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Electronic Spectra of Organic Molecules and their Interpretation. Part I. Effect of Terminal Methyl and Substituted Methyl Groups of Conjugated Systems on K-*Bands.*

By A. BURAWOY and E. SPINNER.

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The effect of methyl and substituted methyl groups at the ends of conjugated systems $\text{A}\cdot\text{CH}_2\cdot[\text{CH}{:}\text{CH}]_n\cdot\text{CH}\cdot\text{A}$ on the position of the corresponding *K*-bands is studied. The dependence of the energy of transition on the facility of the electron migration in one direction of the absorbing conjugated system is demonstrated. Structural modifications of a terminal group which increase its polarisability or the polarity of the absorbing system displace the *K*-band to longer wavelengths. Single bonds of substituted methyl groups ($\text{A}\cdot\text{CH}_2$) participate in the electron migration of the transition and in favourable cases cause red-shifts comparable to those brought about by an additional conjugated double bond ($\text{A}{:}\text{CH}$). These results cannot be explained in terms of electromeric electron displacements or structures involving non-localised bonds, but are accounted for by inductomeric displacements of " localised " electrons.

THE effect of substituents on the position of absorption bands in the electronic spectra of organic compounds is of considerable complexity, since it depends both on the location of the substituent within the absorbing system and on the type of the electronic transition involved, *i.e.*, the type of absorption band under consideration (for the classification of the bands above 2000 Å as *R*-, *K*-, and *B*(enzenoid)- bands, see Burawoy, *Ber.*, 1930, **63**, 3155; 1931, **64**, 464, 1635; 1932, **65**, 941; *J.*, 1939, 1177; *Discuss. Faraday Soc.*, 1950, **9**, 70).

The *K*-bands of comparatively high intensity (ε >5000) are best understood. There is general agreement that qualitatively they are due to transitions involving electron migrations along (the axes of) conjugated systems such as (I) [cf., *e.g.*, Mulliken's N ⟶ V transitions (*J. Chem. Phys.*, 1935, **3**, 522; 1939, **7**, 14, 21, 121, 339, 357, 395); Lewis and Calvin's class I oscillators (*Chem. Rev.*, 1939, **25**, 303); Burawoy, *loc. cit.*, 1950]. As one of us has deduced empirically and supported by considerable evidence, the position of a *K*-band is determined by two factors: (i) the polarity of the absorbing system, *i.e.*, influences increasing its polarity (in the ground state) facilitate the electron migration, stabilise the excited state, and displace the *K*-band to longer wavelengths; (ii) the extension of the absorbing conjugated system or, as will be defined more precisely in this paper, the polarisability of the electrons of the terminal groups or atoms (I; A or B): the higher the polarisability, the greater the displacement to longer wavelengths.

$$\text{(I)}\quad \underset{\longrightarrow}{\text{A}\cdot[\text{CH}{:}\text{CH}]_n\cdot\text{B}}$$

We have investigated the effect of methyl and substituted methyl groups as terminal groups A or B [in (I)] of certain conjugated systems on the position of the corresponding *K*-bands in order to derive information about the relative importance of these two factors, and also to test the justification or otherwise for the valency conception of hyperconjugation.

Methyl Group.—In Table 1 data showing the effect of terminal methyl groups of conjugated systems on the positions of the corresponding *K*-bands are reproduced. In the examples 1—5 the position of the *K*-band is determined by the facility of the electron migration along the absorbing system proceeding from the terminal methyl group as indicated in (II). The introduction of the *p*-methyl group is responsible for appreciable red-shifts due to the two factors mentioned, the increased polarity of the substituted system and the replacement of the terminal H–C electrons by the more strongly polarisable electron system of Me–C, both factors facilitating the electron migration (to the excited state). Similarly, the displacement to longer wavelengths due to the methyl group

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TABLE 1. *Maxima of* K-*bands of compounds* p-X·C_6H_4·H *and* p-X·C_6H_4·Me.

