205. *The Preparation and Ultra-violet Light Absorption of Some Substituted Phenylpropenyl- and Styrylmethyl-carbinols and 1-Phenylbutadienes.*

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In connexion with kinetic studies on anionotropic rearrangements (see following paper), carbinols of the type $C_6H_4R\cdot CH(OH)\cdot CH{:}CHMe$, where R = *o*-Me, *m*-Me, *p*-Me, *p*-F, *p*-Cl, *p*-Br and *p*-MeO, have been prepared by Grignard condensations of appropriate aromatic halides with crotonaldehyde. Quantitative conversions into the isomers $C_6H_4R\cdot CH{:}CH\cdot CH(OH)Me$ are effected by treatment with hydrochloric acid in aqueous dioxan. Dehydration of the carbinols by distillation from potassium hydrogen sulphate yields the dienes $C_6H_4R\cdot CH{:}CH\cdot CH{:}CH_2$, which are characterised by their adducts with maleic anhydride and with benzoquinone. The ultra-violet light absorption properties of the various compounds are discussed and provide evidence for the smaller polarisability of the phenyl nucleus as compared with the ethylenic bond.

The extension of the kinetic studies on anionotropic rearrangements carried out in these laboratories (cf. Braude and Jones, *J.*, 1946, **122**, 128; Braude, Jones, and Stern, *ibid.*, p. 396) required the preparation of substituted phenylpropenylcarbinols (I) and of the isomeric styrylmethylcarbinols (II). Only the parent carbinols (I and II, R = H) have been described

$$C_6H_4R\cdot CH(OH)\cdot CH{:}CHMe \quad (I.) \qquad C_6H_4R\cdot CH{:}CH\cdot CH(OH)\cdot Me \quad (II.)$$

hitherto. A number of substituted phenylvinylcarbinols have been prepared by Burton and Ingold (*J.*, 1928, 904) and Burton (*ibid.*, p. 1650), but the lower mobility of phenylvinyl- as compared with phenylpropenyl-carbinol (Braude, Jones, and Stern, *loc. cit.*) indicated that the vinylcarbinols would be less valuable for kinetic studies than their propenyl homologues.

The simplest route to phenylpropenylcarbinols is by the Grignard condensation of the appropriate aryl halides with crotonaldehyde. Qualitative data in the literature (cf. Runge in Schmidt, "Chemie in Einzeldarstellungen," Vol. 16, Part I, Stuttgart, 1932) indicate that the reactivity of aryl halides towards magnesium varies in the order ArCl < ArBr < ArI. Furthermore, it is said to be enhanced by methyl substituents, decreased by halogen and methoxyl substituents, and completely destroyed by substituents, such as the nitro-group, exerting only electron-attracting effects. The range of compounds accessible by this method is therefore limited. In the present work it was found that the bromotoluenes and *p*-bromofluorobenzene all reacted readily with magnesium in the presence of a small amount of ethyl bromide. *p*-Dibromobenzene and *p*-bromoanisole reacted somewhat less readily, while with *p*-dichlorobenzene the reaction was incomplete even after four days. With *p*-di-iodobenzene the metal slowly disappeared after prolonged treatment, but in contrast to the findings of Bruhat and Thomas (*Compt. rend.*, 1926, **183**, 297; cf. Mihailescu and Caragea, *Chem. Zentr.*, 1930, I, 2248) no significant yield of condensation product with crotonaldehyde could be obtained, some of the di-iodobenzene being recovered unchanged, together with iodobenzene, and intractable residues. Attempts to make *p*-bromonitrobenzene react with magnesium, using Grignard's technique (*Compt. rend.*, 1934, **198**, 625) of adding an equimolecular proportion of ethyl bromide simultaneously with the unreactive halide, only yielded unchanged starting material and small amounts of *pp'*-dibromo-azo- and -hydrazo-benzenes (cf. Werigo, *Annalen*, 1873, **165**, 190; Hepworth, *J.*, 1920, **117**, 1004; Slotta and Heller, *Ber.*, 1930, **63**, 3030). Again, the bromomagnesium derivative of *p*-bromophenol, though soluble in anisole at 100°, failed to react with magnesium.

The Grignard derivatives of the first eight halides mentioned were condensed with crotonaldehyde, special attention being paid to temperature control during the addition of the aldehyde and during the decomposition of the complex with ammonium chloride, in order to avoid the formation of the isomeric styryl derivatives. Thus, even in the preparation of the much less readily isomerised phenylvinylcarbinol, the product contains some cinnamyl alcohol unless the last two stages are carried out below 20°. It is known that, *vice versa*, cinnamylmagnesium chloride reacts partly in the form of phenylvinylcarbinylmagnesium chloride (Gilman and Harris, *J. Amer. Chem. Soc.*, 1927, **49**, 1825) and it may well be, therefore, that the Grignard derivatives themselves undergo some equilibration.

The substituted phenylpropenylcarbinols were isolated in good yields as viscous liquids or low-melting solids. In view of their ready isomerisation in the presence of acids, traces of the latter were excluded by drying over, and distilling from traces of, potassium carbonate.

In the absence of these precautions, some of the rearranged styrylmethylcarbinols and phenylbutadienes are invariably produced, and considerable resinification occurs. This is particularly noticeable with the highly mobile *p*-anisylpropenylcarbinol.

Rearrangement of the phenylpropenylcarbinols was effected by treatment with hydrochloric acid in aqueous dioxan, the corresponding styryl isomers being obtained in almost quantitative yields. In aqueous alcohol a mixture of the carbinols and their ethyl ethers is produced (cf. Braude, Jones, and Stern, *loc. cit.*) and kinetic data (see following paper) indicate that with the chloro- and bromo-carbinols some etherification occurs before, as well as during, rearrangement.

Treatment of the phenylpropenylcarbinols with α-naphthyl *iso*cyanate in the absence of solvent gave the naphthylurethanes of the corresponding styrylmethylcarbinols. In petrol solution and in the presence of traces of pyridine, mixtures of the isomerised and unisomerised naphthylurethanes were obtained. The latter could not be isolated pure, however, as they readily rearrange to the former on attempted recrystallisation. The two types of derivatives are distinguished by their characteristic ultra-violet light absorption (see below).

