(200); and mass spectrum *m/e* 286, 258, and 243.

The final step, pyrolytic conversion of **9** to **10**, is remarkable in that four bridges are formed in one operation in an overall yield of 57%. The efficiency of the benzocyclobutene dimerization makes possible the total synthesis of [2.2.2.2.2](1,2,3,4,5)cyclophane in six steps from readily available starting materials. Thus, there is no difficulty in obtaining [2.2.2.2.2](1,2,3,4,5)cyclophane in sufficient quantity for a full-scale investigation of its physical and chemical properties and this is underway.

Acknowledgment. We thank the National Science Foundation for their support of this investigation. P.F.T. Schirch thanks the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico do Brasil (CNP_q) for a graduate fellowship.

References and Notes

(1) C. J. Brown and A. C. Farthing, *Nature* (*London*), **164,** 915 (1949).
(2) D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, **73,** 5691 (1951).
(3) B. H. Smith, "Bridged Aromatic Compounds", Academic Press, New York, 1964.
(4) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4,** 204 (1971).
(5) S. Misumi and T. Otsubo, *Acc. Chem. Res.*, **11,** 251 (1978).
(6) K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. R. Soc. London, Ser. A.*, **255,** 82 (1960).
(7) A. W. Hanson, *Acta Crystallogr., Sect. B,* **28,** 2287 (1972).
(8) A. W. Hanson, *Acta Crystallogr., Sect. B,* **33,** 2003 (1977).
(9) H. J. Lindner, *Tetrahedron,* **32,** 753 (1976).
(10) Y. Sekine, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.,* following paper in this issue.
(11) R. Gray, L. G. Harruff, J. Krymowski, J. Peterson, and V. Boekeheide, *J. Am. Chem. Soc.*, **100,** 2892 (1978).
(12) L. G. Harruff, M. Brown, and V. Boekelheide, *J. Am. Chem. Soc.*, **100,** 2893 (1978). Cf. A. J. Barkovich, E. S. Strauss, and K. P. C. Vollhardt, *ibid.*, **99,** 8321 (1977); P. Schiess and M. Heitzmann, *Helv. Chim. Acta*, **61,** 844 (1978).
(13) V. Boekelheide and G. Ewing, *Tetrahedron Lett.,* 4245 (1978).
(14) J. D. Hepworth, D. A. Ibbitson, A. J. Williams, and G. Hallas, *J. Chem. Soc., Perkin Trans. 2,* 2298 (1972). Cf. F. Vögtle, J. Grütze, R. Nätscher, W. Wieder, E. Weber, and R. Grün, *Chem. Ber.,* **108,** 1694 (1975).
(15) Satisfactory elemental analyses and spectral data are available for all new compounds. NMR spectra were measured in deuteriochloroform with tetramethylsilane as an internal standard; mass spectra were measured at 70 eV.

Paulo F. T. Schirch, Virgil Boekelheide*
Department of Chemistry, University of Oregon
Eugene, Oregon 97403

Received February 6, 1979

[2.2.2.2.2.2](1,2,3,4,5,6)Cyclophane: Superphane

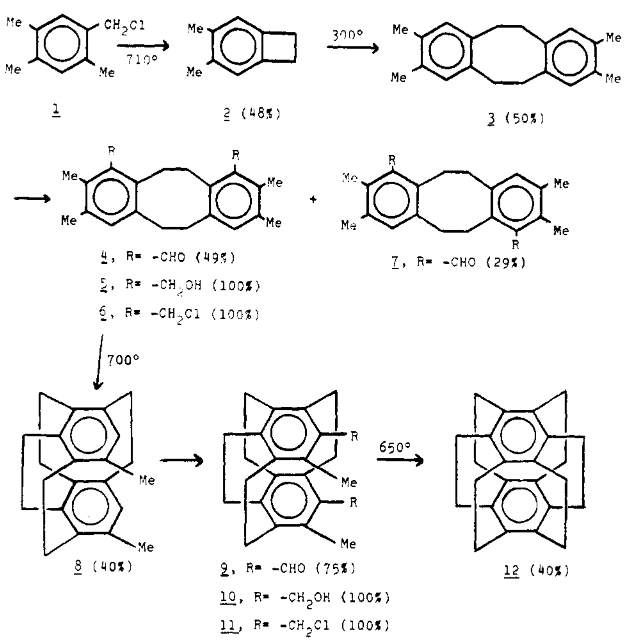
Sir:

