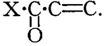
207. *Studies in Light Absorption. Part III. Auxochromic Properties and the Periodic System.*

By Kenneth Bowden, Ernest A. Braude, and E. R. H. Jones.

Existing and new data are collected and discussed concerning the effects of covalently saturated substituents on the ultra-violet light absorption of unsaturated systems. It is shown that the observed bathochromic effects ($\Delta\lambda_X$) are even larger in acyclic ethylenic than in aromatic compounds. They are dependent on the nature of the ethylenic system, increasing with increasing polarisability and electronic mobility of the latter, in the order $X{\cdot}Ph < X{\cdot}C{=}C < X{\cdot}C{=}C{\cdot}C{=}C < X{\cdot}C{=}C{\cdot}C{=}O$, where $X = CR_3$, SiR_3, NR_2, OR, SR, or Hal. ($R = H$ or alkyl.) $\Delta\lambda_X$ bears a definite relationship to the position of the substituent element in the periodic system, reaching a maximum with nitrogen amongst the non-metals of the first period, and increasing on ascending a group; there is thus a pronounced parallelism between the auxochromic effects of substituents and their tautomeric effects on chemical reactivity. Hypsochromic effects are observed when the substituent forms part of certain heterocyclic rings or when it is linked directly to a carbonyl chromophore, *e.g.*, in $X{\cdot}C{=}O$ and  $X{\cdot}\underset{\underset{O}{\|}}{C}{\cdot}C{=}C$.

It has long been recognised that the substitution of certain groups (" auxochromes ") for hydrogen atoms directly attached to covalently unsaturated systems exhibiting selective light absorption in the visible region of the spectrum results in increases in the wave-lengths and intensities of the maxima (" batho- and hyperchromic " effects). The most effective auxochromes, in the classical sense, are groups themselves covalently unsaturated (*e.g.*, $^-C{=}C^-$, $^-C{=}N^-$, $^-NO_2$), but the colour of dyes is also deepened and intensified by certain suitably positioned covalently saturated substituents (*e.g.*, $^-NR_2$, ^-OR, ^-SR), that is, co-ordinatively unsaturated groups containing unshared electron pairs. Similar phenomena are well known in connection with the ultra-violet light absorption of aromatic systems, but aliphatic compounds have only recently been examined from this point of view. It has been shown that amino-substituents in aliphatic ethylenic systems give rise to large batho- and hyper-chromic effects (Bowden, Braude, Jones, and Weedon, this vol., p. 45), and it had previously been observed that alkyl groups which are neither covalently nor co-ordinatively unsaturated also produce small, but definite, bathochromic displacements (Kuhn and Grundmann, *Ber.*, 1937, **70**, 1318; Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76; Gillam *et al.*, *J.*, 1940, 1453; 1941, 1123; 1943, 565; 1945, 432; Braude and Jones, *J.*, 1945, 498; Carr and Stücklen, *Z. physikal. Chem.*, 1934, *B*, 25, 57; Carr, Pickett, and Stücklen, *Rev. Mod. Physics*, 1942, **14**, 260; Price, *Ann. Reports*, 1939, **36**, 47).

In the present communication existing and new data are collected which illustrate the variochromic effects of vicinal carbon, silicon, nitrogen, oxygen, sulphur, chlorine, and bromine substituents in unsaturated aliphatic systems. It is shown that these effects are more marked than those observed in aromatic and heterocyclic compounds and that they can be correlated with the position of the substituent element in the periodic system.

The data in Table I refer to substituents attached to an ethylenic group, the latter being either isolated or

TABLE I.

The Auxochromic Effects of Substituents in Ethylenic Systems.

