81. *Mechanism of Aromatic Side-chain Reactions with Special Reference to the Polar Effects of Substituents. Part XVI.* Hyperconjugation of Groups of the Type* CH_2X *in the Benzaldehyde–Cyanohydrin Equilibria.*

By JOHN W. BAKER, J. A. L. BRIEUX, and D. G. SAUNDERS.

Substituted benzaldehydes of the type $X{\cdot}CH_2{\cdot}C_6H_4{\cdot}CHO$ have been prepared in the *para*-series where X = H, Me, Cl, OH, OMe, CO_2Et, CO_2H, CO_2^-, and NEt_3^+, and in the *meta*-series where X = H, Cl, and OMe, and the values of the equilibrium constants $K = k_2/k_1$, have been determined for the reaction $X{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{:}O + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ in constant-boiling alcohol at 20°. The results provide information regarding the effect of the substituent X on the hyperconjugation of the group CH_2X and are discussed on this basis.

IT has been clearly demonstrated[1] that the equilibrium $R{\cdot}C_6H_4{\cdot}CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R{\cdot}C_6H_4{\cdot}CH(OH){\cdot}CN$ constitutes a very favourable system for determination of the relative mesomeric electron-release (+*M*) effects of the substituents R, even when such substituents

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* Part XV, *J.*, 1952, 2831.

[1] (*a*) Baker and Hemming, *J.*, 1942, 191; (*b*) Baker and Hopkins, *J.*, 1949, 1089; (*c*) Baker, Barrett, and Tweed, Part XV, *J.*, 1952, 2831.

possess dual polar effects of the types $\pm I$, $+M$. This communication records the use of this equilibrium in an attempt to ascertain the effect of various groups X on the H–C hyperconjugation [2] of CH_2 in the group CH_2X. The method depends essentially on the fact that, because of the more extended conjugated system present, mesomeric electron-release by a *para*-substituent R effects relatively greater stabilisation of the free aldehyde *p*-$R\cdot C_6H_4\cdot CHO$ than of its cyanohydrin *p*-$R\cdot C_6H_4\cdot CH(OH)\cdot CN$. Hence the increase in the numerical value of the equilibrium constant, $K = k_2/k_1$, is a measure of the relative mesomeric effect of the group R. In the *meta*-position the inductive effect of the substituent will be the dominating influence (with only minor complications arising from a relayed, second-order mesomeric effect [1b]), so that the ratio of the equilibrium constants K_p/K_m gives a more reliable assessment of the $+M$ effect of the substituent in the *para*-position. Wherever this supplementary test has been applied it has confirmed the order of $+M$ effects deduced from a study of the *para*-series alone.

It was intended to determine such equilibrium constants for substituents of the type CH_2X in both the *meta*- and the *para*-position in benzaldehyde but certain unexpected experimental difficulties in the *meta*-series have, so far, permitted determinations for only three such *meta*-substituted benzaldehydes, *viz.*, when X = H, Cl, and OMe. A much more extended range, X = H, Me, OH, OMe, CO_2Et, CO_2H, CO_2^-, Cl, and NEt_3^+, has been studied in the *para*-series. Since it seems unlikely that further information regarding the *meta*-series will become available in the near future, it is considered desirable to record the results already obtained, especially as they seem to justify certain tentative conclusions regarding the effect of various groups X on the effective hyperconjugation of the two H–C bonds in the whole group CH_2X.

Methods for the preparation of the required aldehydes (most of which are new) varied from case to case and are given in the Experimental section. Certain irregularities in yield obtained by Stephen's method [3] from *p*-chloromethylbenzonitrile led to a more detailed examination in this case. Under usual conditions hydrolysis of the separated aldimine stannichloride with water at 70° gave only a 17% yield of *p*-chloromethylbenzaldehyde. Concentration of the supernatant ether solution, from which the aldimine stannichloride had separated, and hydrolysis of the solid so obtained with water at 30° afforded unchanged *p*-chloromethylbenzonitrile (17%) and *p*-chloromethylbenzamide, characterised by alkaline hydrolysis to ammonia and *p*-hydroxymethylbenzoic acid, conversion into *p*-chloromethylbenzoic acid with nitrous acid, and dehydration to the original nitrile with phosphoric oxide. Continuous ether-extraction of the combined aqueous extracts afforded, in addition to various tin-containing products, *p*-hydroxymethylbenzaldehyde, which is very soluble in water and was characterised as its 2 : 4-dinitrophenylhydrazone. Thus the main causes of the low yield of *p*-chloromethylbenzaldehyde are (1) incomplete reaction of the nitrile or its hydrogen chloride addition product with stannous chloride so that subsequent hydrolysis of the unreduced chloroaldimine affords the amide, and (2) ready hydrolysis of the side-chain chlorine in *p*-chloromethylbenzaldimine stannichloride to give water-soluble *p*-hydroxymethylbenzaldehyde. Modifications in the experimental technique (see p. 410) based on these results increased the yield of *p*-chloromethylbenzaldehyde to 72·5%.