In a review on cyclophanes in 1972, Vögtle stated "the ultimate achievement of work in the cyclophane field would be the synthesis of the fully bridged [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane and its hexaene".[1] We now describe a synthesis of [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane (**12**), for which we propose the trivial name superphane.[2]

The dimerization of benzocyclobutenes, as discussed in an accompanying communication,[3] is a powerful method for preparing multibridged cyclophanes. To take advantage of this we designed a synthesis of superphane as an extension of our recent, simple synthesis of [2.2.2.2](1,2,4,5)cyclophane.[4] The overall plan is outlined in Scheme I.

Gas-phase pyrolysis of 2,4,5-trimethylbenzyl chloride (**1**)[5] at 710 °C and 10^{-2} Torr, following the procedure previously described,[6] gave **2** as white crystals: mp 66-68 °C, NMR δ 6.87 (2 H, s, Ar H), 3.17 (4 H, s, $-CH_2$), and 2.29 (6 H, s, $-CH_3$).[7] The dimerization of **2**, by heating it in diethyl phthalate at 300 °C,[8] yielded **3**: white crystals, mp 238-248 °C; NMR δ 6.83 (4 H, s, Ar H), 2.93 (8 H, s, $-CH_2$), and 2.15 (12 H, s, $-CH_3$). Formylation of **3**, by the Rieche procedure,[9] led to a mixture of two aldehydes which, after separation and purification by chromatography over silica gel, gave **4** in 49% yield as white crystals, mp 195-196 °C, and **7** in 29% yield as white crystals, mp 235-239 °C. Spectral data did not allow a clear decision regarding the correct structural assignments and so each was carried independently through the next three-step sequence.

Scheme I



Sodium borohydride reduction of **4** gave **5**, mp 257-259 °C, and this with thionyl chloride yielded **6**, mp 238-240 °C. Pyrolysis of **6** at 700 °C and 10^{-2} Torr produced the desired tetrabridged cyclophane **8** in 40% yield.[10] Purification of **8** by chromatography over silica gel followed by sublimation gave white crystals: mp 219-220 °C; NMR δ 6.17 (2 H, s, Ar H), 3.01 and 2.88 (4 H each, s, $-CH_2$), 3.25-2.40 (8 H, m, $-CH_2$), and 2.06 (6 H, s, $-CH_3$); UV (CH_2Cl_2) λ_{max} 287 nm (ϵ 384), 295 (sh, 354), and 301 (sh, 319). Formation of **8** not only establishes the correct structure of **4** but also provides an example of the previously unknown class of [2.2.2.2](1,2,3,4)cyclophanes.[11]

Formylation of **8** gave the dialdehyde **9**, mp 305-309 °C dec,[12] and this, on reduction with lithium aluminum hydride, yielded the diol **10**: white crystals, mp 273-275 °C dec. The dichloro derivative **11**, mp 215-217 °C, was then obtained by treatment of **10** with thionyl chloride. Pyrolysis of **11** at 650 °C and 10^{-2} Torr led to a white solid which, after sublimation followed by recrystallization from dichloromethane, gave **12** in 40% yield as hard, white crystals; mp 325-327 °C; ^1H NMR, singlet at δ 2.98, and ^{13}C NMR (proton decoupled), singlets at δ 144.2 and 32.3; UV (CH_2Cl_2) broad maximum at 296 nm (ϵ 421), 306 (sh, 394), and 311 (sh, 324); and mass spectrum, *m/e* 312, 284, 256, 156, 141, and 128.

The simplicity of the ^1H and ^{13}C NMR leave no doubt about the structure of **12**. In the mass spectrum of **12**, the parent molecular ion is by far the strongest signal with apparent fragmentation by successive loss of the ethylene bridges. The envelope of signals at 156, 141, and 128 also suggest that fragmentation is occurring to some extent to give hexaradialene.