			p-X·C_6H_4·H		p-X·C_6H_4·Me		
No.	X	Solvent	λ (Å)	ε	λ (Å)	ε	Δλ
1	H *	H_2O	2035	7,400	2065	7,000	30
2	Ph	C_6H_{14}	2467	19,000	2513	19,100	46
3	COMe	C_6H_{14}	2387	12,500	2466	17,500	79
4	$\text{CMe:}\overset{+}{\text{O}}\text{H}$	H_2SO_4	2950	28,000	3113	30,000	163
5	NO:O	C_6H_{14}	2513	9,500	2645	10,000	132
6	p-MeO·C_6H_4	C_6H_{14}	2595	21,500	2602	23,600	7
7	NH_2	EtOH	2344	8,000	2355	10,000	11
8	O^-	0·1N-NaOH	2345	11,000	2359	9,500	14

* Doub and Vandenbelt, *J. Amer. Chem. Soc.*, 1947, **69**, 2714.

becomes greater with the increasing electron demand by the substituted system, *i.e.*, the increasing polarity of the Me–C bond. The red-shift is smallest in toluene and 4-methyldiphenyl, greater in 4-methylacetophenone and p-methylnitrobenzene, and most pronounced in the oxonium ion of 4-methylacetophenone.

(II) $\underset{\longrightarrow}{\text{Me}\cdot C_6H_4\cdot \text{X-}p}$ (X = H, Ph, COMe, $\text{CMe:}\overset{+}{\text{O}}\text{H}$, NO:O)

(III) $\underset{\longleftarrow}{\text{Me}\cdot C_6H_4\cdot \text{X-}p}$ (X = p-MeO·C_6H_4, NH_2, O^-)

The effect of a p-methyl substituent on the K-bands of aniline, the phenoxide ion, and 4-methoxydiphenyl (nos. 6—8) is different. The methyl group is now at the negative end of the absorbing system, *i.e.*, the electron migration determining the stability of the excited state proceeds into the methyl group as indicated in (III). The polarity of the substituted system and, thus, its polarisability in direction of the electron migration will be reduced (factor 1), which should cause displacement of the K-band to shorter wavelengths. On this, however, is superimposed a red-shift due to the replacement of the H–C electrons by the more strongly polarisable Me–C electrons (factor 2). The latter factor being greater, the overall result is a small displacement to longer wavelengths. In the examples 1—5, factor 2 should be even more preponderant, since the polarity of the C_{Me}–$C_{C:C}$ bond suggests a stronger electronic polarisability towards the aromatic carbon atom.

α-Substituted p-*Nitrotoluene Derivatives.*—An investigation into the effect of substituents in terminal methyl groups on the position of a K-band affords additional evidence for its dependence on the direction of the electron migration and the reality of the twofold function of a terminal group of the absorbing system. The data for α-substituted p-nitrotoluene derivatives (Table 2) show that the K-band of p-nitrotoluene is displaced to *shorter* wavelengths as the electron-attracting power (inductive effect) of the α-substituents (IV; A) increases, *i.e.*, in the order H < Br < Br_2 < Br_3, H < Cl < Cl_2 < Cl_3, and H < NH_2 (in ethanol) < OH < Cl < C:N < $\overset{+}{N}H_3$ < NO_2.

(IV) $\underset{\longrightarrow}{\text{A}\cdot CH_2\cdot C_6H_4\cdot \text{NO:O-}p}$

The introduction of electron-withdrawing substituents into the methyl group reduces the polarity of the A:CH_2–C bond and, to a smaller degree, by inductive transfer, that of the other linkages of the absorbing system relative to the electron migration and, thus, is responsible for a hypsochromic shift of the K-band. The absorption maximum is in no case at shorter wavelengths than for nitrobenzene itself, although in many cases such as ω : p-dinitrotoluene, 4-nitrobenzyl cyanide, and the 4-nitrobenzylammonium ion (IV; A = NO_2, C:N, $\overset{+}{N}H_3$) the substituent A·CH_2 is more strongly electron-attracting than is the hydrogen atom. This illustrates the important contribution of the increased polarisability of the C–C electrons (factor 2) to the red-shift caused by the methyl group, which only in the case of ω : p-dinitrotoluene is just cancelled by the hypsochromic effect due to the reduced polarity of the system (factor 1).

