

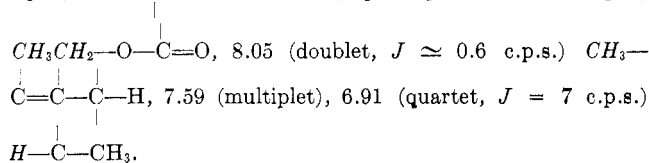
was stirred overnight. Ice-water was then added; the solution partially was neutralized with 40% sodium hydroxide and extracted with methylene chloride. The latter solution was extracted with sodium bicarbonate to remove acidic products, and the solvent was dried over sodium sulfate and removed to yield 2.3 g. of an amber oil. Distillation of the latter afforded the diester **7a**, as a colorless oil: b.p. 109–111° (0.3 mm.); 1.4 g. (38%); $\lambda_{\max}^{\text{EtOH}}$ 244 m μ (ϵ 10,100); $\nu_{\max}^{\text{CHCl}_3}$ 1681, 1730 cm.⁻¹; n.m.r., 8.81 (triplet, $J = 7$ c.p.s.), 8.75 (triplet, $J = 7$ c.p.s.), 6.01 (quartet, $J = 7$ c.p.s.), 5.91 (quartet $J = 7$ c.p.s.), 8.59 (singlet), 8.21 (singlet).

Anal. Calcd. for C₁₄H₂₀O₆: C, 62.67; H, 7.51. Found: C, 62.55; H, 7.61.

The semicarbazone of **7a** was crystallized from aqueous ethanol to give thin plates, m.p. 135–136°.

Anal. Calcd. for C₁₅H₂₄N₃O₆: C, 55.37; H, 7.12; N, 12.92. Found: C, 55.53; H, 7.19; N, 12.72.

B. 3-Carboxy-2,4-dimethylcyclohex-3-en-1-one (8).—The bicarbonate layer from A above was acidified and yielded after extraction with methylene chloride 1.64 g. of oily material. This was combined with material from a duplicate experiment and 2.94 g. of crude acid was distilled. At a bath temperature of 140° (0.7 mm.) gas evolution occurred. The distillate **8**, b.p. 99.5–105° (1.5 mm.), was collected as a colorless oil: $\lambda_{\max}^{\text{EtOH}}$ 220 m μ (ϵ 9300) (with weak base or acid it was not possible to effect isomerization of **8** to the corresponding α,β -unsaturated ketone); $\nu_{\max}^{\text{CHCl}_3}$ 1639, 1709 cm.⁻¹; n.m.r., 8.9 (doublet, $J = 7$ c.p.s.)



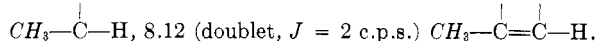
Anal. Calcd. for C₁₁H₁₆O₃: C, 67.32; H, 8.22. Found: C, 67.10; H, 8.28.

The semicarbazone crystallized from ethanol as small plates, m.p. 149.5–150°.

Anal. Calcd. for C₁₂H₁₈N₃O₃: C, 56.90; H, 7.6; N, 16.59. Found: C, 56.79; H, 7.69; N, 16.89.

The residue from the distillation when triturated with petroleum ether (b.p. 30–60°) gave 0.4 g. of a tan solid. Crystallization from ether–petroleum ether yielded 0.1 g. of yellow crystals, m.p. 108–135°. From the ultraviolet spectrum, $\lambda_{\max}^{\text{EtOH}}$ 241 m μ (ϵ 8700), the material is probably mainly **2** (below).

C. 2,4-Dimethyl-3-carboxycyclohex-2-en-1-one (2).—Treatment of 11.5 g. of **5a** with 100 ml. of concentrated hydrochloric acid overnight at room temperature was followed by dilution of the mixture with 100 ml. of water and heating at reflux for 20 hr. The solution was cooled, made alkaline, and extracted with ether. The aqueous solution was then acidified and extracted with methylene chloride. The acid product was crystallized from methylene chloride–petroleum ether to give 2.2 g., m.p. 124–126°. The mother liquor, 2.7 g., yielded an additional 1.0 g. of crystalline material. Recrystallization from the above solvent gave colorless prisms: m.p. 126–128°; $\lambda_{\max}^{\text{EtOH}}$ 245 m μ (ϵ 10,100); $\nu_{\max}^{\text{CHCl}_3}$ 1675, 1700 cm.⁻¹; n.m.r., 8.8 (doublet, $J = 7$ c.p.s.)



