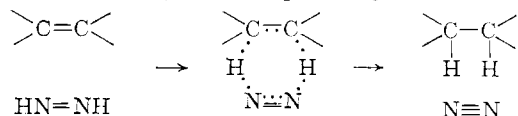For several reasons it is attractive to consider the reduction of multiple bonds by diimide as a *synchronous transport* of a *pair* of hydrogens, *i.e.*, a cyclic addition of two hydrogens either in exact or nearly exact concurrence. Foremost among these are the high stereospecificity and the fact

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]
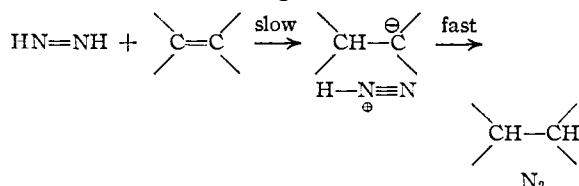
(7) The cyclo-addition path for hydrogenation requires that the *syn*-form of diimide serve as the actual transfer agent and implies either that this isomer is generated directly or that *syn* and *anti* forms are in rapid equilibrium. The unsymmetrical isomer of diimide $H_2N^+ = N^-$ might also operate as a *cis* hydrogenator by cyclo-addition.

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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 tautomerism[1] (I $\rightleftarrows$ II) and in terms of a planar pseudo-aromatic structure involving 1,6-overlap[2] (III). Subsequently, infrared and Raman frequencies have
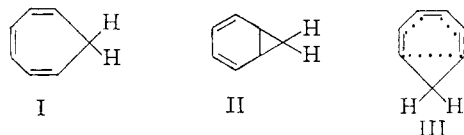
been assigned on the basis of a structure of C_{2v} symmetry (III)[3] and it has been stated that thermochemical data support the view that 1,6-interaction is quite strongly developed.[4] On the other hand, the first workers who obtained heat of hydrogenation data on tropilidene clearly recognized that 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. Kistiakowsky 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 procedures[7-10] 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.), $n^{25}D$ 1.5010, $\lambda_{max}^{C_2H_5OH}$ 268 mμ, log ϵ 3.59) could be distinguished readily from the less predominant material, 2-methylene-3,7,7-trimethyl-3,5-cycloheptadiene (V) (b.p. *ca.* 76° (14 mm.), $n^{25}D$ 1.5185 $\lambda_{max}^{C_2H_5OH}$ 287 mμ, log ϵ 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

IV　　　　　　　　　V　　　　　　　　　VI
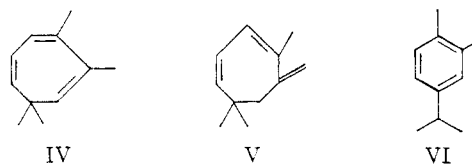
in IV. Further confirmation of the structure of these two olefins comes from the nuclear magnetic resonance spectra which show, in IV, two olefinic methyl groups at 8.06 and 8.21τ and a complicated, seven peak spectrum in the vinyl hydrogen region characteristic of tropilidenes. The latter compound, 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 previously[7-10] 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 Lord[3] 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. Islam and R. A. Raphael, *J. Chem. Soc.*, 4096 (1956).

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

have been expected to produce IV exclusively if IV were truly significantly more stable, suggested that a determination of the equilibration of IV and V under acid catalysis be made. The study of the equilibration was complicated somewhat by the fact that both IV and V rearrange to 4-iso-propyl-o-xylene (VI), whose identity was proved by oxidation[11] to 3,4-xylic acid, m.p. 164–165°. The pseudo-first order rate constant for conversion of either IV or V to VI in 0.25 M toluenesulfonic acid in acetic acid at 25.0° was 1.1×10^{-4} sec.$^{-1}$. Simultaneous with the production of VI, the isomers IV and V approach an equilibrium in which the ratio of IV:V is about 9. During the early stages of the isomerization (the first half-life), the ratio IV:V can be determined quite accurately and has reached the values of 88:12 (starting from 96% pure V) and 92:8 (starting from 97% pure IV). Unfortunately the v.p.c. analytical method becomes highly inaccurate as the substances IV and V become minor components of the reaction mixture, so the further approach to equilibrium cannot be observed.

When the ΔF for V $\rightleftarrows$ IV is calculated using K = 9, a value of -1.3 kcal./mole results. This measurement of an equilibrium between two compounds of a common skeleton and degree of hydrogenation at once eliminates the problems involved in the choice of model compounds for use in calculation of resonance energies from heats of hydrogenation data. Since 1,6-overlap is clearly impossible in V, it follows that the stabilization of IV over V, in the absence of other effects, will measure directly the stabilization effected by 1,6-overlap.