However, it will be noticed that the K-bands of 4-nitrobenzylamine (in hexane), 4-nitrobenzyl iodide, and 4-nitrodiphenylmethane appear at wavelengths slightly longer

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than that of *p*-nitrotoluene, in spite of the electron-withdrawing character of the corresponding substituents which is illustrated by the dissociation constants of acetic acid, iodoacetic acid, and phenylacetic acid (Table 2). Moreover, the displacement to shorter wavelengths caused by the introduction of bromine atoms and, to a smaller degree, of chlorine atoms into *p*-nitrotoluene is also smaller than might have been expected. Braude (*J.*, 1949, 1902) has already pointed out that the inflexion corresponding to the *K*-band of diphenylmethane appears at longer wavelengths than the *K*-band of toluene and discussed it in terms of hyperconjugated structures (cf. also Bowden, Braude, and Jones, *J.*, 1946, 948; Bowden and Braude, *J.*, 1952, 1068).

TABLE 2. *Maxima of* K-*bands of compounds* $p\text{-}NO_2\cdot C_6H_4\cdot X$.

	n-Hexane			Ethanol			$10^5 K$ of
X	λ (Å)	ε	Δ (X-Me)	λ (Å)	ε	Δ(X-Me)	$HO_2C\cdot X$ *
H	2513	9,500	—	2595	9,500	—	17·1
$CH_2\cdot NO_2$	2513	12,500	−132	—	—	—	—
$CH_2\cdot\overset{+}{N}H_3$	—	—	—	2620	11,000	−106	—
$CH_2\cdot CN$	2547	11,000	− 98	—	—	—	342·0
CCl_3	2553	14,600	− 92	—	—	—	20000·0
$CHCl_2$	2560	14,500	− 85	—	—	—	5000·0
CH_2Cl	2581	12,500	− 64	2650	12,000	− 76	155·0
$CH_2\cdot OH$	2610	12,000	− 35	2705	10,000	− 21	15·0
CBr_3	2632	16,500	− 13	—	—	—	—
$CHBr_2$	2635	17,000	− 10	—	—	—	—
CH_2Br	2641	15,000	− 4	2705	12,000	− 21	138·0
$CH_2\cdot NH_2$	2651	12,500	+ 6	2715	10,000	− 11	—
CH_3	2645	10,000	0	2726	10,000	0	1·75
CH_2I	2649	15,000	+ 4	—	—	—	75·0
CH_2Ph	2660	13,500	+ 15	—	—	—	4·88

* Dippy, *Chem. Rev.*, 1939, **35**, 151; La Mer and Downes, *J. Amer. Chem. Soc.*, 1933, **55**, 1840; Ives and Sames, *J.*, 1943, 513; Walden, *Z. phys. Chem.*, 1892, **10**, 638; Ostwald, *ibid.*, 1889, **3**, 418.

These facts show that the α-substituents are not only responsible for a displacement of the *K*-band to shorter wavelengths by reducing the polarity of the absorbing system, but, like groups directly attached to the double bond of a conjugated system, can make appreciable bathochromic contributions due to the greater polarisability of the A–CH_2 electrons. The latter effect, normally only small, cannot be neglected, if the electronic polarisability of the new substituent is high as in C–I, C–Br or C–Ph. This indicates that the electrons of the A–C bonds participate in the electron migration to the excited state (cf. also below).

It is noteworthy that the displacements to shorter wavelengths on introduction of Cl, Br, or NH_2 are *greater* in ethanol than in hexane. This should be attributed to a smaller increase of polarity of the corresponding (less polar) 4-nitrobenzyl derivatives on change to the solvent of higher dielectric constant, and possibly to external hydrogen-bond formation by these substituents (cf. Ungnade, *J. Amer. Chem. Soc.*, 1953, **75**, 432). Hydrogen-bond formation in ethanol should also account for the *smaller* shift to shorter wavelengths of 4-nitrobenzyl alcohol, the latter serving now as hydrogen donor (cf. Burawoy and Chamberlain, *J.*, 1952, 2310).