Anal. Calcd. for C₉H₁₂O₃: C, 64.40; H, 7.10. Found: C, 64.22; H, 7.32.

D. 4-Methyl-3-carboxycyclohex-3-en-7-one (3).—The Michael adduct **5b** (10 g.) was dissolved in 75 ml. of cold concentrated hydrochloric acid and the resulting dark purple solution stood for 48 hr. at 0°. It was then diluted to 150 ml. and refluxed for 2 hr. The aqueous solution was extracted with ethyl acetate and removal of the solvent gave 6.4 g. of a dark oil. Short-path distillation at 180° (bath temperature) afforded material which could be crystallized from ether–petroleum ether to give 0.754 g. of prisms: m.p. 112–114°; $\lambda_{\max}^{\text{EtOH}}$ 222 m μ (ϵ 7600); $\nu_{\max}^{\text{CHCl}_3}$ 1630, 1680, 1715 cm.⁻¹; n.m.r., 7.88 (triplet, $J = 2$ c.p.s.)

Anal. Calcd. for C₈H₁₀O₃: C, 62.32; H, 6.54. Found: C, 62.35; H, 6.60.

The Ultraviolet Absorption Spectra of Some Conjugated Dienes

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Deviations from the relationships known as Woodward rules, which empirically relate the ultraviolet spectra of conjugated dienes, are explained in terms of steric interactions and in terms of some special interactions occurring in the *cis* conformation. This special interaction also rationalizes some of the relations which form the basis of the Woodward rules. Further, a preliminary discussion is presented concerning solvent changes occurring in such systems and concerning the vibrational fine structure observed in the main absorption bands.

The ultraviolet spectra of conjugated dienes have been studied by many authors, notably by Booker, Evans, and Gillam¹ and by Woodward,² who have derived extremely useful empirical rules relating wave length of maximal absorption to substitution of the diene chromophore. These relations have since then been widely employed.³ However, recent accurate spectroscopic data are not available for some of the simpler substituted butadienes. We have therefore redetermined the spectra of a number of such substituted dienes, using carefully purified dienes whenever possible, in an attempt to relate minor spectral changes to structural changes. We were prompted to do this by some preliminary work⁴ which suggested that more careful in-

vestigation of the butadiene spectra might reveal additional empirical relationships, and also by some recent work⁵ which indicates that in certain butadienes the *cis* isomer can be more stable than the *trans* form.

Experimental

The ultraviolet absorption spectra were determined by standard methods in 1-cm. or 5- or 2-mm. cells using a Unicam SP 500, a Beckman Model DU, or a Cary Model 14 spectrophotometer. These instruments were calibrated against standard solutions of potassium chromate and/or potassium nitrate. For each compound at least two independent sets of observations were made. The λ_{\max} values obtained on the different instruments were found to be within 1 m μ of each other. The precision of λ_{\max} values is estimated to be 1 m μ and the precision of ϵ_{\max} values, 5% or better. Absorptivity values for most compounds were

(1) H. Booker, L. K. Evans, and A. E. Gillam, *J. Chem. Soc.*, 1453 (1940).
 (2) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).
 (3) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, pp. 15–21.

(4) W. F. Forbes and R. Shilton, *J. Org. Chem.*, **24**, 436 (1959).
 (5) H. G. Viehe, *Angew. Chem.*, **75**, 793 (1963).