Auxochrome.	Unsubstituted compound.	$\lambda_{max.}$, A.	$\epsilon_{max.}$ ($\times 10^{-3}$).	Substituted compound.	$\lambda_{max.}$, A.	$\epsilon_{max.}$ ($\times 10^{-3}$).	$\Delta\lambda$.	$\Delta\epsilon$ ($\times 10^{-3}$).	Solvent.	Refs.
$-CH_3$	$CH_2{=}CH{\cdot}CH{=}CH_2$	2170	21	$\mathbf{C}H_3{\cdot}CH{=}CH{\cdot}CH{=}CH_2$	2240	26	70	5	H	1
	,,	2170	21	$CH_2{=}C(\mathbf{C}H_3){\cdot}CH{=}CH_2$	2200	24	30	3	H	1
	,,	2170	21	$\mathbf{C}H_3{\cdot}CH{=}CH{\cdot}CH{=}CH{\cdot}\mathbf{C}H_3$	2270	23	100	2	H	1
	$CHMe(OH){\cdot}CH{=}CH{\cdot}C{\equiv}CH$	2230	13	$CHMe(OH){\cdot}CH{=}CH{\cdot}C{\equiv}C{\cdot}\mathbf{Bu^a}$	2280	16	50	3	A	2
	$CH_2{=}CH{\cdot}CMe{=}O$	2100	7	$\mathbf{C}H_3{\cdot}CH{=}CH{\cdot}CMe{=}O$	2240	10	140	3	A	1, 3
	,,	2100	7	$CH_2{=}C(\mathbf{C}H_3){\cdot}CMe{=}O$	2180	8	80	1	A	1, 3
	,,	2100	7	$\mathbf{C}H_3{\cdot}CH{=}C(\mathbf{C}H_3){\cdot}CMe{=}O$	2300	11	200	4	A	1, 3
$-SiR_3$	$CHMe{=}CMe{\cdot}C{\equiv}CH$	2190	9	$CHMe{=}CMe{\cdot}C{-}C{\cdot}\mathbf{Si}Et_3$	2340	15	150	6	H	3
$-NR_2$	$CHBu^a{=}CHEt$	1850	8	$C_5H_{10}\mathbf{N}{\cdot}CH{=}C\ \ Et$†	2280	10	430	2	H	4, 5
	$CH_2{=}CH{\cdot}CH{=}CH_2$	2170	21	$Et_2\mathbf{N}{\cdot}CH{=}CH{\cdot}CH{=}CH_2$	2810	24	640	3	H	1, 5
	$CHMe{=}CH{\cdot}CO_2Et$	2070 *	20	$Et_2\mathbf{N}{\cdot}CMe{=}CH{\cdot}CO_2Et$	2880	31	810	11	A	8, 5
	$CH_2{=}CH{\cdot}CPr^a{=}O$	2140	8	$Et_2\mathbf{N}{\cdot}CH{=}CH{\cdot}CPr^a{=}O$	3070	28	930	20	A	7, 5
	$CH_2{=}CH{\cdot}\underset{\underset{O}{\Vert}}{C}{\cdot}Ph$	2480	11	$Et_2\mathbf{N}{\cdot}CH{=}CH{\cdot}\underset{\underset{O}{\Vert}}{C}{\cdot}Ph$	3430	25	950	14	A	5
$-OR$	$CHMe{=}CH{\cdot}CO_2H$	2040	10	$Me\mathbf{O}{\cdot}CMe{=}CH{\cdot}CO_2H$	2340	14	300	4	A	8, 3
	,,	2040	10	$CHMe{=}C(\mathbf{O}Me){\cdot}CO_2H$	2230	9	190	−1	A	8, 3
	$CHMe{=}CH{\cdot}CMe{=}O$	2170	10	$H\mathbf{O}{\cdot}CMe{=}CH{\cdot}CMe{=}O$	2690	12	520	2	H	1, 6
$-SR$	$CHBu^a{=}CHEt$	1850	8	$Cl(CH_2)_2\mathbf{S}{\cdot}CH{=}CH_2$	2280	7	430	−1	H	4, 3
	$CH_2{=}CH{\cdot}CPr^a{=}O$	2070 *	8	$Et\mathbf{S}{\cdot}CH{=}CH{\cdot}CPr^a{=}O$	2920	15	850	7	H	7, 3
	$CH_2{=}CH{\cdot}\underset{\underset{O}{\Vert}}{C}{\cdot}Ph$	2480	11	$Et\mathbf{S}{\cdot}CH{=}CH{\cdot}\underset{\underset{O}{\Vert}}{C}{\cdot}Ph$	3190	18	710	7	A	7, 3
$-Cl$	$CH_2{=}CH_2$	1750	?	$\mathbf{Cl}{\cdot}CH{=}CH_2$	1850	?	100	?	V	9
	$CH_2{=}CH{\cdot}CH{=}CH_2$	2170	21	$CH_2{=}C(\mathbf{Cl}){\cdot}CH{=}CH_2$	2230	14	60	−7	H	1, 3
	$CHMe{=}CH{\cdot}CO_2H$	2040	10	$CHMe{=}C(\mathbf{Cl}){\cdot}CO_2H$	2220	11	180	1	A	8, 3
	$CH_2{=}CH{\cdot}CMe{=}O$	2100	7	$\mathbf{Cl}{\cdot}CH{=}CH{\cdot}CMe{=}O$	2280	10	180	3	A	3
	$CH_2{=}CH{\cdot}CPr^a{=}O$	2070 *	8	$\mathbf{Cl}{\cdot}CH{=}C(\mathbf{Cl}){\cdot}CPr^a{=}O$	2480	6	410	−2	H	7, 3
$-Br$	$CHMe{=}CH{\cdot}CO_2H$	2040	10	$CHMe{=}C(\mathbf{Br}){\cdot}CO_2H$	2280	7	240	−3	A	8, 3
	$CH_2{=}CH{\cdot}CPr^a{=}O$	2070 *	8	$\mathbf{Br}{\cdot}CH{=}CH{\cdot}CPr^a{=}O$	2370	5	300	−3	H	7, 3
	,,	2070 *	8	$\mathbf{Br}{\cdot}CH{=}C(\mathbf{Br}){\cdot}CPr^a{=}O$	2590	7	520	−1	H	7, 3

