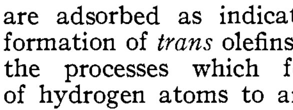
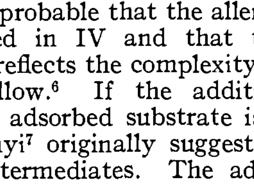
studies have emphasized that adsorption occurs in the least hindered way. Examination of molecular models of I and II shows that in each system adsorption along *a* or *b* (III) is not hindered but adsorption along *c* and *d* is hindered seriously by the methylene groups.[5] The question then arises, why are substantial amounts of *trans* olefins formed from I and II, particularly when the *trans* olefins are far less stable[3] than the *cis* isomers? It is possible that one is badly misled by models. But we believe that it is more probable that the allenes are adsorbed as indicated in IV and that the formation of *trans* olefins reflects the complexity of the processes which follow.[6] If the addition of hydrogen atoms to an adsorbed substrate is a stepwise process as Polanyi[7] originally suggested, consider the potential intermediates. The addition of a hydrogen atom to C-1 (IV) gives a half-hydrogenated state which is identical with the half-hydrogenated state of the corresponding acetylene (triple bond initially between C-2 and C-3) and accordingly we believe that the predominant course of reaction should be the addition of a second hydrogen atom to C-2, without loss of configuration, to yield a *cis* olefin.[8] Alternatively, addition of the first hydrogen atom to C-2 (IV) gives a half-hydrogenated state which without leaving the surface of the catalyst and while still preserving the geometry of the remaining double bond can flatten into an allylic system in which the three trigonal centers are coplanar (or nearly so) and strongly adsorbed on the catalyst.[9] Examination of molecular models indicates that the preferred configuration in the nine- and ten-membered systems should be the (*pseudo*) *cis,trans* form depicted as V.[10]

Addition of a second hydrogen atom to V should be nearly equally probable at C-1 or C-3; the former would give a *cis* olefin and the latter *trans*.

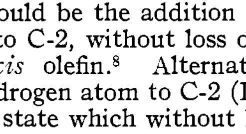
If this picture has any merit, it is clear that whenever species V is formed, *trans* olefin should be a significant product. A pertinent test arises in the hydrogenation of *cis,cis*-1,3-cyclodecadiene[11,12] (VI). This diene must have only one double bond adsorbed on the catalyst, since it cannot have the double bonds coplanar[11] (precluding direct 1,4-addition of hydrogen). Addition of a hydrogen atom to C-2 gives a half-hydrogenated state which should mainly add a second hydrogen atom at C-1 to give *cis*-cyclodecene. Addition of the first hydrogen atom to C-1 should give the same half-hydrogenated state, V, proposed to arise from II. We find that *partial hydrogenation of VI gives at least 38% of trans-cyclodecene.* This result, the formation of a *trans* olefin from a (non-transoid) *cis,cis*-diene, taken with those above strongly suggests that half-hydrogenated species exist on the catalyst for times sufficient to permit attainment of the most stable configuration.[13] Furthermore, we believe that similar configurational arguments can be applied to other medium-ring allylic species.



III



IV, $n = 4,5$



V, $n = 4,5$

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(5) Gardner and Narayana[2] concluded that *only cis*-cyclononene can be formed from I.

(6) Recent studies of hydrogenation which include many pertinent references: (a) J.-F. Sauvage, R. H. Baker and A. S. Hussey, *J. Am. Chem. Soc.*, **83**, 3874 (1961); (b) S. Siegel and G. V. Smith, *ibid.*, **82**, 6087 (1960); (c) R. L. Burwell, Jr., *Chem. Rev.*, **57**, 895 (1957).

(7) I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(8) Burwell[6c] has proposed that such intermediates may lead to *trans* olefins. We find that hydrogenation of cyclodecyne initially gives *ca.* 1% of *trans*-cyclodecene.

(9) (a) Burwell and co-workers have suggested that π-bonded allylic species may be involved in certain exchange reactions of deuterium and hydrocarbons on chromium oxide: R. L. Burwell, Jr., A. B. Littlewood, M. Cardew, G. Pass and C. T. H. Stoddart, *J. Am. Chem. Soc.*, **82**, 6272 (1960). (b) Based on the results of studies of the metal-catalyzed exchange of deuterium into certain polymethylcyclopentanes, Kemball and his co-workers have produced strong arguments for the existence of π-bonded allylic species on metallic surfaces (particularly palladium.) They have proposed that such species can be attached to a single metal atom of the surface and note that the type of bonding should be similar to that in certain known organometallic compounds. J. J. Rooney, F. G. Gault and C. Kemball, *Proc. Chem. Soc.*, 407 (1960); *J. Catalysis*, **1**, 255 (1962). The latter paper includes references to Kemball's earlier work which suggested the intermediacy of some type of triadsorbed alkanes in exchange reactions.