It has long been known that methylstyrylcarbinol can readily be dehydrated to phenylbutadiene (Klages, *Ber.*, 1902, **35**, 2650); in fact, early workers experienced considerable difficulty in obtaining the pure carbinol by the condensation of cinnamaldehyde with methylmagnesium iodide because they omitted to eliminate traces of iodides and of acids which act as dehydration catalysts. In the present work, the rearrangement and subsequent dehydration of the phenylpropenylcarbinols were conveniently carried out in one stage by means of potassium hydrogen sulphate. The carbinol together with about one-tenth of its weight of sulphate is preheated to 80—100° at 10^{-3} mm. until the vigorous rearrangement reaction sets in (5—30 mins.). In the case of the *p*-anisyl- and *p*-bromophenyl-propenylcarbinols the solid styryl isomers are deposited on the sides of the vessel. The temperature is then raised and the phenylbutadiene distils over as the dehydration proceeds. The ease of dehydration appears to vary in the same order as that of the isomerisation of the parent carbinols. The substituted phenylbutadienes are highly refractive liquids or low-melting solids which were purified by micro-fractionation from traces of potassium hydrogen sulphate or by crystallisation, and showed the expected selective high-intensity absorption in the ultra-violet (see below). On heating or on exposure to light and air, they readily resinify, and some difficulty was experienced in obtaining correct microanalyses, particularly for the tolyl compounds.

The dienes were characterised by their reactions with maleic anhydride and with *p*-benzoquinone in benzene solution, giving respectively the phenyltetrahydrophthalic anhydrides and the phenyl-1 : 4 : 9 : 10-tetrahydronaphtha-5 : 8-quinones (cf. Diels and Alder, *Ber.*, 1929, **62**, 2081, 2337). The tetrahydro-quinones are pale yellow owing to their absorption band near 3650 A. (see below), but slowly change on standing into the colourless phenyl-1 : 4-dihydronaphtha-5 : 8-quinols. This double prototropic change is facilitated by exposure to light, and the ease with which it occurs again appears to parallel that of the isomerisation of the phenylpropenylcarbinols. Thus the *p*-anisyl derivative does not even show the expected light absorption maximum at 3650 A. in hexane, chloroform, or benzene solution; maxima near 3300 A. expected for the 1 : 4-dihydronaphthalene derivative (cf. Morton and de Gouveia, *J.*, 1934, 916) appear instead, and only the colourless quinol can be recovered from the solution. Since the last two solvents are not appreciably transparent to light of wave-lengths shorter than 2350 and 3000 A. respectively at the cell thickness used (1 cm.), the wave-length of the photochemically active light seems to be within the region of the 3650 A. band expected for the tetrahydronaphthaquinone.

The light absorption properties of the various compounds were determined in the region 2150—4000 A. In the phenylpropenylcarbinols (Table I), the phenyl and ethylene chromophores are in isolated positions, and would therefore be expected to contribute independently to the ultra-violet light absorption (cf. Braude, *Ann. Reports*, 1945, **42**, 105). The selective absorption of the ethylenic double bond lies well below 2150 A., and the absorption of the carbinols in the region examined should therefore be closely similar to that of the corresponding substituted toluenes, as is found to be the case.

In the styrylcarbinols (Table II, Figs. 2 and 3), the essential chromophore is the styrene system. Styrene exhibits two bands in the region examined, at 2450 and 2920 A. (Pestemer, Langer, and Manchen, *Monatsh.*, 1936, **68**, 326), which can be assigned to the conjugated system and to the partial phenyl chromophore respectively. The styrylcarbinols exhibit similar bands, showing small bathochromic displacements of 10—180 A. due to the substituents, except that a *p*-fluoro-group produces a hypsochromic shift of 30 A. In the naphthylurethanes

(Table III) the absorption originating in the naphthyl residue is superimposed on the styryl absorption and the difference in the absorption of the naphthylurethanes of the styrylcarbinols and of methanol coincides with the absorption of the styrylcarbinols themselves.

TABLE I.

Ultra-violet light absorption of $C_6H_4R{\cdot}CH(OH){\cdot}CH{:}CHMe$ *in ethanol.**

R.				R.			
H	$\lambda_{max.}$, A.	—	2510, 2580	*p*-F	$\lambda_{max.}$, A.	—	2580, 2640, 2700
	$\epsilon_{max.}$	—	450, 450		$\epsilon_{max.}$	—	1450, 1450, 1050
o-Me	$\lambda_{max.}$, A.	2,150	*2590*, 2640, *2700*, *2810*	*p*-Cl	$\lambda_{max.}$, A.	2,220	2590, 2640
	$\epsilon_{max.}$	11,000	480, 510, 400, 130		$\epsilon_{max.}$	11,000	2300, 2300
m-Me	$\lambda_{max.}$, A.	—	2420, 2515, 2580, 2650, *2700*, *2725*	*p*-Br	$\lambda_{max.}$, A.	2,230	2590, 2650
	$\epsilon_{max.}$	—	1050, 1150, 1450, 1450, 1150, 1000		$\epsilon_{max.}$	13,000	1500, 1500
p-Me	$\lambda_{max.}$, A.	2,220	2595, 2645, 2720	*p*-MeO	$\lambda_{max.}$, A.	2,280	2730, 2760, 2815
	$\epsilon_{max.}$	11,000	270, 310, 280		$\epsilon_{max.}$	13,500	2200, 2200, 2100

Ultra-violet light absorption of $R{\cdot}C_6H_4{\cdot}Me$ *in ethanol for comparison.*

p-Me	$\lambda_{max.}$, A.	2,160	2600, 2680, 2740	*p*-MeO	$\lambda_{max.}$, A.	2,240	2800, 2850
	$\epsilon_{max.}$	7,500	330, 500, 620		$\epsilon_{max.}$	10,400	2200, 1530
p-Br	$\lambda_{max.}$, A.	2,200	2620, 2690, 2770				
	$\epsilon_{max.}$	10,500	390, 470, 390				

* In this and subsequent tables figures in italics refer to inflections.

TABLE II.

Ultra-violet light absorption of $C_6H_4R{\cdot}CH{:}CH{\cdot}CH(OH)Me$ *in ethanol.*

R.			
H	$\lambda_{max.}$, A.	2480, 2510	2810, 2910
	$\epsilon_{max.}$	19,000, 19,500	2000, 1550
o-Me	$\lambda_{max.}$, A.	2480, 2550	2880, 2970
	$\epsilon_{max.}$	16,000, 16,000	1300, 700
m-Me	$\lambda_{max.}$, A.	2510, 2550	*2880*, 2960
	$\epsilon_{max.}$	17,500, 17,500	1300, 900
p-Me	$\lambda_{max.}$, A.	*2460*, 2510, 2550	2890
	$\epsilon_{max.}$	19,000, 22,000, 22,000	1600
p-F	$\lambda_{max.}$, A.	2480, 2580	2800, 2950
	$\epsilon_{max.}$	21,000, 15,000	1500, 800
p-Cl	$\lambda_{max.}$, A.	*2510*, 2560, 2590	2900, 2990
	$\epsilon_{max.}$	22,500, 23,000, 23,000	1700, 1150
p-Br	$\lambda_{max.}$, A.	2580	2880, 2990
	$\epsilon_{max.}$	26,000	2300, 1150
p-MeO	$\lambda_{max.}$, A.	2610, 2690	2920
	$\epsilon_{max.}$	25,000, 19,800	3400

TABLE III.

