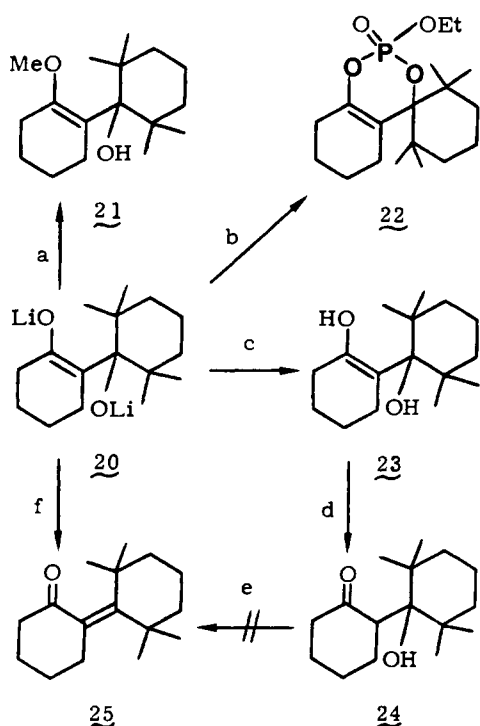


Scheme 1^a

^a Reaction key: (a) excess Me_2SO_4 , HMPA, 60% (MeI fails to react); (b) $\text{Cl}_2\text{PO}_2\text{Et}$, 43%; (c) H_2O , NH_4Cl , 0°C , 55%; (d) silica gel, 25%; (e) $p\text{-TsOH}$, toluene, Δ (retroaldol occurs); (f) $(\text{CF}_3\text{CO})_2\text{O}$, 55%.

dianion **12** adds completely to this ketone to afford intermediate **20** (entry 9). Several reactions of this intermediate are outlined in Scheme 1. Most noteworthy among these is the formation (on aqueous quenching of **20**, reaction c) of the solid hydroxy enol **23**,¹¹ in 55% yield after recrystallization. While isolation of this enol product was unexpected, stable enols have been observed in other hindered molecules¹² and in this case serve to emphasize the extreme crowding in the system. Enol **23** does rearrange on silica gel to the aldol product **24**, but a competing retroaldol reaction destroys most of the product. Attempted dehydration of **24** affords only retroaldol products. Dealing with the troublesome hydroxy ketone **24** can be avoided altogether, however, by quenching intermediate **20** with trifluoroacetic anhydride to obtain the very congested olefin **25** directly in a single step.

Although α -keto dianions add to a variety of ketones, it is important to note that simple methyl ketones (e.g., acetone or 2-octanone) undergo mainly enolization by both dianions **6** and **12** under the conditions described (entry 10). These results are difficult to understand in view of the successful addition of dianion **6** to highly enolizable cyclopentanone. Little effort has thus far been expended on this aspect of the problem, however, as normal kinetic aldol condensations at unhindered ketones generally proceed quite well.¹³ Further studies related to the enolization question, as well as applications of these dianion condensations to synthesis (e.g., tetra-*tert*-butylethylene) are currently under way.

(11) **23**: mp $117.5\text{--}119^\circ\text{C}$; IR (CHCl_3) 3250 (enol OH), 1645 ($\text{C}=\text{C}$) cm^{-1} ; NMR (CDCl_3) δ 2.3–2.0 (m, 4 H, allylic), 1.8–1.5 (m, 10 H), 1.27 (s, 6 H, CH_3), 1.12 (s, 6 H, CH_3). Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{O}_2$: C, 76.14; H, 11.18. Found: C, 76.16; H, 10.87.

(12) Hart, H. *Chem. Rev.* **1979**, *79*, 515.

(13) Gaudemar-Bardone, F.; Gaudemar, M. *J. Organomet. Chem.* **1976**, *104*, 281. See also ref 3.

(14) All new compounds afforded proper combustion or exact mass spectral analysis, as well as suitable IR and NMR spectra. Products **5**,¹⁵ **7**,¹⁶ **10**,¹⁷ and **13**¹⁸ were previously reported compounds.

