A Trifluoromethylated Diphosphabenzvalene: 1,3,4,6-Tetrakis(trifluoromethyl)-2,5-diphosphatricyclo[3.1.0.0^{2,6}]hexene-3

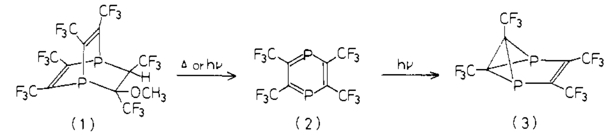
Sir:

Previously, we reported the synthesis of 2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphabenzene (**2**) by the thermolysis of the methanol adduct (**1**) of 2,3,5,6,7,8-hexakis(trifluoromethyl)barrelene[1] and 7,7-dichloro-2,3,5,6-tetrakis(trifluoromethyl)-1,4-diphosphanorbornadiene by thermolysis of **2** with carbon tetrachloride.[2] In this work, we examined the photolysis of **2** and found that the title compound (**3**) was obtained. Compound **3** is the first example of a benzvalene analogue containing heteroatoms in the ring system. Further, photolysis of **1** was found to give **3** through **2**.

The solution of **2** in perfluoropentane, which was obtained in situ by thermolysis of **1** in *n*-hexane, evaporation of solvent, and dissolution of the residue in perfluoropentane in argon atmosphere, was sealed in a Pyrex tube under vacuum and irradiated with a high pressure mercury lamp for 72 h. Separation of the reaction mixture by a trap-to-trap distillation gave colorless oil (**3**), which solidified at −78 °C. The mass spectrum shows that **3** is a valence-bond isomer of **2**: *m/e* 386 (M$^+$), high mass calcd for $C_8F_{12}P_2$ 385.928, found 385.929. Presence of a double bond is confirmed by the IR spectrum ($\nu_{C=C}$ 1620 cm^{-1}). ^{19}F NMR[3] shows that **3** has two kinds of trifluoromethyl groups: δ −10.2 (d, J_{PF} = 22.6 Hz), and −6.0 (t, J_{PF} = 5.2 Hz), intensity ratio 1:1. The former couples with one phosphorus atom and the latter with two. Only one kind of phosphorus was observed in ^{31}P NMR[4]: δ 17.96 (singlet by irradiation of fluorine). These spectral data suggest that **3** is 1,3,4, 6-tetrakis (trifluoromethyl)-2, 5-diphosphatetracyclo-[3.1.0.0^{2,6}]hexene-3. The ^{13}C NMR supports this assignment (Figure 1). Compound **3** is stable against air at room temperature and thermally isomerized to **2**: half-life at 198 °C in hexafluorobenzene is ~75 min.

Compound **1** was found to give **2** at first and then **3** under the same condition as the photolysis of **2** (Scheme I). Prinzbach et al. reported[5] that the homocyclic tricyclo[2.2.2]octadiene compound was converted mainly to intramolecular [2 + 2] cycloadduct. The difference between our result and theirs might be ascribed to the longer P–C bond; two double bonds are too far to add to each other.

Scheme I



Many attempts have been made to obtain valence-bond isomers of azine and diazine compounds, but no heterocyclic analogue of benzvalene has been isolated nor observed spectroscopically. Our isolation of the diphospha analogue of benzvalene might be due to speciality of the phosphorus in the excitation, the longer P–C bond, the difference in hybridation between the first and the second row elements, and/or the perfluoroalkyl effect stabilizing strained ring systems.

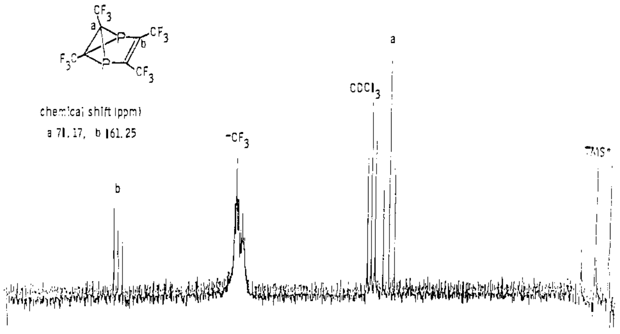


Figure 1. ^{19}F-Decoupled ^{13}C NMR: *, ^{1}H nondecoupled.

