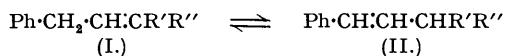


503. Structural Influences determining Tautomeric Equilibria in Phenylpropenes.

By L. BATEMAN and J. I. CUNNEEN.

3-Alkyl substitution in 1-phenylpropene (II; $R' = R'' = H$) leads to the non-styryl-conjugated isomer (I) forming a measurable proportion of the equilibrated mixture in alkaline methyl-alcoholic solution at 165°. The influence of different alkyl groups may be correlated with (a) the extent of CH-bond first-order hyperconjugation, and (b) the operation of a specific effect on replacement of the CH_2 group by CHR. The experimental data permit the magnitude of these factors and also the resonance energy of the styryl unit to be evaluated. These quantities, and reasonable estimates of related quantities, are found to give fairly satisfactory analogous interpretations of the relative heats of hydrogenation of olefins and the equilibria between $\Delta^{\alpha\beta}$ - and $\Delta^{\beta\gamma}$ -unsaturated carboxylic acids, esters, and nitriles.

SYSTEMATIC studies of tautomeric equilibria in purely hydrocarbon three-carbon systems have hitherto been restricted to 1:3-diarylpropenes and condensed arylcycloalkyl structures such as indene (see Baker, "Tautomerism," Routledge and Sons, London, 1934, p. 80 *et seq.*). With the object of determining the power of alkyl groups to influence double-bond migrations, we have now examined the equilibria in the simpler examples (I) \rightleftharpoons (II), where $R' = H$, $R'' = Me$, Pr^i , or Bu^t , and $R' = R'' = H$ or Me .

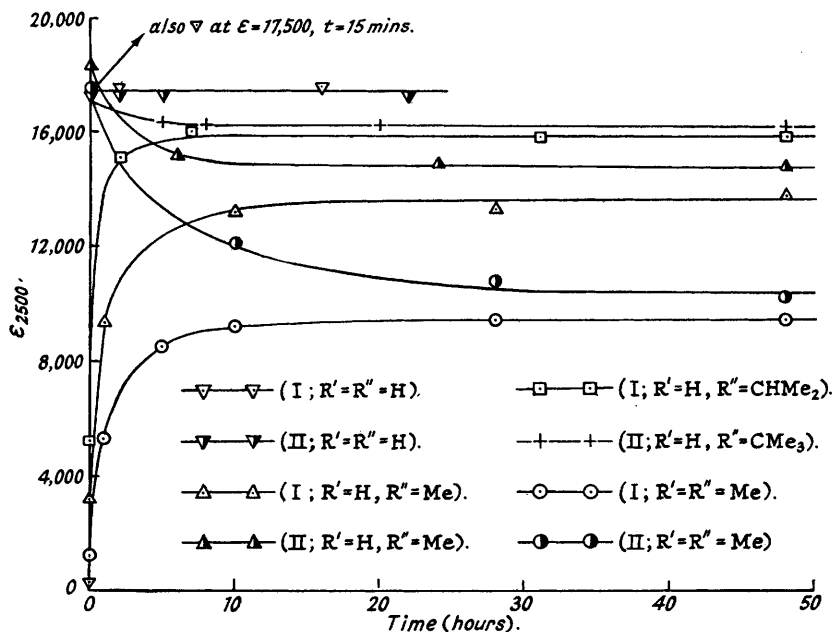


Interconversion of these tautomers occurs readily in methyl-alcoholic alkali at 165° (the half-life periods under the conditions employed being of the order of 1—2 hours), and is conveniently followed quantitatively by estimating the extent of styryl conjugation from ultra-violet absorption measurements. The tautomeric nature of the observed changes has been established by approaching the same equilibrium mixture from hydrocarbons consisting wholly or predominantly of the separate isomers in the cases where $R' = H$, $R'' = Me$; $R' = R'' = H$; and $R' = R'' = Me$, and by showing in the last system that the components are not otherwise modified or destroyed.

As far as we are aware, these experiments provide the first definite demonstration of the deconjugation of the styryl unit in a mobile prototropic or anionotropic system, and it is therefore of some importance to try to define the responsible structural influences.

