

The Reaction of 6,6-Dibromobicyclo[3.1.0]hexane with Methylolithium. Evidence for the Generation of 1,2-Cyclohexadiene and 2,2'-Dicyclohexenylene¹

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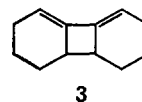
Abstract: The reaction of 6,6-dibromobicyclo[3.1.0]hexane (**1**) with methylolithium in ether gives no products derived from a carbene. At -80° the major products are two $C_{24}H_{32}$ stereoisomers **4a** and **4b**. Structures have been assigned on the basis of spectral properties and degradative studies. In refluxing ether the major product is the $C_{12}H_{16}$ dimer **3a**. These results indicate that **1** leads to the generation of 1,2-cyclohexadiene (**2**) which rapidly dimerizes to form a biradical, 2,2'-dicyclohexenylene (**16**). This biradical undergoes stereospecific cyclization to form only **3a** or, at low temperatures, it accumulates sufficiently to dimerize to only **4a** and **4b**.

A wide variety of allenes can be generated by treatment of *gem*-dibromocyclopropanes with organolithium reagents.³ This reaction undoubtedly proceeds through an α -bromolithium intermediate which as a carbenoid species undergoes elimination of lithium bromide to generate the allene, possibly passing through a carbene or complexed carbene. In cases where the allene would be highly strained, other reactions may intervene. Thus the dibromocarbene adduct of cyclohexene reacts with methylolithium to form an array of products from insertion and coupling, but no products which are derived from an allene intermediate.⁴ In view of this result, the dibromocarbene adduct of cyclopentene (**1**) might be expected to show even less tendency to generate an allene inasmuch as 1,2-cyclohexadiene (**2**), the allene which would be produced, certainly must be extraordinarily strained. Nevertheless, as we discuss below, **1** serves as an efficient source of **2**.

Domnin⁵ attempted to prepare **2** by treatment of 2,3-dichlorocyclohexene with zinc under various conditions. In addition to several halogenated products, he obtained a hydrocarbon fraction which he thought may have been a tetramer of C_6H_8 as well as polymeric material.

Ball and Landor⁶ attempted to prepare **2** by treatment of 1-chlorocyclohexene with sodium amide in liquid ammonia but reported only nonvolatile materials believed to be polymeric. Wittig and Fritze⁷ obtained evidence for the generation of **2** in the treatment of 1-bromocyclohexene with potassium *t*-butoxide in dimethyl sulfoxide. They obtained two stereoisomeric adducts of C_6H_8 with 1,3-diphenylisobenzofuran in 41% combined yield (one adduct slowly dehydrated). In the absence of the trapping agent, they obtained a

7% yield of a C_6H_8 dimer to which they assigned structure **3**.



We have found that analysis of the mixtures of products obtained from the reaction of **1** with methylolithium in ether under a variety of conditions shows that no C_6H_8 compounds are formed; all products have much higher molecular weights.⁸ At -80° the major products prove to be "tetramers" (C_6H_8)₄. In refluxing ether, a dimer (C_6H_8)₂ is the principal product. The same products are obtained in essentially unchanged yields when the reactions are performed in the presence of cyclohexene, isobutylene, and furan; no adducts with these compounds are formed. Styrene proved to be an efficient trapping agent, giving a 76% yield of a 1:1 styrene- C_6H_8 adduct.¹¹ In this paper, we discuss the structures of the tetramers and the dimer and the significance of their formation.

Tetramers. Addition of methylolithium to a dilute solution of **1** in ether at -80° gave a mixture of products which by glpc analysis was shown to consist of mainly tetramers **4** (61%) accompanied by smaller amounts of "trimeric" materials (13%). The reaction was fast since hydrolyzing after 5 min at -80° gave no change in the product composition. Increasing the concentration of **1** (preparative-scale reactions) lowered the yields of **4** to 40–50%. Addition of **1** to methylolithium or the use of butyllithium at -80° led to the same products.

By a combination of crystallization and elution chromatography, **4**, a single peak on glpc, was resolved into two colorless crystalline compounds in a 3:1 ratio: **4a** and **4b**. Elemental analysis, mass spectrometry, and (for **4a**) freezing point depression and vapor

(1) Acknowledgment is made to the National Science Foundation (GP-1306) and to the donors of the Petroleum Research Fund administered by the American Chemical Society (1549-A4) for support of this research.

(2) National Institutes of Health Predoctoral Fellow, 1960–1964.

(3) (a) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); (b) W. R. Moore and H. R. Ward, *ibid.*, **27**, 4179 (1962); (c) L. Skattebøl, *Tetrahedron Lett.*, 167 (1961).

(4) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Amer. Chem. Soc.*, **83**, 2019 (1961).

(5) N. A. Domnin, *J. Gen. Chem. USSR*, **15**, 461 (1945).

(6) W. J. Ball and S. R. Landor, *J. Chem. Soc.*, 2298 (1962).

(7) G. Wittig and P. Fritze, *Ann.*, **711**, 82 (1968); *Angew. Chem.*, **78**, 905 (1966).

(8) We have found that 2-bromo-3-methylcyclohexene⁹ is formed from the alkylation of 2,3-dibromocyclohexene and not from reaction with **1** as initially reported. Compound **1** undergoes facile thermal¹⁰ and Lewis acid catalyzed rearrangement to the allylic isomer. The reaction of the allylic dibromide with other lithium reagents will be described elsewhere (W. R. Moore, L. N. Bell, and W. R. Moser).

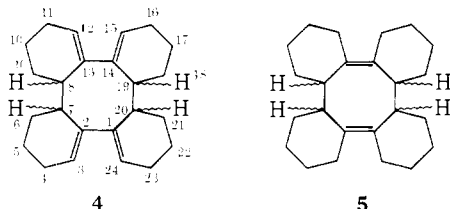
(9) W. R. Moore and H. R. Ward, *Chem. Ind. (London)*, 549 (1961).

(10) J. Sonnenberg and S. Winstein, *J. Org. Chem.*, **27**, 748 (1962).