TABLE I
MAIN ABSORPTION MAXIMA OF SOME ALIPHATIC DIENES AND THE EFFECTS OF METHYL SUBSTITUTION ON THEIR SPECTRA

Compd.	Solvent	λ_{\max} , m μ	ϵ_{\max}	Ref. compd.	$\Delta\lambda$ for δCH_3 , m μ
Group 1					
Butadiene	Cyclohexane	218.5	23,000
	Ethanol	217.5	22,400		
1,3-Pentadiene	Cyclohexane	224	26,400	Butadiene	5.5
	Ethanol	223	25,000		5.5
Isoprene	Cyclohexane	223	26,000	Butadiene	4.5
	Diethyl ether	222.5			
	Ethanol	222.5	22,800		5
2,3-Dimethyl-1,3-butadiene	Water	224			
	Vapor phase	221		Isoprene	
	Cyclohexane	228	22,000		2.5
	Diethyl ether	226.5			
2,4-Hexadiene	Ethanol	226.5	20,300		4
	Water	228			
	Cyclohexane	226.5	24,000	1,3-Pentadiene	2.5
	Ethanol	226	23,800		3
2-Methyl-1,3-pentadiene	Vapor phase	220			
	Cyclohexane	228		1,3-Pentadiene	4
3,4-Dimethyl-1,3-pentadiene ^a	Hexane	239	27,700	4-Methyl-1,3-pentadiene	5
2,4-Dimethyl-1,3-pentadiene	Vapor phase	220.5		4-Methyl-1,3-pentadiene	-3.5
	Cyclohexane	230.5	9,900		-3.5
	Diethyl ether	229	10,000		
	Ethanol	231	10,000		-1.5
2,3-Dimethyl-1,3-pentadiene	Cyclohexane	232.5	22,900	2,3-Dimethyl-1,3-butadiene	4.5
	Ethanol	231.5	19,200		5
Group 2					
4-Methyl-1,3-pentadiene	Vapor phase	224			
	Cyclohexane	234	23,000	1,3-Pentadiene	10
	Ethanol	232.5	22,400		9.5
2,5-Dimethyl-2,4-hexadiene	Vapor phase	238.5			
	Cyclohexane	244	24,000	2,4-Hexadiene	18/2 = 9
	Diethyl ether	242.5	24,000		
	Ethanol	242.5	26,000		16.5/2 = 8
2,4-Dimethyl-1,3-pentadiene	Vapor phase	220.5		2-Methyl-1,3-pentadiene	0.5
	Cyclohexane	230.5	9,900		2.5
Group 3					
2,3,4,5,-tetramethyl-2,4-hexadiene	Cyclohexane	}	No maximum between 210 and 280 m μ .		
	Ethanol				
4-Methyl-2- <i>t</i> -butyl-1,3-pentadiene	Cyclohexane	225	6,600		
	Ethanol	225	6,400		

^a Value from T. Nishida, A. Arai, and I. Ichikizaki, *Bull. Soc. Chem. Japan*, **35**, 572 (1962).

reproducible to 2%. The main ultraviolet maxima are listed in Table I.

Most of the dienes were commercially available. They were redistilled before use and the purity of most of the compounds was checked by vapor phase chromatography (v.p.c.). The v.p.c. unit employed was the F and M model 720 with fraction collection system TCS-3 and an 8 ft. \times 0.5 in. column packed with 15% Carbowax 20M on Diatoport S (60-80 mesh) was used in the purification.

4-Methyl-1,3-pentadiene was prepared by the method of Bachman and Goebel.⁶ It had b.p. 74-75°, n_{D}^{20} 1.4528.

2,4-Hexadiene, prepared by the method of Adams and Geissman,⁷ had b.p. 79-81°, n_{D}^{20} 1.4502.

2,3-Dimethyl-1,3-butadiene was prepared from pinacol by the method given by Vogel.⁸ It had b.p. 68-69° (755 mm.), n_{D}^{20} 1.4369. V.p.c. afforded only a single peak indicating that the compound was at least 99% pure.

2,4-Dimethyl-1,3-pentadiene was prepared by the method of Jitkow and Bogert.⁹ The crude material contained a little carbonyl material which was removed by treatment with Brady's reagent. The diene, after drying with calcium chloride and distillation from sodium, had b.p. 95°, n_{D}^{20} 1.4412. V.p.c. af-

forded only a single peak indicating that the compound was at least 99% pure.