In analysing the results shown in Fig. 1, account must be taken of two minor uncertainties. First, a variation is apparent in the value of ϵ for the several styryl-conjugated isomers. This is undoubtedly due partly to real differences from compound to compound (almost certainly of stereochemical origin) and partly to slight, and variable, contamination with the non-conjugated isomers produced in trivial amounts during their syntheses. For the purpose of deducing the several equilibrium compositions, no significant error is introduced by assuming a uniform value of 17,800, except for propenylbenzene (II; $R' = R'' = H$) where the measurements obviously show that no detectable amount of allylbenzene (I; $R' = R'' = H$) is present in this system at equilibrium. Secondly, our specimens of (I; $R' = H, R'' = Me$) and (I; $R' = R'' = Me$) contained about 10% (as estimated from their infra-red spectra) of the 1:5-diene-type isomers, $Ph \cdot CH_2 \cdot CH_2 \cdot CH \cdot CH_2$ and $Ph \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH_2$, respectively. The latter olefins isomerize much more slowly than do the 1:4-dienes, and hence the conjugation actually developed will tend to be less than the extent characteristic of the system considered. This factor appears to be responsible for the differences observed in equilibrium composition depending on whether

FIG. 1.
Isomerizations in methyl-alcoholic alkali at 165°.



the 1-phenyl- Δ^1 - or 1-phenyl- Δ^2 -isomer is examined in these cases, and accordingly we have given more weight to the results obtained from the former isomers.

The equilibrium data and the associated free-energy changes ($-\Delta G = RT \ln K$) summarized in Table I reveal a qualitative correlation between the tautomeric stability of (I) and the number of CH bonds adjacent to the double bond, *i.e.*, first-order hyperconjugation (Mulliken, Riecke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41) is an effective competing influence opposing the development of styryl conjugation.

The present studies afford in principle an exceptionally sensitive method of defining this relationship quantitatively, but in effect the multiple structural consequences of varying R' and R'' limit the rigour with which this can be done. First, other electronic processes may contribute to the observed effects: as will be discussed later, substitution as such at a double-bonded carbon atom, irrespective of hyperconjugative properties, exerts a powerful influence in stabilizing compounds such as (I) relative to (II). Secondly, the replacement of a C-H by a C-Alkyl group may alter ΔG by modifying the relative disposition of the neighbouring bonds to an unequal extent in (I) and (II). Thirdly, an uncertain approximation is involved in assuming the total hyperconjugation developed to be strictly proportional to the number of α -methylene C-H bonds (as, *e.g.*, by Baker *et al.*, *J.*, 1939, 1150; 1940, 692; 1942, 191), owing partly to ignorance concerning the hyperconjugative power of C-C bonds under different conditions.

Finally, the quantitative aspects of cross-hyperconjugation, *e.g.*, $>C:CH:C(\cdot CH_2)\cdot CH:C<$, are obscure. These features and ambiguities are, however, inherent in all comparable studies of alkyl substitution at the present time, and hence a simplified theory concerned essentially with resultant empirical hyperconjugation changes is of considerable practical value.

Let E_1 denote the resonance energy of conjugation of a phenyl group and a double bond, e_1 that of hyperconjugation between a phenyl group and a C-H bond, e_2 and e_3 that of hyperconjugation between a double bond and a C-H and C-C bond, respectively. If we assume (i) that the resonance energy developed in cross-hyperconjugation is the sum of that developed in the contributing units separately, and (ii) that hyperconjugation involving C-C bonds is negligible except in the absence of C-H bonds, then certain "stabilizing factors" (*s.f.*) can be assigned to the pairs of tautomers (Table II). Equating $s.f._{II} - s.f._I$ with $-\Delta G$ yields values for $E_1 - 2e_1$ and e_2 of 2.1 and 0.26 kcal., respectively. It is of interest to examine the validity of these values, and also whether the present analysis in terms of *s.f.s* is of wider applicability.

TABLE I.

Tautomeric system :		$\epsilon_{25,000}$ at equilibrium.	Proportion of (II) at equilibrium, % (at 165°).	$-\Delta G$ (kcal.).
R' =	R'' =			
H	H	17,400	100 *	—
H	CMe ₃	16,200	91	2.02
H	CHMe ₂	15,900	89	1.83
H	Me	14,600	82	1.32
Me	Me	10,200	57	0.25

* See text (p. 2284).

TABLE II.