(15) Kossanyi, J.; Furth, B.; Morizeer, J. P. *Tetrahedron* **1970**, *26*, 395.

(16) Nozaki, H.; Oshima, K.; Takai, K.; Ozawa, S. *Chem. Lett.* **1979**, 379.

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Acknowledgment. Support of this investigation was provided by the National Cancer Institute, DHEW, under Grant No. 27157, by the National Science Foundation under Grant No. CHE-8111128, by the 3M Corp. under a 3M Corp. Young Faculty Grant, and by the Lubrizol Corp. via a fellowship to K.W.F. (1980–1981).

Registry No. **4**, 74636-48-9; **6**, 74636-46-7; **8**, 80926-16-5; **9**, 80926-17-6; **11**, 80926-18-7; **12**, 74636-49-0; **14**, 80926-19-8; **15**, 80926-20-1; **19**, 80926-21-2; **21**, 80926-22-3; **22**, 80926-23-4; **23**, 80926-24-5; **24**, 80926-25-6; **25**, 80926-26-7; benzaldehyde, 100-52-7; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 2,2-dimethylpropanal, 630-19-3; 2,4,6-trimethylbenzaldehyde, 487-68-3; 2,2,6,6-tetramethylcyclohexanone, 1195-93-3; acetone, 67-64-1; 2-octanone, 111-13-7.

Cyclohepta-1,2,4,6-tetraene

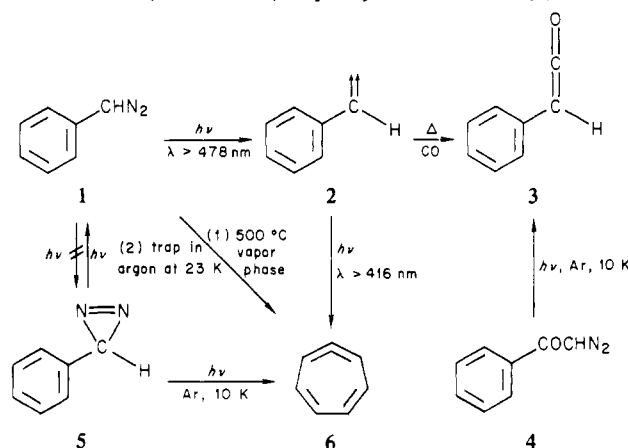
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Despite intense investigation during the past 20 years, spectroscopic observation of phenylmethylene is limited to the ESR spectrum of the triplet ground state,¹ and the structures of the first-formed products from photolysis and thermolysis are not known. We present the infrared and ultraviolet spectra of phenylmethylene and describe the thermal and photochemical ring expansion of phenylmethylene to cyclohepta-1,2,4,6-tetraene.

Irradiation ($\lambda > 478$ nm) of phenyldiazomethane (**1**) matrix-



isolated in argon at 10 K gave phenylmethylene (**2**). The matrix was deposited on cesium iodide for the infrared spectrum (Figure 1a) and on sapphire for the ultraviolet spectrum (Figure 2). The C–H deformations of the phenyl group are changed very little in going from **1** to **2** as is the C–H deformation mode of the methine hydrogen at 445 cm^{-1} . The ultraviolet spectrum of **2** is characterized by highly structured absorptions between 370 and 434 nm with a prominent maximum at 430 nm.² Extinction coefficients were not determined, but the fact that infrared observations could be made on the same matrix shows that the UV extinction coefficients are small. The identity of phenylmethylene was confirmed by an experiment in an argon matrix doped with 0.25% carbon monoxide. After generation of phenylmethylene (infrared monitoring), the matrix was warmed to the softening point, at which point phenylketene (**3**) was formed. Authentic phenylketene was generated by irradiation of diazoacetophenone in argon at 10 K. As a final precaution, phenyldiazirine (**5**) was

(1) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990–4991.

(2) The ultraviolet spectrum is inconsistent with the emission spectrum tentatively ascribed to phenylmethylene.³

(3) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302–1311.