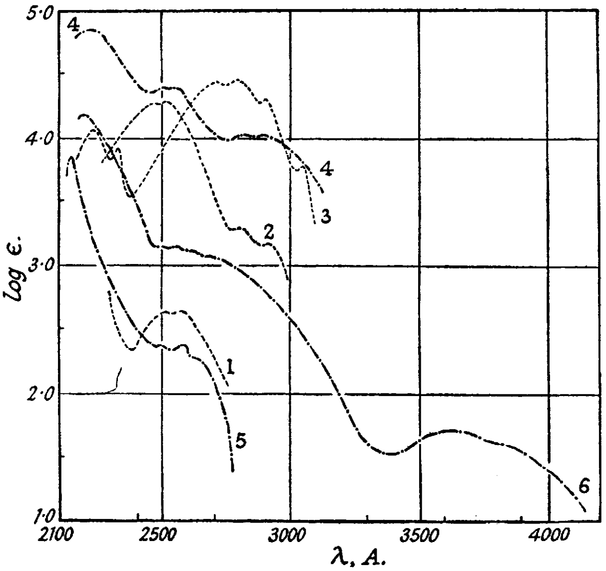
Ultra-violet light absorption of $C_{10}H_7{\cdot}NH{\cdot}CO_2{\cdot}CHMe{\cdot}CH{:}CH{\cdot}C_6H_4R$ *in ethanol.*

R.				
H	$\lambda_{max.}$, A.	2220	2510, 2560	2810, 2900
	$\epsilon_{max.}$	72,000	25,000, 25,000	10,000, 10,000
o-Me	$\lambda_{max.}$, A.	2210	2510	2810, 2910
	$\epsilon_{max.}$	76,000	20,000	9000, 9000
m-Me	$\lambda_{max.}$, A.	2200	2550	2810, 2910
	$\epsilon_{max.}$	75,000	20,000	8600, 8000
p-Me	$\lambda_{max.}$, A.	2210	2550	2800, *2900*, *2960*
	$\epsilon_{max.}$	69,000	20,000	11,000, 9600, 930
p-F	$\lambda_{max.}$, A.	2220	2500	2820, 2910
	$\epsilon_{max.}$	71,000	22,000	7500, 7500
p-Cl	$\lambda_{max.}$, A.	2220	2580	2910
	$\epsilon_{max.}$	68,000	30,000	10,500
p-Br	$\lambda_{max.}$, A.	2220	2580	*2900*
	$\epsilon_{max.}$	71,000	29,000	10,500
p-MeO	$\lambda_{max.}$, A.	2220	2650	2920
	$\epsilon_{max.}$	71,000	35,000	13,000

Ultra-violet light absorption of $C_{10}H_7{\cdot}NH{\cdot}CO_2Me$ *in ethanol for comparison.*

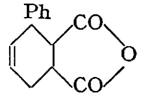
$\lambda_{max.}$, A.	2230	—	2810, 2910
$\epsilon_{max.}$	68,000	—	6800, 6800

FIG. 1.



1. Ph·CH(OH)·CH:CHMe.
2. Ph·CH:CH·CH(OH)·Me.
3. Ph·CH:CH·CH:CH$_2$.
4. Ph·CH:CHMe·O·CO·NH·Naphthyl.

5.



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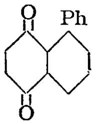
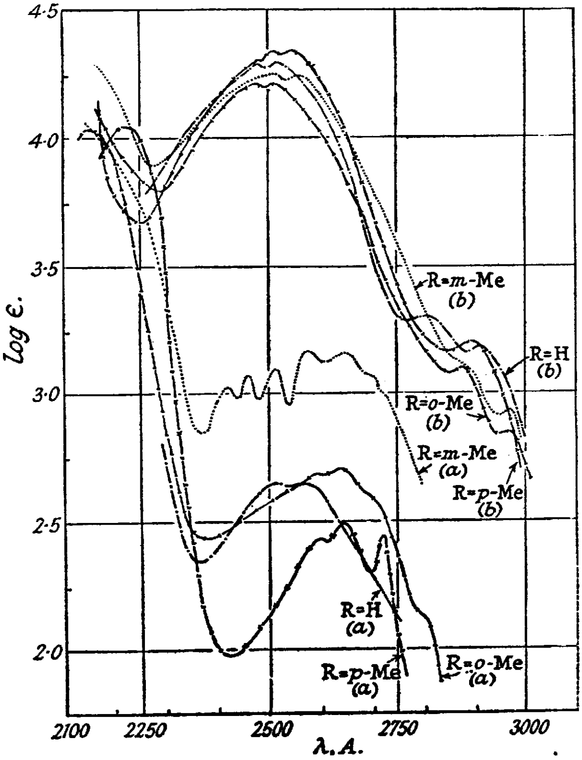


(*In ethanol.*)

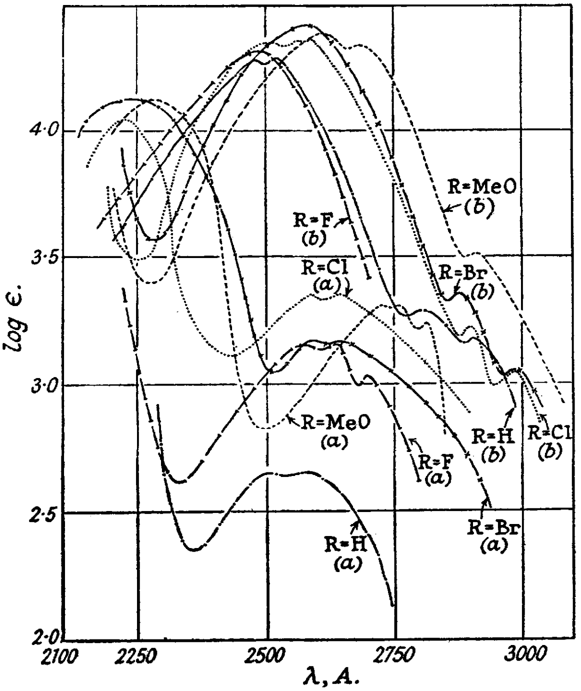
FIG. 2.



(*a*) R·C$_6$H$_4$·CH(OH)·CH:CHMe *and* (*b*) R·C$_6$H$_4$·CH:CH·CH(OH)Me.
(*In ethanol.*)

The phenylbutadienes (Table IV, Figs. 4 and 5) give rise to resolved absorption bands around 2200, 2800, and 3100 A. The last two may be ascribed respectively to the phenylbutadiene and to the partial phenyl chromophore, while the first probably represents a summation of the low wave-length phenyl bands and absorption due to the partial butadiene chromophore. The effects of methyl, chloro-, and bromo-substituents on the 2800 A. bands is smaller even than in the styryl system, while the fluoro-group again has a hypsochromic effect of 30 A., and the methoxy-group a bathochromic effect of 110 A. In the maleic anhydride adducts (Table V), the phenylchromophore is again isolated from the other unsaturated groups in the molecule and the absorption is very similar to that of the phenylpropenylcarbinols. The absorption curves of the benzoquinone adducts (Table VI) are a summation of those due

FIG. 3.