H = *n*-hexane solution, A = ethanol solution, V = vapour. † $C_5H_{10}N$ = piperidyl.

* Calculated empirically, assuming $\lambda_{max.}$ (ethanol) − $\lambda_{max.}$ (hexane) = 70 A. (cf. Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; Evans and Gillam, *J.*, 1945, 432).

[1] Booker, Evans, and Gillam, *J.*, 1940, 1453; Evans and Gillam, *J.*, 1941, 815. [2] Jones and McCombie, *J.*, 1943, 261; Heilbron, Jones, and Raphael, *J.*, 1943, 264. [3] This paper. [4] Platt, Rusoff, and Klevens, *J. Chem. Physics*, 1943, **11**, 535. [5] Bowden, Braude, Jones, and Weedon, this vol., p. 45. [6] Grossmann, *Z. physikal. Chem.*, 1924, **109**, 305. [7] Bowden, Heilbron, Jones, and Weedon, this vol., p. 39. [8] Mohler and Lohr, *Helv. Chim. Acta*, 1938, **21**, 485. [9] Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207.

itself conjugated with another ethylenic or with an acetylenic, carbonyl, or carboxyl group. As far as possible, the compounds chosen to represent the various systems were the simplest of their class, but, where the necessary data were not available, similarly substituted reference compounds have been employed. The bathochromic effects deduced for the elements Si, N, O, and S refer to substituents SiR_3, NR_2, OR, and SR (where R = alkyl), and although the bathochromic effects of alkyl groups and the chromolatory (transmitting) capacities of auxochromes are in any case small, the values will, nevertheless, be slightly larger (*ca.* 50—100 A.) than those appertaining to the simple SiH_3, NH_2, OH, and SH substituents.

From the data in Table I, a number of generalisations clearly emerge. These may be summarised as follows:

(i) Substituents attached to an ethylenic linkage which may either be isolated or form part of a conjugated system increase $\lambda_{max.}$ and usually $\varepsilon_{max.}$.

