

Secondly, the small upfield shift of I relative to 5-fluoroindan (+0.24 and +0.21 ppm) in cyclohexane and DMF, respectively, together with the downfield shift of III relative to 6-fluorotetralin (-0.67 ppm in cyclohexane; -0.43 ppm in DMF) suggests that the inductive field effect of the C-Si bond is extremely small. In fact, the relative downfield shift of III is opposite to what is expected from simple inductive effects emanating from the electropositive silicon. Although it is tempting to attribute the origin of the downfield shift to the likely formal positive charge residing on the carbon atom adjacent to fluorine (due to alternating polarization of the π system), recent experimental results indicate that ^{19}F chemical shifts in structurally similar aryl fluorides are sensitive to geometrical distortion.⁹ The chemical-shift difference between III and 6-fluorotetralin undoubtedly reflects a conformational subtlety between the two systems.^{6,10}

The conclusions from this study are in agreement with the recent proposals of Eaborn and coworkers² and Traylor and coworkers.³ Our recent suggestion¹⁰ that the large "hyperconjugative $\sigma-\pi$ " interaction of metallo substituents in the neutral ground state is due to the inductive effect (field and π -inductive effects) needs reappraisal along the present lines. Our work in this area continues.

Acknowledgment. We are extremely grateful to Dr. I. Rae of Monash University for his services in obtaining the ^{19}F nmr spectra and are grateful to the Australian Research Grants Committee for their partial support of this work.

(9) W. Adcock, J. Alste, and M. A. Zeb, unpublished work.

(10) An inspection of Dreiding models shows that whereas the benzylic hydrogens in 6-fluorotetralin (half-chair) are staggered around 8 H, they are eclipsed in III (half-boat) leading to "peri-like" interactions as in naphthalene.

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A Directed Synthesis of

cis-anti-cis-Tricyclo[6.4.0.0^{2,7}]dodecatetraene
(*o,o'*-Dibenzene). Thermal Rearrangement of a
Blocked Dibenzene to a Caged (CH)₁₂ Precursor¹

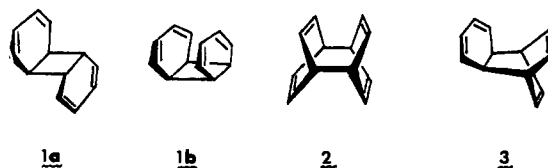
Sir:

There is special interest in the cycloaddition dimers of benzene, a subset of the (CH)₁₂ series,² because the

(1) This work was supported in part by grants from the National Science Foundation (GP 11017X) and the Hoffmann-La Roche Foundation.

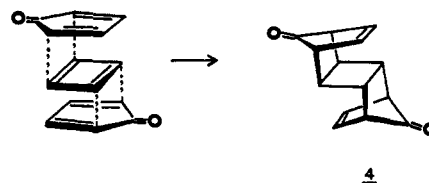
(2) For references to examples of (CH)₁₂, see (a) G. Schröder and W. Martin, *Angew. Chem., Int. Ed. Engl.*, **5**, 130 (1966); (b) G. Schröder, *ibid.*, **2**, 481 (1963); (c) J. N. Labows, Jr., J. Meinwald, H. Röttele, and G. Schröder, *J. Amer. Chem. Soc.*, **89**, 612 (1967); (d) L. A. Paquette and J. C. Stowell, *ibid.*, **93**, 5735 (1971); *Tetrahedron Lett.*, 4159 (1969); (e) H. Röttele, W. Martin, J. F. M. Oth, and G. Schröder, *Chem. Ber.*, **102**, 3985 (1969); (f) G. Schröder, W. Martin, and H. Röttele, *Angew. Chem., Int. Ed. Engl.*, **8**, 69 (1969); (g) E. Le Goff and S. Oka, *J. Amer. Chem. Soc.*, **91**, 5665 (1969); (h) J. F. M. Oth, H. Röttele, and G. Sch-

concerted thermal dissociations of the *anti-o,o'*, *syn-o,o'*, and *p,p'* isomers **1a**, **1b**, and **2** to two molecules of benzene are "forbidden" by orbital symmetry, but that of the *o,p'* isomer **3** is "allowed."³ The rates of dis-



sociation therefore could provide an estimate of the magnitude of the orbital symmetry forces in a cycloreversion reaction. The first preparation of a member of this series is due to Schröder, who found the *anti-o,o'* dimer **1a** (9% yield) among the thermal transformation products of [12]annulene.^{2e,f,h,i,4} We report here a directed synthesis of **1a** by a method which affords the hydrocarbon free of side products and which, because of a new rearrangement developed en route, may be adaptable to the *syn* isomer **1b** and other (CH)₁₂ compounds.