α-Substituted p-*Toluidine Derivatives.*—These conclusions are convincingly confirmed by the effect of substituted methyl groups at the " receiving " end of the electron migration. The maxima of the *K*-bands of α-substituted *p*-toluidine derivatives (V) are shown in Table 3. In these compounds the introduction of electron-withdrawing substituents (B) into the methyl group increases the polarity of the C–CH_2B bond and, by inductive transfer, that of the other linkages of the absorbing system relative to the direction of the electron migration. This results in displacements of the *K*-band of *p*-toluidine to *longer* wavelengths, increasing in the order of the electron-attracting power of the substituents, *i.e.*, $H < Ph < NH_2 \sim OH < CN < NH_3^+$. Again, the rather high red-shift of the *K*-band of 4-aminobenzylamine (B = NH_2) and, in particular, of 4-aminodiphenylmethane (B = Ph) is accounted for by the comparatively high polarisability of the electron system of the C–NH_2 and C–Ph groups. In contrast to the cases of 4-nitrobenzylamine and 4-nitrodiphenylmethane, this contribution here enhances the red-shift due to the increased

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polarity of the absorbing system. Unfortunately, the instability of α-halogeno-*p*-toluidines precluded the extension of this investigation to C–Hal bonds.

(V) $\underrightarrow{p\text{-}NH_2\cdot C_6H_4\cdot CH_2\cdot B}$ $\underrightarrow{p\text{-}MeO\cdot C_6H_4\cdot C_6H_4\cdot CH_2\cdot B\text{-}p}$ (VI)

α-Substituted 4-Methoxy-4′-methyldiphenyl Derivatives.—We have, therefore, investigated the α-substituted derivatives of 4-methoxy-4′-methyldiphenyl, in which the electron migration responsible for the position of the *K*-band again involves an electron recession into the methyl group (VI; B = H). Maxima of the *K*-bands of the various compounds are reproduced in Table 3.

TABLE 3. *Maxima of* K-*bands.*

	$p\text{-}H_2N\cdot C_6H_4\cdot X$ in ethanol			$p\text{-}MeO\cdot C_6H_4\cdot C_6H_4\cdot X\text{-}p$ in hexane		
X	λ (Å)	ε	$\Delta_{(X-Me)}$	λ (Å)	ε	$\Delta_{(X-Me)}$
H	2344	8,000	—	2595	22,000	—
CH_3	2355	11,000	0	2602	23,600	0
CH_2Ph	2400	13,000	+ 45	2632	28,000	+ 30
$CH_2\cdot NH_2$	2410	10,500	+ 55	—	—	—
$CH_2\cdot OH$	2410	12,000	+ 55	2638	24,500	+ 36
$CH_2\cdot CN$	2424	10,500	+ 79	2657	23,000	+ 55
$CH_2\cdot SH$	—	—	—	2672	27,000	+ 70
$CH_2\cdot \overset{+}{N}H_3$	2455	11,500	+100	—	—	—
CH_2Cl	—	—	—	2712	23,000	+110
$CHCl_2$	—	—	—	2761	23,000	+159
CH_2Br	—	—	—	2767	23,500	+165
CH_2I	—	—	—	2910	23,500	+308
$CH{:}CH_2$	—	—	—	2867	26,500	+265
COMe	—	—	—	2980	28,000	+378
CHO	—	—	—	3047	28,000	+445

As already explained, 4-methoxy-4′-methyldiphenyl absorbs at only slightly longer wavelengths than 4-methoxydiphenyl (Δ, 7 Å). Electron-withdrawing α-substituents (B) cause much greater red-shifts. With substituents of low polarisability the displacement increases with the electron-withdrawing effect, as in the *p*-toluidine series, *e.g.*, in the order H < Ph < OH < CN. However, the phenyl substituent in 4-benzyl-4′-methoxydiphenyl is again responsible for a greater displacement of the *K*-band to longer wavelengths than could have been expected from its inductive effect alone, *i.e.*, from factor 1.

Similarly, the chloride (B = Cl) absorbs at longer wavelengths than the cyanide (B = CN), although the electron-withdrawing effect of CN is greater than that of Cl (cf. the dissociation constants of cyanoacetic acid and chloroacetic acid in Table 2). Most important, the red-shift of the *K*-band increases considerably from the chloride to the bromide and iodide, and from the alcohol to the thiol. The displacements increase as one ascends within a group in the Periodic Table, although the electron affinity decreases. The red-shifts due to factor 1 are obviously enhanced by another effect increasing in the opposite order. This is the polarisability of the C–B electrons (factor 2) which increases in the order CN < Cl < Br < I and OH < SH. It clearly demonstrates that these electrons participate in the electron migration of the transition.

