adsorbed pyrene, currently being carried out, will help to clarify these shifts in the triplet energy states.

The results demonstrate that the flash photolytic technique can be extended to photolysis in the adsorbed state and that significant changes can be anticipated in the lifetime, spectra, and, perhaps, the chemistry of adsorbed excited species. Work is in progress to extend this investigation to shorter times using a laser flash and to study the behavior of radical and ionic transients in the adsorbed state.

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Paul L. Piciulo, James W. Sutherland*
Department of Energy and Environment
Brookhaven National Laboratory, Upton, New York 11973
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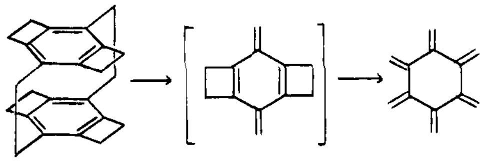
[2.2.2.2.2](1,2,3,4,5)Cyclophane

Sir:

Di-*p*-xylylene and its crystal structure were first reported just 30 years ago.[1] The importance of this observation was immediately recognized by Cram,[2] who introduced the cyclophane nomenclature and systematically prepared a large number of structures having aromatic rings held face to face in rigid cages. The value of cyclophanes as models for testing all manner of questions of bonding, strain, and π-π electron interactions has resulted in a phenomenal growth of interest in the field.[3-5] From the beginning, one of the most intriguing questions has been the nature of the π-electron interaction when two aromatic rings are crowded together face to face and the limit to which such crowding can be forced. Whereas the mean planar distance between benzene rings in [2.2]paracyclophane is 3.09 Å,[6] it is only 2.80 Å in [2.2.2](1,3,5)cyclophane-1,9-diene,[7] and 2.69 Å in [2.2.2.2](1,2,4,5)cyclophane.[8] The theoretical calculations of Lindner predict that [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane will have a mean planar distance between rings of only 2.60 Å with the molecule having a total strain energy of 60–79 kcal/mol.[9] Thus, the change in geometry and strain energy as additional bridges are added is of special interest.

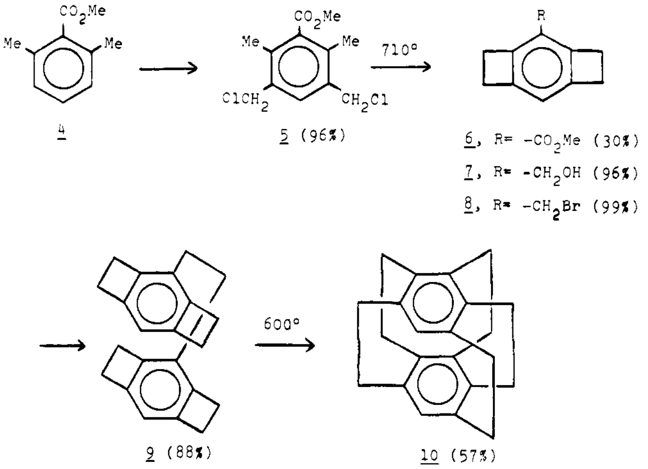
The preparation of multibridged cyclophanes in the normal way of adding a bridge at a time is exceedingly long, and so the synthesis of higher examples of multibridged cyclophanes has awaited the development of new methods. We now report that the dimerization of benzocyclobutenes provides an efficient and relatively short method for synthesizing multibridged cyclophanes. In this communication we describe the preparation of [2.2.2.2.2](1,2,3,4,5)cyclophane (**10**) and, in the accompanying communication, the synthesis of [2.2.2.2.2.2](1,2,3,4,5,6)cyclophane (superphane).[10]

The concept of using the dimerization of benzocyclobutenes to introduce multiple bridges in cyclophanes was first proposed for the case of [2.2](3,6)benzo[1,2;4,5]dicyclobutenophane (**1**).[11] Unfortunately, pyrolysis of **1** led to hexaradialene (**3**),[12] presumably due to the preferential cleavage to the *p*-xylylene intermediate **2** rather than to the desired multi-*o*-xylylene intermediate. Subsequently, the basic idea of benzocyclobutene dimerization to prepare multibridged cyclophanes was demonstrated by a simple, practical synthesis of [2.2.2.2](1,2,4,5)cyclophane.[13] Therefore, we turned our attention to the benzycyclobutene derivative **9**, which can no longer undergo thermal cleavage to a *p*-xylylene intermediate.



1 2 (?) 3

As summarized in the reaction scheme, chloromethylation of methyl 2,6-dimethylbenzoate (**4**)[14] readily gave **5** as white crystals, mp 105–106 °C.[15] Gas-phase pyrolysis of **5** at 710 °C and 10^{-2} Torr, following the procedure described previously,[11] led to **6** (white crystals, mp 98.5–99.5 °C). Reduction of **6** with lithium aluminum hydride yielded **7** (white crystals, mp 109–110 °C), which on treatment with phosphorus tribromide gave **8** (white crystals, mp 60–62 °C). Conversion of **8** to the Grignard by treatment with magnesium in tetrahydrofuran followed by addition of anhydrous ferric chloride gave the coupling product **9** as white crystals: mp 198.5–199.5 °C; NMR δ 6.63 (2 H, s, Ar H), 3.04 (16 H, s, $-CH_2$), and 2.77 (4 H, s, $-CH_2$). Pyrolysis of 174 mg of **9** at 600 °C and 0.05 Torr yielded a white solid which, after chromatography over silica gel using a benzene-hexane mixture for elution, gave 100 mg (57%) of [2.2.2.2.2](1,2,3,4,5)cyclophane (**10**) as white crystals: mp 334–336 °C dec; NMR δ 6.05 (2 H, s, Ar H), 2.92 (4 H, s, $-CH_2$), 2.82 (8 H, d, J = 2.5 Hz), and 2.56–3.33 (8 H, AA′BB′, $-CH_2$); UV (THF) λ_{max} 294 (ϵ 352) and 313 nm



4 5 (96%)

6, R= $-CO_2Me$ (30%)
7, R= $-CH_2OH$ (96%)
8, R= $-CH_2Br$ (99%)

9 (88%) 10 (57%)

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(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.

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

Received February 6, 1979

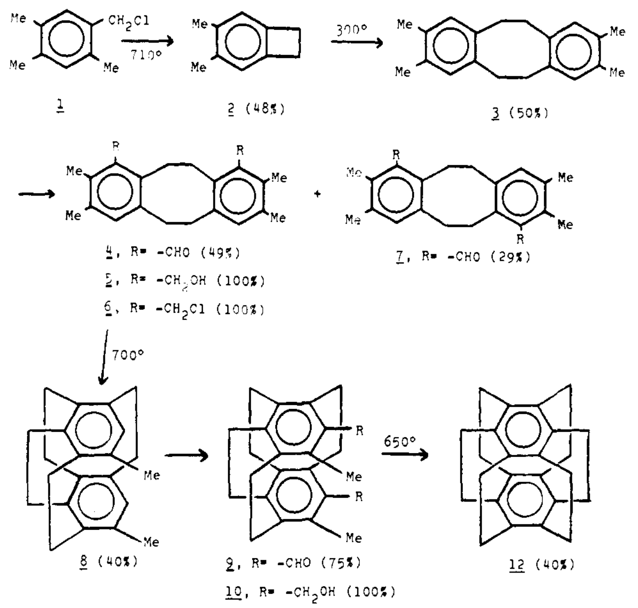
[2.2.2.2.2.2](1,2,3,4,5,6)Cyclophane: Superphane

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.

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.

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

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