The key step in each of two synthetic approaches we have studied is the unmasking of a disguised cyclohexadiene system. Conceptually, the first route involves the construction of a precursor of the tricyclic skeleton by addition of two cyclopentadienone equivalents to a cyclobutadiene unit to give **4**. The synthetic steps



consist of KO-*t*-Bu-Me₂SO dehydrohalogenation of the dimethoxytetrachlorocyclopentadienone (DMTC)-3,4-dichlorocyclobutene adduct⁶ to a pentachlorodiene,⁷ dechlorination to the tricyclic ketal **5**,⁷ Diels-Alder addition of another mole of DMTC followed by dechlorination to **6**,⁷ and hydrolysis to the volatile, crystalline diketone **4**.⁷

Pyrolysis of **4** (102° in C₆D₆NO₂) or photolysis (2537 Å, -15°, a temperature at which **1a** is thermally stable^{2e,f,h,i}) give only benzene and CO. Whether **1a** is an intermediate in these reactions cannot be stated with confidence, since it undergoes pyrolytic and photochemical cycloreversion to benzene under the above conditions more readily than diketone **4** decarbonylates.

Pyrolysis of **4** in the presence of excess dimethylacetylene dicarboxylate suppresses the formation of benzene and gives the diadduct **7** of **1a**, identified by

röder, *Tetrahedron Lett.*, **61** (1970); (i) J. F. M. Oth, J. M. Gilles, and G. Schröder, *ibid.*, **67** (1970).

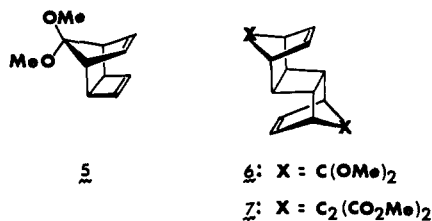
(3) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N.Y., 1970; (b) *cf.* also D. Bryce-Smith, *J. Chem. Soc. D.*, 806 (1969).

(4) Dibenzene **1a** is a plausible but at present not obligatory intermediate in the formation⁵ of its maleic anhydride (MA) bisadduct or benzene from the action of NaI on 3,6,9,12-tetramethanesulfonoxycyclo[6.4.0.0^{2,7}]dodeca-4,10-diene in the presence or absence of MA, respectively.

(5) E. H. Gold and D. Ginsburg, *J. Chem. Soc. C*, 15 (1967).

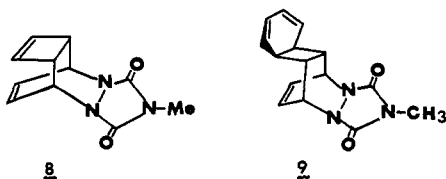
(6) M. Avram, I. G. Dinulescu, G. H. D. Mateescu, and C. D. Nenitescu, *Rev. Roum. Chim.*, **13**, 505 (1966).

(7) All new substances reported had the correct molecular composition by either combustion analysis (Alfred Bernhardt) or high-resolution mass spectrometry (for which we thank Dr. W. J. McMurray of the Division of Health Science Resources at Yale).



melting point and by comparison of ir and nmr spectra with those of an authentic sample kindly supplied by Professor Schröder. Observation of the course of this reaction by nmr spectroscopy provides evidence that diadduct formation occurs by generation and entrapment of first one and then the other of the cyclohexadiene moieties. This suggests that in the absence of dienophile a similar stepwise decarbonylation may occur and that the resulting monoketone may decompose without ever forming **1a**.

The alternative route avoids this difficulty by the use of two different masking groups, the second of which can be removed under very mild conditions. Debromination of the cyclooctatetraene⁸ dibromide-*N*-methyltriazolinedione adduct with zinc gives **8**.^{7,9} The cyclobutene double bond of this intermediate can be made to function selectively as a dienophile toward α -pyrone,¹⁰ and the resulting lactonic adduct⁷ suffers smooth decarboxylation at 160° in *o*-dichlorobenzene to give the singly-masked precursor **9**.⁷



Hydrolysis of **9** with boiling KOH-*i*-PrOH gives the corresponding semicarbazide, which can but need not be isolated. Direct treatment of the neutralized hydrolysis mixture with CuCl₂¹¹ under N₂ at 0° gives (presumably *via* the unstable azo compound) the dibenzene **1a** in 35% yield.