(11) W. R. Moore and W. R. Moser, *ibid.*, **35**, 908 (1970).

pressure lowering in benzene established that the compounds both had the molecular formula $C_{24}H_{32}$. Their mass spectra were very similar and their glpc retention times were identical.¹² Nmr spectra¹³ of **4a** and **4b** established that both have four vinyl, twelve allylic, and sixteen nonallylic protons. Both compounds absorb strongly in the far-ultraviolet¹³ but neither shows a maximum above 190 nm. Quantitative microhydrogenation of **4a** over platinum in acetic acid established the presence of 4.0 double bonds per molecule, a number verified by quantitative¹⁴ bromination.

At this point, based on both spectral data and mechanistic considerations, it appeared clear to us that the tetramers were two of the stereoisomers having the general formula **4**. At first inspection, **4** would not



appear to fit the ultraviolet data inasmuch as it has two tetrasubstituted butadiene moieties which might be expected to give an intense absorption maximum at *ca.* 235 nm. However, examination of molecular models shows that the conjugated double bonds of **4** (all stereoisomers) must be substantially skewed and as a consequence the absorption must suffer a large shift to shorter wavelengths.¹⁵

The major tetramer **4a** was reduced rapidly by lithium in liquid ammonia containing tetrahydrofuran and *t*-butyl alcohol to a crystalline tetrahydro derivative (isolated in 38% yield) and a residual oil.¹⁶ The nmr and ultraviolet spectra of the crystalline compound indicate that it must have two tetrasubstituted double bonds (di-1,4 reduction) and thus it must be one of the stereoisomers of general structure **5**.

Ozonolysis of **5** gave a single volatile product, which was shown to be the crystalline stereoisomer of bicyclohexyl-2,2'-dione (**6**).¹⁷ Criegee and Reinhardt¹⁸ have provided evidence recently that this crystalline compound is the *meso* isomer **6a** as would be predicted on the basis of earlier work.¹⁹

(12) Both compounds underwent rearrangement to unidentified materials if the chromatographic conditions were not carefully controlled.

(13) Spectral data are given in the Experimental Section.

(14) H. M. Buckwalter and E. C. Wagner, *Org. Anal.*, **3**, 237 (1956).

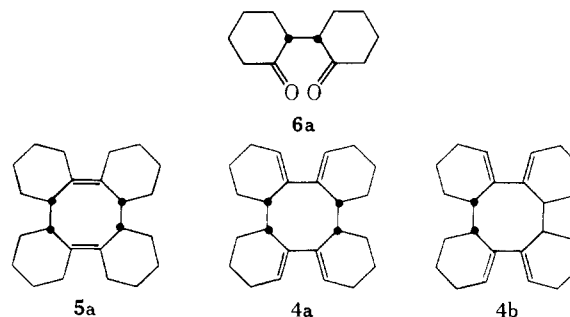
(15) 2,3-Di-*t*-butylbutadiene, a diene which must be skewed, has a maximum at 185 nm ($\log \epsilon$ 3.8) with a shoulder at 209 nm ($\log \epsilon$ 3.4) in the gas phase; H. Wynberg, A. DeGroot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963).

(16) Glpc analysis indicated the presence of three compounds formed in yields of 8, 39, and 8%. The nmr spectrum of the mixture is consistent with the assignment of one tetra- and one trisubstituted double bond to the major component and two trisubstituted double bonds to each of the minor components. The fact that **4a** underwent a significant amount of 1,2 reduction must be a reflection of the skewed 1,3-diene moieties.

(17) (a) Both the crystalline and the noncrystalline isomers were prepared^{17b} for comparison by oxidation of cyclohexanone with di-*t*-butyl peroxide. (b) C. G. Moore, *J. Chem. Soc.*, 236 (1951).

(18) R. Criegee and H. G. Reinhardt, *Chem. Ber.*, **101**, 102 (1968).

(19) Previous work²⁰ had indicated that the crystalline isomer is the more stable, a conclusion we have verified by base-catalyzed isomerization of the liquid isomer **6b** to the crystalline compound. Based on the work of Kharasch and coworkers,²¹ who investigated the stereochemistry of several pairs of *meso*- and *dl*-1,4-diketones and found that in every case the *meso* isomer was the higher melting and more stable, the



Since ozonolysis of **5** gave only **6a** under conditions which did not isomerize **6b**, **5** must have either the *cis-syn-cis* configuration²² or the *cis-anti-cis* configuration. However, examination of molecular models shows that the latter would be an extremely strained configuration, while the former, with the eight-membered ring in a twisted tub conformation, is essentially strain free. Thus we assign the *cis-syn-cis* configuration **5a** to **5** which thus leads to the assignment of the *cis-syn-cis* configuration to **4a**, an assignment which is supported by mechanistic considerations.

Reduction of the minor tetramer **4b** with lithium in ammonia gave a mixture of at least five tetrahydro isomers. The nmr spectrum of the mixture shows that there are two olefinic protons per molecule, which indicates that only 1,2 reduction occurred. Examination of molecular models shows that while all of the stereoisomers of **4** are reasonably strain free, the *cis-anti-cis* isomer appears to be most apt to exist in conformations having a minimal tendency toward achieving near planarity of at least one of the 1,3-diene units. This effect should favor 1,2 over 1,4 reduction. Furthermore, both mono- and di-1,4 reduction of the *cis-anti-cis* isomer would lead to badly strained molecules, a situation which does not exist for any of the other stereoisomers of **4**. Inasmuch as *only* 1,2 reduction occurred, we have assigned the *cis-anti-cis* configuration to **4b** and believe that mechanistic considerations support this assignment.

Dimer. Addition of a solution of dibromide **1** in ether to a solution of methyl lithium in refluxing ether afforded a 55% yield of a crystalline dimer (C_6H_8)₂, 10% yield of trimeric material, and 5% yield of tetrameric material.