(*a*) *p*-R·C_6H_4·CH(OH)·CH:CHMe *and* (*b*) *p*-R·C_6H_4·CH:CH·CH(OH)Me.
(*In ethanol.*)

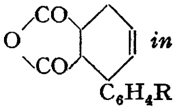
TABLE IV.

Ultra-violet light absorption of C_6H_4R·CH:CH·CH:CH_2 *in ethanol.*

R.				
H	λ$\lambda_{\text{max.}}$, A.	2230, 2330	2710, 2800, 2900	3050
	$\epsilon_{\text{max.}}$	12,000, 8500	28,000, 28,300, 27,000	6000
o-Me	$\lambda_{\text{max.}}$, A.	2230	2810	*
	$\epsilon_{\text{max.}}$	12,500	25,000	
m-Me	$\lambda_{\text{max.}}$, A.	2170, 2285, 2350	2790	*3110*
	$\epsilon_{\text{max.}}$	16,600, 14,400, 10,000	29,000	7200
p-Me	$\lambda_{\text{max.}}$, A.	2270, 2340	*2730*, 2810, 2880	3090
	$\epsilon_{\text{max.}}$	11,300, 9250	28,900, 30,000, 28,000	8000
p-F	$\lambda_{\text{max.}}$, A.	2180	2730, 2770	*
	$\epsilon_{\text{max.}}$	12,800	30,000, 30,000	
p-Cl	$\lambda_{\text{max.}}$, A.	2270, 2340	2810, *2860*	*3120*
	$\epsilon_{\text{max.}}$	12,200, 7500	32,000, 31,000	5700
p-Br	$\lambda_{\text{max.}}$, A.	*2200*, 2270	2810, 2860	*
	$\epsilon_{\text{max.}}$	13,600, 12,000	31,000, 30,000	
p-MeO	$\lambda_{\text{max.}}$, A.	2220	2840, 2910	*
	$\epsilon_{\text{max.}}$	16,000	35,000, 35,000	

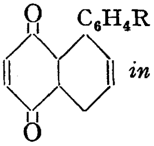
* Absorption beyond 3100 A. not determined.

TABLE V.

Ultra-violet light absorption of  *in ethanol.*

R.			
H	$\lambda_{max.}$, A.	2,150	*2480*, 2580, *2650*
	$\epsilon_{max.}$	7,800	260, 270, 190
o-Me	$\lambda_{max.}$, A.	2,130	2630, 2710
	$\epsilon_{max.}$	11,500	250, 160
m-Me	$\lambda_{max.}$, A.	2,145	2650, 2730
	$\epsilon_{max.}$	11,000	330, 260
p-Me	$\lambda_{max.}$, A.	2,180	*2600*, 2640, 2730
	$\epsilon_{max.}$	10,000	320, 350, 320
p-F	$\lambda_{max.}$, A.	—	2600, 2650, 2710
	$\epsilon_{max.}$	—	120, 155, 135
p-Cl	$\lambda_{max.}$, A.	2,230	*2470*, 2600, 2670, 2770
	$\epsilon_{max.}$	12,500	280, 320, 350, 250
p-Br	$\lambda_{max.}$, A.	2,230	2600, 2660, 2770
	$\epsilon_{max.}$	14,000	350, 350, 200
p-MeO	$\lambda_{max.}$, A.	2,280	2650, 2700, 2720, 2760, 2820
	$\epsilon_{max.}$	11,500	200, 270, 270, 270, 230

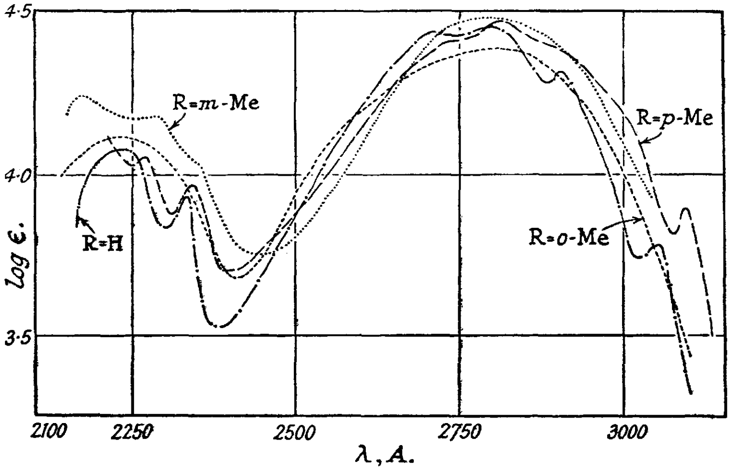
TABLE VI.

Ultra-violet light absorption of  *in* n-*hexane.*

R.				
H	$\lambda_{max.}$, A.	2,200	2500, 2560, *2610*, *2690*	3640, *3780*
	$\epsilon_{max.}$	15,500	1450, 1400, 1300, 1100	53, 43
o-Me	$\lambda_{max.}$, A.	2,200	2600, 2810, 2910	3650
	$\epsilon_{max.}$	16,500	1400, 1100, 1100	60
p-Me	$\lambda_{max.}$, A.	2,220	2580, *2820*	3640, *3760*
	$\epsilon_{max.}$	19,000	1650, 850	55, 50
p-F	$\lambda_{max.}$, A.	2,180	2550, 2600, 2900	3650
	$\epsilon_{max.}$	23,000	2600, 1800, 850	80
p-Cl	$\lambda_{max.}$, A,	2,250	2550, 2820, 2920	3650
	$\epsilon_{max.}$	24,000	1500, 900, 900	55
p-Br	$\lambda_{max.}$, A.	2,230, 2,270	2490, 2560	3650
	$\epsilon_{max.}$	27,500, 27,000	2400, 2000	55

to their separate phenyl and dihydro-quinone systems, the latter giving rise to bands near 2500 and 3600 A., *i.e.*, displaced by *ca.* 200 A. with respect to those shown by the open-chain diacetyl-ethylene system (Braude, *J.*, 1945, 490) (Fig. 1).

FIG. 4.

