

The dideuterioethylenes were geometrically pure and contained less than 2 per cent. monodeuterioethylene.

The vapor pressures of *cis*- and *gem*-dideuterioethylene are equal to within a few hundredths of a per cent. The *trans* compound value is greater than either the *cis* or the *gem* by 0.1% at the low temperatures and 0.05% at 180°K. The vapor pressure of *trans*-dideuterioethylene is 1.2% greater than that of ethylene at 130°K. and 1.6% greater at 180°K.

The existence of a difference between the equivalent structural geometric isomers, *cis*-, *trans*- and *gem*-dideuterioethylenes, the larger vapor pressure of the dideuterio compounds, and the largest pressure for the *trans*-dideuterioethylene support the structural theory of vapor pressure of isotopic molecules.² In the theory, a difference in the first quantum effect $(h/kT)^2$ between non-equivalent isotopic isomers, e.g., $N^{15}N^{14}O^{16}$ and $N^{14}N^{15}O^{16}$ was predicted and found.³ No such difference is to be expected in this approximation between equivalent isotopic isomers. The difference between the equivalent isomers can be interpreted in terms of quantum effects of the order $(h/kT)^4$ or in terms of the zero point energy difference of the liquid and gas. Both descriptions are equivalent and confirm a decrease in the C-H molecular stretching frequencies on condensation.⁴ The facts that the dideuterioethylenes are but 1.5% more volatile than ethylene and the *trans* is the most volatile is a consequence of stiffening of planar and out of plane bending motions of the hydrogen atoms by the intermolecular forces. The mathematical theory can be phrased as follows: condensation favors the clustering of deuterium within the molecule. This explanation is further confirmed by the difference in temperature coefficients of P_{trans}/P_{cis} vs. P_{trans}/P_{ord} .

A detailed description of the experiments and a full exposition of the applicable theory will be submitted for publication shortly.

(2) J. Bigeleisen, *J. Chem. Phys.*, **34**, 1485 (1961).

(3) J. Bigeleisen and S. V. Ribnikar, *ibid.*, in press.

(4) G. Glockler and M. M. Renfrew, *ibid.*, **6**, 170 (1938).

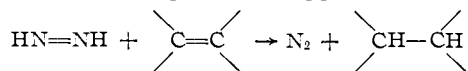
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CHEMISTRY OF DIIMIDE. II. STEREOCHEMISTRY OF HYDROGEN TRANSFER TO CARBON-CARBON MULTIPLE BONDS

Sir:

In Part I¹ we have proposed that diimide (HN=NH) is the active hydrogenator in the reduction of unsaturated linkages by mixtures of hydrazine and oxidizing agents such as oxygen-copper ion and hydrogen peroxide-copper ion



Of special note are the following points:

(1) E. J. Corey, W. L. Mock and D. J. Pasto, *Tetrahedron Letters*, **11**, 353 (1961); see also S. Hünig, H. Müller and W. Thier, *ibid.*, in press (1961).

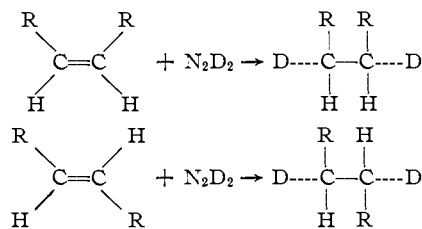
1. Reduction of multiple bonds also can be effected by decarboxylation of potassium azodiformate (KOOCN=NCOOK) in aqueous media, a process which quite clearly involves the formation of diimide.²

2. Diimide itself possesses a finite lifetime; its decomposition into N₂ and H₂ appears not to be inevitable, and is probably even less favorable than intermolecular hydrogen transfer as exemplified by self-annihilation giving molecular nitrogen and hydrazine.^{2,3}

3. Diimide has been implicated^{4,5} as an intermediate in the oxidation of hydrazine by reagents such as are effective for hydrogenation of multiple bonds with hydrazine.

We now report that the steric course of this remarkable addition of hydrogen is *quite generally cis*, a finding in accord with the behavior expected of a hydrogenating agent which derives its reactivity from formation of a very stable molecule after the transfer of a pair of hydrogens.