(10) Non-bonded interactions appear to make the *cis,cis* forms unfavorable. The *trans,trans* forms (strained for $n = 4$) can result only from rotation about a double bond or the equivalent in V and thus seem precluded.

(11) A. T. Blomquist and A. Goldstein, *J. Am. Chem. Soc.*, **77**, 998 (1955), who first prepared VI, reported total hydrogenation to cyclodecane.

(12) We have prepared VI by the isomerization of II.[1]

(13) There is no indication of isomerization of VI to the apparently strained and less stable *cis,trans*-1,3-cyclodecadiene.[11] For reasons which will be presented later, we believe that there is no reason to propose that the *cis,trans*-diene is a major undetected or undetectable intermediate in the hydrogenation of VI.

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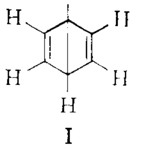
RECEIVED JULY 26, 1962

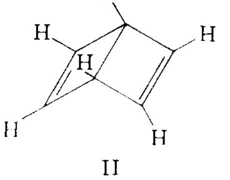
CHEMISTRY OF DEWAR BENZENE. 1,2,5-TRI-*t*-BUTYLBICYCLO[2.2.0]HEXA-2,5-DIENE

Sir:

Originally mentioned by Sir James Dewar in 1867 as one of several alternatives to the preferred Kekulé formulation for benzene,[1] the bicyclo[2.2.0]hexa-2,5-diene structure (I) has persisted conceptu-



I



II

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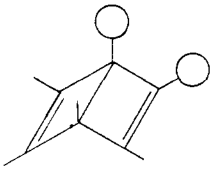
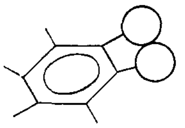
(1) For historical descriptions, see (a) C. K. Ingold, *J. Chem. Soc.*, 121, 1133 (1922); (b) G. W. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 117–118.

ally (planar, and best as an electronically modified version)[1b] as a minor resonance contributor to the hybrid state of the aromatic nucleus. As a non-planar structure, *i.e.*, a valence bond tautomer (II) of the benzenoid system, bicyclo[2.2.0]hexa-2,5-diene should be capable of independent, if precarious, existence. In this contribution we describe a hydrocarbon the properties of which lead us to propose that it is the first isolated member of the "Dewar benzene" class.[2,3]

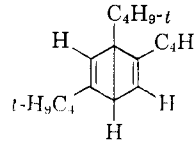
Of the various bicyclohexadiene structures which can be imagined, the simple parent would be expected to be the most unstable relative to benzene; however, bulky substituents at positions 1 and 2 should alter the energy relationship of the pair so as to stabilize, by virtue of steric factors, the non-aromatic member, as can be appreciated from formulas III and IV. It seemed that an *o*-di-*t*-butylbenzene, several examples of which recently have been described,[4] constituted a suitable example of the aromatic member (IV) of the above type of valence bond pair and thus might serve as a precursor of the non-aromatic isomer (III).


III


IV

Irradiation by means of a Hanovia Type L ultraviolet lamp (Vycor filter) of 1,2,4-tri-*t*-butylbenzene[4] in ether solution resulted in significant transformation of the aromatic material to a new hydrocarbon, which was separated from other products[5] by thin layer chromatography (silica gel/cyclohexane). The new hydrocarbon, a liquid at room temperature but solid below 0°, was distilled (10^{-7} mm.) at room temperature, and was used in this state of purity for most of the experiments described below (calcd. for $C_{18}H_{30}$: C, 87.73; H, 12.27. Found: C, 87.47, 87.52; H, 12.22, 12.31).

