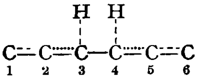
504. *Tautomeric Equilibria in* 1 : 3(4) : 8-*Triene-type Olefins. An Investigation of Double-bond Interaction through Two Methylene Groups.*

By L. Bateman, J. I. Cunneen, and (in part) J. A. Lyons.

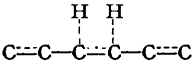
Recent evidence and theories concerned with the existence of some structural peculiarity in 1 : 5-dienes are summarized. An attempt to determine directly whether these dienes are characteristically stabilized by resonance or otherwise is then reported. The experimental basis is to determine the effect on the tautomeric equilibria between 3-substituted 1-phenylprop-1- and -2-enes (see preceding paper) of a double bond, or equivalent unsaturated unit, situated two methylene groups distant from the displaceable Δ^2-double bond. Our results show conclusively that such stabilization is less than is expressed by a free-energy difference (at 165°) of 0·1 kcal.

A remarkable feature of Jeffrey's *X*-ray crystallographic investigation of the molecular structure of geranylamine hydrochloride, $CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}NH_3Cl$ (*Proc. Roy. Soc.*, 1945, *A*, **183**, 388) was the finding that the $CH_2{-}CH_2$ bond (1·44 A.) was much shorter than the length considered characteristic of a " normal " non-conjugated C–C single bond (1·54 A.). Lesser contractions (to 1·51 A.) were also apparent in the bonds joining the central CH_2 groups to the methine carbon atoms. Another compound possessing a 1 : 5-diene unsaturation pattern, *viz.*, dibenzyl, was found later to exhibit similar variations of bond length, the distance between the CH_2 groups being 1·48 A., and between a CH_2 and a Ph group, 1·50 A. (*idem, ibid.*, 1947, *A*, **188**, 222). The accuracy of these measurements is not readily specified. Jeffrey estimated possible errors of ±0·04 and ±0·01 A. in the quoted bond lengths in the two structures, respectively. More recently, however, refinement in the analysis of the experimental data and critical consideration of the limits of error in the case of dibenzyl have led Cruickshank (*Acta Cryst.*, 1949, **2**, 65) to conclude (i) that the $CH_2{-}CH_2$ and $CH_2{-}Ph$ bond lengths given above need revision to 1·510 A. and 1·523 A., respectively, and (ii) that the relatively small contractions thus indicated are statistically significant. In geranylamine hydrochloride, therefore, the bond shortening would appear to be real and substantial, but may well be less than half that originally believed.

An explanation by Bateman and Jeffrey (*Nature*, 1943, **152**, 446) of this structural abnormality in terms of hyperconjugation had the following basis. Chemical-equilibria studies (Baker and Hemming, *J.*, 1942, 191), supported by dipole-moment data (Smyth *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 89, 1931), had shown that the delocalisation of C–H bond electrons when conjugated with an unsaturated centre exists as a mesomeric effect, as well as a powerful electromeric process influencing reactivity (Baker and Nathan, *J.*, 1935, 1844; Hughes, Ingold, and Taher, *J.*, 1940, 949; see also Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093). Since a 1 : 5-diene consists of two such units joined head-to-head, it seemed reasonable to envisage that the electronic distribution, rather than being as depicted in (I) with the $C_{(3)}{-}C_{(4)}$ bond insulating the two resonating systems, would tend towards that represented by (II) in order to promote more extensive resonance throughout the carbon chain. This tendency might be expected to develop as the length of the carbon chain increases, and the possible significance in this sense of the finding that the refractivity properties of natural rubber lie between those characteristic of mono-olefins and non-conjugated diolefins on the one hand and conjugated diolefins on the other has been pointed out by Wood and Tilton (Proc. Rubber Tech. Conf., London, 1948, p. 142). Somewhat similar ideas in this or related contexts have been put forward by Szwarc (*Faraday Soc. Discussion*, 1947, **2**, 41), Hinshelwood (*ibid.*, p. 113), Dhar *et al.* (*loc. cit.*, p. 2103), and Dewar (" The Electronic Theory of Organic Chemistry," Oxford, 1949, p. 158). The last author interprets analogously the peculiar alternation in reactivity shown by several series of αω-disubstituted alkanes—a phenomenon which may also be associated with unusual variations in bond length (Morrison and Robertson, *J.*, 1949, 980, 987, 993, 1001). On the other hand, Walsh (*J.*, 1948, 389) regards the situation in 1 : 5-dienes



(I.)