(ii) The bathochromic effects depend primarily on the nature of the element vicinal to the ethylenic group, varying in the order C < Si, O < S, Cl < Br, and C < N > O > Cl, *i.e.*, increasing on ascending a group of the periodic system, and reaching a maximum with nitrogen in the first period (see also Table I*a*).

(iii) The effect of any one substituent also depends on the nature of the conjugated ethylenic system to which it is attached, increasing in the order $\mathrm{X{\cdot}C{=}C} < \mathrm{X{\cdot}C{=}C{\cdot}C{=}C} < \mathrm{X{\cdot}C{=}C{\cdot}C}\lessdot^{O}_{O} < \mathrm{X{\cdot}C{=}C{\cdot}C{=}O}$ (see also Table I*a*).

(iv) Substituents in conjugated ethylenic systems produce larger bathochromic effects when they are located at the end of the system than when they are " cross-conjugated."

(v) The effects of two and more substituents are roughly additive.

TABLE I*a*.

Summary of Bathochromic Effects ($\Delta\lambda_X$, A.) *of Substituents* (*X*) *in Ethylenic Systems* (*R = alkyl group*).

	Substituent X.						
Substituted system.	CH_3.	SiR_3.	NR_2.	OR.	SR.	Cl.	Br.
$\mathrm{X{\cdot}C{=}C}$	50	—	400	—	450	50—100	—
$\mathrm{X{\cdot}C{=}C{\cdot}C{=}C}$	50	150[1]	650	—	—	60	—
$\mathrm{X{\cdot}C{=}C{\cdot}C}\lessdot^{O}_{O}$	—	—	800	300	—	200	250
$\mathrm{X{\cdot}C{=}C{\cdot}C{=}O}$	100	—	950	500	850	200	300

[1] Assumed to be the same as in the conjugated vinylacetylene system.

These relationships may be compared with those obtaining when auxochromes are attached to chromophoric systems other than of the open-chain ethylenic type:

(i) In benzene derivatives the largest displacements of the 2000 A. band (regarded as displaced ethylenic absorption) are produced by the amino- and the thiol group, while in all other cases the maximum remains below 2200 A. and has not been recorded (Table II). The low-intensity 2550 A. band (ascribed to the benzenoid chromophore) is displaced by all auxochromic substituents but in a different order from that found in aliphatic systems, namely $CH_3 < NH_2 > OH > F$, OH > SH, F > Cl > Br > I, *i.e.*, $\Delta\lambda_X$ again reaches a maximum with nitrogen in the first period, but decreases on ascending a group of the periodic system.

TABLE II.

The Effect of Auxochromes on the Phenyl Chromophore.

(Solvent: *n*-hexane.)

	$\lambda_{max.}$, A.†	$\varepsilon_{max.}$	$\lambda_{max.}$, A.†	$\varepsilon_{max.}$
Ph·H [1]	1980	8000	2560	250
$Ph{\cdot}CH_3$ [2]	*	*	2620	300
$Ph{\cdot}NH_2$ [2]	2300	8000	2800	200
Ph·OH [3]	*	*	2750	200
Ph·SH [3]	2350	8500	2690	700
Ph·F [4]	*	*	2670	1650
Ph·Cl [4]	*	*	2650	300
Ph·Br [4]	*	*	2650	250
Ph·I [4]	*	*	2580	800

* Not recorded.

† Values refer to the highest peaks of regions of resolved absorption.

[1] Henri, *J. Phys. Radium*, 1922, **3**, 181. [2] Scheibe, *Ber.*, 1926, **59**, 2617. [3] This paper. [4] Conrad-Billroth, *Z. physikal. Chem.*, 1932, **19**, 76.

(ii) In five-membered heterocyclic compounds where the substituent is linked by single bonds to the ends of the conjugated system, the high-intensity absorption near 2000 A., probably representing a displaced band due to the ethylenic group, is but little affected, while the low-intensity absorption near 2400 A., ascribed to the conjugated diene system, is strongly reduced in intensity in pyrrole and furan, and slightly intensified in thiophen (Table III), $\lambda_{max.}$ remaining almost unchanged. Similarly, in tricyclic dyes formally derived from diphenylmethane or diphenylamine by joining the *o* : *o'*-positions through O, S, or NR groups, the introduction of the latter results, on the average, in hyperchromic effects of —690, —720, and —1570 A. respectively (Lewis, *J. Amer. Chem. Soc.*, 1945, **67**, 770).