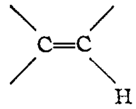
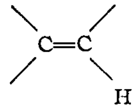
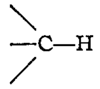
The volatility and chromatographic behavior of the irradiation product suggested that it was monomeric, and this surmise was confirmed by mass spectrometric determination (parent peak 246)[6] and by its osmometric molecular weight (274 in benzene solution at 39°).[7] On being heated at 200° for 15 minutes, the photo hydrocarbon was converted in good yield to 1,2,4-tri-*t*-butylbenzene, as evidenced by thin-layer chromatographic, infrared spectral and mixed m.p. comparison. In accordance with the favored structure (V), only end absorption (λ^{ether} 220 mμ, $\epsilon = 1800$) appeared in the usual ultraviolet region (> 215 mμ). Carbon–carbon double bond stretching peaks appear in the high wave length infrared region (6.26 and 6.46 μ) uniquely characteristic of cyclobutene systems.[8]



V

The proton magnetic resonance spectrum of the new hydrocarbon (Table I) provided further important clues as to its structural nature. In addition to a peak for a single proton appearing in the methine region (6.80 τ), signals ascribable to olefinic hydrogens appear at 3.87 and 3.95 τ; further, the higher field olefinic proton and the methine hydrogen split each other, whereas the lower field olefinic proton is unsplit. It is evident that there must be *two* tri-substituted double bonds in the molecule, implying that the ring system is bicyclic.[9] Assuming nonconjugation of the double bonds and without considering chemical plausibility, a number

TABLE I[a]

Peak (τ p.p.m.)	Area	Spin-spin splitting	Assignment
3.87	1	Singlet, with minor shoulders	
3.95	1	Doublet (J = ~1.0 cps.)[b]	
6.80	1	Doublet (J = ~1.0 cps.)[b]	
8.94	9	Singlet	*t*-C_4H_9
9.02	18	Singlet	2*t*-C_4H_9

[a] Spectrum obtained on a 60 mc. Varian instrument using a carbon tetrachloride solution at room temperature. Values relative to tetramethylsilane (τ = 10.0). [b] As evidenced by the irregular nature of each of these two peaks, secondary splitting is also involved, probably between the lowest field proton with each of the other non-*t*-butyl hydrogens.

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(2) For previous attempts to detect experimentally this type of ring system, see E. C. Taylor, W. W. Paudler and I. Kuntz, *J. Am. Chem. Soc.*, **83**, 2967 (1961); E. C. Taylor, R. O. Kan and W. W. Paudler, *ibid.*, **83**, 448 (1961); and also C. E. Berkoff, R. C. Cookson, J. Hudec and R. O. Williams, *Proc. Chem. Soc.*, 312 (1961).

(3) For related cases, see O. L. Chapman and D. J. Pasto, *J. Am. Chem. Soc.*, **80**, 6685 (1958) and references therein; E. F. Ullman and J. E. Milks, *ibid.*, **84**, 1315 (1962).

(4) C. Hoogzand and W. Hübel, *Tetrahedron Letters*, No. 18, 637 (1961).

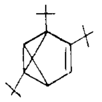
(5) As evidenced by its yellow color and ultraviolet spectrum (λether 260 mμ) a small yield of fulvenoid material was formed during the irradiation process. Fulvene itself has been reported as a photolysis product of benzene (H. J. F. Angus, J. M. Blair and D. Bryce-Smith, *J. Chem. Soc.*, 2003 (1960).

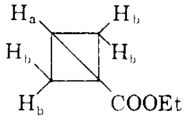
(6) Kindly provided by Prof. C. Djerassi, Stanford University.

(7) Kindly provided by R. W. Rinehart, The Upjohn Company.

(8) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

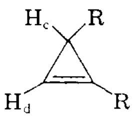
(9) Although it does not contain the two double bonds apparently demanded by the n.m.r. data, structure i, a novel yet reasonable irradiation possibility, warrants comment. The values given by K. B. Wiberg and R. P. Ciula (*J. Am. Chem. Soc.*, **81**, 5261 (1959)) for the ring protons in ethyl bicyclo[1.1.0]butane-1-carboxylate (ii), (H_a, 8.03 τ; H_b 7.68 and 8.94 τ) are not, however, in line with the critical two in our case, one of which falls at far lower fields.


i

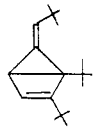


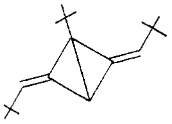
ii

of structures loosely accommodating the above data can be entertained. Of these, save for the [2,2.0]-bicyclohexa-2,5-diene system, all feature one or two three-membered rings; and except for two cases (alkylidenecyclopropanes VII and VIII), all are cyclopropene types (VI). Other investigators[10] have measured the chemical shifts of various hydrogens on the latter ring system, with the finding that a proton (H_c) on the saturated ring carbon appears at 8.6–8.7 τ, while a hydrogen (H_d) on the double bond falls at 3.0–3.4 τ. The proton resonances of the photo hydrocarbon lie distinctly outside these ranges and, beyond that, are reasonable for the proposed structure (V) (cyclobutene exhibits an olefinic proton peak at 4.03 τ and methylene resonance at 7.46 τ, $J = 0 \pm 0.2$ cps.).[8] As a possibility, structure VII is photochemically sound[5] and might be considered consistent with the physical data described above; however, thermal conversion to starting benzenoid material of VII or of its valence tautomer, tri-*t*-butylfulvene, seems unlikely.[11] Structure VIII appears even less plausible, both on the grounds of photochemical improbability as well as expected non-reversion to aromatic precursor. Thus anticipated structure V remains as the most acceptable of the various candidates.