(II.)

quite differently, *viz.*, that the presence of electronegative substituents X in $CH_2X{\cdot}CH_2X$ leads, as a general principle, to a strengthening of the C–C bond. We fail to understand why the CH_2–CH_2 bond rather than the X–CH_2 bond is considered to be mainly affected, for Walsh himself attributes the added bond strength of vinyl compared with alkyl derivatives to just the same cause, and also why electron attraction at *both* ends of a bond should produce a strengthening effect.

Attempts to trace manifestations of the bond shortening in ultra-violet absorption characteristics were first made by Bateman and Koch (*J.*, 1944, 600), who found that geranylamine hydrochloride, in common with hydrocarbon 1 : 5-dienes, absorbs almost identically with comparable mono-olefins in the region 2100—2800 A. This establishes either (i) that the structural abnormality is unique to the crystalline state and does not persist when the molecules are in solution, or (ii) that the light-absorption properties of the 1 : 5-double bonds remain unchanged at the wave-lengths given. The latter is not the remote possibility it might seem on first thoughts because even the spectral consequences of C–H bond hyperconjugation cannot yet be definitely described (cf. Bateman and Koch, *loc. cit.*). Koch (*J.*, 1948, 1123) subsequently extended these investigations to 1 : 6-diphenylhexa-1 : 5-diene (dicinnamyl), where the incorporation of the ethylenic double bonds in styryl units might well enhance the electronic interaction postulated above and at the same time permits the first intense ($N \rightarrow V$ type) absorption band to be accurately characterized by the usual spectrophotometric techniques. Compared with 1-phenylprop-1-ene (propenylbenzene), the absorption maximum of dicinnamyl exhibits a bathochromic shift (from 2470 to 2550 A.) and a slight increase in intensity, which together are suggestive of chromophore interaction. However, even interposition of six saturated carbon atoms between the styryl groups (in 1 : 10-diphenyldeca-1 : 9-diene) produces a similar intensification of absorption though at a reduced wave-length displacement ($\lambda_{max.}$ 2505 A.). Koch concluded therefore that these changes result largely from " weight " or " chain-length " effects and that the extent to which electronic transmission through the saturated carbon atoms is responsible (if at all) remains uncertain. Braude (*J.*, 1949, 1902) has disagreed with this conclusion and argues that Koch's observations actually support his own in demonstrating incomplete electronic insulation by the $-CH_2{\cdot}CH_2-$ unit (of an unspecified nature although valency-bond resonance is thought to be an important factor). The decadiene case is dismissed by postulating some interspatial interaction of the styryl groups. This viewpoint, resting on the validity of this arbitrary postulate, lacks conviction in the absence of supporting evidence, and needs more data and advances in interpretation to gain acceptance.

The only claim to have obtained definite, and quantitative, chemical evidence of the bond contraction in 1 : 5-dienes is by Szwarc (*loc. cit.*). He found that the CH_2–CH_2 bond energy in dibenzyl, calculated by subtracting twice the resonance energy of the benzyl radical (deduced from toluene pyrolysis experiments) from the C–C bond energy in ethane, was 11 kcals. less than that derived from thermochemical data, and interpreted this difference as a measure of bond shortening in good agreement with Jeffrey's data—these imply a difference of 14 kcals. on the basis of Skinner's bond length–bond strength relationship (*Trans. Faraday Soc.*, 1945, **41**, 645). Apart from the fact that comparison with Jeffrey's data is now invalid, we question whether Szwarc's deductions are sufficiently free from uncertainty to make such agreement significant. The interpretative complexities of this type of experiment are well illustrated by a recent study of the pyrolysis of dibenzyl itself (Horrex and Miles, *Faraday Soc. Discussion*, in the press).

