ferent intensity are observed with the more intense at higher field. ε-Heptachlorocyclohexane has two axial hydrogens adjacent to an axial chlorine, one axial hydrogen adjacent to two axial chlorines and two equatorial hydrogens highly surrounded by chlorine. Its spectrum shown in Fig. 1 fits the steric interpretation.

In the γ-isomer, which contains four axial hydrogens each pair of which adjoins an axial chlorine and one equatorial hydrogen highly surrounded by chlorine, a complex spectrum is obtained. This seems to be due to an interaction between chemical shift and spin–spin coupling and the peaks cannot be assigned with certainty.[16]

The δ-isomer has two axial hydrogens adjacent to one axial chlorine, one axial hydrogen adjacent to two axial chlorines, and two equatorial hydrogens partly surrounded by chlorines. If the ring converts to its other conformation the equatorial hydrogens become axial and adjacent to two axial chlorines, while the hydrogen in this environment previously becomes equatorial. However, the two axial hydrogens adjacent to one axial chlorine become equatorial and largely surrounded by chlorine. The carbon atoms attached to these hydrogens adjoin the disubstituted ring carbon atom which might cause a chemical shift to lower field because of an inductive effect. If the inductive effect and rapid ring interconversion occur, a single proton resonance peak might be expected. Without the inductive effect ring interconversion would still give rise to two peaks since the conformations are not equivalent. However, only a single peak was found.

After a correction for chemical shift it is found that ring protons in a similar environment have their resonance absorption in the same region. This is shown in Table II. The axial hydrogens adjacent to one substituent in the δ- and *myo*-isomer are the only discrepancy.

TABLE II

STERIC EFFECT ON RING PROTON ABSORPTION

Axial hydrogen alone	52 (β 6)	37 epi	39 (α 7)
	47 (δ 6)	48-*scyllo*	
		41 *myo*	
Axial hydrogens with 1 axial substituent	23 (α 6)	29-L	26 (a 7)
	47 (δ 6)	41-*myo*	20 (γ 7)[b]
	32 (ε 6)	13 *neo*[a]	30 (ε 7)
Axial hydrogen with 2 axial substituents		22-*epi*	8 (ε 7)
Equat. hydrogen largely surrounded by subst.	26 (δ 6)	21-*myo*	0 (γ 7)[b]
	25 (ε 6)		22 (ε 7)
Equat. hydrogen partly surrounded by subst.	39 (α 6)	45-L	
		35-*epi*	

[a] Doubtful due to weak signal and hot solution. [b] Only approximate because of chemical shift spin–spin interaction.

Conclusion.—In hexasubstituted cyclohexanes where the inductive effect is the same for all the ring protons several absorption peaks may be observed. These can be correlated with the proximity of substituents which shift the resonance of the more sterically hindered protons to a lower field. A similar effect is observed in the proton resonance spectra of the heptachlorocyclohexanes.

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ITHACA, N. Y.

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[16] H. M. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Resonance Energies of Conjugated Acetylenes

BY MAURICE M. KREEVOY

RECEIVED SEPTEMBER 4, 1958

Inductive and resonance effects on the heats of hydrogenation of substituted acetylenes have been evaluated. Inductive effects are about twice as large as those in olefin hydrogenation, and the Baker–Nathan effect per α-hydrogen is about half again as large, but resonance effects due to conjugation are slightly smaller. Resonance effects due to conjugation are a function of the dimensions of the π-bond system but, to a good approximation, independent of the nature of the atoms involved. All this is in good accord with the predictions of simple L.C.A.O.–M.O. theory.

Flitcroft and Skinner recently have measured the heats of hydrogenation of a number of substituted acetylenes.[1,2] They observed that for all compounds containing the structural feature —C≡C—COX, the heat of hydrogenation was *higher* (*i.e.*, *more* heat was given off) than for the corresponding unsubstituted acetylene.[1] They correctly concluded that inductive effects (ionic–covalent resonance) were responsible for this apparent anomaly. The present paper shows that a set of resonance energies for conjugated acetylenes which are all of the proper sign and of a reasonable magnitude can be obtained if inductive and resonance effects are assumed to be additive and inductive and Baker–Nathan effects are quantitatively accounted for. (In this paper the experimentally observed stabilization of a molecule containing one or more hydrogen atoms alpha to a π-electron system will be called the Baker–Nathan effect.)