The reduction of maleic and fumaric acids either by deuteriohydrazine-oxidizing agent or by potassium azodiformate-deuterium oxide affords stereospecifically *meso*- and *dl*-2,3-dideuteriosuccinic acids, respectively. The deuteriated succinic acids were assayed by infrared analysis, being readily distinguished by their markedly different absorption in the 8-9 μ region⁶; only the product of *cis*-addition was detectable and we estimate that these reductions are at least 97% stereospecific.



Similarly, reduction of *cis*- and *trans*-2-butene-1,4-diols produced only *meso*- and *dl*-2,3-dideuterio-butane-1,4-diols, respectively, isolated (after permanganate oxidation) and analyzed as the corresponding succinic acids.

Reduction of *cis*- and *trans*-stilbenes was also stereospecific in the deuteriated system, affording *meso*- and *dl*-1,2-dideuterio-1,2-diphenylethanes respectively. The stereochemistry of these deuteriated ethanes was determined by ozonolysis and oxidation to the succinic acids.

cis-Hydrogenation also was observed in the reaction of dimethylmaleic acid with hydrazine-hydrogen peroxide which afforded only *meso*-2,3-dimethylsuccinic acid. Further, reduction of acetylenic linkages also appears to be a *cis* addition. Partial hydrogenation of diphenylacetylene gave a mixture of starting material, *cis*-stilbene and 1,2-diphenylethane; no *trans*-stilbene could be isolated or detected by infrared analysis.

(2) C. V. King, *J. Am. Chem. Soc.*, **62**, 379 (1940).

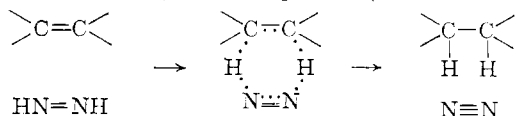
(3) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **28**, 719 (1958).

(4) L. F. Audrieth and B. F. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, New York, N. Y., 1951, Chapter 6.

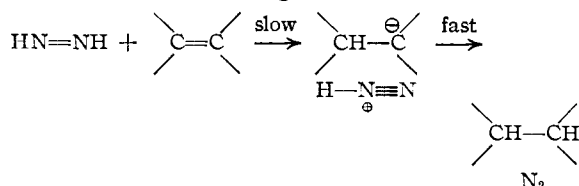
(5) W. C. E. Higginson in "Recent Aspects of the Inorganic Chemistry of Nitrogen," Chemical Society Special Publication No. 10, 1957, p. 95.

(6) C. R. Childs and K. Bloch, *J. Org. Chem.*, **26**, 1630 (1961).

For several reasons it is attractive to consider the reduction of multiple bonds by diimide as a *synchronous transport* of a pair of hydrogens, *i.e.*, a cyclic addition of two hydrogens either in exact or nearly exact concurrence. Foremost among these are the high stereospecificity and the fact



that such a mechanism fully couples the driving force of nitrogen formation with the addition reaction.⁷ The extreme alternative of a two step process, seems especially unlikely for the reduction of isolated olefinic linkages.⁸



(7) The cyclo-addition path for hydrogenation requires that the *syn*-form of diimide serve as the actual transfer agent and implies either that this isomer is generated directly or that *syn* and *anti* forms are in rapid equilibrium. The unsymmetrical isomer of diimide $\text{H}_2\text{N}^+ = \text{N}^-$ might also operate as a *cis* hydrogenator by cyclo-addition.

(8) We thank the National Science Foundation for fellowships to W. C. M. (predoctoral) and D. J. P. (postdoctoral) and the Higgins Fund of Harvard University for generous financial support.

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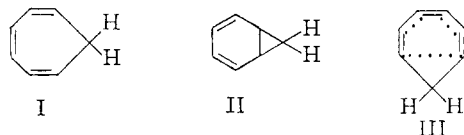
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EVIDENCE FOR THE MAGNITUDE OF THE 1,6-OVERLAP ENERGY IN A SUBSTITUTED TROPILIDENE

Sir:

There has been considerable discussion regarding the intimate structure of tropilidene and related molecules. The system has been discussed in terms of the concept of valence tautomerism¹ ($\text{I} \rightleftharpoons \text{II}$) and in terms of a planar pseudo-aromatic structure involving 1,6-overlap² (III). Subsequently, infrared and Raman frequencies have



been assigned on the basis of a structure of C_{2v} symmetry (III)³ and it has been stated that thermochemical data support the view that 1,6-interaction is quite strongly developed.⁴ On the other hand, the first workers who obtained heat of hydrogenation data on tropilidene clearly recognized that the resonance energy (6.7 kcal.)⁵ was closely commensurate with the resonance energy of a non-cyclic triene in which 1,6-overlap is non-

(1) E. J. Corey, H. J. Burke and W. A. Remers, *J. Am. Chem. Soc.*, **77**, 4941 (1955).