2,5-Dimethyl-2,4-hexadiene was obtained from the Borden Chemical Co. It had b.p. 134°, n_{D}^{20} 1.4742.

A compound assumed to be 2,3,4,5-tetramethyl-2,4-hexadiene was prepared from 2,3,5-trimethylhex-2-en-4-one (b.p. 175°, 91° at 44 mm., n_{D}^{20} 1.4401; prepared by the general method of Colonge and Mostafavi¹⁰ from 2-methyl-2-butene, isobutyryl chloride, and stannic chloride) and methyl magnesium iodide followed by dehydration: yield 50%, b.p. 143-144°, n_{D}^{20} 1.4486.

Anal. Calcd. for C₁₀H₁₈: C, 86.9; H, 13.1. Found: C, 86.5; H, 13.3.^{11a}

Results

Deviations from Woodward Rules.—The spectra listed in Table I show that generally the introduction of an alkyl substituent in a butadiene system gives rise to a bathochromic wave-length displacement in the absorption spectrum. However, as previously pointed out,⁴ this displacement is not constant. In particular, a second methyl group, introduced into the system to

(6) G. B. Bachman and C. G. Goebel, *J. Am. Chem. Soc.*, **64**, 787 (1942).

(7) R. Adams and T. A. Geissman, *ibid.*, **61**, 2083 (1939).

(8) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co. Ltd., London, 1951.

(9) O. N. Jitkow and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 1979 (1941).

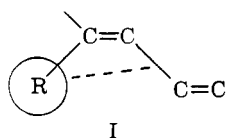
(10) J. Colonge and K. Mostafavi, *Bull. soc. chim. France*, **6**, 335 (1939).

(11) (a) Cf. E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3331 (1955).
(b) K. Hirayama, *J. Am. Chem. Soc.*, **77**, 373 (1955).

afford the chromophoric system $=C(CH_3)_2$, frequently gives a considerably larger displacement than the first methyl substituent (see Table I, groups 1 and 2, and compare Hirayama's formula^{11b} for a wave length of maximal absorption in which the parameters 0.13 for R and 0.17 for R' are used for compounds with structure $\begin{matrix} R \\ R' \end{matrix} > C=O$).

Steric Interactions.—Table I also shows that the wave-length displacement, brought about on alkyl substitution, which, according to the Woodward rules should remain approximately constant, may become much smaller for the more highly substituted butadienes. For example, inspection of the spectra of 2,4-dimethyl-1,3-pentadiene and of 4-methyl-1,3-pentadiene in cyclohexane solution shows that the introduction of a methyl substituent actually gives rise to a hypsochromic wave-length displacement. This observation suggests that compounds like 2,4-dimethyl-1,3-pentadiene exist, because of steric interactions, predominantly in a non-planar conformation, presumably *s-trans*¹² but possibly also *s-cis*. The hypothesis that Woodward rules do not apply to sterically hindered compounds of this type also receives support from the spectrum of 4-methyl-2-*t*-butyl-1,3-pentadiene in which the wave length of maximal absorption is yet further displaced to shorter wave length (see group 3 of Table I). This type of steric effect has been referred to as a type II steric effect.¹³ For compounds like 2,3,4,5-tetramethyl-2,4-hexadiene where steric interactions are yet further enhanced, as predicted,¹⁴ no maximal absorption occurs between 210 and 280 $m\mu$ indicating that the coplanarity of the double bonds is destroyed. These spectral effects of steric interactions are further illustrated in Fig. 1 which also shows the progressively reduced absorption intensities with increased steric interactions.