Unconjugated Acetylenes.—Taft and Kreevoy[3] have suggested that the heats of hydrogenation of non-conjugated acetylenes to saturated hydro-

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[1] T. L. Flitcroft and H. A. Skinner, *Transactions of the Faraday Society*, **54**, 47 (1958).

[2] T. L. Flitcroft, H. A. Skinner and M. C. Whiting, *ibid.*, **53**, 784 (1957).

[3] R. W. Taft, Jr., and M. M. Kreevoy, THIS JOURNAL, **79**, 4011 (1957).

carbons at 82° in the gas phase can be represented by eq. 1

$$\Delta H - \Delta H_0 = \rho^*\Sigma\sigma^* + h(n - n_0) \qquad (1)$$

where σ^* is a constant characteristic of a substituent and measuring its ability to supply electrons.[4] The summation is taken over the two R groups of R—C≡C–R. The parameter $\rho^* = -5.53$ and is characteristic of the reaction. It is a measure of the difference in electron-withdrawing power between an sp bond and an sp^3 bond. The parameter $h = 0.59$ and is a measure of the Baker–Nathan stabilization of an acetylenic compound by a single α-hydrogen atom. The number of α-hydrogen atoms in the general acetylenic compound, RC≡CR, is n and the corresponding number in dimethylacetylene (6) is n_0. For dimethylacetylene $n = n_0$, $\Delta H = \Delta H_0$, and $\Sigma\sigma^* = 0$. Equation 1 correlates the heats of hydrogenation of nine substituted acetylenes[5] at 25° in the vapor phase with good precision. The parameters for the 25° data were evaluated by the method of least squares[6] and have the values: $\rho^* = -5.06 \pm 0.18$; $h = 0.61 \pm 0.05$. These do not differ from the parameters appropriate to the 82° data by more than their combined uncertainties. The correlation coefficient for the 25° data is 0.99[7] and the average difference between observed and calculated heats of hydrogenation is 0.3 kcal./mole, about the same as the estimated uncertainty of the experimental data.[5]

The heats of hydrogenation of solid but-3-ynoic acid and pent-3-ynoic acid are -72.4 ± 1.1 and -65.8 ± 1.2 kcal./mole, respectively.[1] Subtracting -65.1 kcal./mole, the heat of hydrogenation of dimethylacetylene, $\Delta\Delta H$ for these compounds is -7.3 and -0.7 kcal./mole. The values calculated from Eq. 1 with the given parameters are -10.3 and -6.0 kcal./mole. The difference is thought to be due principally to differences in heats of fusion and vaporization between the saturated and the acetylenic carboxylic acids. These differences have been estimated and corrected for as follows: The entropy of fusion, ΔS_{fus}, has been assumed the same for the saturated and the acetylenic compounds and both the heat and the entropy of fusion have been assumed temperature independent for both compounds. With these assumptions the differences in heats of fusion, ΔH_{fus}, are given by eq. 2. The entropy of fusion

$$\Delta H_{\text{fus}}^{\text{sat}} - \Delta H_{\text{fus}}^{\text{ace}} = (T_{\text{fus}}^{\text{sat}} - T_{\text{fus}}^{\text{ace}})\Delta S_{\text{fus}} \qquad (2)$$

is obtainable in the usual way for the saturated acids from their known melting points[8] and heats of fusion.[1] From the known melting points, T_{fus}, of the acetylenic acids[9,10] $\Delta H_{\text{fus}}^{\text{sat}} - \Delta H_{\text{fus}}^{\text{ace}}$ is then -0.8 and -1.1 kcal./mole for the 4- and 5-carbon acids. The difference between the heat of vaporization of liquid but-3-ynoic acid and liquid butyric acid was estimated by Trouton's rule applied to the boiling points at 5 mm.[9b,11,12] and is -1.1 kcal./mole. The boiling point of pent-3-ynoic acid is not known so it was assumed that the difference between the heats of vaporization of the 5-carbon acids is also -1.1 kcal./mole. Using these values the vapor phase ΔH's become -9.2 and -2.6 kcal./mole for the 4- and 5-carbon acids, respectively. The agreement between these and the calculated values cited above is probably as good as could be expected in view of the cited uncertainty in the measured values and the many uncertainties in the conversion from the solid to the vapor phase.