VI


VII


VIII

Experiments on the preparation and detection of Dewar benzene itself will be presented later.

Acknowledgment.—The authors are grateful to Dr. C. Hoogzand, European Research Associates, Brussels, for a gift of one gram of tri-*t*-butylbenzene; to the Petroleum Research Foundation for financial support; and to Dr. A. Storni for valuable assistance.

(10) For example, G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003 (1961), and personal communications from Prof. Closs.

(11) J. H. Day, *Chem. Rev.*, **53**, 179 (1953).

(12) National Institutes of Health Predoctoral Fellow.

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RECEIVED AUGUST 13, 1962

BOOK REVIEWS

Crystallometry. By P. TERPSTRA, D. Sc., Sometime Professor of Crystallography and Mineralogy in the University of Groningen, and L. W. CODD, M.A. Academic Press Inc., 111 Fifth Avenue, New York 3, N. Y. 1961. xv + 420 pp. 18.5 × 25.5 cm. Price, $12.00.

Crystallometry is the quantitative examination of crystals with an optical goniometer to determine the angles between the faces. The data are then summarized in the form of projections and face pole figures. Terpstra and Codd have prepared a detailed volume on this topic written in a textbook style. However, the authors also intended that the book prove useful in a self teaching program. The present English version constitutes a second edition of an earlier Dutch version, first published in 1954.

Crystallometry is presented in great detail. The authors appear to have taken scrupulous care not to stray into adjacent disciplines even when these techniques are closely related to crystallometry and in fact may be considered as extensions of the optical technique. The style is easy to follow, it is almost chatty in many places. There are numerous excellent figures (273). The book seems to have been very carefully edited; the authors made good use of bold-face type in calling attention to significant conclusions. They also prepared many tabular summaries, and worked out selected problems in detail to illustrate the techniques which could be used at the different stages of the development of the subject. There is no overabundance of reference. However, those which have been included were carefully selected and should prove useful to the reader; references to literature include some papers which appeared in 1960. At the end of the book, the authors have assembled a chapter of significant questions and included the answers. The typography of the book is excellent and the paper and binding are of high quality. The English edition has been modernized in several respects. W. L. Bond's technique, based on matrix algebra, for reducing crystallographic data to a form required for plotting projections has been included. Detailed descriptions are given of modern goniometers. In Chapter 4 the elements of crystal symmetry are described and a useful compilation of the various notations is presented. No proofs were included.

The basic limitation of this book is that it is so narrow in scope. The authors sing the praises of crystallometry with evangelical fervor, although they recognize this narrowness. In several places (p. 129 and p. 162) they call attention to the limitation of the method but nonetheless laud a preoccupation with one aspect of the optical examination of crystals. Why is the goniometer to be preferred to the polarizing microscope for the identification of crystals? If one is concerned with the symmetry of a crystal, why not establish whether it is optically isotropic and why not attempt to measure the indices of refraction? The book would have been much more useful were some of the excessive details of crystallometry replaced by brief discussions of methods for the determination of crystal densities and simple tests for judging whether a crystal is piezo or pyroelectric. The authors do mention these techniques as additional and helpful devices which occasionally must be "dragged in" to establish the crystal symmetry. One concession to other techniques is a final chapter of ten pages on the use of Laue diagrams for plotting stereographic projections. The question remains whether it is proper to give students such a distorted impression.

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Thermodynamics, Second Edition. By GILBERT NEWTON LEWIS and MERLE RANDALL. Revised by KENNETH S. PITZER, Professor of Chemistry, University of California, Berkeley, and LEO BREWER, Professor of Chemistry, University of California, Berkeley. McGraw-Hill Book Company, Inc., 330 West 42nd Street, New York 36, N. Y. 1961. xii + 723 pp. 16.5 × 23.5 cm. Price, $12.50.

The first edition of Lewis and Randall was many books in one. It was a text book, a guide book, a prospectus to lure both the young and the adult chemist, a hand-book for setting up and for using a system of bookkeeping, a table of all entries in the book, and a case book of the authors'