TABLE III.

	$\lambda_{max.}$, A.	$\epsilon_{max.}$	$\lambda_{max.}$, A.	$\epsilon_{max.}$
*cyclo*Pentadiene [1]	2000	10,000	2440	2500
Pyrrole [2]	2100	15,000	2400	300
Furan [2]	2000	10,000	2500	1
Thiophen [2]	Not recorded		2350	4500

[1] Scheibe and Grieneisen, *Z. physikal. Chem.*, 1934, *B*, **25**, 52; Henri and Pickett, *J. Chem. Physics*, 1939, **7**, 439 (measurements in vapour phase and hexane solution). [2] Menczel, *Z. physikal. Chem.*, 1927, **125**, 161 (measurements in hexane solution).

(iii) Substituents directly attached to a carbonyl group also produce effects quite different from those observed when they are attached to an ethylenic bond (cf. Herold, *Z. physikal. Chem.*, 1932, **18**, 277; Burawoy, *J.*, 1939, 1177). The carbonyl group itself gives rise to two maxima, one at about 1900 A. (ε = *ca.* 10,000) which may be compared to the band near 1800 A. exhibited by olefins and most other compounds containing a multiple linkage, and the other at 2900 A. (ε = *ca.* 20) which is peculiar to the carbonyl group (Wolf, *Z. physikal. Chem.*, 1929, *B*, **2**, 35, *et seq*; Mohler, *Helv. Chim. Acta*, 1937, **20**, 285). Only the low-intensity bands have been recorded for compounds of the type R·CO·X, $\lambda_{max.}$ being decreased, most strongly by the amino- and hydroxyl groups, in the order X = NH_2, OH > Cl > CH_3 (Table IV). In α : β-ethylenic carbonyl compounds, a methyl group attached at the carbonyl carbon atom exerts a small bathochromic effect on the band due to the conjugated system; other substituents again have the opposite effect, though in the different order Cl > OH > NR_2.

TABLE IV.

The Effect of Auxochromes on the Carbonyl Chromophore.

	X·CH=O (vapour or liquid).				
X	H.	CH_3.	NH_2.	OH.	Cl.
$\lambda_{max.}$	295 [1]	290 [2]	*205 [3]	205 [3]	235 [3]
$\epsilon_{max.}$	~10	10	160	45	50
	CHMe=CH·CX=O (in alcohol).				
X	H.	CH_3.	NEt_2.	OH.	Cl.
$\lambda_{max.}$	217 [4]	224 [5]	215 [6]	204 [7]	<210 [6]
$\epsilon_{max.} \times 10^{-3}$	16	10	11	10	> 8

* Inflexion.

[1] Purvis and McCleland, *J.*, 1912, **101**, 1810. [2] Conrad-Billroth, *Z. physikal. Chem.*, 1933, *B*, **23**, 315. [3] Ley and Arends, *ibid.*, 1931, *B*, **12**, 132. [4] Hausser, Smakula, Kuhn, and Hoffer, *ibid.*, 1935, *B*, **29**, 371. [5] Evans and Gillam, *J.*, 1941, 815. [6] This paper. [7] Mohler and Lohr, *Helv. Chim. Acta*, 1938, **21**, 485.

A characteristic property of the ethylenic group and of most other chromophores containing multiple linkages is their ability to transmit conjugation. This chromolatory effect is also shown to varying degrees by auxochromes containing unshared electron pairs. It is well known that in dyes the bathochromic effect of amino-substituents increases in the order NH_2 < NHEt < NEt_2 (cf. Wizinger, " Organische Farbstoffe," Dümmler, Berlin, 1933), *i.e.*, that nitrogen transmits the bathochromic effect of alkyl groups. It has also been shown (Part II, Braude and Jones, *loc. cit.*) that the >NH-group will to a large extent transmit conjugation between two chromophoric systems. Table V shows that this also applies to the –O– and –S– groups, the chromolatory capacity varying in the order N > S > O. No chromolatory effects are displayed, on the

TABLE V.