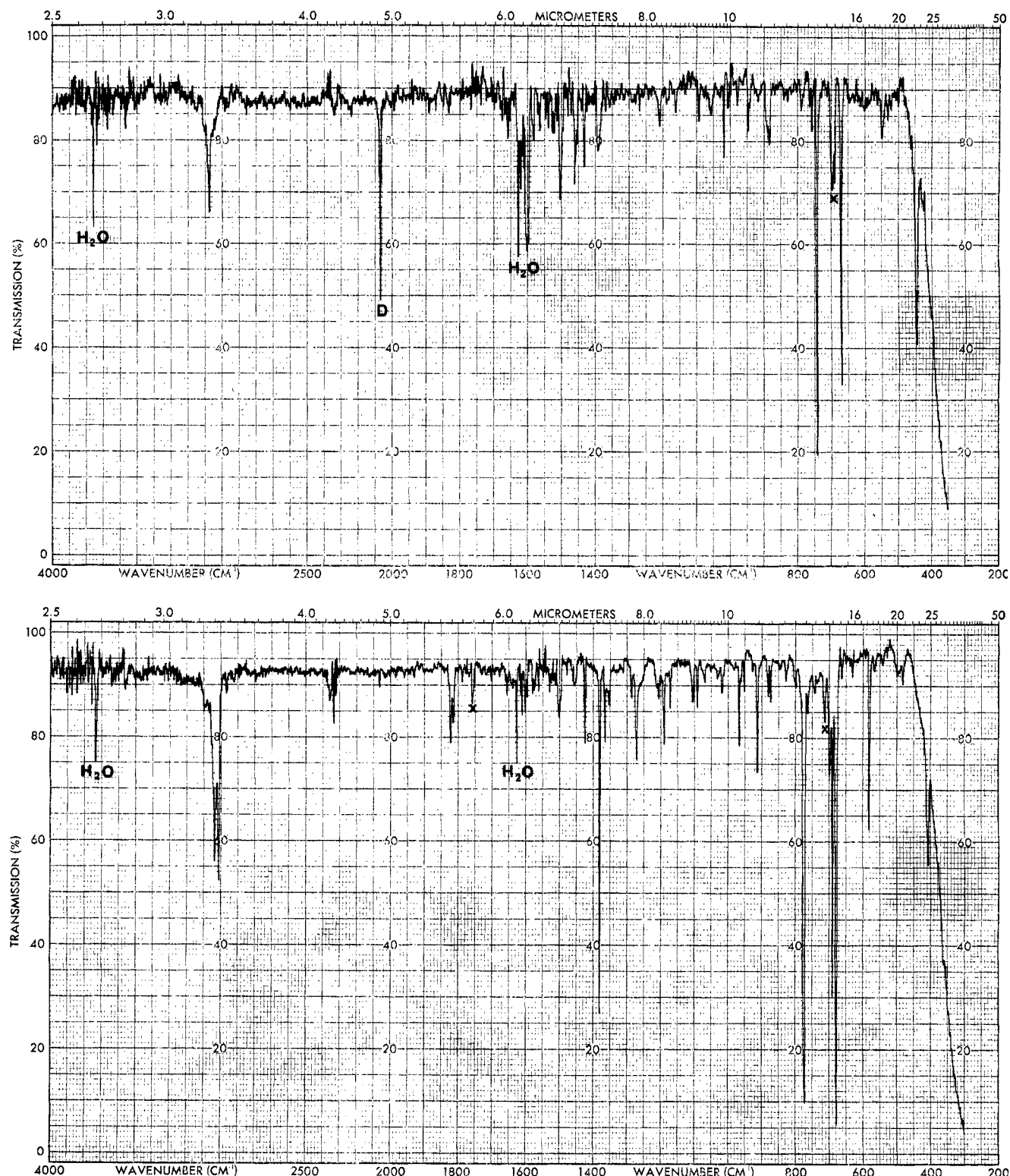


Figure 1. (a) Infrared spectrum of phenylmethylene matrix isolated in argon at 10 K. Residual phenyldiazomethane is designated D. An impurity band is marked X. (b) Infrared spectrum of cyclohepta-1,2,4,6-tetraene matrix isolated in argon at 10 K. Impurity bands are marked X.

prepared and deposited in argon. The infrared spectrum of **5** showed that it was not formed in the irradiation of **1**.