This " polarisability " effect of the C–Hal electrons is much more important in this series than in the *p*-nitrotoluene series. Whereas 4-nitrobenzyl iodide absorbs at approximately the same wavelength as *p*-nitrotoluene, factors 1 and 2 cancelling each other, in 4-bromomethyl- and 4-iodomethyl-4′-methoxydiphenyl factor 2 makes much the greater contribution. The displacements of the *K*-band due to the increased polarity in in the ground state could be expected to be much smaller for the bromide and iodide than those found for the cyanide or chloride (55 and 110 Å respectively), but the observed displacements are 165 and 308 Å respectively. This shows that the polarisability of the CH_2–Hal electrons towards the C atom is smaller than that in the opposite direction. (A consideration of the different polarities of the CH_2–Hal bonds in the two series would only reinforce this conclusion).

In order to assess the contribution of the electronic polarisability of the C–Br and, in

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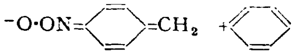
particular, of the C–I bond in its proper perspective, we have prepared and examined the spectra of 4-formyl-4′-methoxy-, 4-acetyl-4′-methoxy-, and 4-methoxy-4′-vinyldiphenyl (VI; $CH_2B = CH{:}O$, $CMe{:}O$, $CH{:}CH_2$). The maxima of the *K*-bands are compared in Table 3. They show that the displacement of the *K*-band due to the introduction of the CH_2I group into 4-methoxydiphenyl is appreciably greater than that produced by the $CH{:}CH_2$ group and almost as great as that caused by the COMe or CHO group, although in the latter cases the displacement is partly due to the increased polarity of the absorbing system. The effect of a C–I bond here is comparable to and even greater than that of a double bond.

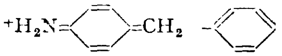
Discussion.—Analysis shows that the effect of a terminal group on the position of *K*-bands depends on its polarisability and its influence on the polarity of the absorbing system, both factors varying the facility of the electron migration in the direction which determines the stability of the excited state. According to wave-mechanics, an electron passes on excitation into a new orbital divided by an (additional) nodal plane into two parts possessing wave-functions of opposite sign. In symmetrical systems such as atoms or the hydrogen molecule, the probability of finding the excited electron on either side of the nodal plane is equal, but in unsymmetrical systems the excited orbital can be expected to extend more to one side of the nodal plane. Our observations afford experimental evidence that the stability of the excited state is decided by the migration of the electron into the more stable part orbital of longer " life time," although the matter is slightly more complicated in the polyelectronic systems discussed in this paper.

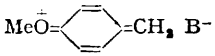
The observation that in substituted methyl groups the single bonds (A–C or C–B) partake in the electron migration within systems such as (VII) and that their polarisability may cause redshifts comparable to those due to multiple linkages such as $C{:}C$ and $C{:}O$ (VII; $CH_2B = C{:}C$, $C{:}O$) is of considerable theoretical significance, since it cannot be accounted for by the widely accepted theoretical interpretations of electronic spectra which are based on structures involving non-localised bonds and on the assumption that only the π-electrons of the absorbing systems are important or need to be considered for the electron transition.

(VII) $$\underrightarrow{A\cdot CH_2\cdot[CH{:}CH]_n\cdot CH_2\cdot B}$$

The observed effects are far too great to be attributed to some kind of hyperconjugation. Attempts to apply this conception to substituted methyl groups, in order to account for the considerable spectroscopic effects of single bonds, or at least for the contribution due to their polarisability, are also unsatisfactory, because they would make it necessary to assume that in the excited state and, to a smaller degree, in the ground state idealised structures such as (VIII) and (IX) would make an inportant contribution and that the contribution


(VIII)


(IX)


(X)

of structures (X) would increase in the order $Cl^- < Br^- < I^-$. This would be inconsistent with the known relative and absolute electron affinities and ionisation potentials of atoms (for the inadequacy of the conception of hyperconjugation, see also Burawoy and Spinner, *J.*, 1954, 3752; 1955, in the press; Sweeney and Schubert, *J. Amer. Chem. Soc.*, 1954, **76**, 4625).