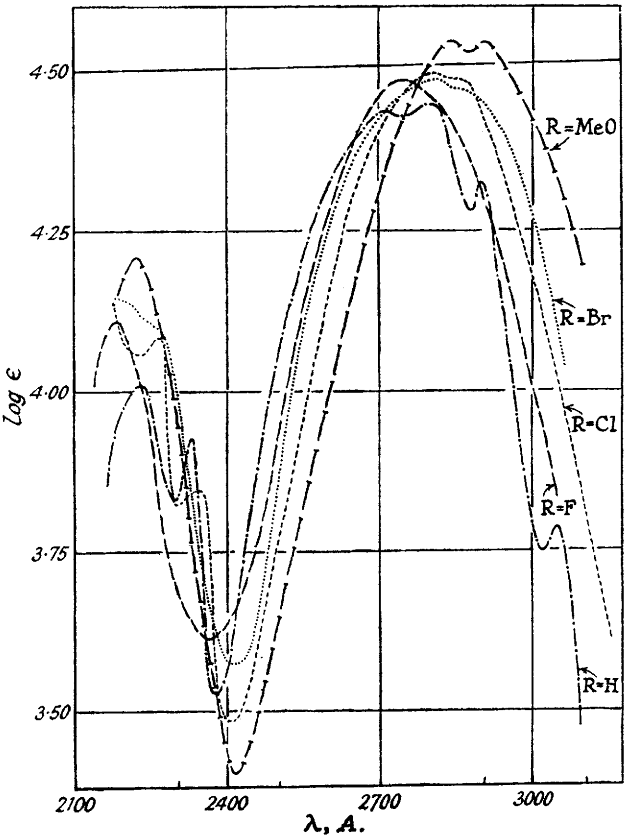


$R\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CH_2$. (*In ethanol.*)

The variochromic effects of the nuclear substituents on the principal bands in the phenylpropenylcarbinols, styrylmethylcarbinols, and phenylbutadienes are summarised in Table VII.

(The exact values of $\Delta\lambda$ are somewhat arbitrary owing to the vibrational structure. The highest peaks have been taken as characteristic of a group, and where two peaks of equal intensity are shown, the one at higher wave-length has been used for computing $\Delta\lambda$.) These effects are generally smallest (10—50 A.) for a methyl substituent, a little larger (10—90 A.) for the halogen groups, and largest (70—180 A.) for the methoxyl group. A number of other regularities appear, but their generality is too limited to warrant separate discussion. The fact, however, that the variochromic effects of nuclear substituents in the styryl and phenylbutadiene systems are no greater than in the phenyl one and smaller than in corresponding

FIG. 5.



p-R·C_6H_4·CH:CH·CH:CH_2. (*In ethanol.*)

TABLE VII.

The variochromic effects of nuclear substituents.

R.	C_6H_4R·CH(OH)·CH:CHMe : " Phenyl " band.	C_6H_4R·CH:CH·CH(OH)Me : " Styrene " band.	" Phenyl " band.	C_6H_4R·CH:CH·CH:CH_2 : " Phenylbutadiene " band.	" Phenyl " band.
		$\lambda_{max.}$, A.			
H	2580	2510	2810	2800	3050
		$\Delta\lambda_{max.}$, A.			
o-Me	+ 60	+ 40	+ 70	+ 10	—
m-Me	+ 50	+ 40	+ 70	+ 10	+ 60
p-Me	+ 65	+ 40	+ 80	+ 10	+ 40
p-F	+ 60	— 30	— 10	— 30	—
p-Cl	+ 60	+ 80	+ 90	+ 10	+ 70
p-Br	+ 70	+ 70	+ 70	+ 10	—
p-MeO	+ 180	+ 100	+ 110	+ 110	—

systems where the substituents are directly attached to acyclic ethylenic double bonds (cf. Bowden, Braude, and Jones, *J.*, 1946, 948) is of interest. Since the conjugating and transmitting capacity of a group is related to its polarisability (cf. Braude, *loc. cit.*), it provides spectral evidence for the lower polarisability of the phenyl nucleus as compared with an aliphatic ethylenic group.

EXPERIMENTAL.

(Light-absorption data are only given when not included in Tables I—VI.)

o-*Tolylpropenylcarbinol* (I; R = *o*-Me).—Freshly distilled crotonaldehyde (20 g.) in ether (40 c.c.) was added to *o*-tolylmagnesium bromide (from Mg, 6·5 g.) in ether (250 c.c.) during one hour at 0°; the solution was then stirred for 3 hours and treated with excess of ammonium chloride solution. Isolation of the product with ether, drying over anhydrous potassium carbonate, and distillation from a trace of potassium carbonate yielded o-*tolylpropenylcarbinol* (30·5 g.), b. p. 61°/0·001 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5392 (Found: C, 81·2; H, 8·7. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%).

o-*Methylstyrylmethylcarbinol* (II; R = *o*-Me).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 12 hours at 30° yielded o-*methylstyrylmethylcarbinol* (1·35 g.), b. p. 66°/0·005 mm., $n_{\mathrm{D}}^{22^\circ}$ 1·5590 (Found: C, 81·75; H, 8·55. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *a-naphthylurethane* (0·6 g.), obtained by treating the carbinol (0·33 g.) with a-naphthyl *iso*cyanate (0·35 g.), crystallised from petrol (b. p. 80—100°) in needles, m. p. 104° (Found: C, 79·9; H, 6·5; N, 4·2. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·2%).

1-(o-*Tolyl*)*buta*-1 : 3-*diene*.—*o*-Tolylpropenylcarbinol (4 g.) was distilled from potassium hydrogen sulphate (0·8 g.) at 10^{-2} mm. The *diene* after fractionation had b. p. 37°/0·01 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·6008 (Found: C, 91·0; H, 8·5. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* (0·65 g.) was obtained by refluxing the diene (0·5 g.) with maleic anhydride (0·25 g.) in benzene (3 c.c.) for 5 minutes. It crystallised from petrol (b. p. 80—100°) in fine needles, m. p. 92° (Found: C, 73·9; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·3%).

p-*Benzoquinone adduct*. A solution of the diene (5·0 g.) and *p*-benzoquinone (3·5 g.) in benzene (15 c.c.) was boiled for a few minutes. On cooling, and evaporation of the solvent under reduced pressure, crystals separated which were washed with a little methanol to remove a small amount of quinhydrone. Recrystallisation from petrol (b. p. 80—100°) afforded pale yellow plates of 1-(o-*tolyl*)-1 : 4 : 9 : 10-*tetrahydronaphthaquinone* (3·7 g.), m. p. 93·5° (Found: C, 80·9; H, 6·25. $C_{17}H_{16}O_2$ requires C, 80·95; H, 6·4%). On allowing the quinone (1 g.) to stand overnight with acetic anhydride (25 g.) and zinc chloride (0·5 g.) and dilution with water, 1-(o-*tolyl*)-1 : 4-*dihydronaphthaquinol diacetate* (1 g.) was obtained; it crystallised from petrol (b. p. 80—100°) or alcohol, and had m. p. 141° (Found: C, 74·9; H, 6·1. $C_{21}H_{20}O_4$ requires C, 74·9; H, 6·0%). Light absorption in alcohol: Maxima at 2180, 2650, and 2720 A., ϵ = 25,000, 800, and 720, respectively.