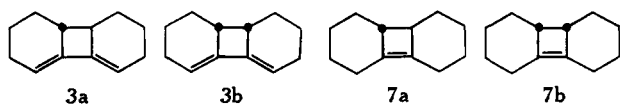
The elemental analysis, the mass spectrum (M^+/e 160), the ultraviolet maximum at 238 nm ($\log \epsilon$ 4.16), quantitative microhydrogenation (two double bonds), and the nmr spectrum (two olefinic protons) taken together established that the dimer must be one of the stereoisomers of **3**, the compound which Wittig and Fritze⁷ obtained in low yield from treatment of 1-bromocyclohexene with base. The dimer was shown to be the *trans* isomer **3a** by treatment with lithium in refluxing anhydrous ammonia to give **7a**, the result of 1,4 reduction, as the only product. The *trans* fusion of **7a** was established by spectral comparison with the *cis* isomer **7b**.²³ Subsequently, Criegee and Reinhardt¹⁸ have reduced the dimer obtained by Wittig

crystalline isomer of **6** could be assigned the *meso* configuration with some confidence.

(20) S. G. P. Plant, *J. Chem. Soc.*, 1595 (1930).

(21) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, **70**, 1269 (1948).

(22) Relative configurations are given by 7,8-*cis* or -*trans*; 8,19-*syn* or -*anti*; 19,20-*cis* or -*trans*.



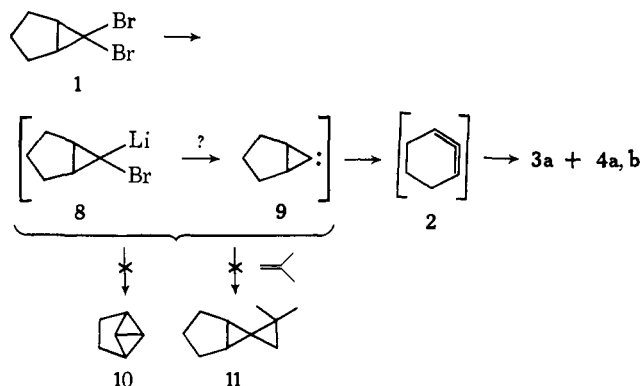
and Fritze⁷ and provided chemical evidence that the 1,4-reduction product²⁴ which results is the *trans* isomer **7a** by showing that it undergoes pyrolytic (conrotatory) ring opening to 1,1'-bicyclohexenyl at a much higher rate than does the *cis* isomer **7b**.

The yield of dimer **3a** fell to 17% when the reaction was carried out at -18° and no more than a trace of **3a** could have been present when the reaction was performed at -80° . Interestingly, employing *n*-butyllithium in place of methyllithium in refluxing ether gave only 20% **3a** along with increased amounts of trimers and **4a, b**. We believe that this change mainly reflects the greater reactivity of butyllithium (compared to methyllithium) causing a sufficiently fast reaction with **1** that mixing was not adequate to prevent relatively high local concentrations of reactive intermediates.²⁵

Discussion

The formation of **3a** and **4a, b** and the absence of carbene products such as **10** and **11** in reactions of **1** with methyllithium indicate that either the α -bromolithium species **8** or the carbene **9** must undergo ring opening to 1,2-cyclohexadiene (**2**) (Scheme I).

Scheme I



Products analogous to **10** and **11** are formed upon treatment of 7,7-dibromobicyclo[4.1.0]heptane (**12**) with methyllithium⁴ and no evidence for the intermediacy of 1,2-cycloheptadiene has been found. Since 1,2-cyclohexadiene (**2**) would appear to be more highly strained than 1,2-cycloheptadiene, the generation of **2** was not expected. The most important factor operating toward opening the three-membered ring of **8** and/or **9** is probably the relief of strain in the bicyclo[3.1.0]hexane system. Thus, **1** undergoes facile re-

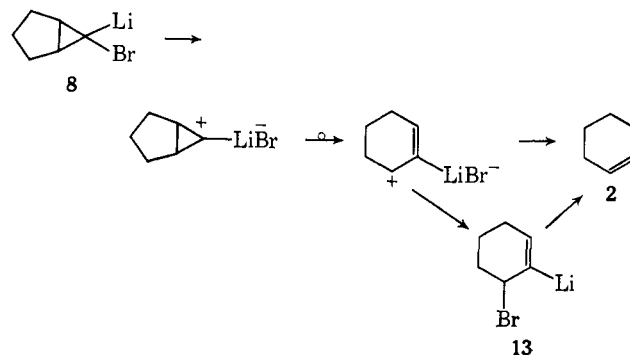
(23) (a) Comparison of the infrared and nmr spectra of the *trans* isomer **7a** with those of the *cis* isomer **7b**^{23b} clearly indicated that they are different and in fact the nmr spectra permit a clear assignment of configuration. (b) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltie, *J. Amer. Chem. Soc.*, **88**, 2742 (1966). (c) We wish to acknowledge an exchange of spectra (1963-1964) with Professor W. G. Dauben who subsequently reported^{23b} the assignment of stereochemistry to **7a** and **7b** we had made at that time, based on the chemical shifts of the tertiary allylic protons. However, because the report^{23b} of the spectral comparison unfortunately is in error and similar analyses are very important in related work,³¹ we have given a corrected description and a brief analysis in the Experimental Section.

(24) Criegee and Reinhardt¹⁸ added a solution of **3a** in methanol-pentane to sodium in ammonia at -70° and obtained **7a** in 34% yield along with 1,2-reduction products. In this case then the reduction is cleaner at a higher temperature in the anhydrous solvent.