***s-cis* and *s-trans* Conformations.**—For extended conjugated systems it was at first thought that the main long wave-length ultraviolet absorption band in the *trans* isomer occurs at longer wave length and with greater absorption intensity than in the *cis* isomer.¹⁵⁻¹⁷ However, for simple systems such as 1,3-pentadiene or crotonic acid, the absorbing properties of the *cis* and *trans* forms are similar to a first approximation. This is not unexpected since in molecules of that type the over-all length of the conjugated system and hence the transition moment for both *cis* and *trans* forms are similar. If, in addition, both forms are approximately coplanar, the spectral characteristics will be determined by secondary interactions in the ground and excited states. It is now postulated that one such interaction occurs if a methyl or similar group is *cis* to the central



(12) *s-cis* and *s-trans* conformations denote *cis-trans* isomerism about a single bond possessing some double bond character.

(13) W. F. Forbes and R. Shilton, *J. Am. Chem. Soc.*, **81**, 786 (1959), and references cited therein.

(14) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955).

(15) L. Crombie, *Quart. Rev.*, **6**, 101 (1952), and references cited therein.

(16) D. Holme, E. R. H. Jones, and M. C. Whiting, *Chem. Ind. (London)*, 928 (1956).

(17) P. Naylor and M. C. Whiting, *J. Chem. Soc.*, 4006 (1954).

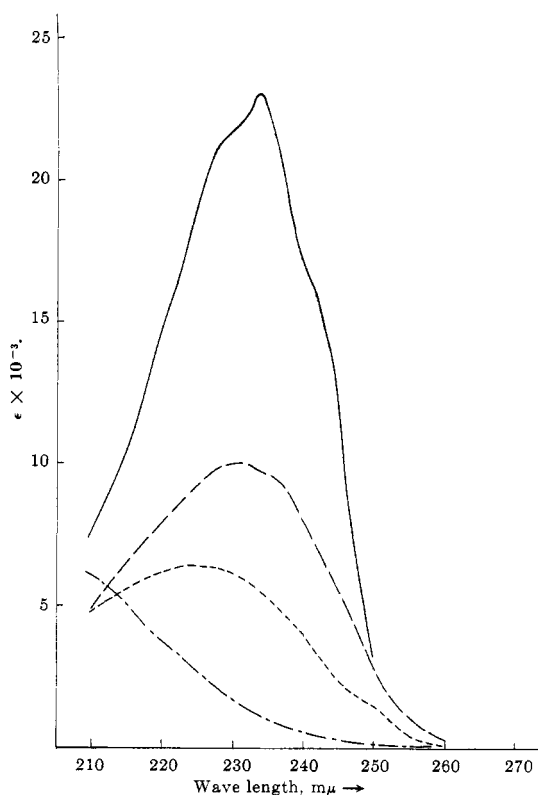


Fig. 1.—The ultraviolet absorption spectra in cyclohexane solution of 4-methyl-1,3-pentadiene (—), 2,4-dimethyl-1,3-pentadiene (---), 4-methyl-2-*t*-butyl-1,3-pentadiene (— · — ·), and 2,3,4,5-tetramethyl-2,4-hexadiene (· · · ·).

single bond in conjugated butadienes, as shown in structure I, and that such interaction can give rise to a displacement to longer wave length of about 5 $m\mu$.

This additional empirical rule can account for a number of observations. First, replacing $=CH(CH_3)$ by $=C(CH_3)_2$ generally gives a larger displacement than replacing $=CH_2$ by $=CH(CH_3)$ (see Table I), since only in the former case must the methyl group be placed in a position as shown in structure I. Next, it accounts for the observation that under certain conditions compounds like *cis*-1,3-pentadiene,¹⁸ *cis,cis*-2,4-hexadienol,¹⁹ or *cis,cis*-2,4-hexadienoic acid²⁰ absorb at slightly longer wave length than the corresponding *trans* isomer. In such *cis* isomers steric interactions may tend to oppose electronic interactions, and it is not surprising that a variety of spectral differences between *cis* and *trans* forms have been reported, which sometimes depend on the environmental conditions. These considerations also account for a number of anomalous observations. For example, it suggests one of the reasons why simple cyclic conjugated cycloalkadienes absorb at longer wave length than might have been anticipated²¹; the contributing reason may be that in these compounds a conformation similar to that shown in structure I is enforced. Also, the anomalously large wave-length displacements which occur on β,β' -disubstitution of methyl vinyl ketone with neopentyl groups²² can be explained by as-

(18) P. L. Nichols, Jr., S. F. Herb, and R. W. Riemenschneider, *J. Am. Chem. Soc.*, **73**, 247 (1951).