One of us has already shown that the valency conception of non-localised bonds is in disagreement with numerous observations and is superfluous. The constitutive changes of covalent linkages and of their bond properties such as the bond energies, interatomic distances, dipole moments, as well as chemical changes, can be accounted for by the principles of the classical structural theories. They involve only inductive electron displacements and are caused by changes of the effective nuclear charges (the screening) of the participating atoms, *i.e.*, by changes of the repulsive interactions of electrons and nuclei which should also inhibit electronic delocalisation (Burawoy, *Trans. Faraday Soc.*, 1944, **40**, 537; *Discuss. Faraday Soc.*, 1951, **10**, 104; *Chem. and Ind.*, 1944, 434; " Contribution à l'Étude de la Structure Moléculaire," Liège, 1947—1948, p. 73; cf. also Lennard-Jones and Pople, *Discuss. Faraday Soc.*, 1951, **10**, 9).

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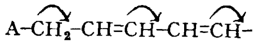
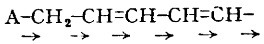
The results of the present investigation afford additional support for this view. Thus, the electron migrations to the excited state in conjugated systems are not electromeric (as in XI), nor do they involve many-centred (non-localised) orbitals, but consist of inductomeric displacements of "localised" electrons (as in XII). According to this view a single bond should fulfil qualitatively and, if of sufficiently high electronic polarisability, quantitatively the same function as a double bond, as is, indeed, observed.

(XI) 
$A{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}$

 (XII)
$A{-}CH_2{-}CH{=}CH{-}CH{=}CH{-}$

On this basis, an absorbing conjugated system can be considered as a complex system of interacting smaller polarisable units (electron pairs or even the single electrons). An increase of the polarisability of any of these units either by an increase of the polarity of a bond or on replacement by other more strongly polarisable units will facilitate the electron migration and stabilise the excited state, *i.e.*, cause a red-shift of the *K*-band. In later parts of this series, these conclusions will be further supported by an analysis of the effect of other terminal groups on the position of *K*-bands and will be justified by a theoretical interpretation.

EXPERIMENTAL

Spectra were determined with a Hilger E3 quartz spectrograph fitted with a Spekker photometer, a tungsten-steel high-tension spark being employed as the source of light. If not otherwise stated, compounds investigated were obtained by known methods and purified. They had the physical characteristics previously reported, except that 4-aminobenzylamine obtained by Amsel and Hofmann (*Ber.*, 1886, **19**, 1285) as a liquid was found to be a highly hygroscopic solid, m. p. 37°, giving a urea derivative of m. p. 199—200° (Amsel and Hofmann give 197°).

p-*Nitrobenzotrichloride*.—Antimony pentachloride (3 c.c.) was added slowly to *p*-nitrobenzotribromide (5 g.) (Fisher, *J. Amer. Chem. Soc.*, 1934, **56**, 2470); the mixture was heated at 80° for 20 min., poured on ice and extracted with ether. After being washed with 10% aqueous sodium hydrogen carbonate and water and dried, the ether was removed and the residue of of p-*nitrobenzotrichloride* (0·7 g., 22%) recrystallised from light petroleum (b. p. 40—60°) forming needles, m. p. 47° (Found: C, 35·4; H, 2·1; N, 5·4; Cl 43·6. $C_7H_4O_2NCl_3$ requires C, 35·0; H, 1·7; N, 5·8; Cl, 44·2%).

4-p′-*Methoxyphenylbenzoyl Chloride*.—4′-Methoxydiphenyl-4-carboxylic acid (34·2 g.) (Fieser and Bradsher, *J. Amer. Chem. Soc.*, 1936, **58**, 1738, 2337) and thionyl chloride (250 g.) were refluxed gently for 2 hr. The excess of thionyl chloride was removed under reduced pressure and from the residue 4-p′-*methoxyphenylbenzoyl chloride* (27 g., 73%) was extracted with dry light petroleum (b. p. 60—80°). The same product was also obtained by the action of phosphorus pentachloride. It crystallised from light petroleum as plates, m. p. 100° (Found: Cl, 14·7. $C_{14}H_{11}O_2Cl$ requires Cl, 14·4%).