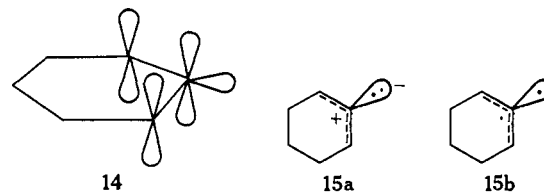
(25) Specifically, the concentration of **16** (see Discussion) would build up, favoring reactions leading to higher molecular weight products.

arrangement to 2,3-dibromocyclohexene while **12** is completely stable under comparable conditions^{8,10} and the silver ion catalyzed solvolytic rearrangement of **110** is much faster than the corresponding reaction of **12**. Since the tendency to rearrange is clearly associated with the generation of a positive charge on the cyclopropane ring, **8** may undergo a related rearrangement to **13** prior to formation of **2** (Scheme II).²⁶

Scheme II



The most reasonable shape for **2** is that of a planar or nearly planar ring which is essentially hexagonal; *i.e.*, the allene linkage is twisted and bent. Both C-1 and C-3 should be sp^2 hybridized as in a normal allene, but C-2 would be expected to change from sp to sp^2 hybridization⁶ or close to the latter (**14**). On this basis, the parallel p orbitals at C-1, C-2, and C-3 define an



allylic system, leaving a nonbonding orbital at C-2. The latter, because of relatively high s character, would be expected to be lower in energy than the nonbonding allylic orbital, suggesting that the lowest singlet state of **2** can be represented as **15a**. Promotion of one electron from the nonbonding sp^2 hybrid at C-2 to the nonbonding allylic orbital gives **15b**, for which the triplet state should be the lower energy state. Depending upon the magnitude of the singlet-triplet splitting, either **15a** or **15b** may be the ground state.²⁷ Neither represents a low-energy species. Formally **15a** is equivalent to a cyclohexenyl cation minus a proton and **15b** is equivalent to a cyclohexenyl radical minus a hydrogen atom. Both formal representations imply high reactivity.

In order to account for the formation of **3a** and **4a, b** and the shift from **3a** at "high" temperatures to **4a, b**

(26) Species **13**, if formed, must undergo loss of LiBr to generate **2**; it cannot account for the formation of **3a** directly because coupling of **13** would give a nonconjugated isomer of **3a**. We believe that no organometallic species are involved in the product-forming stages of these reactions and will elaborate on this conclusion in a discussion of other ways to generate **2**; W. R. Moore and L. N. Bell, in preparation.

(27) (a) A referee has suggested that although single electron orbital energies would appear to favor **15a**, decreased electron interaction in **15b** would lead to an energy lowering sufficient to make the latter the ground state. A related discussion of carbene orbital energies has been given by R. Hoffmann, *et al.*, *J. Amer. Chem. Soc.*, **90**, 1485 (1968) (in particular, see footnote 5). (b) The results of experiments involving trapping of **2** in styrene suggest that **2** as generated in this system is a singlet.¹¹

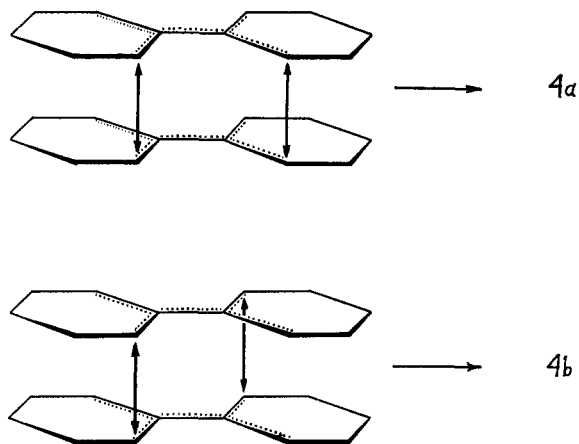
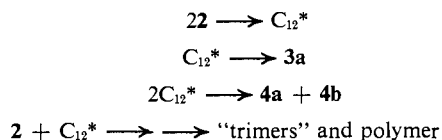


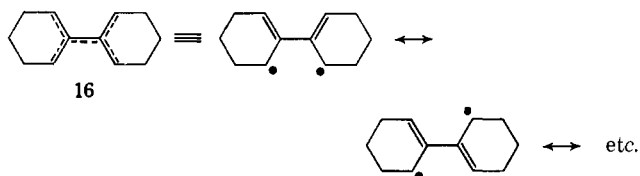
Figure 1. Orientation of **16** in dimerization. Vertical double-headed arrows show points where bonds are made.

at low temperatures, at least one intermediate in addition to **2** is necessary. We believe that a simple mechanism can correctly interpret these results (Scheme III). Dimerization of **2** must give a species C_{12}^*

Scheme III



which can either isomerize to **3a** or dimerize to **4a, b**. We believe that the reactive intermediate C_{12}^* must be **16**, 2,2'-dicyclohexenylene.^{28a} Conrotatory closure of **16** gives **3a**. Only the *trans* isomer **3a** has been detected in these reactions, but it appeared possible



that either we missed the *cis* isomer **3b** or it was not stable to the reaction conditions. Examination of models clearly indicates (perhaps surprisingly) that the *cis* isomer **3b** must be significantly more strained than the *trans* isomer **3a**. The cyclobutane ring can pucker to relieve strain in **3a** but not in **3b**. However, in other studies we have succeeded in synthesizing **3b** (and **3a** too) independently and have shown that **3b** is stable to the reaction conditions and is not formed when **1** is treated with methylolithium.^{28b}

We believe that the only rational way to arrive at tetramers **4a** and **4b** is by dimerization of **16**; stepwise additions of C_6 units cannot logically lead to only two C_{24} compounds. Yet, we emphasize that *only two* C_{24} compounds were formed and they are stereoisomers. If any other isomers of **4a, b** were undetected, they had to be present in very small amounts. Because we can see no reason why multistep dimerization of **16** should

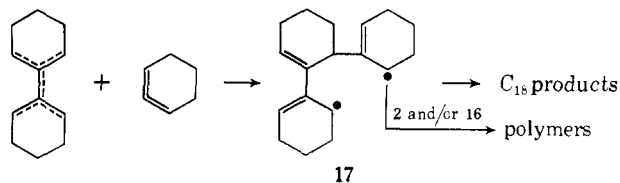
(28) (a) Following Berthier,^{28b} we will refer to the parent species C_6H_6 as 2,2'-diallylene, or simply diallylene, rather than as 2,2'-diallyl to avoid confusing this species with the stable molecule diallyl (1,5-hexadiene) or as "tetramethylenethane," a name which is difficult to employ as a basis for naming more complex species. (b) W. R. Moore, L. N. Bell, and G. P. Daumit, work in progress.

not lead to all five stereoisomers of **4**, we believe that **16** must undergo a concerted or near-concerted dimerization which restricts the number of products.