(2) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *ibid.*, **78**, 5448 (1956).

(3) M. V. Evans and R. C. Lord, *ibid.*, **82**, 1876 (1960).

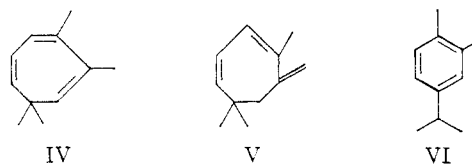
(4) A. G. Harrison, L. R. Honnen, H. J. Dauben and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

(5) J. Conn, G. Kistlakowsky and E. Smith, *ibid.*, **61**, 1868 (1939).

existent. More recent workers have excused the low value of the resonance energy on the basis of the underestimation of the strain energy involved in attainment of the planarity requisite for effective delocalization or on improper choice of model compounds for the heat of hydrogenation.⁶

In sum, the question of the degree of 1,6-overlap in tropilidenes is in a rather uncertain state, depending as it does upon the comparison of closely similar, highly uncertain quantities. I now wish to report an experiment which gives a direct estimate of the importance of 1,6-overlap in tropilidenes.

The preparation of 2,3,7,7-tetramethyl-1,3,5-cycloheptatriene (IV) by published procedures⁷⁻¹⁰ gave rise to a mixture of olefins as evidenced by vapor phase chromatography (v.p.c.). It proved possible to separate the two olefins by preparative v.p.c. on a didecyl phthalate column at 125° and to obtain samples of each isomer (satisfactory analyses were obtained) of > 95% purity. The predominant material, 2,3,7,7-tetramethyl-1,3,5-cycloheptatriene (IV) (b.p. *ca.* 74° (13 mm.), n_D^{25} 1.5010, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 268 μ , $\log \epsilon$ 3.59) could be distinguished readily from the less predominant material, 2-methylene-3,7,7-trimethyl-3,5-cycloheptatriene (V) (b.p. *ca.* 76° (14 mm.), n_D^{25} 1.5185, $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 287 μ , $\log \epsilon$ 4.04), by virtue of strong infrared bands at 1553, 835, 811, 766 and 715 cm^{-1} in IV which are lacking in V and at 3080, 1581, 899, 826, 755 and 709 cm^{-1} in V which are lacking



in IV. Further confirmation of the structure of these two olefins comes from the nuclear magnetic resonance spectra which show, in IV, two olefinic methyl groups at 8.06 and 8.21 τ and a complicated, seven peak spectrum in the vinyl hydrogen region characteristic of tropilidenes. The latter compound, V, shows only one vinyl methyl group at 8.12 τ and a saturated methylene group at 7.88 τ (area ratio *ca.* 3:2) and a much simpler vinyl hydrogen spectrum with three peaks at 4.54, 5.01 and 5.27 τ . Further indication of the close relationship of IV and V comes from their interconversion and transformation to a common product (see below). It may be noted that the properties reported by each of the sets of workers who had reported IV previously⁷⁻¹⁰ show that they actually had a mixture of IV and V at hand, though only the first of these workers so reported. The infrared spectrum of 3,4,7,7-tetramethyltropilidene (*sic*) recorded by Lord³ is identical with that of our sample of IV of about 97% purity by v.p.c.

The fact that both IV and V were isolated from acid catalyzed dehydration, conditions which might

(6) R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *ibid.*, **79**, 4127 (1957).

(7) E. J. Corey, H. J. Burke and W. A. Remers, *ibid.*, **78**, 180 (1956).

(8) K. Alder, K. Kaiser and M. Schumacher, *Ann.*, **602**, 80 (1957).

(9) J. R. B. Campbell, A. M. Islain and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

(10) H. Rupe and W. Kerkovius, *Ber.*, **44**, 2702 (1911).