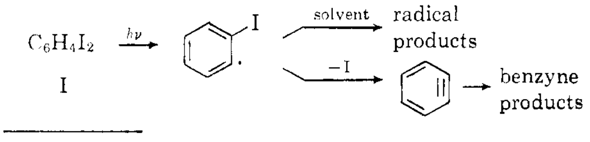
acterized in 42% yield as biphenyleneiodonium sulfate, identified by a comparison of m.p. and infrared spectrum with those of an authentic sample.[9] A similar photolysis in benzene for 175 hours gave a small amount of biphenyl, identified by m.p. and ultraviolet spectrum; 2-iodobiphenyl as the major product, identified by infrared and ultraviolet spectra; and 4% triphenylene[10] (two aromatic rings assumed to come from solvent), identified by m.p., infrared and ultraviolet spectra and m.p. of trinitrobenzene derivative. Triphenylene could not be detected by careful adsorption chromatography and ultraviolet analysis of the reaction mixture from the 43 hour photolysis. In a control experiment the photolysis of 2-iodobiphenyl in benzene for 60 hours gave 7% triphenylene (one aromatic ring from solvent) and 67% recovered 2-iodobiphenyl. These data clearly imply that triphenylene is formed by further reaction of 2-iodobiphenyl rather than directly from I.

The photolysis of I for 41 hours in benzene containing an equimolar amount of tetracyclone gave 2-iodobiphenyl as the major product and approximately a 10% yield of the expected Diels–Alder adduct of benzyne and tetracyclone, 1,2,3,4-tetraphenylnaphthalene,[7] identified by a comparison of m.p. and infrared and ultraviolet spectra with those of an authentic sample, which must arise from I since the photolysis of tetracyclone in benzene gave no tetraphenylnaphthalene. Photolysis of I for 65 hours in distilled furan gave a complex mixture from which well-defined products could not be isolated. It was possible to demonstrate the presence of small amounts of the anticipated adduct, 1,4-dihydronaphthalene-1,4-endoxide,[11] by converting it to α-naphthol.[11] The latter was identified by a comparison of its ultraviolet spectrum and the ultraviolet and visible spectra of the azo dye resulting from coupling with diazotized sulfanilic acid with those derived from authentic α-naphthol. A control experiment showed that α-naphthol was not formed from the photolysis of furan in the absence of I. In all of these experiments biphenylene was carefully sought by adsorption chromatography and spectrophotometric analysis. The characteristic ultraviolet absorption[12] of biphenylene was never observed.

The observed products clearly suggest the formation of both the 2-iodophenyl radical and benzyne[13] in the course of the reaction. It seems possible that the 2-iodophenyl radical is an intermediate common to both the "radical path" and the "benzyne path." Thus, it can either react directly with solvent or lose an iodine atom and give benzyne. In the absence of tetracyclone or furan, free iodine presumably functions as an efficient benzyne scavenger and leads to the regeneration of starting material. Another possible interpretation of the observed results is that the 2-iodophenyl radical is not an intermediate in the formation of benzyne, but that both the radical and benzyne arise directly from I. The two modes of photolytic decomposition in question would presumably proceed from different excited states. The present data do not permit a clear decision concerning the relative merits of these two schemes. Further experiments are in progress.[14]



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[9] J. Collette, D. McGreer, R. Crawford, F. Chubb and R. B. Sandin, *J. Am. Chem. Soc.*, **78**, 3819 (1956).

[10] C. M. Buess and D. D. Lawson, *Chem. Revs.*, **60**, 313 (1960).

[11] G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).

[12] W. Baker, M. P. V. Boarland and J. F. W. McOmie, *J. Chem. Soc.*, 1476 (1954).

[13] It is conceivable, but not particularly likely for steric reasons,[2] that the observed Diels–Alder adducts are the result of a two-step radical addition mechanism.