Irradiation of phenylmethylene (**2**) at shorter wavelengths ($\lambda > 416$ nm) gave a new substance with substantially altered C-H deformation modes.⁴ The absorptions characteristic of the phenyl

group and the methine were replaced by a considerably more complex pattern (Figure 1b). The structured UV absorption vanished leaving a broad, intense maximum at 271 nm (Figure 2). Irradiation of phenyldiazirine (**5**) in argon and thermolysis of phenyldiazomethane (**1**) at 500 °C followed by trapping in argon gave the same product obtained from phenylmethylene (**2**).

(4) In the early experiments a band at 1760 cm⁻¹ was observed and attributed to bicyclo[4.1.0]hepta-2,4,6-triene since it occurred at the same frequency as ν_{CC} in authentic cyclopropenes including the benzobicyclo[4.1.0]hepta-2,4,6-trienes.⁶ This 1760-cm⁻¹ band is due to reactions involving oxygen since rigorous exclusion of oxygen eliminates it completely.

(5) West, P. R. Part 1: "Photochemical Transformations of Aryl Diazo-methanes". Part 2: "Preparation and Characterization of Strained Cyclo-alkynes", Ph.D. Thesis, University of California at Los Angeles, Los Angeles, CA, 1980.

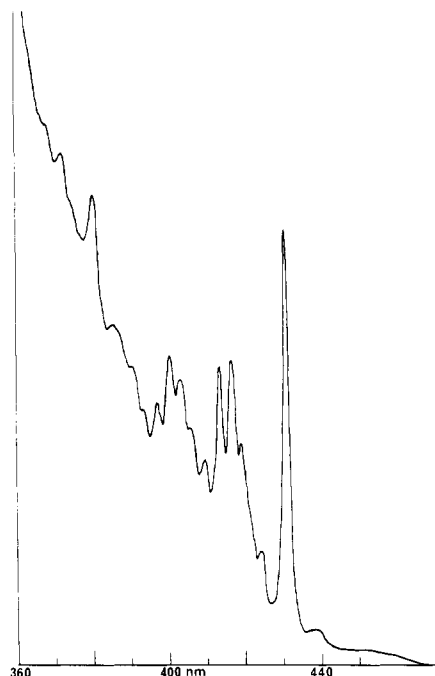


Figure 2. Ultraviolet spectrum of phenylmethylene (2) matrix isolated in argon at 10 K.

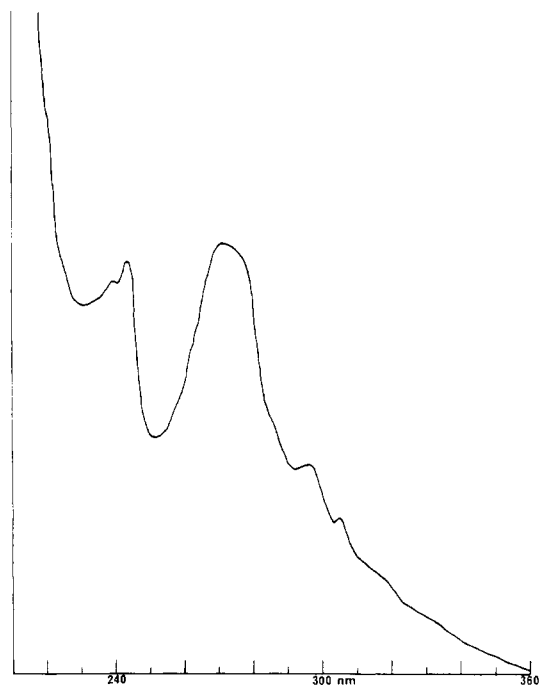
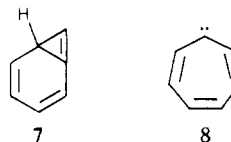