m-*Tolylpropenylcarbinol* (I; R = *m*-Me).—Freshly distilled crotonaldehyde (9·5 g.) in ether (50 c.c.) was added to *m*-tolylmagnesium bromide (from Mg, 3·2 g.) during one hour at 0°, and the solution stirred for 3 hours. Working up in the usual manner and distillation from a trace of potassium carbonate yielded m-*tolylpropenylcarbinol* (17 g.), b. p. 76°/0·01 mm., $n_{\mathrm{D}}^{19^\circ}$ 1·5384 (Found: C, 81·8; H, 8·7. $C_{11}H_{14}O$ requires: C, 81·45; H, 8·7%).

m-*Methylstyrylmethylcarbinol* (II; R = *m*-Me).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% dioxan (50 c.c.) for 24 hours at 30° yielded m-*methylstyrylmethylcarbinol* (1·30 g.), b. p. 69°/0·005 mm., $n_{\mathrm{D}}^{18^\circ}$ 1·5608 (Found: C, 81·7; H, 8·65. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *a-naphthylurethane* crystallised from petrol (b. p. 80—100°); m. p. 96° (Found: C, 79·8; H, 6·6; N, 4·2. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·25%).

1-(m-*Tolyl*)*buta*-1 : 3-*diene*.—*m*-Tolylpropenylcarbinol (2·5 g.) was distilled from potassium hydrogen sulphate (0·25 g.) at 10^{-2} mm. Fractionation of the product from potassium hydrogen sulphate (0·1 g.) yielded the *diene* (1·8 g.), b. p. 80°/0·005 mm., $n_{\mathrm{D}}^{17^\circ}$ 1·5980 (Found: C, 89·5; H, 8·5. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* was obtained by treating the diene (0·5 g.) with maleic anhydride (0·3 g.) in benzene (3 c.c.). Crystallisation from light petroleum (b. p. 60—80°) yielded the adduct (0·7 g.) in long needles, m. p. 78° (Found: C, 74·35; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

p-*Tolylpropenylcarbinol* (I; R = *p*-Me).—Freshly distilled crotonaldehyde (35 g.) in ether (70 c.c.) was added to *p*-tolylmagnesium bromide (from Mg, 12 g.) in ether (300 c.c.) during one hour at 0°, and the solution stirred for 3 hours. Isolation of the product in the usual manner afforded p-*tolylpropenylcarbinol* (65 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 55° (Found: C, 81·55; H, 8·65. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%).

p-*Methylstyrylmethylcarbinol* (II; R = *p*-Me).—Treatment of the above carbinol (1 g.) with 0·001M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 15 hours at 30° yielded p-*methylstyrylmethylcarbinol* (0·86 g.), which crystallised from light petroleum (b. p. 40—60°) in needles, m. p. 43° (Found: C, 81·3; H, 8·55. $C_{11}H_{14}O$ requires C, 81·45; H, 8·7%). The *a-naphthylurethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 135°, or from methanol, m. p. 127° (Found: C, 79·45; H, 6·4; N, 4·05. $C_{22}H_{21}O_2N$ requires C, 79·75; H, 6·4; N, 4·25%).

1-(p-*Tolyl*)*buta*-1 : 3-*diene*.—*p*-Tolylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·2 g.) at 10^{-2} mm. The diene, b. p. 78°/0·005 mm., solidified at room temperature and after crystallisation from aqueous methanol had m. p. 26° (Found: C, 90·6; H, 8·55. $C_{11}H_{12}$ requires C, 91·6; H, 8·4%). The maleic anhydride *adduct* was obtained by treating the diene (1·5 g.) with maleic anhydride (1 g.) in benzene (10 c.c.). Crystallisation from petrol (b. p. 80—100°) yielded the adduct (2·3 g.) in long needles, m. p. 117° (Found: C, 74·6; H, 5·8. $C_{15}H_{14}O_3$ requires C, 74·35; H, 5·8%).

p-*Benzoquinone adduct*. Treatment of the diene (2·2 g.) with *p*-benzoquinone (1·8 g.) in benzene (10 c.c.) afforded p-*tolyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (2·8 g.), which crystallised from petrol (b. p. 80—100°) in pale yellow plates, m. p. 114° (Found : C, 81·4; H, 6·3. $C_{17}H_{16}O_2$ requires C, 81·0; H, 6·4%).

p-*Fluorophenylpropenylcarbinol* (I, R = *p*-F).—*p*-Bromofluorobenzene (58 g.) (Schieman and Pilarsky, *Ber.*, 1931, **64**, 1343) in ether (250 c.c.) was added slowly to a suspension of magnesium (8·0 g.) in ether (150 c.c.) containing ethyl bromide (0·5 g.) and stirred for 4 hours in an atmosphere of nitrogen. Freshly distilled crotonaldehyde (23 g.) in ether (50 c.c.) was added to the ice-cold suspension during 2 hours, and stirring continued overnight. On working up in the usual manner, p-*fluorophenylpropenylcarbinol* (37 g.) was obtained, b. p. 59°/0·001 mm., $n_D^{18^\circ}$ 1·5175 (Found : C, 72·2; H, 7·0. $C_{10}H_{11}OF$ requires C, 72·25; H, 6·7%). Active hydrogen (Zerewitinoff) : 1·02

p-*Fluorostyrylmethylcarbinol* (II; R = *p*-F).—Treatment of the above carbinol (1·5 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 36 hours at 30° yielded p-*fluorostyrylmethylcarbinol* (1·4 g.), b. p. 78°/0·01 mm., $n_D^{20^\circ}$ 1·5411, which solidified on standing at room temperature and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 42° (Found : C, 72·3; H, 6·95. $C_{10}H_{11}OF$ requires C, 72·25; H, 6·7%). The α-*naphthylurethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 116° (Found: C, 75·5; H, 5·7; N, 4·1. $C_{21}H_{18}O_2NF$ requires C, 75·2; H, 5·4; N, 4·2%).