(I).	<i>s.f.</i>	(II).	<i>s.f.</i>	<i>s.f.</i> _{II} - <i>s.f.</i> _I .
Ph·CH ₂ ·CH:CH·CMe ₃ ...	$2e_1 + 2e_2 + 3e_3$	Ph·CH:CH·CH ₂ ·CMe ₃ ...	$E_1 + 2e_2$	$E_1 - 2e_1 - 3e_3$
Ph·CH ₂ ·CH:CH·CHMe ₂ ...	$2e_1 + 3e_2$	Ph·CH:CH·CH ₂ ·CHMe ₂	$E_1 + 2e_2$	$E_1 - 2e_1 - e_2$
Ph·CH ₂ ·CH:CH·Me	$2e_1 + 5e_2$	Ph·CH:CH·CH ₂ Me	$E_1 + 2e_2$	$E_1 - 2e_1 - 3e_2$
Ph·CH ₂ ·CH:CMe ₂	$2e_1 + 8e_2$	Ph·CH:CH·CHMe ₂	$E_1 + e_2$	$E_1 - 2e_1 - 7e_2$

Taking $E_1 - 2e_1 = 2.1$ kcal., we have $e_3 < 0.03$ kcal. There can be little error in assuming $e_1 \sim e_2$, and hence in concluding that $E_1 = 2.6$ kcal. This value is less than half that deduced by Pauling and Sherman (*J. Chem. Physics*, 1933, 1, 606) from heats of combustion (but for amendment see Cottrell and Sutton, *ibid.*, 1947, 15, 685), but nearly twice that deduced by Dolliver, Evesham, Kistiakowsky, and Vaughan (*J. Amer. Chem. Soc.*, 1937, 59, 831) from heats of hydrogenation. All these estimates are subject to similar or related ambiguities, and therefore the different data must be analysed equivalently for proper comparison.

In Table III a selection of the extensive data of Kistiakowsky and his collaborators (*loc. cit.*; *J. Amer. Chem. Soc.*, 1935, 57, 65, 876; 1936, 58, 137, 146; 1938, 60, 440) is compared with values of $-\Delta H$ calculated on the assumption that the value for ethylene (*D*) is changed by substitution as follows: Substitution as such at a CH₂ group, irrespective of its nature, introduces a negative $-\Delta H$ term, *S*, which is taken equal to 1.5 kcal. In 1:1- or 1:2-disubstituted ethylenes, the *S* contribution is doubled, but further substitution is considered to be without effect in this respect. Further negative terms are identified with the resonance energies E_1 , e_1 (0.3 kcal.), E_2 (that of the butadienoid unit), e_2 (0.3 kcal.), and E_a (that of the benzene ring); E_2 and E_a are determined from examples (11) and (16) as 5.1 and 39.0 kcal., respectively.* Unfortunately, the present technique as applied to the systems studied does not readily allow the equilibria to be determined over a sufficiently wide temperature range to yield accurate values of ΔH . However, comparison of the hydrogenation data with our ΔG values is not seriously unreasonable, since calculations by Kilpatrick, Rosen, Pitzer, and Rossini (*J. Res. Nat. Bur. Stand.*, 1946, 36, 559) suggest that ΔS differences will not exceed one-quarter of the

* Earlier interpretations of these data emphasise the *cis*-character of the double bonds in the Kekulé formula for benzene, and E_a has been estimated by the imprecise comparison: $3(-\Delta H$ for cyclohexene) - $(-\Delta H$ for benzene). In the present treatment, differences between *cis*- and *trans*-isomers are ignored, partly because no decision can be made as to the extent to which *S* or e_2 or both are effected and partly because our main interest, the value of E_1 , is unaffected by this complication. Our tacit assumption that *S* remains the same in the aromatic and aliphatic olefins considered therefore introduces some uncertainty into the value of E_a deduced, but the fact that $-\Delta H$ calculated for cyclohexene on the above basis (28.4 kcal.) is in good agreement with experiment (28.6 kcal.) suggests that the error is likely to be small.

observed ΔG differences. With this in mind and with recognition that the additive analysis adopted is undoubtedly an over-simplification, the correlation between the observed and calculated values of $-\Delta H$ is regarded as satisfactory, and particularly so that the value of E_1 derived (3.4 kcal.) agrees fairly well with that deduced above.

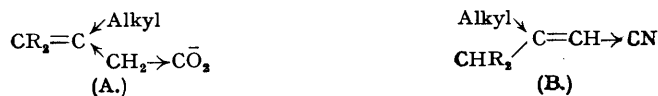
Data more closely comparable with our own are provided by the work of Linstead, Kon, and their collaborators on the equilibria between $\Delta^{\alpha\beta}$ - and $\Delta^{\beta\gamma}$ -isomers of unsaturated carboxylic acids (in alkaline solution), esters, and nitriles (summarized in Gilman, "Organic Chemistry," Wiley and Sons, 2nd edition, 1944, p. 1042). Some of the extensive results are presented in Table IV, where E_4 , E_5 , and E_6 are the resonance energies of conjugation of a double bond with a carboxylate ion, carboxyl, and nitrile group, respectively, and e_4 , e_5 , and e_6 are the corresponding hyperconjugation energies. On comparing the conjugating power of these substituent groups with that of an ethylenic double bond, it appears reasonable to take E_4 as 1.5 kcal., $E_5 = E_6$ as 2.0 kcal., and $e_4 = e_5 = e_6$ as 0.2 kcal. To avoid needless repetition and to maintain consistency with Table II, the substitutional factor S is introduced as a *negative s.f.* in compounds containing vinyl groups. The isomeric compositions found and calculated in

TABLE III.