Determination of the equilibrium constants was effected by the method previously described, with tri-*n*-propylamine as the catalyst, but modifications were necessary in some cases because of secondary reaction of the benzyl side-chain with the reagents used in the determination of hydrogen cyanide. Thus with $CH_2Cl\cdot C_6H_4\cdot CHO$ a small, experimentally-determined correction was necessary for the reaction of the side-chain chlorine with silver nitrate under strictly standardised conditions of titration. Because of the much greater reactivity of bromine and iodine, equilibrium determinations with the bromomethyl- and iodomethyl-derivatives were not possible. With *p*-$^+NEt_3\cdot CH_2\cdot C_6H_4\cdot CHO\}Cl^-$ there is a large correction for the reaction of the chloride ion with silver nitrate. In the study of the aldehydo-acid, *p*-$HO_2C\cdot CH_2\cdot C_6H_4\cdot CHO$, the basic catalyst would be removed by conversion into the salt and hence the very slow equilibration of the cyanohydrin reaction had to be

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[2] Cf. Baker, " Hyperconjugation," Clarendon Press, Oxford, 1952, p. 96.

[3] Stephen, *J.*, 1925, **127**, 1874.

followed over a long period. For such reasons the values of the equilibrium constants may not be quite as accurate as those previously determined in more straightforward cases, but the consistency of the values obtained in a number of determinations (Table) indicates that they are sufficiently reliable as data from which conclusions may be drawn regarding the relative mesomeric electron-release of the various groups.

The results are given and analysed in the Table. The values of ΔF are calculated from the usual relation $\Delta F = -\boldsymbol{R}T \ln K$.

Equilibrium constants $K = k_2/k_1$ *for the reaction* $X\cdot CH_2\cdot C_6H_4\cdot CHO + HCN \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X\cdot CH_2\cdot C_6H_4\cdot CH(OH)\cdot CN$ *in constant-boiling alcohol at* 20°. *Catalyst* = 2 *drops* (~0·003M) *of* NPr^n_3 *in* 50 *ml. of a solution initially* 0·1M *with respect to aldehyde and* ~0·16M *with respect to* HCN.

X [a]	10^3K (mole l.$^{-1}$)	No. of determns.	10^{-2} ΔF (cal.)	$10^{-2}\delta(\Delta F) = \Delta F_H - \Delta F_{CH_2X}$ (cal.)	$10^{-2}\delta$ (ΔF) per H (cal.)
H *p* [b]	8·74 ± 0·08	4	27·6	−3·9	−1·3
m	5·5 ± 0·1	6	30·3	−1·2	−0·4
CO_2^-	8·96 ± 0·1	3	27·4	−4·1	$-2{\cdot}0_5$
Me [b]	8·18 ± 0·03	—	28·0	−3·5	$-1{\cdot}7_5$
OH	7·57 ± 0·16	7	28·4	−3·1	−1·5
MeO *p*	3·81 ± 0·07	5	32·4	+0·9	+0·45
m	3·7 ± 0·1	5	32·6	+1·1	$+0{\cdot}5_5$
CO_2Et	5·22 ± 0·21	6	30·6	−0·9	$-0{\cdot}4_5$
CO_2H	6·64 ± 0·21	2	29·2	−2·3	$-1{\cdot}1_5$
Cl *p*	8·34 ± 0·21	8 [c]	27·9	−3·6	−1·8
m	4·9 ± 0·4	2	30·9	−0·6	−0·3
NEt_3^+	12·52 ± 0·11	7 [d]	25·5	−6·0	−3·0
(CH_2X = H) [b]	4·47 ± 0·11	—	31·5	—	—

[a] In *p*-position except where otherwise shown. [b] Baker and Hemming [1a] whose value for *p*-$Me\cdot C_6H_4\cdot CHO$ was 8·98. [c] NPr^n_3 = 0·0015M. [d] Catalyst = 0·003M-NEt_3.