The purpose of the present work was to try to devise a direct experimental test of the existence of any unique stabilization of the 1 : 5-diene unit. If shortening of the central C–C bond results from some electronic process involving the flanking ethylenic groups, then a factor exists opposing disruption of the unit and therefore opposing any isomerization involving double-bond displacement. Acyclic terpenoid hydrocarbons of this type are known to be so resistant to such changes (Farmer, *Trans. Faraday Soc.*, 1942, **38**, 358) that quantitative study is greatly impeded, and the occurrence of multiple displacements (cf. the isomerization of hexa-1 : 5-diene to hexa-2 : 4-diene, Faworsky, *J. pr. Chem.*, 1891, **44**, 208) might obscure the data sought. These difficulties can be overcome by arranging that some structural condition fixes one of the double bonds and that the second is a member of a 1 : 4-diene system in which the other member is also fixed. The olefins (III) and (V) possess these features; isomerization in alkaline media at moderate temperatures will therefore be restricted to shifts of the more central ethylenic double bonds to produce the corresponding styryl isomers (IV) and (VI). The interconversion of similar tautomers at 165° is described in the preceding paper, where it is shown that the composition of an equilibrated isomeric mixture affords a sensitive empirical measure of the relative extent of conjugation and C–H bond hyperconjugation in the two isomers. Thus (VII) and (VIII) co-exist at equilibrium in the proportion 43 : 57 (at 165°). Now (III) and (V) differ from (VII) only in possessing one less α-methylenic hydrogen atom and hence, according to our analysis of the controlling influences (p. 2285), *and if no special energy term intrudes,* the corresponding proportions of (III) to (IV) and (V) to (VI) should be approximately 35 : 65.

$\mathrm{PhCH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2Ph}$ (III.)

$\mathrm{PhCH{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Ph}$ (IV.)

$\mathrm{PhCH_2{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$ (V.)

$\mathrm{PhCH{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$ (VI.)

$\mathrm{PhCH_2{\cdot}CH{:}CMe_2}$ (VII.)

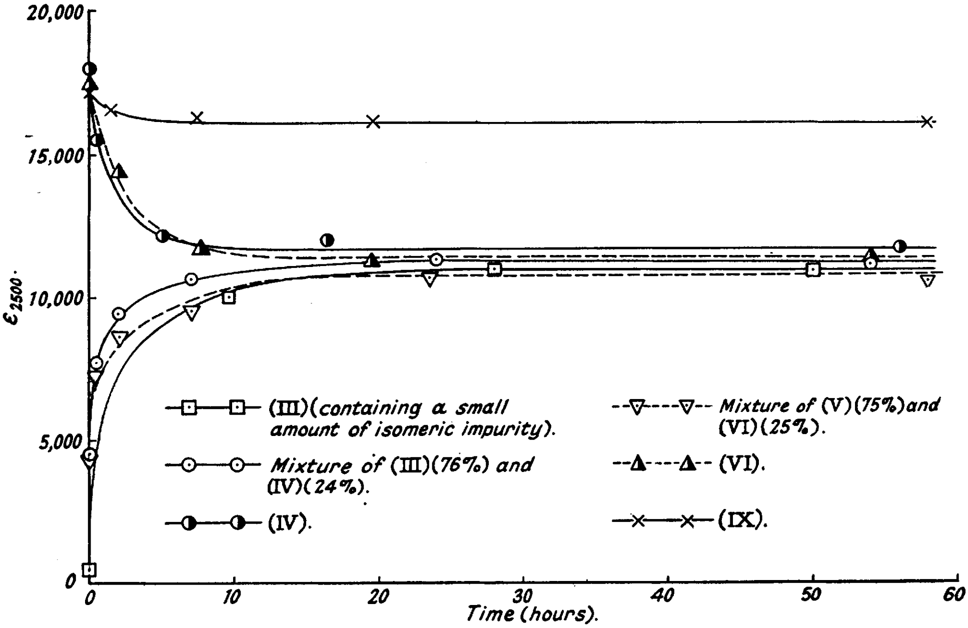
$\mathrm{PhCH{:}CH{\cdot}CHMe_2}$ (VIII.)

$\mathrm{PhCH{:}CH{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}$ (IX.)

A free energy of only 1 kcal. opposing the destruction of the 1 : 5-diene system would change this ratio to 63 : 37 and 6 kcals.; *i.e.*, Skinner's estimate of the increase in C–C bond strength on contraction from 1·54 to 1·51 A.—if no partly compensating bond lengthening occurs elsewhere—would cause (III) and (V) to be virtually the sole components (99·8%).