It is clear, however, that IV is stabilized relative to V to some extent in that the olefinic bond involved in the isomerization is trisubstituted in IV and only disubstituted in V. On the other hand, Dreiding models indicate that the strain energy involved in making the triene system in IV coplanar is larger than that involved in making the triene coplanar in V, since in this latter case the triene system can approximate coplanarity even though the seven-membered ring remains strongly puckered at the 1 and 7 positions. (The λ_{max} of V at higher wave length than that of IV probably reflects this.) It is difficult to assess the relative importance of these two opposing effects, so that one cannot decide in which direction, or by how much, it is necessary to modify the experimentally determined value of 1.3 kcal./mole stabilization of tropilidene by 1,6-overlap.[12] Nevertheless, it is clear that 1,6-overlap is by no means the major factor in this system that it has been postulated to be.

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(11) O. Kruber, Ber., 57, 1008 (1924).

(12) If one makes the prima facie reasonable assumption that a measure of the stabilization of IV over V due to strain and degree of substitution will be given by that of methylcycloheptene over methyl-enecycloheptane, with amounts to 2.3 kcal./mole,[13] it follows that 1,6-overlap is actually destabilizing by 1.0 kcal./mole. It is evident that this extreme assumption is unjustified.

(13) R. B. Turner and R. H. Garner, J. Am. Chem. Soc., 80, 1424 (1958).

LONG-RANGE PROTON SPIN-SPIN INTERACTIONS: THE ^{13}CH$_3$ SATELLITES IN ACETONE

Sir:

Several examples of resolvable nuclear magnetic resonance absorption lines arising from the coupling between protons separated by four or more bonds recently have been reported.[1,2,3] We have observed such a coupling in acetone which, we believe, arises from a coupling mechanism different from those operating in the previously analyzed systems. The acetone coupling depends upon a mechanism related to the one recently proposed by Karplus[4] for unsaturated systems but different in that the unsaturated bond is not a link in the connective bond chain between the protons.

The proton resonance spectrum[5] of acetone consists of a single sharp line, which arises from the six equivalent methyl protons, surrounded symmetrically by two weak satellite groups at ± 63.6 cps., which arise as a result of the ^{13}C–H coupling in the 2.2 mole per cent. of acetone molecules containing one ^{13}CH$_3$ group. Under high resolution the ^{13}CH$_3$ groups each split into a well-resolved 1:3:3:1 quadruplet with a spacing of 0.54 ± 0.05 cps. This quadruplet is the result of long-range spin–spin coupling of the ^{13}CH$_3$ protons to the non-equivalent ^{12}CH$_3$ protons four sigma bonds away. This spacing is equal to the coupling constant A_{HH} between protons on the two methyl groups.

A coupling of similar magnitude was observed in acetoxime, $(CH_3)_2C\!\!=\!\!NOH$, in saturated tetrachloroethylene solution; however, the solution was relatively dilute and accurate measurements were not feasible because of an unfavorable signal-to-noise ratio. On the other hand, the ^{13}CH$_3$ satellites of the related alcohol $(CH_3)_2CHOH$ show no evidence of an appreciable coupling between the methyl groups. We estimate a value of A_{HH} not greater than 0.2 cps., based on the observed line widths.

Previous examples of resolvable long-range proton–proton coupling through sigma-bonded systems[1] have involved compounds in which there are fixed or highly favored conformations of the molecules with respect to rotation about the carbon–carbon bonds through which the protons interact. This is to be expected in view of the dependence of the magnitude of coupling constants on the dihedral angle between bonding orbitals on adjacent carbon atoms.[6] In acetone, however, the internal rotation frequency about the carbon–carbon bonds is very much greater than the proton resonance frequencies used, the barrier to rotation being approximately 2.8 kcal./mole. Furthermore, the C–C–C bond angle differs from 120° by not more

(1) D. R. Davis, R. P. Lutz and J. D. Roberts, J. Am. Chem. Soc., 83, 246 (1961).

(2) J. N. Shoolery, L. Johnson and W. A. Anderson, J. Mol. Spectroscopy, 5, 110 (1960).

(3) (a) E. B. Whipple, J. H. Goldstein and W. E. Stewart, J. Am. Chem. Soc., 81, 4761 (1959); (b) E. B. Whipple, J. H. Goldstein and L. Mandell, J. Chem. Phys., 30, 1109 (1959).

(4) M. Karplus, J. Am. Chem. Soc., 82, 4431 (1960); J. Chem. Phys., 33, 1842 (1960).

(5) All spectra were observed at 40 Mc. with a Varian Associates Model V4300-B high resolution n.m.r. spectrometer. Frequency measurements were made by the sideband method using a calibrated Hewlett-Packard Model 200D audiofrequency oscillator.

(6) M. Karplus, J. Chem. Phys., 30, 11 (1959).