Olefin.	Factors composing $-\Delta H$.	$-\Delta H$ (kcal.) (at 82°).	
		Found.	Calc.
1. $\text{CH}_2\text{:CH}_2$	D	32.58	—
2. $\text{CH}_2\text{:CHMe}$	$D - S - 3e_2$	30.12	30.2
3. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Me}$	$D - S - 2e_2$	30.34	30.5
4. $\text{CH}_2\text{:CH}\cdot\text{CHMe}_2$	$D - S - e_2$	30.33	30.8
5. $\text{CH}_2\text{:CMe}_2$	$D - 2S - 6e_2$	28.34	27.8
6. $\text{CH}_2\text{:CMe}\cdot\text{CH}_2\text{Me}$	$D - 2S - 5e_2$	28.49	28.1
7. $\text{CH}_2\text{:CMe}\cdot\text{CHMe}_2$	$D - 2S - 4e_2$	28.00	28.4
8. $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{CHMe}$	$D - 2S - 5e_2$	27.95	28.1
9. $\text{CMe}_2\cdot\text{CHMe}$	$D - 2S - 9e_2$	26.92	26.9
10. $\text{CMe}_2\cdot\text{CMe}_2$	$D - 2S - 12e_2$	26.63	26.0
11. $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CH}_2$	$2D - 2S - E_2$	57.07	(57.1) *
12. $\text{CH}_2\text{:CH}\cdot\text{CH}\cdot\text{CHMe}$	$2D - 3S - E_2 - 3e_2$	54.11	54.7
13. $\text{CH}_2\text{:CMe}\cdot\text{CMe}\cdot\text{CH}_2$	$2D - 4S - E_2 - 6e_2$	53.87	52.3
14. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$	$2D - 2S - 4e_2$	60.79	61.0
15. $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$	$2D - 2S - 4e_2$	60.52	61.0
16. PhH	$3(D - 2S) - E_a$	49.80	(49.8) *
17. $\text{Ph}\cdot\text{CH}_2\text{Me}$	$3(D - 2S) - E_2 - 2e_2$	48.92	49.2
18. $\text{Ph}\cdot\text{CH}\cdot\text{CH}_2$	$3(D - 2S) - E_a + D - S - E_1$	77.48	(77.5) *

* Arbitrary agreement in order to obtain E_2 , E_a , and E_1 , respectively.

accordance with the principles described above are in good agreement, except in those carboxylates and nitriles where (I) is a β -alkyl- $\Delta^{\beta\gamma}$ -compound. With the former substituent the proportion of (I) found is higher than that calculated; with the latter the reverse is true. It is almost certain, therefore, that inductive effects are superimposed upon those hitherto considered: in examples 6, 8, 10, and 11, the electron repulsions of the carboxylate ion and β -alkyl groups reinforce each other to satisfy the inductive electron demand of the double bond in the $\Delta^{\beta\gamma}$ -structure (A), whereas they are in opposition in the $\Delta^{\alpha\beta}$ -isomer; in example 19, the



electron attraction of the CN group and repulsion of the β -alkyl group are mutually stimulated by relay through the $\alpha\beta$ -double bond (B). Two facts supporting this explanation are (i) the greater influence of a β -ethyl compared with a β -methyl substituent in favouring (A) (cf. 6 with 8 and 10 with 11), and (ii) the absence of similar features in systems containing the less polar carboxyl group. These irregularities provide another illustration of what appears to be a general principle, *viz.*, that many systems are potentially responsive to both inductive and hyperconjugative influences, the former coming into prominence in the more polar molecules, the latter in the less (cf. $\alpha\beta$ -elimination reactions proceeding in accordance with Hofmann's rule in 'onium compounds, and with Saytzeff's rule in alkyl halides; Dhar, Hughes, Ingold, Mandour, Maw, and Woolf, *J.*, 1948, 2093).

The Structural Factor S.—A special feature of the above interpretations is the emphasis given to S . The importance of this factor in determining the relative stability of vinyl and alkylvinyl isomers is already evident, and is further illustrated by the allylbenzene (I; $R' =$

TABLE IV.