The isomerizations observed on heating (III) (containing *ca.* 7% of 3-methylene-1 : 5-diphenylpentane), (IV), and a mixture rich in (III) (containing none of the vinylic isomer) in alkaline methyl-alcoholic solution at 165° are shown in the figure; they obviously conform to the same pattern as earlier results (cf. figure, p. 2284). The slightly lower ε at equilibrium observed with the first mixture partly reflects the inertness of the vinylic constituent (cf. p. 2284). To confirm the validity and check the sensitivity of this procedure, (IX) has been similarly examined. This olefin is a substituted *iso*butylstyrene, and actually is found to yield nearly the same equilibrium proportion of its 1-phenyl-Δ^2-isomer (9·5%) as the parent compound (11%; p. 2285). The significant facts disclosed, however, are that the equilibrium mixtures produced from (III) and (IV) and from (V) and (VI) have identical isomeric compositions containing 36% of the non-conjugated forms, and this composition is almost exactly that predicted above on the assumption that the 1 : 5-diene unit is without special effect.

Isomerisations in methyl-alcoholic alkali at 165°.



The conclusion from this work is unequivocal : no energy of the magnitude associated with a detectable C–C bond contraction stabilizes chemically the 1 : 5-diene systems examined, and no increase in energy occurs in any individual bond which is not associated with, and almost exactly balanced by, a decrease in another (or others) or with special intermolecular forces. This accords with the near identity of the heat of hydrogenation of hexa-1 : 5-diene with twice that of but-1-ene (Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Amer. Chem. Soc.*, 1936, **58**,

146) and also with the absence of definite spectroscopic manifestations. It is not inconsistent with the *X*-ray evidence from closely similar systems provided that the qualifying conditions are obeyed. If the bond contraction is real, then the theoretical explanation of Dhar *et al.* (*loc. cit.*; cf. in this connection, Denbigh, *Nature*, 1944, **154**, 642; Wang, *J. Chem. Physics*, 1939, **7**, 1012) is the most acceptable of those hitherto advanced.

EXPERIMENTAL.

3-*Methyl*-1 : 5-*diphenylpent*-2-*ene* (III).—Fractionation of the product obtained on heating 3-methyl-1 : 5-diphenylpentan-3-ol (from dibenzylacetone and methylmagnesium iodide) with aqueous sulphuric acid (30%) at 100° yielded this hydrocarbon (admixed with *ca.* 7% of its 3-methylenepentane isomer), b. p. 126°/0·5 mm., n_D^{14} 1·5605, ε_{2500} 540 (Found : C, 91·3; H, 8·5. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%).

3-*Methyl*-1 : 5-*diphenylpent*-1-*ene* (IV).—3-*Bromo*-1-*phenylbutane*, b. p. 116—118°/14 mm., n_D^{22} 1·5351, was obtained from 1-phenylbutan-3-ol and phosphorus tribromide by reaction first at −10°, then at 100° (Found : C, 56·7; H, 6·3; Br, 37·4. $C_{10}H_{13}Br$ requires C, 56·4; H, 6·1; Br, 37·5%). The Grignard derivative prepared from this bromide (76 g.) and magnesium (9 g.) in ether (250 ml.) was run rapidly on to powdered solid carbon dioxide (300 g.). After treatment of the mixture with ice and hydrochloric acid, and extraction first with ether, then with sodium carbonate solution, followed by acidification of the latter extract, 1-phenylbutane-3-carboxylic acid (25 g.), b. p. 105—107°/0·006 mm., n_D^{20} 1·5113, was obtained (Found : C, 74·3; H, 8·0%; equiv., 179. Calc. for $C_{11}H_{14}O_2$: C, 74·2; H, 7·9%; equiv., 178). By reaction with lithium aluminium hydride in ether, this acid was converted almost quantitatively into 2-methyl-4-phenylbutan-1-ol, b. p. 135°/11 mm., n_D^{16} 1·5173, which gave the corresponding *bromide*, b. p. 129°/14 mm., n_D^{18} 1·5344 (Found : C, 58·2; H, 6·6; Br, 35·2. $C_{11}H_{15}Br$ requires C, 58·2; H, 6·6; Br, 35·3%), with phosphorus tribromide. The Grignard derivative of this bromide (22·7 g.) reacted readily with benzaldehyde (10·7 g.) in ether to give 3-*methyl*-1 : 5-*diphenylpentan*-1-*ol* (17 g.), b. p. 135—136°/0·01 mm., n_D^{16} 1·5506 (Found : C, 85·2; H, 9·0. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%). Dehydration of this alcohol (3·8 g.) with sodium hydrogen sulphate (1·9 g.) at 160° for 1 hour yielded 3-*methyl*-1 : 5-*diphenylpent*-1-*ene* (2 g.), b. p. 110°/0·01 mm., n_D^{18} 1·5710, ε_{2500} 18000 (Found : C, 91·4; H, 8·6. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