4-p-*Methoxyphenylbenzyl Alcohol*.—The acid chloride (25 g.) in dry ether (750 c.c.) was added during 2 hr. to a stirred mixture of lithium aluminium hydride (3 g.) and dry ether (400 c.c.). The mixture was refluxed for another hour, poured on ice, and acidified with dilute sulphuric acid. 4-p-*Methoxyphenylbenzyl alcohol*, being only sparingly soluble in ether, separated (16 g., 74·5%). Alternate recrystallisation from ethanol and light petroleum (b. p. 60—80°) gave plates, m. p. 164° [Found: C, 78·6; H, 6·2%; *M* (Rast), 214. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·6%; *M*, 214·2]. This compound can also be prepared on a small scale by direct reduction of 4-*p*-methoxyphenylbenzoic acid.

4-p-*Methoxyphenylbenzyl Chloride*.—A solution of the alcohol (4·5 g.) and thionyl chloride (3·5 g.) in chloroform (70 c.c.) was heated at 40° for 1 hr. and refluxed for 15 min. After cooling, it was washed with water, aqueous sodium hydrogen carbonate, and again with water, dried (Na_2SO_4), and evaporated. The residue was extracted with hot light petroleum (b. p. 60—80°) from which the *chloride* separated on cooling (4·0 g., 92%). It crystallised from light petroleum as plates (or clusters of needles), m. p. 103·5—104° (Found: C, 72·0; H, 5·6; Cl, 15·0. $C_{14}H_{13}OCl$ requires C, 72·3; H, 5·6; Cl, 15·2%).

4-p-*Methoxyphenylbenzyl Bromide*.—A solution of the alcohol (1 g.) and phosphorus pentabromide (3·5 g.) in chloroform (25 c.c.) was heated at 40° for 30 min. and then raised to the b. p. This gave the *bromide* (0·8 g., 62%), plates (from light petroleum), m. p. 114° (Found: C, 60·6; H, 4·7; Br, 28·8. $C_{14}H_{13}OBr$ requires C, 60·65; H, 4·7; Br, 28·8%).

4-p-*Methoxyphenylbenzyl Iodide*.—The chloride (1·0 g.) in acetone (10 c.c.) was mixed with potassium iodide (1·0 g.) in water (6 c.c.) and acetone (60 c.c.), set aside in the dark for 4 hr.,

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and then boiled for 5 min. After cooling, it was poured into water (1 l.), a solution of sodium thiosulphate (3 g.) added, and the precipitate of *iodide* filtered off without delay (1·0 g., 70%). Recrystallisation in semidarkness from light petroleum (b. p. 60—80°) gave light-sensitive pale yellow needles, m. p. 114° to 122° (decomp.), depending on the rate of heating (Found: C, 52·4; H, 4·3; I, 38·8. $C_{14}H_{13}OI$ requires C, 51·9; H, 4·0; I, 39·15%).

4-p-*Methoxyphenylbenzyl Cyanide*.—A solution of the chloride (0·6 g.) and sodium cyanide (1·2 g.) in acetone (15 c.c.) and water (10 c.c.) was refluxed for 3 hr. After filtration, water was added and the precipitated *cyanide* was collected (0·3 g., 50%). Alternate crystallisation from light petroleum and ethanol gave plates, m. p. 128—129° (Found: C, 80·2; H, 5·9. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9%).

4-p-*Methoxyphenyltoluene-ω-thiol*.—A solution of sodium sulphide nonahydrate (1 g.) in water (3 c.c.) and ethanol (15 c.c.) was saturated with hydrogen sulphide. 4-*p*-Methoxyphenylbenzyl chloride (1 g.) in ethanol (30 c.c.) was added and the mixture refluxed for 10 min. After cooling and addition of water (100 c.c.), the precipitate was filtered off, washed with water, and extracted with a solution of sodium hydroxide (1 g.) in ethanol (50 c.c.) and water (110 c.c.). The solution was acidified quickly by the addition of concentrated hydrochloric acid (10 c.c.), and the precipitated *thiol* (0·4 g., 40%) collected and washed with water. Crystallisation from ethanol or light petroleum gave white plates, m. p. 103—104° (Found: C, 72·4; H, 6·4. $C_{14}H_{14}OS$ requires C, 73·0; H, 6·1%).