Conjugated Acetylenes.—For heats of hydrogenation of olefins and free energies of hydrogenation of carbonyl compounds it has been shown[13] that $\rho^*\Sigma\sigma^*$ is a measure of inductive effects in conjugated compounds also, and that the Baker–Nathan effect can be estimated by $h(n-n_0)$. If this is also true for heats of hydrogenation of acetylenes, the changes in resonance energy, $\Delta H\psi$, accompanying hydrogenation, are given by eq. 3. In each case the reaction is accompanied by a loss in resonance energy and $\Delta H\psi$ should be a good approximation of that loss. Since resonance

$$\Delta H\psi = (\Delta H - \Delta H_0) - 5.06\Sigma\sigma^* - 0.61(n - n_0) \qquad (3)$$

energies are always negative, $\Delta H\psi$ should always be positive. The values of $\Delta H\psi$ given by eq. 3 are tabulated. The experimental heats of hydrogenation are those of ref. 1 except where otherwise noted. In general, heats of hydrogenation based on older heats of combustion are not included. The various devices which have been used to convert solid and liquid state data to the gas phase are listed in the footnotes to the table, and in general parallel the methods used for the non-conjugated acids cited above.

The losses in resonance energy accompanying the hydrogenation of the corresponding olefins, $\Delta H\psi$ (olefin), are also tabulated, as are the calculated losses in resonance energy, $\Delta E\psi$.

Calculations of $\Delta E\psi$ were made by the naive L.C.A.O.–M.O. method with all π-bond resonance integrals, β, taken equal and the Coulomb integral for oxygen assumed to be more negative than that of carbon by 1/2 β. In carbon subnitride the

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(4) (a) R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953); (b) R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

(5) These are: acetylene itself, six monoalkyl acetylenes, two dialkyl acetylenes and propargyl alcohol. All of the data except that for propargyl alcohol were taken from F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun and G. Pimentel, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., pp. 479, 480, 465, 466, and bear an estimated uncertainty of 0.20 to 1.00 kcal./mole. The value for propargyl alcohol was obtained by combining the heats of combustion of propargyl alcohol (M. S. Kharasch, *Bur. Stand. J. Res.*, **2**, 359 (1929)) and 1-propanol (F. D. Rossini, *Bur. Stand. J. Res.*, **13**, 189 (1934)) and probably has an uncertainty of about 1 kcal./mole.

(6) W. A. Pavelich, Ph.D. Thesis, The Pennsylvania State University, June, 1955.

(7) H. H. Jaffé, *Chem. Revs.*, **53**, 253 (1953).

(8) J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Houston, Tex., 1950, pp. 387, 390.

(9) (a) I. Heilbron, E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 606 (1949); (b) J. H. Wotiz, J. S. Matthews and J. A. Lieb, THIS JOURNAL, **73**, 5503 (1951).

(10) E. R. H. Jones, G. H. Whitman and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

(11) E. W. Washburn, editor, "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 219.

(12) It is recognized that Trouton's rule does not generally apply to associated liquids such as those under consideration here. Nevertheless $\Delta H_{\text{vap}}/T_{\text{p}}$ ought to be quite similar for two such closely related compounds.

(13) M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4016 (1957).

Effect of Conjugation, $\Delta H\psi$, on Heats of Hydrogenation of Acetylenes, $R_1-C\equiv C-R_2$

R_1	R_2	$\Delta H\psi$ obsd., kcal./mole	$\Delta H\psi$[a] olefin	$\Delta E\psi$ (β = −13.5 kcal./mole
H	C_6H_5	4[b]	4.3	5.8
H	$COOCH_3$	2[b,c]	5.7	6.6
n-C_4H_9	$CH=CH_2$	5[b,d]	5.1	6.3
n-C_3H_7	$COOCH_3$	5[b]	5.7	6.6
n-C_4H_9	$C\equiv C$-n-C_4H_9	10[b,e,f,g]		12.6
C_6H_5	C_6H_5	11[h,i] 12[j]	12.5	12.6
p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	9[h,j,k,l]		12.6
o-$CH_3C_6H_4$	o-$CH_3C_6H_4$	9[h,j,k,m]		12.6
C_6H_5	COOH	8[h,n,o]		12.8
COOH	COOH	12[h,o,p]		13.4
C_6H_5	$C\equiv CC_6H_5$	19[h,j,k,q]		19.9
$C\equiv N$	$C\equiv N$	23[b,r,s]		26.6