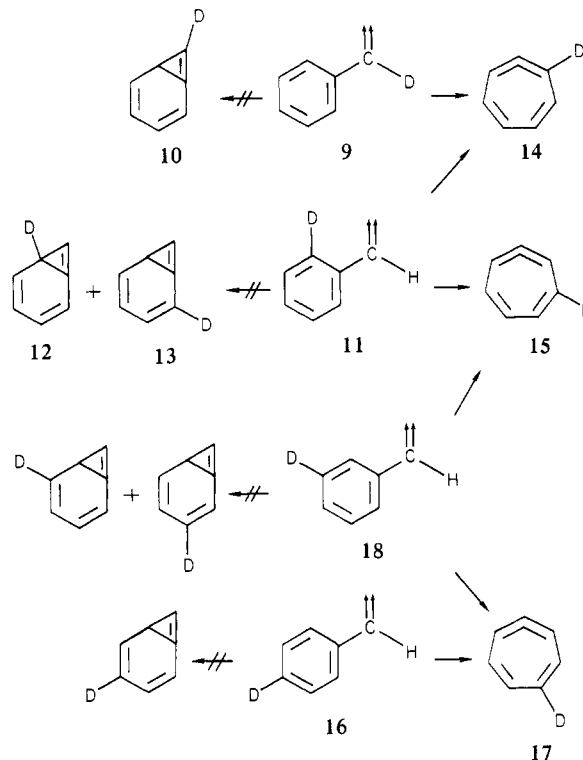
Figure 3. Ultraviolet spectrum of cyclohepta-1,2,4,6-tetraene matrix isolated in argon at 10 K.

Three structures have been considered for the primary product from phenylmethylene, cyclohepta-1,2,4,6-tetraene⁶ (6), bicyclo[4.1.0]hepta-2,4,6-triene⁸ (7), and cycloheptatrienylidene⁹ (8). The product, on warming to room temperature, does not give



heptafulvalene but does give a yellow solid which contains a dimer (m/e 180). Untch had argued earlier that heptafulvalene might be formed from an initial 2 + 2 dimer of 6.⁶ In an argon matrix containing carbon monoxide, warming the product does not produce a ketene. It thus seems reasonable that the product is not cycloheptatrienylidene (8). This conclusion is in agreement with calculations that place cyclohepta-1,2,4,6-tetraene (6), with C_2 symmetry, 13.8⁷ and 15.8¹⁰ kcal/mol lower in energy than planar cycloheptatrienylidene (8). The product shows weak bands at 1824 and 1816 cm^{-1} , very similar to the allene bands of 1-aza-1,3,4,6-cycloheptatetraene.¹¹ This observation together with the absence of the $\sim 1750\text{-cm}^{-1}$ band, ν_{CC} , characteristic of bicyclo[4.1.0]hepta-2,4,6-triene derivatives⁵ and other cyclopropenes¹² with one olefinic hydrogen suggested that the product was cyclohepta-1,2,4,6-tetraene. This conclusion was established by deuterium-labeling studies which rigorously exclude bicycloheptatriene (7).

Cyclization of α -deuteriophenylmethylene (9) would give a single



deuteriobicycloheptatriene (10), and cyclization of (o -deuteriophenyl)methylene (11) would give two bicycloheptatrienes (12, 13). There is thus no common product from (α -deuteriophenyl)methylene and (o -deuteriophenyl)methylene if the product is formed by simple cyclization. In sharp contrast, ring expansion of (α -deuteriophenyl)methylene (9) would give only 1-deuteriocyclohepta-1,2,4,6-tetraene (14),¹³ and ring expansion of (o -deuteriophenyl)methylene (11) would give 14 and 4-deuterio-

(6) The only person to consider cyclohepta-1,2,4,6-tetraene as a possible primary product is K. Untch (see ref 7, footnote 10): Untch, K.; Matthews, G.; Hylton, T. First International Symposium on the Chemistry of Non-benzenoid Aromatic Compounds, Sendai, Japan, Aug 1970. Untch, K., private communication.

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(12) Closs, G. L. *Adv. Alicyclic Chem.* **1966**, *1*, 53-127.