(19) L. Crombie, S. H. Harper, and R. J. D. Smith, *J. Chem. Soc.*, 2754 (1957).

(20) J. L. H. Allan, E. R. H. Jones, and M. C. Whiting, *ibid.*, 1862 (1955).

(21) E. A. Braude, *Chem. Ind. (London)*, 1557 (1954).

(22) P. Arnaud and M. Montagne, *Compt. rend.*, **251**, 998 (1960).

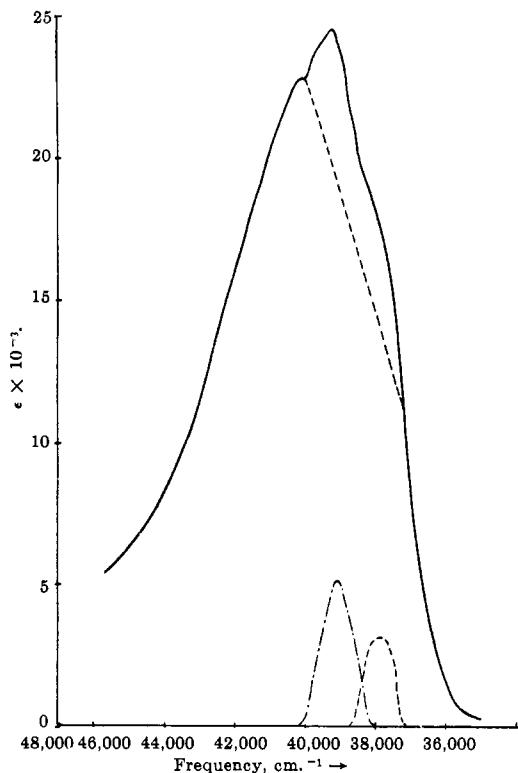
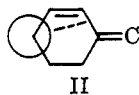


Fig. 2.—The resolution of the spectrum of 2,5-dimethyl-2,4-hexadiene in cyclohexane solution at 24° (wave-number units).

suming that steric interactions increase the $\text{C} > \text{C} =$ angle so that the group *cis* to the central single bond is brought closer to it.

More generally, the hypothesis can explain the displacement of 5 μ which it is necessary to add for each exocyclic double bond in calculating empirically the absorption of a diene using Woodward rules. That is, the additional displacement may be due to the enforced presence of a methylene group *cis* to the central single bond as shown in structure II.



A possible mechanism for this interaction postulated to occur in conformation I is that the alkyl or related group, because of its partial positive charge, exerts a field effect on the central single bond thereby attracting electrons towards this bond which in turn facilitates the electronic excitation. It is possible that the stability of the *cis* form of some 1-mono- and of some 1,4-dihalogen-1,3-butadienes can be rationalized in a related way, rather than to postulate intramolecular hydrogen bonding between the halogen atom and the ethylenic hydrogen atom⁵; or at least, that the attractive forces postulated for the halodiene systems are not the only interactions contributing to the stability of the *cis* forms.

Solvent Changes.—The largest solvent effect is observed on comparing the spectra in the vapor phase and in cyclohexane solution. A solvent orientation effect presumably contributes to this spectral change, and it is noteworthy that the wave-length displacement tends to be less for symmetrically substituted butadienes such

as 2,3-dimethyl-1,3-butadiene and 2,5-dimethyl-2,4-hexadiene than for unsymmetrically substituted butadienes such as 4-methyl-1,3-pentadiene (see Table I). Hence the displacements appear to be related to the dipole moment and/or polarizability of the molecule, which is in accord with previous observations.^{23,24}