The outstanding characteristic of the cyclophanes previously prepared has been the "bent and battered" nature of their benzene rings. In contrast, superphane cannot relieve strain to any appreciable extent by distorting its benzene rings. Thus, studies of the physical and chemical properties of superphane should give an interesting insight on the effects of severe strain with planar benzene rings. One of the real advantages of the

0002-7863/79/1501-3126$01.00/0

benzocyclobutene dimerization method is that it is highly efficient and relatively short so that adequate quantities of superphane are readily available for such studies.

With the syntheses of [2.2.2.2](1,2,3,4)-, [2.2.2.2.2]-(1,2,3,4,5)-, and [2.2.2.2.2.2](1,2,3,4,5,6)cyclophanes described in these two communications, all of the possible isomers of the $[2^n]$ series of cyclophanes are now known.[13] However, the benzocyclobutene dimerization method should have broad application for the syntheses of known cyclophanes,[14] as well as for multibridged cyclophanes containing polycyclic and heterocyclic moieties. This potential is being explored.

Acknowledgment. We thank the National Science Foundation for their support of this investigation.

References and Notes

(1) F. Vögtle and P. Neumann, *Angew. Chem.*, **84**, 75 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 73 (1972).
(2) We are indebted to Professor H. Hopf for suggesting this trivial name to us.
(3) P. F. T. Schirch and V. Boekelheide, *J. Am. Chem. Soc.*, preceding paper in this issue.
(4) V. Boekelheide and G. Ewing, *Tetrahedron Lett.*, 4245 (1978).
(5) L. I. Smith and C. W. MacMullen, *J. Am. Chem. Soc.*, **58**, 629 (1936).
(6) R. Gray, L. G. Harruff, J. Krymowski, J. Peterson, and V. Boekelheide, *J. Am. Chem. Soc.*, **100**, 2892 (1978). Cf. P. Schiess, M. Heitzmann, S. Rutschmann, and R. Stäheli, *Tetrahedron Lett.*, 4569 (1978).
(7) Satisfactory spectral data, elemental analyses, and/or high-resolution mass spectra are available for all new compounds being reported. NMR spectra were measured in deuteriochloroform solutions with tetramethylsilane as an internal standard; and mass spectra were measured at 70 eV.
(8) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4267 (1959).
(9) A. Rieche, H. Gross, and E. Höft, *Chem. Ber.*, **93**, 88 (1960).
(10) When **7** was carried through the same sequence, pyrolysis of the corresponding dichloro derivative gave only polymer.
(11) Shortly after completing the synthesis of **8**, we learned from Professor H. Hopf, University of Würzburg, that his research group has successfully prepared the parent molecule, [2.2.2.2](1,2,3,4)cyclophane.
(12) This is accompanied by the corresponding monoaldehyde (25% yield), mp 182–183 °C.
(13) The preparation of the remaining member, [2.2.2](1,2,3)cyclophane, is described in the Undergraduate Thesis of B. Neuschwander, University of Oregon, 1978.
(14) See, for example, the preparation of [2.2.2](1,2,4)cyclophane (G. D. Ewing and V. Boekelheide, *J. Chem. Soc., Chem. Commun.*, in press).

Y. Sekine, M. Brown, V. Boekelheide*
Department of Chemistry, University of Oregon
Eugene, Oregon 97403
Received February 6, 1979

Heterogeneous Photosynthetic Production of Amino Acids from Methane–Ammonia–Water at Pt/TiO_2. Implications in Chemical Evolution

Sir:

Previous studies from this laboratory have demonstrated that irradiation of platinized n-type TiO_2 suspensions with a xenon lamp or sunlight can promote several solution reactions, such as the photo-Kolbe reaction, in which acetic acid is decomposed to methane and CO_2.[1,2] Recent experiments employing spin trapping methods and electron spin resonance detection during illumination of aqueous solutions containing such suspensions[3] have demonstrated the intermediacy of hydroxyl radicals under these conditions.[4] The presence of such a reactive intermediate suggested the possibility of synthesis of amino acids by irradiation of methane–ammonia–water mixtures in the presence of semiconductor powder suspensions; electrical discharges through similar gaseous mixtures are known to produce amino acids.[5,6]