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(3) Benzotrifluoride as internal standard.

(4) 85% H_3PO_4 as external standard.

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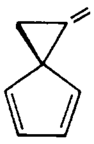
Synthesis and Properties of 1-Methylenespiro[2.4]hepta-4,6-diene. A Facile and Bond-Selective Sigmatropic Ring Expansion

Sir:

We have prepared 1-methylenespiro[2.4]hepta-4,6-diene (**1**) by the photochemical cycloaddition of diazocyclopentadiene to allene at low temperature. The material is a potential source of a substituted trimethylenemethane diradical for which considerable stabilization of the zwitterionic singlet state **4** might be expected.[1] The spirotriene **1** is unstable and undergoes a facile sigmatropic ring expansion to the bicyclic triene **2** which dimerizes in a Diels–Alder fashion to produce a highly strained and thermally labile kinetic dimer. This unprecedented low temperature ring expansion is quite possibly assisted by strain relief of the methylenecyclopropane and results in the migration of the allylic rather than the vinylic σ bond. Derivatives of bicyclo[3.2.0]hepta-1,3-diene (**5**) are extremely unstable.[2] All attempts to generate the parent system have yielded only spiro[2.4]heptadiene **6** via an unusually fast ring contraction which is apparently driven by relief of the considerable strain of the bridgehead double bond of **5**. In marked contrast, protonation of the bicyclo[3.2.0]heptatrienyl anion (**7**) apparently produces **8** as an unstable intermediate which promptly dimerizes in a [2 + 2] fashion across the strained double bond rather than undergoing the sigmatropic ring contraction.[3] It has been suggested that the latter pathway is energetically unfavorable because of the strain associated with the formation of the cyclopropene ring (E_s = 55 kcal/mol).[4] In this respect, it is interesting that the recently prepared spiro[2.4]heptatriene derivatives **9** do not ring expand under the conditions of isolation.[5] This suggests the interesting possibility that the migratory apptitude of the vinyl σ bonds may be low even though the ring expansion is conceivably exothermic.



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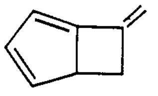

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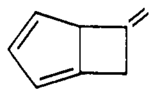

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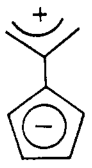

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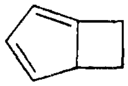

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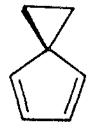

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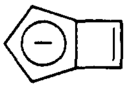

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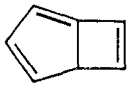

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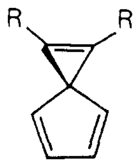
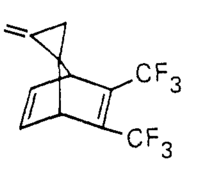


9

R = Me, Et

Irradiation (450-W Hg lamp, Pyrex) of a solution of freshly prepared diazocyclopentadiene[6] in liquid allene (2 M, −55 °C) led to the formation of an unstable material subsequently identified as **1** by its characteristic spectral data and chemical reactions.[7] When a solution of **1** in pentane was warmed to 0 °C in the presence of excess hexafluoro-2-butyne, a mixture of Diels-Alder adducts (**10** and **11**) was obtained.[8]

The spirotriene **1** was unstable ($t_{1/2}^{0.5\,^{\circ}\mathrm{C}} = 5$ h) and rapidly dimerized upon standing. The dimer from **1** was highly unsymmetrical as evidenced by its complex spectral data.[9] The ^{1}H NMR spectrum exhibited a particularly striking AB pattern the upfield portion of which at τ 7.72 appeared as a doublet (J = 16 Hz) which was further split into regular quintets. The low field portion was a 12-line pattern (d, d, t, J = 16, 8, 2.6 Hz) when observed at 360 MHz. The large 16-Hz splitting is most consistent with a geminal coupling. Microhydrogenation of the purified dimer led to the rapid uptake of 4 mol of hydrogen to produce a saturated derivative.