(13) The allene bands at 1824 and 1816 cm^{-1} shifted to 1820 and 1810 cm^{-1} on deuteration. This shift is far below the 40-50- cm^{-1} shift expected for deuteration of cyclopropenes,^{5,12} but it is reasonable for deuteration of allenes.¹⁴

(14) Anderson, C.; Stolevik, R.; Burnvoll, J.; Cyryn, S.; Hagen, G. *Acta Chem. Scand.* **1967**, *21*, 1759-1766.

cyclohepta-1,2,4,6-tetraene (15). The cyclization model and the ring expansion model thus make strikingly different predictions.¹⁵ Irradiation of (*o*-deuteriophenyl)diazomethane gives first (*o*-deuteriophenyl)methylene (11, two rotamers) and then 14 and 15. Subtraction of the infrared spectrum of 14 from the infrared spectrum of the mixture of 14 and 15 gives the spectrum of 15.¹⁶ The identity of 15 is established by independent synthesis. Irradiation of (*p*-deuteriophenyl)diazomethane gives (*p*-deuteriophenyl)methylene (16) and then 5-deuteriocyclohepta-1,2,4,6-tetraene (17). The infrared spectrum of 17 is different from that of either 14 or 15. Irradiation of (*m*-deuteriophenyl)diazomethane gives (*m*-deuteriophenyl)methylene (18) and then simultaneously 15 and 17. Subtraction of the infrared spectrum of 17 from that of the mixture of 15 and 17 gives an infrared spectrum of 15 identical with that from 11. The observation of a common product from 16 and 18 and from 11 and 18 again illustrates the point that cyclization of the aryl methylenes to the bicycloheptatrienes is inconsistent with the results.

The data presented above make it clear that the product formed in the thermolysis and photolysis of phenylmethylene is cyclohepta-1,2,4,6-tetraene.

Acknowledgment. This research was supported by Grant CHE79-00964 from the National Science Foundation and by Grant GM24427 from the National Institute of General Medical Sciences, National Institutes of Health.

Registry No. 1, 766-91-6; 2, 3101-08-4; 3, 3496-32-0; 4, 3282-32-4; 5, 42270-91-7; 6, 52783-93-4.

(15) A ring-expansion, cyclization mechanism leading to bicycloheptatrienes can also be considered. This mechanism has been excluded for 1-naphthylmethylene and 2-naphthylmethylene, which form bicycloheptatrienes by cyclization.⁵ The deuterium-labeling data require ring expansion as a first step.

(16) The subtraction of infrared spectra was accomplished with a Perkin-Elmer Data Station coupled to a 580-B spectrometer.

Acute Bonding Deviation in Square-Planar d⁸ Palladium(II) Complexes¹

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The square-planar coordination of d⁸ palladium(II) complexes has been well documented;³ further, it has been assumed that with bidentate 2,2'-bipyridine ligands, coordination is restricted to the orthogonal N electrons.⁴ In the case of dichloro(2,2'-bipyridine)palladium(II), these assumptions are quite valid;⁵ however, with 6,6'-disubstitution on bipyridine, herein described, drastic deviation from an overall planar configuration is established.

(1) Chemistry of Heterocyclic Compounds. Part 78. Previous related paper in this series: Newkome, G. R.; Kohli, D. K.; Fronczek, F. R. *J. Am. Chem. Soc.* **1982**, *104*, 994.

(2) (a) On leave from University of Delhi, Delhi, India, 1980-1981. (b) On leave from Bloomsburg State College, Bloomsburg, PA, 1980.

(3) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972; p 994. Huheey, J. E. "Inorganic Chemistry: Principles of Structure and Reactivity"; Harper and Row: New York, 1972; p 375.

(4) Brandt, W. W.; Dwyer, F. P.; Gyarfas, E. C. *Chem. Rev.* **1954**, *54*, 959.