Chromolatory (*Transmitting*) *Effect of Auxochromes.*

(Solvent: Alcohol.)

	$\lambda_{max.}$, A.	$\epsilon_{max.} \times 10^{-3}$.	$\lambda_{max.}$, A.	$\epsilon_{max.} \times 10^{-3}$.	$\Delta\lambda_{Et.}$*
Ph·CO·CH=CH·NH_2	2420	11	3240	19	—
Ph·CO·CH=CH·NHEt	2420	11	3380	23	140
Ph·CO·CH=CH·NEt_2	2420 2450	12	3430	26	95
					$\Delta\lambda_{Ph.}$*
Ph·CO·CH=CH·NH·Ph	2420 2450	18	3740	31	500
Ph·CO·CH=CH·O·Ph	2670 †	15	2820 2910	18 18	(~200)
Ph·CO·CH=CH·S·Ph	2560	14	3350	19	(~300)
Ph·CO·CH=CH·SO_2·Ph	2450	16	2800 †	4	(~0)

* $\Delta\lambda_{Et.}$ $\Delta\lambda_{Ph}$ = displacements of long wave-length band with respect to parent compounds, *e.g.*, Ph·CO·CH=CH·NH_2, Ph·CO·CH=CH·OH, and Ph·CO·CH=CH·SH.

† Inflexion.

other hand, by the methylene and sulphone groups in which the central atom carries no unshared electron pairs. Similar results have been obtained by Chaix (*Bull. Soc. chim.*, 1933, **53**, 700) in an examination of the ultra-violet light absorption of systems Ph·X·Ph, where $X = CH_2$, NH, O, S, Se, SO, SeO, and SO_2.

DISCUSSION.

Selective absorption in the near ultra-violet region of the spectrum (1800—4000 A.) corresponds to energy increments of between 70 and 160 kg.-cals./mol., intermediate between those required for the photo-ionisation of single covalent bonds and those required for vibrational or rotational transitions. Quanta of this magnitude are involved in the displacement of *mobile electrons* (Lennard-Jones, *Proc. Roy. Soc.*, 1937, *A*, **158**, 280), *i.e.*, electrons *more* mobile than ordinary bonding electrons. The unsaturation electrons of multiple bonds are the most important type of mobile electrons encountered in organic compounds, and it has long been known that the juxtaposition of two or more groups containing multiple bonds gives rise to displacements of the selective absorption towards, and eventually into, the visible region, *i.e.*, to a lowering of the energy requirements of the electronic transitions. These increases in mobility in the classical conjugated systems are paralleled by corresponding changes in other physical properties, *e.g.*, refractivity and heats of formation, and in chemical reactivity, and may be ascribed to enhanced resonance (Bury, *J. Amer. Chem. Soc.*, 1935, **57**, 2115; Pauling, *Proc. Nat. Acad. Sci.*, 1939, **25**, 577).

The bathochromic effects of substituents such as NH_2, OR, and halogens must similarly be attributed to interaction between the unsaturation electrons of the multiple bond and the unshared electron pair of the substituent, resulting in increased resonance and decreased transition energies. Deviations from additivity in physical properties are observed, as well as chemical reactions reminiscent of those found in conjugated systems of two multiple linkages (cf. Bowden, Braude, Jones, and Weedon, *loc. cit.*). These effects disappear if the free electron pair becomes shared; thus the light absorption of compounds XNR_2 (where X is a substituted ethylenic group) reverts to that of XH in strongly acid solutions, and the amine oxide (French and Gens, *J. Amer. Chem. Soc.*, 1937, **59**, 2600) and sulphone groups exert hardly any bathochromic action.