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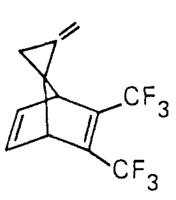

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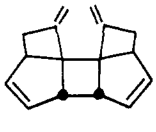

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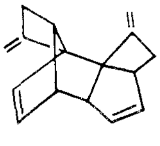

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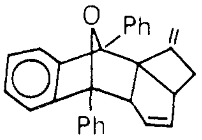

14

The kinetic dimer was itself thermally labile and cleanly rearranged upon attempted GLC purification or in refluxing benzene ($t_{1/2}^{80\,^{\circ}\mathrm{C}} = 8$ h) to produce a new but now highly symmetrical $C_{16}H_{16}$ material.[10] Consideration of the spectral data suggested that the rearranged dimer was a [2 + 2] cycloaddition product formally derived from the bicyclic triene **2**. This was confirmed by x-ray analysis[11] and the structure assigned as **12**.[12]

With the structure of the symmetrical dimer **12** in hand, it was observed that many prominent features of its NMR spectrum were also reproduced exactly in the spectrum of the kinetic dimer. Particularly striking was the position and distinctive band shape of the AB pattern for the geminal allylic protons of the methylene cyclobutane rings in **12** which also appeared in the kinetic dimer. Consideration of all of the spectral data in conjunction with that of appropriate model compounds led to the tentative structural assignment of **13** as that of the kinetic dimer.[14]

The distinctive presence of bicyclo[3.2.0]heptyl moiety in both dimers **12** and **13** strongly suggested that the spirotriene **6** was undergoing a rate determining 1,5-sigmatropic ring expansion prior to rapid dimerization. In an effort to trap the intermediate, the triene **1** was allowed to warm to 25 °C in the presence of 2,5-diphenylisobenzofuran. Under these conditions virtually no dimer was produced and a single 1:1 adduct was isolated. The structure of the adduct was assigned as **14** on the basis of consistent spectral and analytical data: ^{1}H NMR ($CDCl_3$) τ 2.12–3.14 (m, 14 H), 4.57 (d, t, J = 5.5, 1.3 Hz, 1 H), 5.26 (t, J = 2.6 Hz, 1 H), 7.78 (d, p, J = 16, 2.5 Hz, 1 H). The NMR data was so similar to that of the dimer **12** that the presence of a common structural unit seems unavoidable. Extensive decoupling was possible due to the widely separated resonances and these results were completely consistent with structure **14**.

It now seems that the spirotriene **1** unlike **6** is unstable and undergoes a facile (E_a = 19.6 kcal/mol) and unprecedented 1,5-sigmatropic ring expansion to the bicyclic triene **2**. The reaction is apparently bond selective and involves the migration of the allylic rather than the vinylic bond, since no evidence for the formation of an adduct of **3** was obtained even in the presence of excess trapping reagents. This selectivity is interesting in light of the recent report by Semmelhack and coworkers[15] describing kinetic evidence for an increased migratory aptitude of a vinyl bond (relative to either alkyl or allyl) in a series of spiro[4.4]nona-1,3-diene derivatives. It is, however, in complete accord with the recent topochemical prediction of Epiotes and Shaik[16] who suggest that, for 1,5-sigmatropic migrations in substituted cyclopentadienes, it is the group with the lowest ionization potential which preferentially migrates. Application of the criterion to the sigmatropic rearrangement of **1** predicts allyl (*IP* ~8.1 eV) rather than vinyl (*IP* ~8.7 eV)[17] migration as is observed.

Acknowledgment is made to the Stanford Magnetic Resonance Laboratory for the 360-MHz NMR spectrum of **13** and to the NSF and NIH for support from Grants GR 23633 and RR 00711, respectively, in this regard. The authors also acknowledge helpful discussions with Professor J. Brauman of Stanford University.