Irradiation of 20 mL of aqueous 2 M NH_4Cl or NH_3 (~28%) solutions, deaerated first with nitrogen or argon, under slow continuous bubbling of methane in the presence of 100 mg of Pt/TiO_2[7] with a 2.5-kW xenon lamp operated at 1.6 kW for 64–66 h produced a mixture of amino acids. The total yield of amino acids was ~0.5 μmol for the NH_4Cl and ~0.2 μmol for the aqueous NH_3, with the mixture consisting of glycine, alanine, serine, aspartic acid, and glutamic acid. Analysis was carried out with a Beckman Model 120C amino acid analyzer and the identity and amount of acid was estimated by comparison with a standard mixture.[8] An additional, as yet unidentified, peak was found in the irradiated mixture sample which was not present in the standard. Several control experiments were also carried out to eliminate the possibility of sample contamination or other paths as the source of the amino acids (Table I).

Table I. Effect of Solution, Light, and Catalyst on Photosynthesis of Amino Acids

solution composition[a]	catalyst[b]	illumination[c]	amino acids yield, μmol
NH_3, H_2O, CH_4	Pt/TiO_2	Xe lamp, 66 h	~0.2
2 M NH_4Cl, CH_4	Pt/TiO_2	Xe lamp, 64 h	~0.5
	Control Experiments		
2 M NH_4Cl, CH_4	Pt/TiO_2	none, 66 h	none[d]
2 M NH_4Cl, CH_4	none	Xe lamp, 66 h	none[d]
2 M NH_4Cl, CH_4	TiO_2(a,u)	Xe lamp, 66 h	none[d]
2 M NH_4Cl	none	none	none[d]

[a] 20 mL of deaerated solution under continuous addition of CH_4. [b] 100 mg of Pt/TiO_2[7] or unreduced anatase(a,u). [c] 2.5-kW xenon lamp operated at 1.6 kW. [d] Less than 1 nmol.

The results demonstrate the heterogeneous photosynthesis of amino acids under irradiation with visible and near-UV light. The action spectrum for this reaction probably corresponds to that found for the photo-Kolbe reaction with Pt/TiO_2, with a threshold at 420 nm.[9] The mechanism of the process, which is currently under investigation, begins with production of holes and electrons upon light absorption by the TiO_2. Oxidation leading to the amino acids then could proceed upon production of OH radicals, and probably other intermediates (e.g., $\cdot NH_2$). Reaction of OH radicals with methane leading to CH_3 radicals is well documented.[10] Reduction occurs at the Pt sites, leading to H atoms[4] and, ultimately, under these reducing conditions, to H_2. The absence of reaction with unplatinized TiO_2 can be ascribed to inefficient reductive sites for hydrogen production in this case, as has been previously found for other photocatalytic processes.[1] Photocatalytic oxidation at TiO_2 alone could probably take place in the presence of easily reducible substances, such as oxygen or ferric iron. The overall reaction as described here at Pt/TiO_2, however, is photosynthetic, involving a net storage of light energy. For example for the overall reaction

$$2CH_4 + NH_3 + 2H_2O \rightarrow H_2NCH_2COOH + 5H_2$$

$\Delta G^\circ = 55.4$ kcal/mol.[11]

The results reported here may also be relevant to the initial stages of chemical evolution and the prebiological synthesis of organic compounds from components of the reducing Precambrian atmosphere.[12,13] While previous experiments have shown similar synthesis using rather energetic sources, e.g., electric discharges or UV light,[5,6] these results demonstrate this synthesis in solution with radiation characteristic of the terrestrial solar spectrum.[14] The continuous production of such species by inorganic systems such as TiO_2 under solar irradiation could have been a source of nutrients for the initially evolved heterotrophic organisms and served as an abiotic form of photosynthesis until biological photosynthetic systems based on chlorophyll evolved; other aspects of the chemical evolution of photosynthesis have been discussed recently.[16] Heterogeneous photoprocesses such as those described could also have contributed to the nonbiological production of early Precambrian oxygen; arguments against total biological sources for atmospheric oxygen have appeared.[17] While Pt/TiO_2 itself

0002-7863/79/1501-3127$01.00/0