A Mixture of (III) *and* (IV).—3-*Methyl*-1 : 5-*diphenylpentan*-2-*ol* (28 g.), b. p. 132—134°/0·005 mm., n_D^{18} 1·5565, was prepared from the Grignard derivative of 3-bromo-1-phenylbutane (79 g.) and phenylacetaldehyde (42 g.) in ether (Found : C, 84·9; H, 8·7%). The olefinic mixture obtained on dehydrating this with sodium hydrogen sulphate under the conditions given above had b. p. 98—100°/0·006 mm. (Found : C, 91·6; H, 8·5. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%). It had ε_{2500} 4800, indicating that 26% of (IV) was present, but it contained no vinylic impurity.

3 : 7-*Dimethyl*-1-*phenylocta*-1 : 6-*diene* (VI).—3 : 7-Dimethyl-1-phenyloct-6-en-1-ol, b. p. 100—102°/0·01 mm., n_D^{16} 1·5132 (Found : C, 83·2; H, 10·3. Calc. for $C_{16}H_{24}O$: C, 82·8; H, 10·4%), prepared from citronellal and phenylmagnesium bromide, was dehydrated by heating with sodium hydrogen sulphate at 160° for 1 hour under nitrogen. Fractionation of the product from sodium gave the required olefin, b. p. 80°/0·01 mm., n_D^{20} 1·5287 (Found : C, 89·7; H, 10·3. Calc. for $C_{16}H_{22}$: C, 89·7; H, 10·3%).

A Mixture of (V) *and* (VI).—2-Methylhept-2-en-6-ol, b. p. 73°/10 mm., n_D^{18} 1·4498, obtained by reducing methylheptenone with lithium aluminium hydride, on reaction with phosphorus tribromide, afforded 6-bromo-2-methylhept-2-ene, b. p. 60°/12 mm., n_D^{19} 1·4711 (Found : C, 50·1; H, 8·0; Br, 41·5. Calc. for $C_8H_{15}Br$: C, 50·2; H, 7·9; Br, 41·9%). A Grignard reaction with this bromide and phenylacetaldehyde gave 3 : 7-*dimethyl*-1-*phenyloct*-6-*en*-2-*ol*, b. p. 97—98°/0·006 mm., n_D^{17} 1·5155 (Found : C, 82·5; H, 10·3%). This was not smoothly dehydrated over oxalic acid and sodium hydrogen sulphate (charring occurred and oxygen-containing compounds were produced), but heating it with boric acid at 160° gave an ester which decomposed at 340° yielding the required mixture, b. p. 75°/0·01 mm. (Found : C, 89·5; H, 10·6. Calc. for $C_{16}H_{22}$: C, 89·7; H, 10·3%). It had ε_{2500} 4340, indicating the presence of 25% of (VI).

4 : 8-*Dimethyl*-1-*phenylnona*-1 : 7-*diene* (IX).—The Grignard derivative of citronellyl bromide (Wagner-Jauregg and Arnold, *Annalen*, 1937, **529**, 274) was treated with benzaldehyde to give 4 : 8-dimethyl-1-phenylnon-7-en-1-ol, b. p. 110°/0·01 mm., n_D^{15} 1·5085 (Found : C, 83·0; H, 10·6. Calc. for $C_{17}H_{26}O$: C, 82·9; H, 10·6%). Dehydration of this alcohol occurred readily over sodium hydrogen sulphate at 160°, the resulting *hydrocarbon* having b. p. 89—90°/0·01 mm., n_D^{16} 1·5250 (Found : C, 89·3; H, 10·7. $C_{17}H_{24}$ requires C, 89·5; H, 10·5%).

Isomerisation Conditions and Procedure.—These were as described in the preceding paper except that the absorptions at 2500 A. were mostly determined on a Hilger Uvispek Photoelectric Spectrometer.

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