Assuming that **16** is planar²⁹ or nearly so³⁰ we believe that dimerization occurs in a concerted fashion with two molecules of **16** stacked like slices of bread in a sandwich permitting maximum interaction of π orbitals (Figure 1). *Bond making can then occur in two and only two ways, giving rise to only 4a and 4b* (Figure 1).

Trimeric and polymeric products must arise from reaction of **2** with **16**. In this case, it seems likely that a biradical **17** is formed which either gives rise to several C_{18} isomers or reacts with **2** and **16** to give polymers (Scheme IV).

Scheme IV



The shift in products from dimer **3a** at "high" temperatures to tetramers **4a, b** at low temperatures suggests that there is a temperature-dependent barrier to closure of **16** to **3a**, allowing it to accumulate sufficiently at low temperatures to favor dimerization to **4a, b**. Furthermore, this barrier must be such that **16** closes *only* to **3a** and no **3b** is formed. Because **3b** is more strained than **3a** and recognizing that an un-sophisticated perusal of models suggests that it is "easier" to close **16** to **3a** than to **3b**, one might argue that the stereoselectivity is based solely on strain. On the other hand, as both we³¹ and Jacobs³² have pointed out elsewhere, a diallylene such as **16** may close in a stereospecific fashion which is determined by orbital symmetry. We indicated a mild preference for disrotatory closure of possible diallylene intermediates in the dimerization of 1,2-cyclohexadiene.³¹ In the present case we feel that the evidence for the intermediacy of a diallylene species **16** is compelling, but the closure is clearly conrotatory. This fact means that one or more of the following statements must be true (others could be added): (a) the dimerization of 1,2-cyclohexadiene (and similar allenes) does not involve diallylene intermediates; (b) the stereospecific sequence presented for 1,2-cyclohexadiene³¹ should be inverted to disrotatory formation of a diallylene followed by conrotatory closure; (c) strain is the determining factor, overriding any other effects, in causing closure of **16** to **3a**; (d) an "orthogonal" diallylene^{32,33} (in which the two allyl moieties are in

(29) Various calculations of the electronic structure of diallylene have assumed a planar molecule. All have predicted a triplet ground state: (a) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950); (b) G. Berthier, *J. Chim. Phys.*, **52**, 11 (1955); (c) A. Streitwieser and J. L. Brauman, "Supplemental Tables of MO Calculations," Vol. 1, Pergamon Press, New York, N. Y., 1965, p. 7.

(30) While all treatments of diallylene indicate stabilization²⁹ gained by planarity, because of nonbonded repulsions, diallylenes probably are twisted. However, as in the case with biphenyls, modest twisting will not greatly affect the molecular properties. The conclusions we draw concerning dimerization of **16** are not changed by employing a moderately twisted model.

(31) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969).

(32) (a) O. J. Muscio, Jr. and T. L. Jacobs, *Tetrahedron Lett.*, 2867 (1969); (b) T. L. Jacobs, J. R. McClenon, and O. J. Muscio, Jr., *J. Amer. Chem. Soc.*, **91**, 6038 (1969).

mutually perpendicular planes) is formed and it undergoes conrotatory closure; (e) **16** is in a different electronic state from that of diallylene intermediates arising from thermal dimerization of normal allenes and thus **16** closes in the opposite sense. We recognize that additional studies are necessary to provide a valid basis for judgment, but at this point we wish to comment on the last two points.

Gajewski³³ and Jacobs^{32b} have suggested that orthogonal diallylenes may be intermediates in allene dimerizations and in the thermal rearrangement of 1,2-dimethylenecyclobutanes. Thus it is possible that **16** is formed as an orthogonal singlet diallylene which can undergo orbital symmetry allowed conrotatory closure to **3a**. However there still would have to be a significant energy barrier to closure or else dimerization of **16** could not compete effectively with ring closure. Furthermore, as examination of molecular models will show, an orthogonal diallylene cannot lead to the stereochemistry found for tetramers **4a, b**. Hence if an orthogonal singlet diallylene is formed, it appears that it must undergo rapid transformation to a different intermediate, namely to a triplet diallylene which we assume would be planar. A planar triplet species²⁹ could not only lead to the tetramers **4a, b**, but it also might undergo ring closure. While orbital symmetry considerations suggest^{31,32a} that a planar singlet diallylene would undergo disrotatory closure to the ground state of the 1,2-dimethylenecyclobutane ($\psi_1^2\psi_2^2\psi_3^2 \rightarrow \sigma^2\phi_1^2\phi_2^2$), a triplet diallylene would be expected to undergo conrotatory closure to a triplet state of the diene ($\psi_1^2\psi_2^2\psi_3\psi_4 \rightarrow \sigma^2\phi_1^2\phi_2\phi_3$). Although this process appears to be endothermic,³⁴ if the energy barrier were not too great (e.g., 10 kcal) and inter-system crossing ($\sigma^2\phi_1^2\phi_2\phi_3 \rightarrow \sigma^2\phi_1^2\phi_2^2$) were rapid, overall conversion of a triplet diallylene to the ground-state dimethylenecyclobutane could occur. While ring closure of triplet species is not the norm, it may be possible in this case.

Experimental Section³⁷

6,6-Dibromobicyclo[3.1.0]hexane (1). Dropwise addition of 278 g (1.1 mol) of bromoform in 100 ml of pentane to a well-stirred slurry of 1.2 mol of potassium *t*-butoxide in 68 g (1.0 mol) of cyclopentene and 300 ml of pentane at -15° followed by hydrolysis,

(33) J. J. Gajewski and C. N. Shih, *J. Amer. Chem. Soc.*, **89**, 4532 (1967); (b) J. J. Gajewski and C. N. Shih, *ibid.*, **91**, 5900 (1969).