The observed spectral change in this series of compounds, on altering the solvent from cyclohexane to diethyl ether or ethanol, is usually a slight displacement to shorter wave length (see Table I and *cf.* ref. 24). A possible rationalization of this unusual spectral change is that the electropositive part of the more polar solvent molecule interacts with the π -electron cloud of the butadiene chromophore; this tends to lower the energy of the ground state. In the electronic excited state, however, these "bonded" solvent molecules will as a first approximation not appreciably affect the energy level of the excited state because of the Franck-Condon principle which implies that during electronic excitation the molecules do not have time to rearrange themselves. That is, approximately one-half of the solvent molecules will facilitate the excitation but approximately one-half will hinder excitation because of the juxtaposition of like charges. Since therefore in a polar solvent, compared with a nonpolar solvent, the excited states remain energetically similar whereas the energy of the ground state is lowered, the over-all effect on a molecule with a center (or approximate center) of symmetry will be a widening of the energy levels corresponding to a displacement towards shorter wave length. The observed blue shift of *ca.* 1 μ , moreover, corresponds to an energy of *ca.* 0.5 kcal./mole which is of the order of the strength of the bond formed between a π -electron system and, for example, a hydroxyl group.²⁵

Fine Structure in the Main Absorption Band of Conjugated Dienes.—All these dienes, except those in which steric interactions are considerable, show, in addition to the highest peak, inflections at shorter and at longer wave length; the latter is often poorly defined. We shall refer to these peaks as B⁻, B, and B⁺ in order of increasing wave length. The spacing between B⁻ and B is 4–5.5 μ , and from B to B⁺ is 6–9.5 μ , and Table II also shows that the ratios of intensity of B⁻ to B and of B⁺ to B are approximately constant. In the vapor state, as anticipated, the fine structure is better resolved.

The spectra of the dienes which show a triple peak can be resolved graphically into three peaks of similar energy difference and intensity ratios. This has been done by making B⁻ the most intense peak in the resolved spectra which then affords the two peaks B and B⁺ with much lower intensity. Incidentally, we are unable to perform such resolution with B as the most intense peak. The process is illustrated in Fig. 2, and Table II lists the results in wave-number units.

Many published absorption spectra for a wide variety of compounds also show a triple peak similar to that of

(23) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

(24) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(25) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **33**, 427 (1960), and references cited therein.

(26) L. Dorfman, *Chem. Rev.*, **53**, 47 (1953).

(27) D. J. Cram and M. F. Antar, *J. Am. Chem. Soc.*, **80**, 3109 (1958).

(28) P. M. Everitt, D. M. Hall, and E. E. Turner, *J. Chem. Soc.*, 2286 (1956).

TABLE II
POSITIONS AND INTENSITIES OF RESOLVED PEAKS IN THE SPECTRA OF DIENES IN CYCLOHEXANE SOLUTION

Compd.	$\nu_{\max}, \text{cm.}^{-1} \times 10^{-3} (\epsilon)$						Difference, $\text{cm.}^{-1} \times 10^{-3}$		Intensity ratios		
	B ⁻		B		B ⁺		B ⁻ -B	B-B ⁺	B ⁻ -B	B ⁻ -B ⁺	B-B ⁺
Butadiene	46.7	(23,000)	45.4	(9700)	44.0	(7500)	1.3	1.4	2.4	3.1	1.3
Isoprene	45.6	(20,000)	44.5	(7000)	43.0	(7900)	1.1	1.5	1.9	2.7	1.4
2,3-Dimethyl-1,3-butadiene	45.0	(15,800)	43.7	(5900)	42.5	(5500)	1.2	1.1	2.9	3.8	1.3
2,5-Dimethyl-2,4-hexadiene	42.1	(22,700)	40.8	(7700)	39.5	(4900)	1.6	1.5	3.3	4.0	1.2
1,3-Pentadiene	46.2	(24,300)	44.5	(9900)	43.0	(8800)	1.7	1.5	2.5	3.0	1.2

the dienes²⁶⁻²⁸ in as much as the energy differences, expressed in wave numbers, are of the same order. The fine structure has generally been attributed to vibrational sub-levels. Carr, Pickett, and Stücklen²⁹ and Dale³⁰ have examined the vapor phase spectra of a number of dienes and have quoted a figure of 1130-1450 cm.^{-1} for the vibrational spacings, using unresolved

bands. Our data (see Table II) are in agreement with this.