Discussion.—Most of the somewhat sparse evidence for the hyperconjugation effects of groups of the type CH_2X is derived from reaction rates and thus applies to the total $+T$ effect, *i.e.*, mesomeric plus electromeric. Partial-rate factors for the nitration of ethyl phenylacetate [4] show that, in this compound, the group $\cdot CH_2\cdot CO_2Et$ has a negligible inductive effect whilst appreciable activation of the *ortho*- and *para*-positions reveals a considerable $+E$ effect due to hyperconjugation of the two H–C bonds. Similar results for benzyl chloride [4] indicate a strong $-I$ effect superimposed on a $+E$ (hyperconjugative) effect for the group $\cdot CH_2Cl$. For groups $\cdot CH_2R$ (R = alkyl), Berliner and Berliner [5] have explained the different polar effects on the rates of bromination of aromatic compounds by assumption of a second-order type of hyperconjugation but Baddeley, Chadwick, and Rawlinson [6] pointed out that an alternative explanation, based on the geometric requirements of first-order hyperconjugation of the H–C_α bonds, is possible.[7] Theoretical calculations,[8] based on electrostatic field effects in the transition state, of the percentage of *meta*-isomeride produced in electrophilic substitution in benzene derivatives are in agreement with experimental values for those groups which have neither unshared electron pairs nor hyperconjugating H–C bonds, but for the groups Me, $CH_2\cdot CN$, $CH_2\cdot NH_3^+$ $CH_2\cdot NO_2$, and $CH_2\cdot CH_2\cdot NO_2$ the theoretical values are all much higher than the experimental, indicating considerable *ortho-para*-activation arising from hyperconjugation of the CH_2X group with the benzene ring in the transition state of substitution. Relative rates (C_6H_6 = 1) for the unimpeded *para*-bromination of compounds PhR with molecular bromine were determined by Robertson, de la Mare, and Swedlund [9] who, for groups of the $-I$, $+T$ type, found R = CH_2Ph, 51; $CH_2\cdot CO_2Et$, 2·3; CH_2Cl, 0·76; $CH_2\cdot CN$, 0·17. Increasing inductive electron-attraction in the series Ph < CO_2Et < Cl < CN partly

[4] Ingold and Shaw, *J.*, 1949, 575.

[5] Berliner and Berliner, *J. Amer. Chem. Soc.*, 1949, **71**, 1195 and later papers.

[6] Baddeley, Chadwick, and Rawlinson, *Nature*, 1949, **164**, 833; cf. Baddeley and Gordon, *J.*, 1952, 2190.

[7] Cf. Baker, ref. 2, p. 53.

[8] Sixma, *J. Chem. Phys.*, 1951, **19**, 1209.

[9] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

accounts for the reduction of velocity in this series, but the overall activation by $CH_2{\cdot}CO_2Et$ evidently arises from hyperconjugation, whilst the deactivating $-I$ effect of CH_2Cl and $CH_2{\cdot}CN$ is probably partly compensated by an activating $+E$ effect of these groups. Similar results [10] for the rate of addition of bromine to allyl derivatives of the type $\underset{\alpha}{\overset{\curvearrowright}{CH_2X}}\overset{}{—}\underset{\beta}{CH}\overset{\curvearrowright}{=}\underset{\gamma}{CH_2}$ were :

X	F	Cl	Br	CN
k_2^{25}	2·9	1·6	1·0	0·23

It was shown that attack is initiated by electrophilic bromine at C_γ and is thus facilitated by electron-release by CH_2X. Hence the group CH_2F exhibits a greater electron-releasing capacity than CH_2Br and CH_2Cl in spite of the increasing $-I$ effect $Br < Cl < F$. Such results suggest that hyperconjugative electron-release by the group CH_2X *may* be increased by increasing electron-*attraction* of X.