(34) This predicted endothermicity is based on the fact that activation energy for the (degenerate) thermal rearrangement of 1,2-dimethylenecyclobutane is about 47 kcal³⁵ and the assumption that the triplet energy of 1,2-dimethylenecyclobutane would be about 50–55 kcal.³⁶

(35) W. von E. Doering and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **89**, 4534 (1967).

(36) Typical *cis*-1,3-dienes have triplet energies about 53 kcal/mol; cf. D. F. Evans, *J. Chem. Soc.*, 1735 (1960); G. S. Hammond and R. S. H. Liu, *J. Amer. Chem. Soc.*, **85**, 477 (1963).

(37) Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Models 21, 237, and 337 spectrophotometers; nmr, Varian A-60 spectrometer; uv, Cary Model 14 spectrophotometer; mass, Consolidated Electrodynamics Model 21-130 mass spectrometer (ionizing potential of 70 V). Glpc columns were generally 0.5×200 cm and 1.5×200 cm (homemade apparatus, thermal conductivity) or 0.2×150 cm and 0.2×300 cm (Wilkins A-600, flame ionization) employing acid, basic, or neutral Chromosorb P or W and the following liquid phases: Carbowax 20M (C-20M), SE-30 silicone rubber (SE-30), and ethylene glycol adipate (EGA). Internal standard were employed using appropriate response factors; peak areas were measured with a planimeter. Melting points are corrected and boiling points are not. All reactions employing organometallic reagents, active metals, or pyrolysis, were conducted under an atmosphere of nitrogen or helium. Methylolithium was prepared from methyl bromide.

short-path distillation (1 mm, bath 50°), and fractional distillation gave 204 g (85%) of colorless **1**, bp 77° (6 mm), n_D^{25} 1.5568 (lit.¹⁰ n_D^{25} 1.5568). The compound was stored at -15° under nitrogen to avoid isomerization.

cis-syn-cis-Pentacyclo[18.4.0.0^{2,7}.0^{8,13}.0^{14,19}]tetracosatetraene-2-, 12,14,24 (**4a**) and *cis-anti-cis*-Pentacyclo[18.4.0.0^{2,7}.0^{8,13}.0^{14,19}]tetracosatetraene-2,12,14,24 (**4b**). Methylolithium (1 M, 0.03 mol) in ether was added dropwise to a well-stirred solution of 58.8 g (0.245 mol) of **1** in 2 l. of anhydrous ether maintained at -80° . Upon completion of the addition, the reaction mixture was allowed to warm to room temperature. Water was added and the ether layer was separated, washed with water, and dried ($MgSO_4$). Evaporation of the ether gave an oil (kept under nitrogen) which was dissolved in methylene chloride. After 2 days at -10° , 6.73 g (34%) of a crystalline white solid was collected, mp 131 – 134° . Recrystallization from methylene chloride gave 6.49 g of **4a**, mp 132.5 – 134° ; ir (CS₂) 3010, 1635, 800 cm⁻¹ (plus many other fingerprint bands); nmr (CDCl₃) δ 5.41 (4 H, triplet, $>C=CHCH_2-$), 1.8–2.6 (12 H), two broad overlapping bands, major band centered at 2.03 ($>C=CHCH_2-$) and minor centered at 2.19 ($-CH=CCH<$), 1.15–1.83 (16 H, broad band, $-CH_2CH_2-$); uv (heptane) apparent λ_{max} 187 nm (log ϵ 4.41), no max above 190 nm; λ (log ϵ) 195 (4.36), 205 (4.20), 215 sh (4.12), 225 (4.00), 235 (3.75), 245 (3.30), 255 (2.60) nm; mass spectrum m/e 320 (M⁺); molecular weight cryoscopic in benzene, 325; vapor pressure lowering (osmometer), 324. Hydrogenation over platinum in acetic acid at 25° (1 atm) resulted in the uptake of 4.0 mol of hydrogen per mole of **4a**.

Anal. Calcd for C₂₄H₃₂: C, 89.94; H, 10.06. Found: C, 89.95; H, 10.06.

Acetone was added to the mother liquor from the crystallization until no further solid precipitated giving 2.86 g of a white powder, nonvolatile in glpc on 2% EGA (260°) and 5% SE-30 (340°). Concentration of the mother liquor gave 9.38 g of an oil which was chromatographed on Woelm activity I alumina using petroleum ether as an eluent and following the development by glpc, yielding 2.24 g (11%) of a white solid, mp 82 – 86° . This material gave a single peak on glpc (2% EGA, 175°; 2% SE-30, 200°). Two recrystallizations from concentrated methylene chloride gave 1.09 g of **4b**: mp 84.5 – 86° ; ir (CS₂) 3010, 1655 (w), 1630, 800 cm⁻¹ (plus many other fingerprint bands); nmr (CDCl₃) δ 5.35 (4 H, complex, $>C=CH-$), 2.95 (*ca.* 1 H, broad multiplet) and 1.95 (*ca.* 11 H, broad band), both allylic protons,³⁸ 1.6 (*ca.* 16 H, broad band overlapping 1.95 band, $-CH_2CH_2-$); uv (heptane) no maxima above 190 nm; λ (log ϵ) end 187 (4.35), 195 (4.30), 205 (4.24), 215 (4.11), 225 (3.94), 235 (3.88), 245 (3.68), 255 (3.26), 265 (2.60); mass spectrum m/e 320 (M⁺).

Anal. Calcd for C₂₄H₃₂: C, 89.94; H, 10.06. Found: C, 90.01; H, 9.98.

Numerous attempts were made to effect dehydrogenation of **4a** to tetraphenylene using a variety of quinones and noble metals. Although several reactions produced mixtures which included a material with the same glpc retention time as tetraphenylene, the mixtures were too complex to permit isolation of the compound for conclusive identification; collection by glpc was not feasible inasmuch as lightly coated columns with a flame ionization detector using a few micrograms of sample were necessary.

It was necessary to keep the preheater temperature of the glpc instrument below 230° to prevent rearrangement of **4a** and **4b**; e.g., at 300° (preheater), **4a** gave mainly a new peak with a shorter retention time and **4b** gave mainly a new peak with a longer retention time (SE-30).