1-(p-*Fluorophenyl*)*buta*-1 : 3-*diene*.—*p*-Fluorophenylpropenylcarbinol (2·5 g.) was distilled from potassium hydrogen sulphate (0·25 g.) at 10^{-2} mm. The product was fractionated from potassium hydrogen sulphate (0·1 g.) and p-*fluorophenylbutadiene* (1·7 g.) was obtained, b. p. 37°/0·001 mm., $n_D^{22^\circ}$ 1·5788, which solidified on cooling and had m. p. 16—16·5° (Found : C, 80·4; H, 6·6. $C_{10}H_9F$ requires C, 80·65; H, 6·5%). The maleic anhydride *adduct* (0·25 g.) was obtained by treating the diene (0·18 g.) with maleic anhydride (0·12 g.) in benzene (5 c.c.). Crystallisation from petrol (b. p. 80—100°) yielded the adduct in needles, m. p. 113° (Found : C, 68·5; H, 4·7. $C_{14}H_{11}O_3F$ requires C, 68·3; H, 4·5%).

p-*Benzoquinone adduct.* The diene (1·2 g.) was treated with *p*-benzoquinone (0·67 g.) in benzene (5 c.c.). Crystallisation from petrol (b. p. 80—100°) afforded 1-p-*fluorophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (0·93 g.) as very pale yellow needles, m. p. 90° (Found: C, 74·8; H, 5·3. $C_{16}H_{13}O_2F$ requires C, 75·0 H, 5·1%).

p-*Chlorophenylpropenylcarbinol* (I; R = *p*-Cl).—*p*-Dichlorobenzene (74 g.) in ether (400 c.c) was slowly added to a suspension of magnesium (12 g.) in ether (100 c.c.) containing ethyl bromide (0·5 g.) and refluxed for 96 hours. Freshly distilled crotonaldehyde (35 g.) in ether (70 c.c.) was added during one hour at 0°, and the solution was stirred for 3 hours. Working up in the usual manner yielded unchanged *p*-dichlorobenzene (23 g.) and p-*chlorophenylpropenylcarbinol* (28 g.), b. p. 89°/0·005 mm., $n_D^{21^\circ}$ 1·5471 (Found: C, 65·9; H, 6·2; Cl, 19·3. $C_{10}H_{11}OCl$ requires C, 65·7; H, 6·05; Cl, 19·4%). Active hydrogen (Zerewitinoff) : 1·02.

p-*Chlorostyrylmethylcarbinol* (II; R = *p*-Cl).—Treatment of the above carbinol (1 g.) with 0·01M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 40 hours at 30° yielded p-*chlorostyrylmethylcarbinol* (0·87 g.), which separated from light petroleum (b. p. 40—60°) in needles, m. p. 63° (Found : C, 65·95; H, 6·0. $C_{10}H_{11}OCl$ requires C, 65·75; H, 6·1%). α-*Naphthylurethane.* (i) A mixture of *p*-chlorostylrylmethylcarbinol (0·5 g.) and α-naphthyl *iso*cyanate (0·5 g.) was kept in a sealed tube for 5 days. The *urethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 128° (Found : C, 71·5; H, 5·35. $C_{21}H_{18}O_2NCl$ requires C, 71·6; H, 5·6%). (ii) *p*-Chlorophenylpropenylcarbinol (0·5 g.) was treated with α-naphthyl *iso*cyanate (0·5 g.). The oily product after one crystallisation from aqueous ethanol had m. p. 69°. On successive crystallisations from ethanol and finally petrol, the m. p. rose to 128° [undepressed by the product obtained under (i)], and the light absorption maximum, not originally present, at 2580 A., ε = 30,000 (see Table III), appeared.

1-(p-*Chlorophenyl*)*buta*-1 : 3-*diene*.—*p*-Chlorophenylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·5 g.) at 10^{-2} mm., and the product fractionated. The *diene* (1·55 g.), b. p. 49°/0·002 mm., $n_D^{20^\circ}$ 1·6202, solidified on cooling and had m. p. 18·5° (Found : Cl, 21·75. $C_{10}H_9Cl$ requires Cl, 21·55%). The maleic anhydride *adduct*, obtained by the routine method and crystallised from petrol (b. p. 80—100°), had m. p. 108° (Found : Cl, 13·3. $C_{14}H_{11}O_3Cl$ requires Cl, 13·5%).

p-*Benzoquinone adduct.* Treatment of the diene (1·6 g.) with *p*-benzoquinone (1·2 g.) yielded the pale yellow adduct, 1-p-*chlorophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (1·8 g.); after being washed with methanol and crystallised from petrol (b. p. 80—100°) it had m. p. 110° (Found : C, 70·35; H, 4·8; Cl, 12·85. $C_{16}H_{13}O_2Cl$ requires C, 70·45; H, 4·8; Cl, 13·0%).

p-*Bromophenylpropenylcarbinol* (I; R = *p*-Br).—*p*-Dibromobenzene (60 g.) in ether (150 c.c.) was slowly added to a suspension of magnesium (6 g.) in ether (100 c.c.) containing ethyl bromide (0·5 g.) and refluxed for 24 hours. Freshly distilled crotonaldehyde (17 g.) in ether (50 c.c.) was added during one hour at 0° and the solution was stirred for 3 hours. Working up in the usual manner yielded unchanged *p*-dibromobenzene (5 g.) and p-*bromophenylpropenylcarbinol* (26 g.), b. p. 92°/0·002 mm., n_D^{22} 1·5739, which solidified on cooling and after crystallisation from light petroleum (b. p. 40—60°) had m. p. 27° (Found : C, 52·7; H, 5·15; Br, 36·0. $C_{10}H_{11}OBr$ requires C, 52·9; H, 4·9; Br, 35·2%).

p-*Bromostyrylmethylcarbinol* (II; R = *p*-Br).—Treatment of the above carbinol (1·5 g.) with 0·1M hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 12 hours yielded p-*bromostyrylmethylcarbinol* (1·4 g.) as needles, from light petroleum (b. p. 40—60°), m. p. 66° (Found : C, 53·2; H, 5·0. $C_{10}H_{11}OBr$ requires C, 52·9; H, 4·9%). The α-*naphthylurethane* (0·55 g.) crystallised from petrol (b. p. 80—100°) in needles, m. p. 139° (Found : C, 64·0; H, 4·55; N, 3·85. $C_{21}H_{18}O_2NBr$ requires C, 63·65; H, 4·55; N, 3·55%).