	(I).		(II).		s.f.	-S	s.f.	s.f. II -s.f. I.	-ΔG (kcal.).*		Equilibrium proportion of (I), %.	
	Found.	Calc.	Found.	Calc.					Found.	Calc.	Found.	Calc.
1. CH ₃ :CH·CH ₂ ·CO ₂ ⁻	2e ₂ + 2e ₄	3e ₂	CHMe:CH·CO ₂ ⁻	E ₄ + 3e ₂	E ₄ + e ₂ - 2e ₄ + S	2	2	2.91	2.9	32	2	
2. CHMe:CH·CH ₂ ·CO ₂ ⁻	5e ₂ + 2e ₄	2e ₃	CH ₂ Me:CH·CH·CO ₂ ⁻	E ₄ + 2e ₃	E ₄ - 3e ₂ - 2e ₄	43	43	0.56	0.2	26	43	
3. CH ₂ Me:CH·CH·CO ₂ ⁻	4e ₂ + 2e ₄	2e ₃	CH ₂ Me:CH ₂ :CH·CO ₂ ⁻	E ₄ + 2e ₃	E ₄ - 2e ₂ - 2e ₄	34	34	0.78	0.5	19	10	
4. CHMe:CH·CHMe·CO ₂ ⁻	4e ₂ + e ₄	e ₄	CH ₂ Me:CH·CH·CMe·CO ₂ ⁻	E ₄ + 5e ₂	E ₄ + e ₂ - e ₄	7	7	1.08	1.6	11	7	
5. CH ₂ Me:CH·CH·CHMe·CO ₂ ⁻	3e ₂ + e ₄	e ₄	CH ₂ Me:CH ₂ :CH·CMe·CO ₂ ⁻	E ₄ + 5e ₂	E ₄ + 2e ₂ - e ₄	43	43	1.56	1.9	62	43	
6. CHMe:CMc·CH ₂ ·CO ₂ ⁻	8e ₂ + 2e ₄	2e ₄	CHMe ₂ :CH·CH·CO ₂ ⁻	E ₄ + 8e ₂	E ₄ - 3e ₂ - 2e ₄	79	79	-0.36	0.2	79	79	
7. CMc·CH·CH ₂ ·CO ₂ ⁻	8e ₂ + 2e ₄	2e ₄	CHMe ₂ :CH·CH·CMe·CO ₂ ⁻	E ₄ + 8e ₂	E ₄ - 7e ₂ - 2e ₄	43	43	-0.95	-1.0	78	43	
8. CHMe:C(CH ₂ Me):CH ₂ ·CO ₂ ⁻	7e ₂ + 2e ₄	2e ₄	CHMe:C(CH ₂ Me):CH·CO ₂ ⁻	E ₄ + 4e ₂	E ₄ - 3e ₂ - 2e ₄	72	72	-0.99	0.2	78	72	
9. CMc(CH ₂ Me):CH·CH ₂ ·CO ₂ ⁻	7e ₂ + 2e ₄	2e ₄	CHMe(CH ₂ Me):CH·CO ₂ ⁻	E ₄ + e ₂	E ₄ - 6e ₂ - 2e ₄	72	72	-0.95	-0.7	28	72	
10. CHMe:CMc·CHMe·CO ₂ ⁻	7e ₂ + e ₄	e ₄	CH ₂ Me:CMc·CMe·CO ₂ ⁻	E ₄ + 8e ₂	E ₄ + e ₂ - e ₄	10	10	0.70	1.6	50	10	
11. CHMe:C(CH ₂ Me):CHMe·CO ₂ ⁻	6e ₂ + e ₄	e ₄	CH ₂ Me:C(CH ₂ Me):CMe·CO ₂ ⁻	E ₄ + 7e ₂	E ₄ + e ₂ - e ₄	16	16	0	1.6	8	16	
12. CH ₂ Me:CH·CH·CH ₂ ·CO ₂ Et	4e ₂ + 2e ₅	2e ₅	CH ₂ Me:CH·CH·CH·CO ₂ Et	E ₅ + 2e ₅	E ₅ - 2e ₂ - 2e ₅	2	2	1.45	1.0	5	2	
13. CH ₂ Me:CH·CH·CHMe·CO ₂ Et	3e ₂ + 2e ₅	e ₅	CH ₂ Me:CH ₂ :CH·CMe·CO ₂ Et	E ₅ + 5e ₂	E ₅ + 2e ₂ - e ₅	24	24	1.76	2.4	25	24	
14. CHMe:CMc·CH ₂ ·CO ₂ Et	8e ₂ + 2e ₅	2e ₅	CH ₂ Me:CMc·CH·CO ₂ Et	E ₅ + 5e ₂	E ₅ - 3e ₂ - 2e ₅	70	70	0.66	0.7	~90	70	
15. CMc·CH·CH ₂ ·CO ₂ Et	8e ₂ + 2e ₅	2e ₅	CHMe ₂ :CH·CH·CO ₂ Et	E ₅ + e ₂	E ₅ - 7e ₂ - 2e ₅	3	3	-1.37	-0.5	5.5	3	
16. CHMe:CMc·CHMe·CO ₂ Et	7e ₂ + e ₅	e ₅	CH ₂ Me:CMc·CMe·CO ₂ Et	E ₅ + 8e ₂	E ₅ + e ₂ - e ₅	~2	~2	1.57	2.1	14	~2	
17. CH ₂ :CH·CH ₂ :CN	2e ₂ + 2e ₆	2e ₆	CHMe:CH·CN	E ₆ + 3e ₂	E ₆ + e ₂ - 2e ₆ + S	16	16	2.3	3.4	24	16	
18. CH ₂ Me:CH·CH·CH ₂ :CN	4e ₂ + 2e ₆	2e ₆	CH ₂ Me:CH ₂ :CH·CH·CN	E ₆ + 2e ₂	E ₆ - 2e ₂ - 2e ₆	1.08	1.08	1.08	1.0	~1	1.08	
19. CHMe:CMc·CH ₂ :CN	8e ₂ + 2e ₆	2e ₆	CH ₂ Me:CMc·CH·CN	E ₆ + 5e ₂	E ₆ - 3e ₂ - 2e ₆	2.7	2.7	2.7	0.7	79	24	
20. CMc·CH·CH ₂ :CN	8e ₂ + 2e ₆	2e ₆	CHMe ₂ :CH·CH·CN	E ₆ + e ₂	E ₆ - 7e ₂ - 2e ₆	-0.79	-0.79	-0.79	-0.5	79	79	