A hypothetical rearrangement scheme for effecting a face-to-face juxtaposition of the two cyclohexadiene moieties would involve reversible ring opening of the tricyclic system of the anti isomer **1a** to a bicyclo[6.4.0]dodecapentaene and recyclization in the syn form **1b**. This is impractical in the hydrocarbon system because of the instability of **1a**, but a related anti \rightarrow syn rearrangement can be effected in the protected compound **9**. Prolonged heating of **9** at 160° results in gradual conversion to the hexacyclic derivative **10**.⁷ The nmr spectrum of this substance shows an N-Me singlet (3 H, δ 3.05) and six two-proton absorptions at δ 6.24, 4.28, 2.93, 2.69, 2.34, and 2.17. Its mass spectrum shows a strong parent peak at *m/e* 269 (base peak of the spectrum), in contrast to that of **9**, which shows a relatively weak parent peak and a base peak at *m/e* 78,

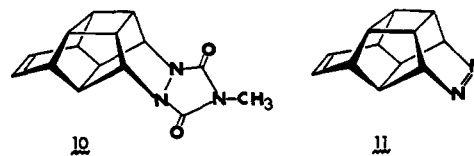
(8) We are grateful to Dr. H. Pommer and the Badische Anilin und Soda Fabrik, Ludwigshafen, for a generous sample of cyclooctatetraene.

(9) For the *N*-phenyl analog, see D. G. Farnum and J. P. Snyder, *Tetrahedron Lett.*, 3861 (1965).

(10) Prepared according to H. E. Zimmerman, G. L. Grunewald, and R. M. Pauffer, *Org. Syn.*, 46, 101 (1966).

(11) Cf. M. Heyman, V. T. Bandurco, and J. P. Snyder, *J. Chem. Soc., D*, 297 (1971). We are indebted to these authors for personal communication of further details of their method of azoalkane synthesis.

corresponding to C₆H₆⁺. This rearrangement must involve a bicyclooctadiene \rightarrow cyclooctatriene valency tautomerism in the anti compound **9**, reclosure in the syn stereochemistry, and intramolecular entrapment of the cyclohexadiene by a Diels-Alder reaction. Hydrolysis and oxidation of **10** give the pentacyclic azo compound **11**.⁷ Although efforts to eliminate N₂ from



11 so far have been unsuccessful, methods for converting this azo compound or similar substances with other masking groups to **1b** (and/or **2**, which is related hypothetically to **1b** by Cope rearrangement) or to other (CH)₁₂ compounds are under investigation.

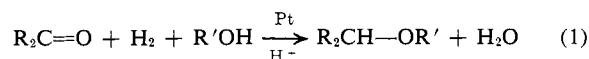
(12) Supported by a Predoctoral Fellowship (GM-40, 824), sponsored by the National Institute of General Medical Sciences, 1968-1971.

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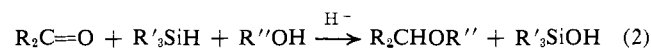
Silane Reductions in Acidic Media. I. Reduction of Aldehydes and Ketones in Alcoholic Acidic Media. A General Synthesis of Ethers

Sir:

Acetals and ketals,¹ aldehydes and ketones,² and esters and lactones³ have been reduced to ethers using a variety of reducing agents. Of these methods the catalytic hydrogenation of aldehydes and ketones in alcoholic acidic media (eq 1) appears to provide the most



general and convenient route to symmetrical and unsymmetrical ethers.² However, hydrocarbon formation competes with ether production, and yields are low when aldehydes are reduced or when the alcohol used is larger than propyl.^{2a} We wish to report that trialkylsilanes reduce aldehydes and ketones in alcoholic acidic media to ethers. In a reaction analogous to that given in eq 1, the use of alcohols directs product formation to the ethers and trialkylsilanol (eq 2).



In a typical experiment 1.0 ml of 97% sulfuric acid was added dropwise to a stirred solution of methanol (2.5 ml) containing benzaldehyde (5.0 mmol) and triethylsilane (5.5 mmol) at 0°. The resulting heterogeneous⁴ solution was warmed to room temperature

(1) (a) W. L. Howard and J. H. Brown, Jr., *J. Org. Chem.*, 26, 1026 (1961); (b) E. L. Eliel, V. G. Badding, and M. N. Rerick, *J. Amer. Chem. Soc.*, 84, 2371 (1962); (c) I. A. Kaye and I. C. Kogon, *ibid.*, 73, 4893 (1951); (d) E. Frainnet and C. Esclamadon, *C. R. Acad. Sci.*, 254, 1814 (1962).

(2) (a) M. Verzele, M. Acke, and M. Anteunis, *J. Chem. Soc.*, 5598 (1963); (b) M. Acke and M. Anteunis, *Bull. Soc. Chim. Belges*, 74, 41 (1965).

(3) G. R. Pettit and D. M. Piatak, *J. Org. Chem.*, 27, 2127 (1962), and previous articles in this series.

(4) Silane and silanol are only partially soluble in the reaction medium.