1-(p-*Bromophenyl*)*buta*-1 : 3-*diene*.—*p*-Bromophenylpropenylcarbinol (2 g.) was distilled from potassium hydrogen sulphate (0·5 g.) at 10^{-2} mm. The product was fractionated, giving the *diene* (1·5 g.), b. p. 88°/0·001 mm., which solidified at room temperature, and crystallised from aqueous methanol; m. p. 29° (Found : C, 57·05; H, 4·7. $C_{10}H_9Br$ requires C, 57·45; H, 4·35%). The maleic anhydride *adduct*, obtained as usual and crystallised from petrol (b. p. 80—100°), formed fine needles, m. p. 138·5° (Found : C, 55·0; H, 3·65. $C_{14}H_{11}O_3Br$ requires C, 54·75; H, 3·6%).

p-*Benzoquinone adduct.* Treatment of the diene (0·5 g.) with *p*-benzoquinone (0·25 g.) in benzene (5 c.c.) gave the adduct, 1-p-*bromophenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (0·45 g.), which crystallised from petrol (b. p. 80—100°) in pale yellow rectangular plates, m. p. 105° (Found : C, 60·4; H, 3·95. $C_{16}H_{13}O_2Br$ requires C, 60·6; H, 4·15%).

p-*Anisylpropenylcarbinol* (I; R = *p*-MeO).—*p*-Bromoanisole (35 g.) in ether (100 c.c.) was added slowly to a suspension of magnesium (4·45 g.) in ether (250 c.c.) containing ethyl bromide (0·5 g.) and stirred overnight in an atmosphere of nitrogen. Freshly distilled crotonaldehyde (12 g.) in ether (25 c.c.) was added during one hour at 0° and the solution was stirred for 3 hours. Working up in the usual manner and final distillation from a trace of potassium carbonate yielded p-*anisylpropenylcarbinol* (23·5 g.), b. p. 100°/0·005 mm., $n_D^{17^\circ}$ 1·5454, which partly solidified on standing at 0°; m. p. 13—15° (Found : C, 74·45; H, 8·0. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·9%). Active hydrogen (Zerewitinoff) : 1·01.

p-*Methoxystyrylmethylcarbinol* (II; R = *p*-MeO).—Treatment of the above carbinol (1 g.) with 0·001M-hydrochloric acid in 60% aqueous dioxan (50 c.c.) for 3 hours at 30° yielded p-*methoxystyrylmethylcarbinol* (0·95 g.), in needles from light petroleum (b. p. 40—60°); m. p. 79° (Found : C, 73·95; H, 7·9. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·9%). Active hydrogen (Zerewitinoff) : 1·02. The α-*naphthylurethane* (0·4 g., 0·8 g. respectively) was obtained by warming (i) *p*-anisylpropenylcarbinol (0·5 g.) and (ii) *p*-methoxystyrylmethylcarbinol (0·5 g.) with α-naphthyl *iso*cyanate (0·5 g.), and crystallised from petrol (b. p. 80—100°) in needles, m. p. 101° (Found : N, 4·1. $C_{22}H_{21}O_3N$ requires N, 4·05%).

1-(p-*Anisyl*)*buta*-1 : 3-*diene*.—*p*-Anisylpropenylcarbinol (1 g.) was warmed with potassium hydrogen sulphate at 10^{-2} mm. for about 5 minutes, and then rapidly distilled. p-*Anisylbutadiene* (0·7 g.) solidified on standing and was crystallised from aqueous methanol, m. p. 46° (Found : C, 82·2; H, 7·45. $C_{11}H_{12}O$ requires C, 82·45; H, 7·55%). Knorr (D.R.-P. 544388; *Chem. Abs.*, 1932, **26**, 2467) gives b. p. 124°/6 mm. for the diene obtained by dehydration of *p*-anisylallylcarbinol. The maleic anhydride *adduct* crystallised from petrol (b. p. 80—100°) in fine needles, m. p. 145° (Found : C, 70·0; H, 5·4. $C_{15}H_{14}O_4$ requires C, 69·75; H, 5·45%).

p-*Benzoquinone adduct*. Treatment of the diene (0·53 g.) with *p*-benzoquinone (0·33 g.) in benzene (5 c.c.) yielded 1-p-*anisyl*-1 : 4 : 9 : 10-*tetrahydronaphthaquinone* (0·38 g.), pale yellow plates from petrol (b. p. 80—100°); m. p. 103° (Found : C, 76·35; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·05; H, 6·0%). Light absorption in *n*-hexane : Maxima at 2280, 2680, and 3250 A., ε = 23,300, 2500, and 230, respectively. The absorption may be ascribed to the isomer, 1-*p*-anisyl-1 : 4-dihydronaphtha-5 : 9-quinol (needles, m. p. 168°), which is produced on irradiation with ultra-violet light during the absorption measurements and separates from the solution on standing or evaporation.

1-*Phenylbuta*-1 : 3-*diene*.—Freshly distilled cinnamaldehyde (40 g.) in ether (120 c.c.) was added to methylmagnesium iodide (from Mg, 8 g.) in ether (200 c.c.). Decomposition of the complex with excess of ammonium chloride solution, isolation with ether, distillation from a trace of potassium hydrogen sulphate, and finally fractionation afforded pure phenylbutadiene, b. p. 45°/0·5 mm., $n_D^{17^\circ}$ 1·6125, which solidified on cooling and had m. p. 4° (Klages, *Ber.*, 1904, **37**, 2309, gives b. p. 86°/11 mm.; Muskat and Herrman, *J. Amer. Chem. Soc.*, 1931, **53**, 252, give b. p. 86°/11 mm., n^{28° 1·5950; Emerson, *J. Org. Chem.*, 1945, **10**, 464, gives b. p. 89—94°/14 mm., $n_D^{25^\circ}$ 1·6010). The low refractive indices recorded by these authors are probably due to the presence of considerable proportions of undehydrated styrylmethylcarbinol or of polymers of the diene (cf. Stobbe and Reiss, *Ber.*, 1912, **45**, 3496; Wright, *J. Org. Chem.*, 1936, **1**, 457). Light absorption : see Table IV (Stobbe and Reiss, *loc. cit.*, and Smakula, *Angew. Chem.*, 1934, **47**, 657, give maximum at 2800 A., ε = 24,000). The maleic anhydride adduct, crystallised from petrol (b. p. 80—100°), had m. p. 120° (Diels and Alder, *Ber.*, 1929, **62**, 2081, give m. p. 120°).

p-*Benzoquinone adduct*. Phenylbutadiene (2 g.) was treated with *p*-benzoquinone (2 g.) in benzene (20 c.c.), and the solution boiled for some minutes. On cooling and evaporation of the solvent under reduced pressure, crystals separated, which were washed with methanol to remove a small amount of quinhydrone. *Phenyl*-1 : 4 : 9 : 10-*tetrahydronaphtha*-5 : 8-*quinone* (2·25 g.) crystallised from petrol (b. p. 80—100°) in pale yellow rectangular plates, m. p. 101° (Found : C, 80·7; H, 5·9. $C_{16}H_{14}O_2$ requires C, 80·65; H, 5·9%).

Styrylmethylcarbinol α-naphthylurethane. Prepared from styrylmethylcarbinol (Braude, Jones, and Stern, *J.*, 1946, 396) (0·5 g.) and α-naphthyl *iso*cyanate (0·5 g.), the *urethane* crystallised from petrol (b. p. 80—100°) in needles, m. p. 89·5° (Found : C, 79·25; H, 6·1; N, 4·2. $C_{21}H_{19}O_2N$ requires C, 79·45; H, 6·05; N, 4·4%).

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