In all cases, the yields of glpc volatile products were too low to account for all of the starting material. But the balance of the material could always be accounted for as a nonvolatile polymer. Attempts to recrystallize such residual materials were unsuccessful.

Addition of 8 mmol of methylolithium in 4 ml of ether to 4.3 mmol of **1** in 25 ml of ether at -80° with a reaction time of 5 min followed by addition of methanol at -80° gave 45% **4a, b** and 5% trimeric material.

Addition of 24 mmol of **1** in 20 ml of ether to 80 mmol of methylolithium in 80 ml of ether at -80° gave essentially the same product ratios as above.

Addition of 10 mmol of methylolithium in 5 ml of ether to 7.2 mmol of **1** in 300 ml of ether at -80° gave on glpc analysis (5% SE-30, program temperature, tetraphenylene internal standard, average of several reactions): very small amounts of materials in

(38) We believe that the material is pure and that the δ 2.95 band may reflect a fraction of the molecules in conformations (models) which put a tertiary allylic proton in the deshielding region of two double bonds.

the C₁₂ region (total ca. 2%), 13% trimeric materials and 61% **4a, b** (single peak). No more than a trace of **3a** was present.

Addition of 15 mmol of *n*-butyllithium (Foote Mineral Co.) in 8 ml of hexane to 7.7 mmol of **1** in 50 ml of ether at -80° gave 4% of materials with retention times slightly greater than that of **3a** (no more than a trace of which was present), 8% trimeric material, and 47% **4a, b**. No change in the products was observed on using pentane as a solvent or using *n*-butyllithium prepared from butyl bromide and lithium in ether.

Reduction of 4a with Lithium in Ammonia. A solution of 3.21 g (10.0 mmol) of **4a** in 15 ml of tetrahydrofuran was added dropwise with stirring to a refluxing solution of 0.8 g (0.1 g-atom) of lithium, 100 ml of anhydrous ammonia, 25 ml of tetrahydrofuran, and 15 ml of *t*-butyl alcohol. After 15 min, ammonium chloride was added until the blue color was gone. Ether was added, the ammonia was distilled, water was added, and the ether layer was separated. The ether solution was washed, dried, and evaporated leaving a white semisolid residue which was dissolved in methylene chloride and allowed to stand for 2 days at -10°. The crystalline white solid which formed was collected, mp 151.5–155°, and recrystallized from methylene chloride giving 1.23 g (38%) of *cis-syn-cis-pentacyclo[18.4.0.0.0.0.0.0.0.14.19]tetracosadien-1,13* (**5a**): mp 153.5–155°; ir (CS₂) 855 cm⁻¹; nmr (CCl₄) δ 1.0–3.0 only with major band centered at 1.53; uv (heptane) λ_{max} 204 nm (log ε 4.28). The compound gave a single glpc peak (2% EGA, 175°; 2% SE-30, 200°).

Anal. Calcd for C₂₄H₃₆: C, 88.82; H, 11.18. Found: C, 88.71; H, 11.30.

Compound **5a** decolorized a solution of bromine in carbon tetrachloride. Hydrogenation of **5a** over platinum (from platinum oxide) in 1:1 cyclooctane acetic acid at 50° required 1 week and gave a minimum of five compounds on glpc analysis (2% SE-30; 200°).

Evaporation of the mother liquor from **5a** gave an oil which could not be induced to crystallize from a variety of solvents. Short-path distillation gave 1.75 g (53%) of a colorless glass. Glpc analysis (2% EGA, 178°) showed three compounds, relative retention times (amount): 1.00 (14%), 1.23 (72%), 1.43 (14%). Each compound reacted rapidly with bromine in carbon tetrachloride: uv (heptane) λ_{max} 193 nm (log ε 4.20); nmr (CCl₄) δ 5.25–5.84 (>C=CH-) and 0.6–3.0 (broad and complex). The ratio of olefinic to nonolefinic protons was 1.00/28.2. For a total of 36 protons per molecule this means that the three compounds have an average of 1.23 olefinic protons per molecule. Assuming that the major component has one tetra- and one trisubstituted double bond and both of the minor components have two trisubstituted double bonds, based on the glpc analysis the mixture would have an average of 1.28 olefinic protons per molecule.

Anal. Calcd for C₂₄H₃₆: C, 88.82; H, 11.18. Found: C, 88.83; H, 11.21.

In another reduction, the reaction mixture was analyzed after 0.5, 5, and 10 hr and found to have the same composition given above. A quantitative recovery of **5a** was obtained when it was subjected to reduction conditions for 3 hr.

Because **4a** is not soluble in ammonia and has very limited solubility in the mixed solvents, the procedure given above (adding **4a** in THF to the lithium-mixed solvent system) is essential if reduction is to be complete; reduction apparently occurs before **4a** can precipitate.

Reduction of 4b with Lithium in Ammonia. A solution of 173 mg (0.54 mmol) of **4b** in 2 ml of tetrahydrofuran was added dropwise with stirring to a refluxing solution of 0.1 g of lithium in 50 ml of anhydrous ammonia, 25 ml of tetrahydrofuran, and 10 ml of *t*-butyl alcohol. Work-up and glpc analysis (2% EGA, 184°) showed a minimum of five compounds. Short-path distillation (0.05 mm, bath 150°) afforded 171 mg (97%) of a colorless glass: ir (CS₂) 3010 (sh), 1628, 799, 820 cm⁻¹; nmr (CCl₄) δ 4.9–5.7 (2.06 ± 0.10 H, complex, >C=CH-), 0.5–3.3 (34 H, broad and complex); uv (heptane) λ_{max} 193 nm (log ε 4.12).

Anal. Calcd for C₂₄H₃₆: C, 88.82; H, 11.18. Found: C, 89.15; H, 10.85.