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(7) Spectral data **1**: ^{1}H NMR ($CDCl_3$, −25 °C) τ 3.53 (m, 2 H), 3.90 (m, 2 H), 4.53 (t, J = 2.5 Hz, 1 H), 4.67 (t, J = 2.5 Hz, 1 H), 7.68 (t, J = 2.5 Hz, 2 H); UV (pentane, −25 °C) λ_{max} 261 nm (ϵ 2700), 208 (sh, ϵ 7500).
(8) Consistent analytical and spectral data were obtained for all new compounds. Complete spectral data are available upon request.
(9) Spectral data for **13**: ^{1}H NMR (CCl_4) τ 3.88–4.26 (m, 3 H), 4.46 (br d, J = 5.8 Hz, 1 H), 5.16–5.35 (m, 3 H), 5.43 (t, J = 2.1 Hz, 1 H), 6.76–6.57 (m, 5 H), 7.72 (d, p, J = 15.7, 2.6 Hz, 1 H), 7.98 (m, 2 H); IR (neat) 3060, 2960, 1675, 1605, 1575, 1425, 1350, 1310, 1170, 1100, 935; 880 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 154.2, 147.2, 138.1, 136.9, 133.3, 132.0, 105.7, 102.1, 76.2, 70.5, 62.0, 49.6, 48.3, 40.7, 35.1, 29.1; UV (pentane) end absorption.
(10) Spectral data for **12**; mp 54–55 °C; ^{1}H NMR (CCl_4) τ 4.22 (d, d, J = 5.5, 2.5 Hz, 1 H), 4.63 (br d, J = 5.5 Hz, 1 H), 4.93 (t, J = 2.5 Hz, 1 H), 5.22 (t,

$J = 2.6$ Hz, 1 H), 6.49 (br s, 1 H), 6.87)br m, 1 H), 7.31 (d, d, t, $J = 16, 8, 2.6$ Hz, 1 H), 7.88 (d, p, $J = 16, 2.6$ Hz, 1 H); UV (pentane) end absorption.

(11) X-ray data to be published separately.

(12) A similar head-to-head syn dimer has been reported by Cava and coworkers[13] as one product resulting from the protonation of the norbiphenylene anion.

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(14) Although the isolated dimer appears homogeneous, the spectral data does not allow an unambiguous choice between the four possible geometrical isomers of **13** at this time.

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Book Reviews

Critical Stability Constants. Volume I. Amino Acids. By A. E. MARTELL and R. M. SMITH, (Texas A&M University). Plenum Press, New York, N.Y. 1974. xiii + 469 pp. $23.00.

This large volume is the first of three dealing with the stability constants of ligands. It is a compilation of metal complex equilibrium constants of the amino carboxylic acids and their corresponding enthalpy and entropy values.

The book is arranged in a logical order going from the simple to the complex amino acids. All tables and data are presented with similar organization and, with the use of an excellent index, are easily found.

Data selected for the volume were judged by the authors to be the most reliable and up-to-date of the published literature values. This and the succeeding volumes would be a valuable addition to the working library of the analytical chemist.

G. R. Powell, *Eastman Kodak Company*

Chemical Control of Insect Behavior. Edited by H. H. SHOREY (University of California, Riverside) and J. J. MCKELVEY, JR. (Rockefeller Foundation, New York). Wiley-Interscience, New York, N.Y. 1977. xii + 414 pp. $19.50.

The latest volume in Wiley's Environmental Science and Technology Series, this book presents a valuable review (through the 1975 literature) of the field of insect control by the use of pheromones and related insect behavior regulating compounds. It consists of a well-organized series of articles by an international assemblage of specialists in chemical ecology, insect physiology and behavior, and pest management studies. As such, it provides in a very readable format a thorough introduction to the concepts, terminology, and current research problems facing the diverse groups whose research contributes to this field.