On the other hand Burton and Ingold [11] determined the proportions of αβ- and αδ-dihydro-compounds formed by reduction of substituted vinylacrylic acids with metal amalgams in alkaline and acid media. In interpretation of these results, de la Mare, Hughes, and Ingold [12] postulated that, since the direction of electron distribution in hyperconjugation is unambiguously $\overset{\curvearrowright}{Alk}—C\overset{\curvearrowright}{=}C$, the importance of such hyperconjugation in groups CH_2X would decrease in the series $X = CO_2^- > H > CO_2H$. This implies that hyperconjugation is greater the larger is the electron-*release* effect of X.

It is recognised that, just as the polarisability component ($+E$) of hyperconjugation may vary according to the electron-demand of the reaction (cf. for example, the difference between nitration with NO_2^+ and bromination with molecular bromine [9]), so the permanent polarisation ($+M$) may be greater the more extended is the conjugated system to which the group is attached.[1b] Hence the extended conjugated system in benzaldehyde may evoke a greater degree of hyperconjugation than is present in the vinylacetic acids. The results in the Table suggest that, in our system at least, electron-release by the group X is *not* the factor which increases the degree of hyperconjugation of the whole group CH_2X, since the strongly electron-attracting ammonium pole in $CH_2{\cdot}NEt_3^+$ seems to confer even greater hyperconjugation on the whole group than does the strongly electron-repelling anion in the group $CH_2{\cdot}CO_2^-$. Reasons have already been adduced [1b] why a $-I$ effect should destabilise the free aldehyde relative to its cyanohydrin (and hence lower the value of K), and were experimentally confirmed for the unequivocally $-I$ groups, halogen and nitro, in the *meta*-position. The much higher K value observed in the cation p-$^+NEt_3{\cdot}CH_2{\cdot}C_6H_4{\cdot}CHO$ would thus appear to arise from a considerable $+M$ (hyperconjugative) effect of the group $CH_2{\cdot}NEt_3^+$.

There is now considerable support for the original view [13] that the degree of hyperconjugation decreases as the number of hyperconjugated H–C bonds is reduced. Hence, to get a consistent standard for the effect of the substituent X on the relative degree of hyperconjugation of group CH_2X, in comparison with that of CH_3, the changes in free energy of dissociation of the cyanohydrin for a single hyperconjugated H–C bond are given in the last column of the Table. It is recognised that this value will include contributions to the relative stability of the free aldehyde from the inductive effect of CH_2X. In the Table the groups are arranged in the order * of decreasing $+I$ (or increasing $-I$) effects of X and hence, presumably, of CH_2X also. Sole operation of this inductive effect should thus, for the *para*-substituents, cause a gradual decrease in the (negative) value of $\delta(\Delta F)$ in passing down the Table. Irregularities observed must be due to some other polar factor, most probably hyperconjugation.

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* The less obvious differences in this order are justified by various observations in the literature.[14]

[10] Swindale, Swedlund, and Robertson, *J.*, 1950, 812; Robertson, Heyes, and Swedlund, *J.*, 1952, 1014.

[11] Burton and Ingold, *J.*, 1929, 2022.

[12] de la Mare, Hughes, and Ingold, *J.*, 1948, 25.

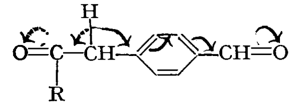
[13] Baker and Nathan, *J.*, 1935, 1844; Baker, *J.*, 1939, 1150.

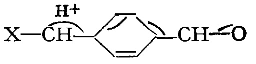
[14] References quoted by Saunders, Thesis, Leeds, 1955.

Before discussing the superficially random effects of X revealed by these *K* values it should be noted that the closely similar values of *K* for *p*-Me (8·74) and *p*-CH_2Cl (8·34) are confirmed by the close similarity of their ratios K_p/K_m which are, respectively, 1·6 and 1·7. Although slender, this evidence supports our contention that the values of *K* for other *para*-substituents do give at least a correct qualitative order of their $+M$ effects, even where results for the *meta*-derivative are not available. The differences in the $\delta(\Delta F)$ values for *meta*- and *para*-substitution indicate that the mean relative stabilisations of the aldehyde to the cyanohydrin for each hyperconjugated H–C bond in the groups Me and CH_2Cl are, respectively, 90 and 150 cal./mole, values of the expected order of magnitude.