4-*Benzyl-4'-methoxydiphenyl*.—To a boiling solution of 4-*p*-methoxyphenylbenzophenone (8 g.) (Fieser and Bradsher, *loc. cit.*) in absolute ethanol (1 l.), sodium (40 g.) was added during 30 min. After cooling, carbon dioxide was passed into the solution until a sample diluted with water was not alkaline to phenolphthalein. The sodium hydrogen carbonate was filtered off and the filtrate concentrated to 80 c.c. On cooling, 4-*benzyl*-4'-*methoxydiphenyl* separated (5·5 g., 70%). It crystallised from methanol as plates, m. p. 100—100·5° (Found: C, 87·2; H, 6·8. $C_{20}H_{18}O$ requires C, 87·6; H, 6·6%).

4-p-*Methoxyphenylbenzaldehyde*.—Chromium trioxide (5·2 g.) was dissolved in *tert.*-butyl alcohol (14 g.), benzene (35 c.c.) was added, and the water removed with anhydrous sodium sulphate. The solution of *tert.*-butyl chromate was added to 4-*p*-methoxyphenylbenzyl alcohol (10 g.) in benzene (500 c.c.) at 45°, the mixture being kept at this temperature for another hour and at room temperature for 24 hr. A solution of hydrazine sulphate (5·2 g.) in 10% sulphuric acid (400 c.c.) was added and the mixture stirred for 1 hr. The benzene layer was separated, washed, dried ($MgSO_4$), and evaporated. The residual *aldehyde* (8·1 g., 82%) was obtained after alternate crystallisation from light petroleum and ethanol as needles, m. p. 104—105° (Found: C, 79·1; H, 5·6. $C_{14}H_{12}O_2$ requires C, 79·2; H, 5·7%).

4-p-*Methoxyphenylbenzylidene Dichloride*.—To a solution of the benzaldehyde (2 g.) in chloroform (12 c.c.) phosphorus pentachloride (6 g.) was added and the mixture refluxed for 15 min. After cooling, it was shaken with ice-water, aqueous sodium hydrogen carbonate, and water. After drying ($MgSO_4$), the chloroform was removed and the residual *dichloride* (1·3 g., 52%) crystallised from light petroleum (b. p. 40—60°) as plates, m. p. 113—114° (Found: C, 63·1; H, 4·5; Cl, 26·2. $C_{14}H_{12}OCl_2$ requires C, 62·9; H, 4·5; Cl, 26·5%). Attempts to prepare the dibromide were unsuccessful.

4-(1-*Hydroxyethyl*)-4'-*methoxydiphenyl*.—A hot solution of 4-*p*-methoxyphenylacetophenone (Fieser and Bradsher, *loc. cit.*) (5·0 g.) in benzene (100 c.c.) was added slowly to lithium aluminium hydride (1·5 g.) in dry ether (125 c.c.). After 6 hours' refluxing, ice and dilute sulphuric acid were added, and the organic layer was separated, washed with 10% aqueous sodium hydroxide, and water, dried ($MgSO_4$), and concentrated to 10 c.c. On cooling, the *alcohol* (4 g., 80%) separated. Crystallisation from light petroleum (b. p. 60—80°) gave needles, m. p. 121—122° (Found: C, 79·1; H, 6·9. $C_{15}H_{16}O_2$ requires C, 78·9; H, 7·1%).

4-p-*Methoxyphenylstyrene*.—The preceding alcohol (3·0 g.) and phosphorus pentabromide (8·0 g.) in chloroform (125 c.c.) were heated at 40° for 1 hr. and subsequently boiled for a few minutes. After being washed with water and 10% aqueous sodium hydrogen carbonate the chloroform solution was dried ($MgSO_4$) and the solvent was removed. The residual bromide (3·3 g., 85%) was crystallised once from light petroleum or carbon tetrachloride. The slightly impure bromide (1·5 g.) was refluxed for 20 min. with a solution of calcium formate (0·4 g.) in 90% formic acid (50 c.c.). On addition of water (25 c.c.) and cooling, 4-p-*methoxyphenylstyrene* separated almost quantitatively. Crystallised from carbon tetrachloride or benzene it had m. p. 173—174° (Found: C, 85·7; H, 6·6. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%).

COLLEGE OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, March* 21*st*, 1955.]