[a] Values taken from ref. 13. [b] Converted from the liquid to the vapor phase by use of Trouton's rule. [c] The hydrogen uptake for this compound was 2–4% below calculated, so this value may be somewhat less reliable than others (ref. 1). [d] The value of σ^* for $CH=CH_2$ was assumed to be the same as that for $CH=CHCH_3$. [e] Data taken from ref. 2. [f] The value of σ^* for $C\equiv C$-n-C_4H_9 was estimated by subtracting 0.05 from σ^* for $C\equiv CC_6H_5$ (1.35); 0.05 is the difference between σ^* for $CH=CHC_6H_5$ and that for $CH=CHCH_3$. [g] The heat of hydrogenation of a single triple bond was obtained by subtracting the heat of hydrogenation of n-$C_4H_9C\equiv C$-n-C_6H_{13} (calculated from eq. 1) from that of n-$C_4H_9C\equiv CC=C$-n-C_4H_9. [h] The boiling point of the acetylene is not known so no correction for differences in the heats of vaporization could be made; if such a correction could be made it probably would lower the tabulated value of $\Delta H\psi$. Converted from the solid to the liquid phase by use of the known heats of fusion of diphenylacetylene and 1,2-diphenylethane (ref. 11, Vol. V, p. 134). [j] Data of Coops and co-workers (J. Coops, G. J. Hoijtink, Th. J. E. Kramer and A. C. Faber, *Rec. trav. chim.*, **72**, 781 (1953); J. Coops, D. Mulder, J. W. Dienske and J. Smittenberg, *ibid.*, **72**, 781 (1953); J. Coops, G. J. Hoijtink and Th. J. E. Kramer, *ibid.*, **72**, 793 (1953)). [k] Corrected from the solid to the liquid state by use of eq. 2, assuming $\Delta S_{fus} = 10$ cal./mole deg. [l] σ^* for p-$CH_3C_6H_4$ was obtained by adding σ for a p-CH_3 group (−0.17) to σ^* for C_6H_5 (+0.625). [m] σ^* for o-$CH_3C_6H_4$ was obtained by adding σ^* for an o-CH_3 group (−0.17) to that for C_6H_5. [n] Corrected from the solid to the liquid state by use of eq. 2; ΔS_{fus} is known for hydrocinnamic acid (ref. 11, Vol. V, p. 134). [o] σ^* for the COOH group was obtained by multiplying that for the CH_2COOH group (1.05) by 2.8. [p] Differences in heats of fusion were neglected because the melting points of the saturated and the acetylenic acid are nearly the same. [q] The heat of hydrogenation of one acetylenic linkage was obtained by subtracting −67.1 kcal./mole, the calculated heat of hydrogenation of $C_6H_5C\equiv CCH_2CH_2C_6H_5$, from the observed heat of hydrogenation. $\Delta H\psi$ for $C_6H_5C\equiv CCH_2CH_2C_6H_5$ was taken as 4 kcal./mole. [r] Data taken from M. S. Kharasch, *Bur. Stand. J. Res.*, **2**, 359 (1929), and private communication with Dr. G. T. Armstrong of the U. S. Bureau of Standards. [s] σ^* for the $C\equiv N$ group was estimated by multiplying that for CH_2CN by 2.8.

Coulomb integral of nitrogen was assumed to be the same as that for carbon. The value −13.5 kcal./mole was used for β. These approximations have been shown to give reliable estimates of the resonance energies of conjugated olefins and carbonyl compounds.[13]

The values of $\Delta H\psi$ are all of the proper sign and in fairly good agreement with calculated values of $\Delta E\psi$. The resonance energy of octa-3-yne-1-ene should be the same regardless of whether it is considered an acetylene or an olefin. Considered an olefin, a value of 6 kcal./mole is obtained by the methods previously described.[13,14] This can be compared with the value 5 kcal./mole tabulated above. Where data for comparable compounds are available, $\Delta H\psi$ for hydrogenation of compounds containing the grouping $-\mathrm{C}\equiv\mathrm{C}-\overset{|}{\mathrm{C}}=\mathrm{X}$ is similar to that for hydrogenation of compounds containing the grouping $-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}=\mathrm{C}$. In accord with the predictions of theory, however, $\Delta H\psi$ for hydrogenation of compounds containing the grouping $-\mathrm{C}\equiv\mathrm{C}-\mathrm{C}\equiv\mathrm{X}$ is about twice that for hydrogenation of compounds containing either the grouping $-\mathrm{C}\equiv\mathrm{C}-\overset{|}{\mathrm{C}}=\mathrm{X}$ or the grouping $-\overset{|}{\mathrm{C}}=\overset{|}{\mathrm{C}}-\overset{|}{\mathrm{C}}=\mathrm{X}$.