Acknowledgment.—The authors are indebted to Dr. R. G. Woolford for advice and assistance and to Mr. D. L. Coffen and Miss Florence Jackman for competent technical assistance in that part of the work which was carried out at the Memorial University of Newfoundland. The authors gratefully acknowledge financial support for this work from the National Research Council of Canada.

(29) E. P. Carr, L. W. Pickett, and H. Stücklen, *Rev. Mod. Phys.*, **14**, 260 (1942).

(30) J. Dale, *Acta Chem. Scand.*, **11**, 265 (1957).

Pyrolysis Studies. XI.^{1,2} Polar Effects of *ortho* Substituents

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Polar σ^0 substituent constants for several substituents have been determined from rate data for vapor phase elimination reactions in which resonance effects are eliminated and proximity effects are minimal. These σ^0 -values agree fairly well with Taft's σ^* -values, and with σ_p^0 -values obtained from other literature data. A table of values is given.

In reactions of simple benzene derivatives the substituents influence the reaction center by a combination of *polar* and *resonance* effects.⁴ Additional *proximity* effects may occur in systems involving *ortho*-substituents.⁵ These proximity effects are likely to be variable for a given *ortho* substituent, being dependent on the nature of the adjacent reaction center, on the particular reaction, and on the reaction conditions (*e.g.*, solvent). This seems to be the main reason why equations of the Hammett type, which have been very successful in correlating rate and equilibrium data for reactions of *meta*- and *para*-substituted benzene derivatives, do not generally apply for similar reactions of *ortho*-substituted compounds.^{6,7}

Before the magnitude of the various proximity effects can be assessed quantitatively, it is necessary to know whether the polar effects and resonance effects are constant from system to system, and, if not, by how much they vary.

Previous studies⁸ have shown that the unimolecular vapor phase pyrolysis of *meta*- and *para*-substituted isopropyl benzoates to propene and the corresponding benzoic acids is an ideal series in which to study polar effects, as the relative rate data correlate accurately with the Taft polar equation $\log k/k_0 = \rho\sigma^0$.^{9,4c} All solvent effects are precluded, and proximity effects are reduced to small secondary steric effects as the eliminations are intramolecular,¹ so that σ^0 -values for the *ortho* substituents, obtained by substitution in the above equation, should give a good quantitative measure of their polar effects.

Experimental

Materials.—The *ortho*-substituted isopropyl benzoates were prepared and purified by the same methods as were used for the corresponding *meta* and *para* compounds.⁸ Th physical properties and analytical data are given in Table I.

Method of Pyrolysis.—The absolute rates of pyrolysis were measured using the apparatus and methods described in full detail previously.^{8,10,11} Each compound was pyrolyzed several

(1) Part X: G. G. Smith and D. F. Brown, *Can. J. Chem.*, **42**, 294 (1964).

(2) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, and at the I.U.P.A.C. Conference, London, July, 1963 (paper Al-125).

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(4) (a) Taft's terminology is used. Cf. R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13. (b) It should be noted that in this treatment, which focuses attention on the Ar-Y bond rather than the X-Ar bond, it is more correct to refer to the effects of the *meta*- and *para*-substituted phenyl groups as a whole. (c) See R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960), section C (2).

(5) Proximity effects may include primary steric effects between the *ortho* substituent and approaching or leaving species, and secondary steric effects such as steric inhibition of resonance, steric interference with internal rotations, and hydrogen bonding.

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1963, Chapter VII.

(7) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963).

(8) G. G. Smith and D. A. K. Jones, *J. Org. Chem.*, **28**, 3496 (1963).

(9) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

(10) G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32**, 703 (1961).

(11) G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.*, **83**, 3647 (1961).