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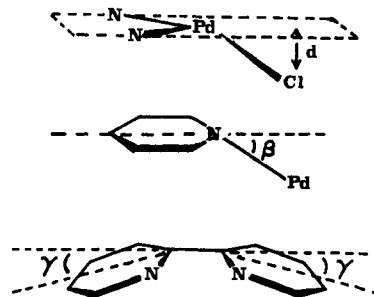
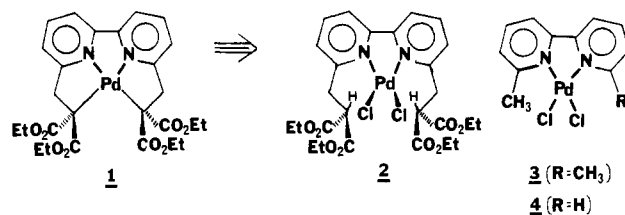


Figure 1. Molecular distortions for (bipyridine)palladium(II) complexes.

Table I. Critical Measurements for the Complexes

| | 2 | 3 | 4 |
|----------------------|------------|-----------|------------|
| Pd-Cl(1), Å | 2.283 (1) | 2.287 (1) | 2.299 (1) |
| Pd-Cl(2), Å | 2.286 (1) | 2.292 (2) | 2.299 (1) |
| Pd-N(1), Å | 2.048 (2) | 2.062 (4) | 2.063 (2) |
| Pd-N(2), Å | 2.040 (2) | 2.050 (4) | 2.023 (2) |
| Cl(1)-Pd-Cl(2), deg | 87.90 (3) | 86.32 (5) | 88.54 (3) |
| N(1)-Pd-N(2), deg | 79.88 (9) | 80.0 (2) | 80.1 (2) |
| N(1)-Pd-Cl(1), deg | 96.15 (7) | 95.9 (1) | 98.17 (6) |
| N(1)-Pd-Cl(2), deg | 168.87 (7) | 167.0 (1) | 173.19 (6) |
| N(2)-Pd-Cl(1), deg | 171.16 (7) | 172.0 (1) | 166.39 (7) |
| N(2)-Pd-Cl(2), deg | 94.62 (7) | 96.2 (1) | 93.70 (6) |
| d ₁ , Å | 0.315 (1) | 0.277 (2) | 0.538 (1) |
| d ₂ , Å | 0.386 (1) | 0.496 (1) | -0.110 (1) |
| β ₁ , deg | 18.5 | 18.8 | 7.3 |
| β ₂ , deg | 18.7 | 16.8 | 15.2 |
| γ ₁ , deg | 10.2 | 7.5 | 6.9 |
| γ ₂ , deg | 10.1 | 8.5 | 6.7 |

Recently we reported the preparation of mono-⁶ and dinuclear⁷ complexes of bipyridine macrocycles as well as the synthesis and biochemical studies of a novel series of stable palladium(II) complexes (1) containing two *cis*-carbon-metal σ bonds.⁸ In light



of the high activity of 1 toward in vitro nicking and binding events in DNA,⁹ we needed to acquire a better molecular picture of not only 1 but also its immediate precursors. The synthesis of 1 proceeds via a stepwise bond-making sequence initiated by complexation of the ligand with either PdCl₂ or PdCl₂(C₆H₅CN)₂.

The orange crystalline complex 2 was characterized by an X-ray crystal structure determination.¹⁰ The geometry of 2 is most unique in that the best plane of the four donor atoms surrounding

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(8) Newkome, G. R.; Onishi, M.; Puckett, W. E.; Deutsch, W. A. *J. Am. Chem. Soc.* **1980**, *102*, 4551.

(9) Simpson, J.; Newkome, G. R.; Deutsch, W. A. *Biochemistry* **1981**, submitted for publication.

(10) Crystal data for 2: C₂₆H₃₂N₂O₃PdCl₂; mw 677.85; monoclinic; space group P2₁/n; a = 12.246 (2), b = 19.644 (13), c = 12.340 (2) Å; β = 97.56 (2)°; Z = 4, d_c = 1.530 g cm⁻³, μ (Mo Kα) 8.52 cm⁻¹; intensities were recorded on an Enraf-Nonius CAD-4 diffractometer and merged to give 3091 unique observed reflections [F > 3σ(F)], R = 0.031. This structure, as well as the others, were solved by the heavy-atom method and refined by full-matrix least-squares methods.