It will be noted that the experimental values of $\Delta H\psi$ are in general a little less than the calculated values. This is probably due to the neglect of differences in overlap integrals arising from differences in bond lengths.[1,15] The discrepancies are barely outside of experimental uncertainty, however, so it did not seem worthwhile to make the more elaborate calculations.

The general agreement between expected values of $\Delta H\psi$ and those found provides support for eqs. 1 and 3, and for the value of ρ^*. In one case (carbon subnitride) the inductive effect, $\rho^*\Sigma\sigma^*$, is over 36 kcal./mole, so that any serious error in ρ^* (or σ^*) would give a completely erroneous value of $\Delta H\psi$. In particular, neglect of inductive effects ($\rho^* \equiv 0$) would lead to a substantial resonance energy of the *wrong sign.*

Kreevoy and Taft[13] suggested the following generalizations for the resonance energies of olefins and carbonyl compounds: that the resonance energy due to the conjugation of two π-bonds is approximately independent of the nature of these bonds; and the resonance energy due to diconjugation is approximately the sum of the resonance energies produced by the groups singly. Within the experimental uncertainty, the tabulated data support these conclusions completely.[16] The average value of $\Delta H\psi$ due to the conjugation of two π-bonds is 4 ± 1 kcal./mole if methyl propiolate is included, 4.7 ± 0.3 if it is excluded. If dodeca-5,7-diyne is considered to contain two conjugated systems of π-bonds, the value becomes 4.8 ± 0.3 excluding methyl propiolate. The average value for diconjugation (considering carbon subnitride to consist of two independent diconjugated systems) is 10.3 ± 1.4 kcal./mole.

It was also suggested[13] that h might be a constant fraction of $\Delta H\psi$ for a single unsaturated substituent. On the other hand, the α-hydrogen bonding theory of the Baker–Nathan effect[17] predicts that $h/\Delta H\psi$ will be 0.07 for olefins and 0.13 for acetylenes. The observed values are 0.08[13] and 0.12,[18] so the theoretical prediction seems to be much more nearly correct. The abso-

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[14] The value of σ^* for $C\equiv C-n$-C_4H_9, + 1.30, was taken from footnote *f* of the table. The heat of hydrogenation of $C_2H_3C\equiv C-n$-C_4H_9, −65.2 kcal./mole, was calculated from eq. 1, and is very similar to that for dimethylacetylene. The heat of hydrogenation of octa-3-yne-1-ene was corrected to the vapor phase by use of Trouton's rule.

(15) C. A. Coulson and V. A. Crawford, *J. Chem. Soc.*, 2052 (1953).

(16) With the possible exception of methyl propiolate, for which there is reason to believe that the experimental data may be in error (ref. 1).

(17) M. M. Krevoy and H. Eyring, THIS JOURNAL, **79**, 5121 (1957).

(18) The value of $\Delta H\psi$ for methyl propiolate was excluded in making this calculation. The value would become 0.15 if it were included.

lute value of h is somewhat lower than that predicted by α-hydrogen bonding theory (0.85),[16] but in view of the general crudeness of the theoretical calculations, this does not seem alarming. In particular, both h and $\Delta H\psi$ may be smaller than predicted due to an improper choice of the resonance integral for the carbon–carbon π-bond, while the ratio $h/\Delta H\psi$ was still correct. On the other hand, the agreement between calculated and observed ratios $h/H\psi$ may be fortuitous.

It is noteworthy that in this, as in previous work on aliphatic compounds,[13] the approximation that Baker–Nathan effects are simply proportional to the number of α-hydrogen atoms seems adequate. However, the data on non-conjugated acetylenes is insufficient to provide a very stringent test for any formulation of this effect. The question of whether alkyl groups attached to the α-carbon atom give rise to a similar, but smaller, effect also cannot be answered.