Following an informative introduction in which basic terms are defined, a series of three articles deals with physiological studies of the chemosensory response system in insects. The next four articles address the integrated behavioral responses of insects to their plant or animal hosts. An article describing possible mechanisms by which insects respond to distant odor sources highlights this section. The discussion next focuses on the role of pheromones in regulating insect sexual behavior, oviposition, and feeding, emphasizing fruitfly and mosquito studies. The subsequent articles concerning Coleoptera and Lepidoptera serve to inform the reader of the extreme complexity of insect behavior patterns and the necessity of learning a great deal more of the pheromone-mediated behavior before successful manipulation of insect populations can become routine.

An article by J. S. Kennedy (Imperial College) discusses means of designing efficient and unambiguous laboratory bioassays for potential behavior regulating compounds. Natural products chemists will be particularly interested in the section which includes articles by R. M. Silverstein and Y. Tamaki discussing their recent research and tabulating known pheromones and synthetic attractants for over 100 species of insects. The final section of six articles provides what may be considered the most valuable contribution this book makes to this rapidly evolving field. These articles provide instructive accounts of the applications of insect attractants and repellents in the control of mosquitos and fruitflies and the economic pests of stored products, agricultural crops, and forests. Perhaps the greatest strength of this book lies in the clarity with which it defines the problems which impede the successful field use of insect behavior regulating compounds. This book is particularly timely in its attempt to establish order and perspective to a complex multidisciplinary field. The authors aptly note in summary that ". . . the contributors to this book isolated and identified certain issues that are likely to influence the future growth and direction of this field".

William R. Bartlett, *Saint John's University (Minnesota)*

Immunology, Aging and Cancer. F. M. BURNET (University of Melbourne). W. H. Freeman and Co., San Francisco, Calif. 1976. viix + 162 pp. $9.95, hardcover; $6.50 soft cover.

The book contains a series of nine lectures presented by the author at the University of California, Irvine, in April 1975. Even though a wide range of topics is contained in a very short series, the discussions are centered on the concept of intrinsic mutagenesis.

In the first four chapters, The Basis of Immunology, Clonal Selection and Antibody Production, T and B Cells, and A Homeostatic and Self-monitoring Immune System, the author presents a broad picture of immunity and immunology as an element in the process of survival.

A preliminary discussion of mutation in Chapter Five is followed by a discussion of the medical aspects of somatic mutation in the next three chapters on aging, a new category of genetic disease, and autoimmune disease. In these chapters as well as in Chapter Nine, "Cancer", the author relates the diseases discussed to error produced during DNA replication and repair by DNA polymerases of varying degrees of error proneness.

An adequate glossary and references cited chapter by chapter at the end of the book will be of value in aiding the nonspecialist reader who wishes to achieve a thorough understanding of the material presented.

T. J. Bond, *Baylor University*

New and Specialty Fibers. Applied Polymer Symposia, No. 29. Edited by J. ECONOMY (IBM Corporation). John Wiley & Sons, Inc., New York, N.Y. 1976. vi + 223 pp. $14.95.

This volume encompasses 19 papers given at the Chicago American Chemical Society meeting in August 1975. It is organized into three sections: filamentary superconductors, high-temperature and reinforcing fibers, and fibers for pollution control applications. The materials discussed are largely inorganic and include: Nb_3Al, V_3Ga, NbTi, Nb_3Sn, Cu-based alloys, V_3Si, Nb_3Ge, NbCN, boron carbide. glass, sapphire alloys, carbon–graphite, and treated cotton. Topics for these fibers include preparation, characteristics, fabrication, and property–structure relationships.

The book is well presented and appears to cover the subject comprehensively. Considerable data are given along with many excellent photomicrographs. There are two papers included which seem a bit incongruous and, perhaps, would best be used elsewhere: (1) the second one in the first section on Nb_3Al was quite short with no experimental data and, as such, was a brief review; and (2) the first one in the third section was a process design evaluation and an engineering study. One of the running titles is in error (in the paper by G. E. Pike et al., NbCN given as $NbCl_5$).

This book is obviously not for distribution to all chemists, but for someone who is acquainted with the areas covered, it is required.

Patrick E. Cassidy, *Southwest Texas State University*