[14] We have been informed by N. Kharasch and W. Wolf that they have independently investigated the photolysis of 1,2-diiodobenzene. Their results, which they have kindly made available to us, will be published shortly.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER J. A. KAMPMEIER
ROCHESTER 20, N. Y. ELAINE HOFFMEISTER

RECEIVED JULY 13, 1962

AN INTERPRETATION OF THE FORMATION OF *trans*-CYCLOALKENES IN THE PARTIAL HYDROGENATION OF CERTAIN CYCLIC DIENES

Sir:

We wish to report certain observations made in the course of studies of the chemistry of cyclic allenes and acetylenes which are relevant to the mechanism(s) of catalytic hydrogenation.

When conventional preparative procedures are employed, partial hydrogenation of 1,2-cyclononadiene (I)[1] and 1,2-cyclodecadiene (II)[1] under one atmosphere of hydrogen in methanol at *ca.* 25° over 10% palladium on charcoal poisoned with pyridine gives exclusively *cis*-cyclononene from I[1,2] and predominantly *cis*-cyclodecene accompanied by some *trans*-cyclodecene from II.[1] However, under the conditions of hydrogenation, we find that the *trans* olefins are isomerized to the thermodynamically more stable *cis* isomers.[3] When aliquots removed during the rapid hydrogenation of I (*ca.* 0.98 equiv. in 4 min.) were analyzed by gas chromatography,[3] a substantial quantity of *trans*-cyclononene was detected. Extrapolation to the beginning of the hydrogenation established that a minimum of 17% of the olefin produced initially was the *trans* isomer. Similarly, we find that at least 32% of *trans*-cyclodecene is produced initially during the hydrogenation of II.[4]

The adsorption of an allene must occur such that the plane of the adsorbed double bond (only one can be involved) is essentially parallel to the surface of the catalyst. Thus, as shown in III, there are four ways an allene can be adsorbed. If adsorption is followed by the *cis* addition of two hydrogen atoms from the surface of the catalyst, two modes of adsorption, *a* and *b*, would give a *cis* olefin and two, *c* and *d*, would give a *trans* olefin. Many

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[1] Some aspects of the chemistry of I and II are discussed in a paper by W. R. Moore and R. C. Bertelson, *J. Org. Chem*,. in press.

[2] P. D. Gardner and M. Narayana, *ibid.*, **26**, 3518 (1961).

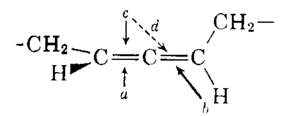
[3] In acetic acid at 25°, *cis/trans* ratios at equilibrium are C_9 *ca.* 650 and C_{10} *ca.* 41; A. C. Cope, P. T. Moore and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

[4] A small amount (*ca.* 5%) of II also isomerized to VI which was reduced more slowly than II.

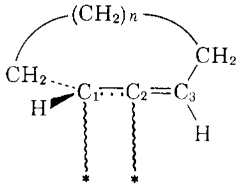
studies have emphasized that adsorption occurs in the least hindered way. Examination of molecular models of I and II shows that in each system adsorption along *a* or *b* (III) is not hindered but adsorption along *c* and *d* is hindered seriously by the methylene groups.[5] The question then arises, 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*.

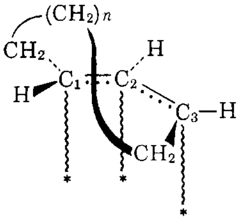
If this picture has any merit, it is clear that whenever species V is formed, *trans* olefin should be a significant product. A pertinent test arises in the hydrogenation of *cis,cis*-1,3-cyclodecadiene[11,12] (VI). This diene must have only one double bond adsorbed on the catalyst, since it cannot have 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.

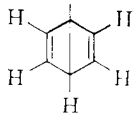
DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS WILLIAM R. MOORE

RECEIVED JULY 26, 1962

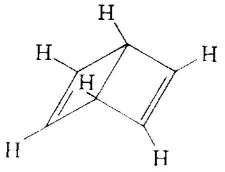
CHEMISTRY OF DEWAR BENZENE. 1,2,5-TRI-*t*-BUTYLBICYCLO[2.2.0]HEXA-2,5-DIENE

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.