In alkyl and alkylsilico-groups, the central atom carries no unshared electron pair. The small but well-defined bathochromic effects which are nevertheless observed have been related to corresponding variations in the heats of hydrogenation of olefins and discussed under the name of " hyperconjugation " (Price and Tutte, *Proc. Roy. Soc.*, 1940, *A*, **174**, 207; Mulliken, Rieke, and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41; Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265). The pronounced influence of alkyl substitution on chemical reactivity has been, in part, ascribed to the partial ionic character of the carbon–hydrogen bonds, but the consequent decrease of the effects in the sequence $Me > Et > Pr^{\beta} > Bu^{\gamma}$ has not been realised in the few spectral measurements so far available (Bateman and Koch, *J.*, 1944, 600).

The carbonyl chromophore is affected by substituents in the opposite way to the ethylenic chromophore. This is clearly due to interaction, amply borne out by other physical as well as chemical evidence (Chaplin and Hunter, *J.*, 1937, 1114; Hunter, *J.*, 1945, 806), between the substituents and the carbonyl oxygen, involving a loss in double-bond character of the carbon–oxygen linkage. This interaction may be of two types: direct co-ordination between X^- and $O{=}$, and hydrogen bond formation when X = NHR or OH. Similar effects have been noted in the substituted *p*-benzoquinones (Part I, *J.*, 1945, 490).

There is thus a close parallelism between the variochromic (as well as chromolatory) effects of substituents on ultra-violet light absorption properties and their so-called " tautomeric " effects on chemical reactivity. Both depend on an increase in the contribution of the resonance form $X^+{=}A{-}B^-$ to a hybrid classically represented by $X{-}A{=}B$. Both are dependent on the capacity for covalency increase of X (cf. Ingold, *Chem. Reviews*, 1934, **15**, 225) and are much larger when X is co-ordinatively unsaturated. Both increase with increasing " basicity," *i.e.*, decreasing control of the unshared electron pair by the atomic nucleus, reaching a maximum with nitrogen amongst the non-metals of the first period, and increasing on ascending a group of the periodic system. On this basis a large bathochromic effect may be predicted for tervalent phosphorus in compounds containing the system $-C{=}C{-}P<$, but no examples are at present known.

EXPERIMENTAL.

For details of the light-absorption measurements see Part I (*loc. cit.*).

Most of the compounds employed in this study are described in the preceding paper. Other materials had the following physical constants: Chloroprene (b. p. 59·5°/760 mm.), thiophenol (b. p. 54°/15 mm., $n_D^{18°}$ 1·5880), methyl β-chlorovinyl ketone (b. p. 72°/100 mm., $n_D^{21°}$ 1·4658), and β-chloroethyl vinyl sulphide (b. p. 45°/15 mm., $n_D^{12°}$ 1·5232). We are indebted to Dr. L. N. Owen for samples of α-methoxycrotonic acid (m. p. 58°), β-methoxycrotonic acid (m. p. 130°), *trans*-α-chlorocrotonic acid (m. p. 99°), and *trans*-α-bromocrotonic acid (m. p. 107°). We are indebted to Dr. S. R. Robinson for the following preparation: 3-*Methyl*-1-*triethylsilicopent*-3-*en*-1-*yne*. Triethylsilicon chloride, prepared from silicon tetrachloride and ethylmagnesium bromide (3·75 mol.), b. p. 142—144°/760 mm. (Found: Cl, 23·4. Calc. for $C_6H_{15}ClSi$: Cl, 23·5%) was treated with the theoretical quantity of the Grignard compound from 1 : 2-dimethylvinylacetylene and ethylmagnesium bromide to give 3-*methyl*-1-*triethylsilicopent*-3-*en*-1-*yne*, b. p. 115—116°/20 mm. (Found: C, 75·1; H, 11·1. $C_{12}H_{22}Si$ requires C, 74·2; H, 11·4%).

The authors wish to thank Professor Sir Ian Heilbron, D.S.O., F.R.S., for his interest, and the Rockefeller Foundation and I.C.I. Ltd., Dyestuffs Division, for financial assistance.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W.7

[*Received, April* 15*th*, 1946.]