reader will find the information contained in these chapters well chosen and basic to the rest of the book.

Chapter III is a practical discussion of apparatus and is designed to aid the worker select equipment that will most efficiently accomplish his aims. Although currently available apparatus is discussed, the author has presented this material from the standpoint of basic considerations, thus avoiding the obsolescence that invariably results from the former practice alone.

In Chapters IV, V, and VI the reader finds the material that can be considered the core material of this two-volume work. It is these chapters that the photomicrographer will turn to first when in need of information regarding a particular type of photomicrography. The range of information extends from low-power photomicrography by reflected light to high-power work with the compound microscope using transmitted light. The somewhat brief comments regarding lighting presented in the above account are supplemented by a very extensive discussion of this important aspect of photomicrography in the following four chapters. Information on light sources, types of illumination, commercial lamps, spectral quality of illuminants, and its control through the use of filters is presented in depth. It is in these chapters that the experienced microscopist will find information and suggestions that make the difference between an ordinary photomicrograph and one of truly professional quality. The final chapter of Volume I deals with the "Eyepiece" photomicrographic camera and a discussion of several commercial models including their use. Perhaps the most interesting part of this chapter deals with methods whereby simple, inexpensive roll-film cameras can be used for the production of good quality photomicrographs. The information presented here should be of particular interest to the amateur as well as the teacher in small institutions where funds for the rather expensive commercial equipment are not available. Volume I closes with three appendices presenting supplementary optical data.

Volume II contains much information for the advanced worker using special methods of microscopy. The methods of dark field, phase contrast, interference, infrared, ultraviolet, and fluorescence microscopy, as well as holomicrography are discussed generally in sufficient depth for the critical reader to obtain a basic understanding of the principles involved and the advantages and disadvantages of the systems. The biologist who is often faced with the problem of taking a photomicrograph of a living specimen in which there is rapid movement and who may wish to use color materials will find the chapter on flash photomicrography of particular interest. A substantial section of the second volume deals with basic photographic techniques, principles, and materials. Much of this material is to be found in the numerous publications of the Eastman Kodak Company and one may question why it is included in these volumes. The convenience of having the information gathered together in one place may, however, justify its inclusion. Cinemicrography is the subject of the final chapter of Volume II. Here the author presents a wealth of information, obviously drawn from personal experience, at a level that will be most helpful to the professional. The cost of equipment and processing as well as its complexity excludes those who would only occasionally make use of cinemicrography. The author was obviously aware of this situation as indicated by his opening sentence wherein he seems to reassure the amateur that hobby quality pictures can be made using inexpensive equipment. Image illuminance and photographic exposure formulas, immersion oils, and detailed directions for the construction of a repetitive sparking illuminator for the far-ultraviolet are presented in the appendices of Volume II.

The illustrations are on the whole informative and well reproduced. There are, however, a few errors which very likely crept in during the printing. For example, it appears that Figures 2–8a and b on page 79 are reversed with respect to the information presented in the text. The same is true of Figures 2–9a and b on page 80. Perhaps the most serious criticism that can be made is that the great wealth of information presented in these two volumes could be considerably better organized. The above criticisms do not detract significantly from the great value of the book and are defects that can be easily rectified in future editions.

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