* At 373° k. for the carboxylates; at 298° k. for the esters and nitriles.

$R'' = H$)-propenylbenzene (II; $R' = R'' = H$) system. The conjugation and hyperconjugation energies being considered as before, but S being neglected, the composition of the equilibrium mixture at 165° should be 6 : 94 parts, respectively, in marked disagreement with experiment (Table I). If allowance is made for S , the predicted composition becomes 1 : 99. In alkenyl systems, S is the dominant factor deciding the equilibrium ($\text{III} \rightleftharpoons \text{IV}$; $X = H$)



which is calculated to be such that 6% of the Δ^1 -isomer is present at 165° , in fair agreement with the estimates made by Kilpatrick *et al.* (*loc. cit.*) based mainly on thermochemical data. When certain mobile anionotropic systems are similarly considered, further interesting conclusions emerge. Thus, the fact that the equilibrium mixture of allylic bromides ($\text{III} \rightleftharpoons \text{IV}$; $X = \text{Br}$) contains approximately 16% of the Δ^1 -isomer at 100° (Young, Richards, and Azorlosa, *J. Amer. Chem. Soc.*, 1939, **61**, 3070; cf. Bateman and Cunneen, *J.*, 1950, 941) is now seen to imply that, relatively to a hydrogen atom, a bromine atom attaches itself preferentially at the secondary rather than the primary carbon atom, as expressed quantitatively by a free-energy difference of about 1 kcal. This order of thermodynamic stability, which is consistent with the weakly developed tendency of n -alkyl halides to isomerize into *sec.*- and *tert.*-compounds, simulates that found for straight- and branched-chain hydrocarbons (Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1945, **34**, 255, 403), and is of course the reverse of the relative ease of homolytic and heterolytic dissociation.

The origin of S is uncertain, but it may well arise from some interaction between the π orbital of the methine carbon atom and the sp^3 orbitals of an adjacent saturated carbon atom, which necessarily has no counterpart when the vinyl substituent is hydrogen. On this view, it would appear to be largely responsible for the effects attributed previously to hyperconjugation (Hughes, Ingold, and McNulty, *J.*, 1940, 899; Dhar *et al.*, *loc. cit.*), although our data indicate that the presence of a carbon atom adjacent to a double bond is much more important as a unique structural feature than the presence of a C-C bond (cf. values of S and e_3). This interaction would imply that a vinylic attachment strengthens a C-C more than it does a C-H bond, and therefore that on passing from (III; $X = H$) to (IV; $X = H$) S measures the change in bonding (exclusive of C-H-bond hyperconjugation) expressed by $(C_{sp^2}C_{sp^2} - C_{sp^2}C_{sp^3}) - (C_{sp^2}H - C_{sp^3}H)$. Definite independent evidence on this point is non-existent, but Roberts and Skinner's critical evaluation of the relevant thermochemical data (*Trans. Faraday Soc.*, 1949, **45**, 339) reveals just such a difference in the respective dissociation energies in molecules where the parallelism between this quantity and the bond energy is probably very close, *viz.*, $\text{CH}_3\cdot\text{CH}_2\text{-Me}$, 82.2; $\text{CH}_2\cdot\text{CH-Me}$, 89.7; $\text{CH}_3\cdot\text{CH}_2\text{-H}$, 97.5; $\text{CH}_2\cdot\text{CH-H}$, 102 kcal. g.-mol.⁻¹.