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MINNEAPOLIS 14, MINN.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Synthesis and Some Reactions of *cis*- and *trans*-Di-*t*-butylethylenes[1]

BY W. H. PUTERBAUGH[2] AND MELVIN S. NEWMAN

RECEIVED SEPTEMBER 10, 1958

Improvements in the syntheses for *cis*- and *trans*-di-*t*-butylethylene, I and II, have been made. The rearrangement of I to II by acidic catalysis proved unusually difficult but was accomplished by heating over a palladium-on-alumina catalyst. The addition of chlorine to *trans*-di-*t*-butylethylene yielded a rearranged product, 2,4-dichloro-2,3,5,5-tetramethylhexane (III).

The strain in *o*-di-*t*-butylbenzene has been estimated to be at least 25 kcal. per mole.[3] To date no authenticated synthesis of *o*-di-*t*-butylbenzene or a derivative thereof has been reported.[4] Since syntheses of both *cis*-di-*t*-butylethylene[5] (I) and *trans*-di-*t*-butylethylene[6] (II) had been reported we thought it desirable to prepare quantities of each in order to study certain chemical and physical properties. The *cis* isomer represents an acyclic analog of *o*-di-*t*-butylbenzene and, as such, would be expected to be highly strained.

We have prepared quantities of *cis*- and *trans*-di-*t*-butylethylene by the methods described[5,6] and were able to effect improvements in each synthesis. Samples of each isomer were supplied to Professor Rossini of Carnegie Institute of Technology for determination of the heats of combustion and to Professor Turner of The Rice Institute for determination of the heats of hydrogenation. The value for the difference in heats of combustion[7] between the *cis* and *trans* isomer is 10.5 ± 0.5 kcal./mole, whereas the value for the difference in heats of hydrogenation[8] is 9.3 kcal. Thus this energy difference is the largest yet found for *cis–trans* isomer acyclic olefins, with the *cis* the higher in energy.[8] In addition samples of I and II were sent to Dr. M. Szwarc of Syracuse University for studies of their behavior when treated with methyl radicals.[9]

We have found that the ease of acid-catalyzed and thermal isomerization of *cis*- to *trans*-di-*t*-butylethylene is not nearly as great as one might expect from the large difference in energy. For example, the *cis* isomer I was recovered unchanged after refluxing for 14 hours in acetic acid containing *p*-toluenesulfonic acid. In addition, the *cis* isomer was recovered unchanged after heating at 200° for 74 hours with 2,3-di-methyl-1,3-butadiene and hexachlorocyclopentadiene in unsuccessful attempts to effect a Diels–Alder reaction. A successful method of isomerization of *cis*- to *trans*-olefin was suggested by the fact that when di-*t*-butylacetylene was hydrogenated to prepare *cis*-di-*t*-butylethylene[5] an appreciable amount of the *trans* isomer II also was produced. Accordingly, when the *cis* isomer was refluxed with 5% palladium-on-alumina for 2 hours, an 80% yield of *trans*-olefin was obtained.

An attempt to convert *trans*-di-*t*-butylethylene (II), to the *cis* isomer I by the method of Hoff, Greenlee and Boord[10] failed when the addition of chlorine to trans-di-*t*-butylethylene (II) yielded a rearranged dichloride III. We assign the structure 2,4-dichloro-2,3,5,5-tetramethylhexane to III because on dehydrohalogenation with potassium amide III yielded 2,3,5,5-tetramethyl-1,3-hexadiene (IV) which afforded 2,3-butanedione (V) on ozonization. Furthermore, on removal of the two

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(1) This research was supported by a grant from the National Science Foundation.

(2) Thiel College, Greenville, Pa.

(3) H. C. Brown, D. Gintis and L. Domash, THIS JOURNAL, **78**, 5387 (1956).

(4) The synthesis of *o*-phenylene-diisobutyric acid represents the first preparation of a highly hindered di-*o*-substituted benzene derivative; see H. A. Bruson, F. W. Grant and E. Bobko, *ibid.*, **80**, 3633 (1958).

(5) G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946).

(6) F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

(7) Unpublished results by Rockenfeller and Rossini, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

(8) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *ibid.*, **80**, 1430 (1958).

(9) A. R. Rader, R. P. Buckley, F. Leavitt and M. Szwarc, *ibid.*, **79**, 5621 (1957); the results reported therein are preliminary.

(10) M. C. Hoff, K. W. Greenlee and C. E. Boord, *ibid.*, **73**, 3329 (1951).