Ozonolysis of 5a. Ozone was passed into a solution of 251 mg (0.77 mmol) of **5a** in 50 ml of methylene chloride at -80° until a blue color was obtained. Aqueous sodium bisulfite was added until a negative starch-iodide test resulted. The organic layer was washed, dried, and analyzed by glpc (2% EGA and 2% SE-30 isothermal and program) showing a single volatile compound (33% yield) with a retention time identical with that of bicyclohexyl-2,2'-dione (**6a**). Short-path distillation (0.1 mm, bath 115°) afforded 88 mg (29%) of a slightly yellow solid with an ir spectrum the same as that of authentic **6a** save for one additional weak band. Three recrystallizations from petroleum ether gave 65 mg of color-

less *meso*-bicyclohexyl-2,2'-dione (**6a**), mp 70.5–72°, no depression on admixture with an authentic sample. The ir spectra of the samples were identical.

Oxidation^{17b} of cyclohexanone with di-*t*-butyl peroxide gave a mixture of **6a**, mp 70.5–72° (lit.^{17b,18,21} 70–71°), and the liquid isomer **6b**. Treatment of the latter with aqueous base isomerized it to **6a**.

trans-Tricyclo[6.4.0.0.0.0.0.0.0.14.19]dodecadiene-2,12 (**3a**). A solution of 9.6 g (0.040 mol) of **1** in 100 ml of ether was added dropwise to a well-stirred refluxing solution of 0.06 mol of methyl lithium in 250 ml of ether. After the addition was completed, the mixture was refluxed for 10 min, then water was added and the ether layer was separated, washed, and dried. Glpc analysis (2% SE-30, program) showed 55% **3a**, 5% trimeric material, and 10% **4a, b** (the balance of the material was accounted for as a nonvolatile residue). Short-path distillation (55°, 0.5 mm) gave a colorless liquid which soon solidified. Sublimation (25°, 0.01 mm) gave 1.6 g of **3a**: mp 55–56°; ir (CCl₄ and CS₂) 3020, 1330, 908, 895, 872, 845, 815, 782 (s), 700 cm⁻¹; nmr (CCl₄) δ 5.29 (2 H, >C=CH-), 0.8–2.5 (14 H, complex); uv (ethanol) λ_{max} 238 (log ε 4.16); mass spectrum *m/e* 160 (M⁺).

Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.21; H, 10.18.

Allowing **3a** to stand under oxygen for 1 week at 25° gave an oil.

Anal. Calcd for C₁₂H₁₆O₂: C, 74.97; H, 8.39. Found: C, 74.72; H, 8.36.

Hydrogenation of **3a** over 30% palladium on carbon in ethanol at 25° (1 atm) resulted in the rapid uptake of 96% of the volume of hydrogen calculated for two double bonds.

The yields of **3a** varied from ca. 45 to 60% when carried out as above, apparently as a function of the stirring and rate of addition of **1**.

When the reaction was carried out at -18°, the yield of **3a** was 17%. In refluxing *n*-heptane the yield was 12%.

Addition of 6.6 mmol of **1** in 15 ml of ether to 10 mmol of butyllithium in 100 ml of refluxing ether gave 20% **3a**, 5% (total) of several materials with retention times close to that of **3a**, 16% trimeric material, and 42% tetramer. Again, the yields varied somewhat with the rate of addition and stirring. Compound **3a** did not react with butyllithium under these conditions.

trans-Tricyclo[6.4.0.0.0.0.0.0.0.14.19]dodecene-1 (**7a**). Sodium was added to a solution of 0.697 g (4.36 mmol) of **3a** in 100 ml of anhydrous ammonia until the blue color persisted. The mixture was stirred for 30 min and worked up in the usual way. Glpc analysis (C-20M) showed the presence of a single compound (83%). Short-path distillation (0.5 mm, bath 60°) afforded 0.521 g (74%) of **7a**, *n*_D²⁰ 1.5124. Glpc analysis (C-20M, 200°, which rearranges **7a** to 1,1'-bicyclohexenyl and 2% EGA, 114°, preheater 120° which does not) indicated that the sample was pure: ir (neat) 1172, 817 cm⁻¹; nmr (CCl₄) δ 0.7–2.5 only (see below); uv (isooctane) λ_{max} 210 nm (log ε 4.49); mass spectrum *m/e* 162 (M⁺).

Anal. Calcd for C₁₂H₁₈: C, 88.82; H, 11.18. Found: C, 88.89; H, 11.12.

The nmr spectrum of **7a** is essentially identical with that of **7b** from ca. δ 1.9 upfield. Compound **7b** shows overlapping bands centered at δ 2.3 (2⁺ H, not 4 H^{23a}), 2.1 (2⁻ H), 1.7 (broad, complex), and 1.2 (broad, complex). The spectrum of **7a** is essentially identical from δ 1.9 upfield. The δ 2.3 band is absent, a small band at δ 2.3 (<< 1 H, not 2 H^{23b}) is clearly part of a broadened AB pattern (*J*_{AB} ~ 12 Hz, geminal coupling) the major part of which is at δ 2.13. The two-proton signal at δ 2.3 in **7b** clearly appears to have shifted to ca. δ 1.85 in **7a**, merging with the downfield portion of the δ 1.7 band. The δ 2.1 band common to both **7a** and **7b** must be due to one of the allylic protons at C-3 and one at C-12 (the geminal partners fall in the ca. δ 1.7 band). The δ 2.3 band of **7b** and the ca. δ 1.85 band of **7a** must arise from the bridgehead allylic protons. Thus the signal from the tertiary allylic protons in **7b** lies about 0.45 ppm downfield from the corresponding signal in **7a**. In the latter case, each of the bridgehead protons is shielded by a *cis*-C-C bond while in **7b** each bridgehead proton is deshielded by a *trans*-C-C bond.

Heating **7a** at 200° for 20 min under nitrogen gave 1,1'-bicyclohexenyl quantitatively (identical ir spectra, glpc retention times). Authentic 1,1'-bicyclohexenyl was prepared³⁹ by dehydration of 1,1'-dihydroxybicyclohexyl,⁴⁰ mp 26–27° (lit.⁴¹ mp 28°).

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(40) E. E. Gruber and R. Adams, *J. Amer. Chem. Soc.*, **57**, 2555 (1935).

(41) E. Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1104 (1935).