EXPERIMENTAL.

Materials.—Allylbenzene (I; $R' = R'' = H$) was distilled from sodium, and had b. p. $45.5-46.5/11$ mm., n_D^{20} 1.5122 (Found: C, 91.3; H, 8.6. Calc. for C_9H_{10} : C, 91.5; H, 8.5%). Propenylbenzene (II; $R' = R'' = H$) was obtained by isomerization of allylbenzene, and had b. p. $65.0-65.2/14$ mm., n_D^{20} 1.5490.

1-Phenylbut-2-ene (I; $R' = H$, $R'' = \text{Me}$). Dehydration of 1-phenylbutan-3-ol (from benzylideneacetone) with 50% aqueous sulphuric acid, and fractionation of the product from sodium, yielded this hydrocarbon admixed with *ca.* 19% of the Δ^1 - and *ca.* 10% of the Δ^3 -isomer. It had b. p. $68-70/13$ mm., n_D^{20} 1.5152 (Found: C, 90.7; H, 9.25. Calc. for $\text{C}_{10}\text{H}_{12}$: C, 90.9; 9.1%).

1-Phenylbut-1-ene (II; $R' = H$, $R'' = \text{Me}$) was prepared (by Dr. D. Barnard) by dehydration of 1-phenylbutan-1-ol (from *n*-propylmagnesium bromide and benzaldehyde; b. p. $73/0.05$ mm.) with anhydrous oxalic acid at 135° (4 hours). It had b. p. $82.0-82.5/18$ mm., n_D^{20} 1.5390 (Found: C, 90.8; H, 9.3. Calc. for $\text{C}_{10}\text{H}_{12}$: C, 90.9; H, 9.1%).

Isomeric mixture of 4-methyl-1-phenylpent-2-ene and its Δ^1 -isomer (I and II; $R' = H$, $R'' = \text{Pr}$). Phenylacetaldehyde (40 g.; freshly distilled) was added dropwise to an ethereal solution of isobutylmagnesium bromide prepared from 45 g. of the alkyl halide and 8 g. of magnesium. The resulting 4-methyl-1-phenylpentan-2-ol (18 g.) had b. p. $123/11$ mm., n_D^{20} 1.5050 (Found: C, 81.0; H, 10.25. $\text{C}_{12}\text{H}_{18}\text{O}$ requires C, 80.9; H, 10.1%). Petyunin (*Chem. Abs.*, 1944, **38**, 950) is reported to have prepared this carbinol *via* the Grignard compound of benzyl chloride and isovaleraldehyde and to have obtained it as a solid, m. p. 129° . Heating of the carbinol (3 g.) with sodium hydrogen sulphate (1.5 g.) at 160° for 1.5 hours yielded a hydrocarbon mixture (0.5 g.), b. p. $91-92/10$ mm., n_D^{20} 1.5109 (Found: C, 90.1; H, 9.85. Calc. for $\text{C}_{12}\text{H}_{16}$: C, 90.0; H, 10.0%).

4:4-Dimethyl-1-phenylpent-1-ene (II; $R' = H$, $R'' = \text{Bu}$). Cinnamyl chloride (30 g.) in ether (60 ml.) was added to the Grignard reagent prepared from *tert.*-butyl chloride (48 g.) and magnesium (12 g.). Fractionation of the rather complex product gave a small yield (1 g.) of the required hydro-

carbon, b. p. 105—107°/12 mm., n_D^{25} 1.5181 (Found : C, 89.3; H, 10.4. $C_{13}H_{18}$ requires C, 89.7; H, 10.3%).

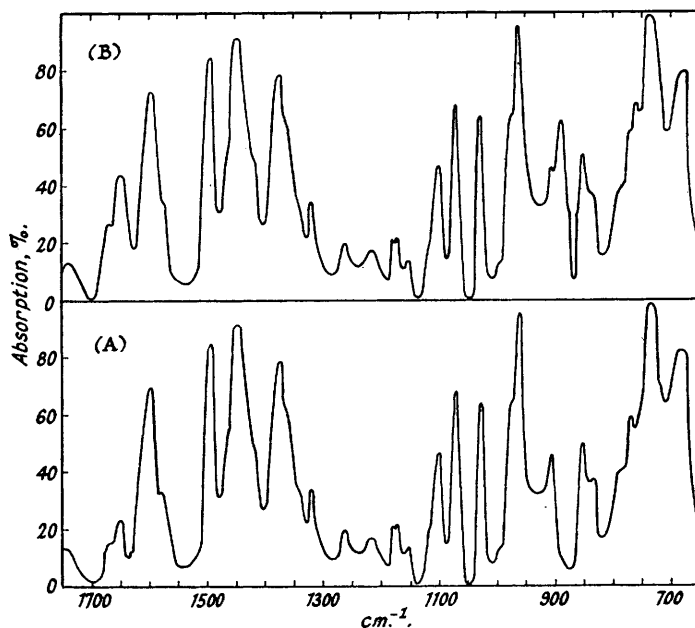
3-Methyl-1-phenylbut-2-ene (I; $R' = R'' = Me$) (prepared by Mr. J. A. LYONS). 2-Methyl-4-phenylbutan-2-ol, obtained from benzylacetone (from benzylideneacetone) and methylmagnesium iodide, was dehydrated with 30% aqueous sulphuric acid at 100°. The product had b. p. 81.2—81.6°/11 mm., n_D^{25} 1.5136 (Found : C, 90.5; H, 9.7. Calc. for $C_{11}H_{14}$: C, 90.4; H, 9.6%), and contained ca. 10% of 2-methyl-4-phenylbut-1-ene (by infra-red spectroscopic analysis).

3-Methyl-1-phenylbut-1-ene (II; $R' = R'' = Me$). 3-Methyl-1-phenylbutan-1-ol, from benzaldehyde and isobutylmagnesium bromide, was dehydrated by being heated with anhydrous oxalic acid at 150° for 2 hours. The resulting hydrocarbon had b. p. 81—83°/12 mm., n_D^{25} 1.5331 (Found : C, 90.6; H, 9.5. Calc. for $C_{11}H_{14}$: C, 90.4; H, 9.6%).

Equilibration Procedure.—An accurately weighed quantity (ca. 0.1 g.) of the hydrocarbon was dissolved in 10 ml. of methyl-alcoholic potassium hydroxide (20%), and ca. 1-ml. portions of the solution were sealed under 10^{-4} mm. pressure in small stout-walled Pyrex tubes. The tubes were heated in a

FIG. 2.

Infra-red absorption spectra. A, Isomerization product from (II; $R' = R'' = Me$). B, Synthetic mixture of (I; $R' = R'' = Me$) (43%) and (II; $R' = R'' = Me$) (57%). Path lengths, ~0.05 mm.



bath of boiling 1 : 3-dibromopropane (b. p. 165°/760 mm.) for various times, and the extinction coefficients of the solutions at 2500 Å. then measured directly on a Hilger Small Quartz Spectrograph and Spekker Photometer. The results are given in Fig. 1. When the solutions of allyl- and propenylbenzene were heated for longer than 24 hours, a slight, steady decrease in absorption intensity (at 2500 Å.) occurred, possibly owing to polymerization of the former compound leading to effective concentration changes. Blank experiments established that the negligible absorption of the alcoholic alkali was not measurably increased by heating for 60 hours under the isomerization conditions, but among several alcohols and glycols examined methyl alcohol was unique in this respect.

Examination of the Products of an Isomerization Reaction.—3-Methyl-1-phenylbut-1-ene (II; $R' = R'' = Me$) (3 g.; $\epsilon_{2500} = 17,700$) in 20% ethyl-alcoholic potassium hydroxide (12 ml.) was heated in an evacuated, sealed tube at 165° for 50 hours. The recovered hydrocarbon (2.8 g., *i.e.*, 93% recovery) had b. p. 82.0—84.5°/12 mm., n_D^{25} 1.5242, ϵ_{2500} 10,500 (in methanol) (Found : C, 90.6; H, 9.55. Calc. for $C_{11}H_{14}$: C, 90.4; H, 9.6%), and its infra-red spectrum (Fig. 2) was practically identical with that of a synthetic mixture of the original olefin (57%) and the Δ^2 -isomer (43%), except for absorption at 890 cm^{-1} in the latter arising from the presence of the Δ^3 -isomer (2-methyl-1-phenylbut-1-ene).

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