In any discussion of these results it is recognised that, although the *K* values are well spaced, the extreme difference in ΔF is only ~700 cal., a small value in relation to various unknown energy and entropy factors such as the change in solvation due to the introduction of integrally charged centres into the molecule. Hence any explanations can be only very tentative. Such uncertainties are, however, unavoidable in any experimental approach to the problem, because of the small energy contributions associated with hyperconjugation even in favourable systems. Two explanations are possible. The first is based on the hypothesis that hyperconjugation of the group CH_2X is *increased* by electron-*attraction* of the group X. This view is supported by the observation that, although the partial-rate factors for the *meta*-position in the nitration of ethyl phenylacetate and benzyl chloride[4] prove an order of $-I$ effects $CH_2Cl > CH_2{\cdot}CO_2Et$, nevertheless the equilibrium *K* value for *p*-chloromethylbenzaldehyde is much larger than that for ethyl *p*-formylphenylacetate, thus revealing a greater hyperconjugation effect by the former group. In the series $X = CO_2^-$, Me, OH, CO_2Et, CO_2H, Cl, NEt_3^+, the inductive electron-release $(+I)$ effect decreases (or $-I$ increases). This factor should cause a gradual and continuous fall in the value of *K*. At the same time the hyperconjugative electron-release of CH_2X will, *ex hypothesi*, increase, and cause a gradual and continuous rise in the value of *K*. Superimposition of these two opposing polar effects would thus cause the value of *K* to pass through a minimum in the above series, in accord with experimental findings. On this view the reduction of hyperconjugative electron-release of groups of the type $CH_2{\cdot}COR$ is regarded as due to crossed hyperconjugation of the CH_2 group with the group COR and with the benzaldehyde residue (see *A*). The greater the $+M$ effect of R in satisfying the electron-demand of the CO group in COR, the smaller should be the competition of the crossed hyperconjugation of the CH_2 group, and hence the hyperconjugation of the whole group $CH_2{\cdot}COR$ with the benzene ring should (as is found) decrease in the order $R = O^- > OH > OEt$. The *total* electron release of the group $CH_2{\cdot}COR$ $(+I, +M)$ will, however, be complicated by a strong $+I$ effect when $R = O^-$.

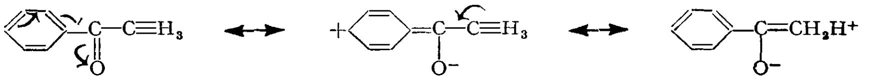
(*A*)





(*B*)

An alternative explanation of our results is possible by a modification of this view if it is tentatively assumed that the main effect of the group X is due not so much to its electron-attracting power as to its ability to stabilise further the negative charge in structures of the general type (*B*) which are involved in hyperconjugation. Rothstein has used a somewhat similar concept to formulate the structures of disulphonylpropenes, and the operation of a $-E$ effect of the sulphone in the transition state of the nitration of alkyl benzyl sulphones (due, in these examples, to the utilisation of the *d*-orbitals of sulphur). A further illustration is provided by the stimulation of the hyperconjugative effects of alkyl groups by the phenyl group in alkyl phenyl ketones,[16] *e.g.* :



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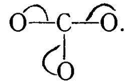
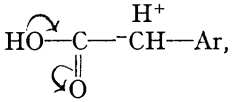
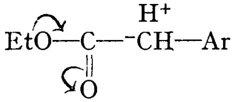
[15] Rothstein, *J.*, 1937, 309; 1953, 3991.

[16] Baker, *Trans. Faraday Soc.*, 1941, **37**, 648.

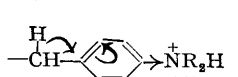
which explains why the cyanohydrin equilibrium constants of the alkyl phenyl ketones Ph·COAlk follow the order of the hyperconjugative effects of the alkyl group (K = Me > Et > Pr^i > Bu^t) whereas in the corresponding alkyl *cyclo*hexyl ketones [17] they are governed by the inductive effect (K = Me < Et < Pr^i).

In our present examples, application of this concept is most obvious in the group $CH_2{\cdot}CO_2^-$ where the structure $^-O{\cdot}CO{\cdot}\overset{H^+}{C^-}H{\cdot}C_6H_4{\cdot}CHO$, in which two negative charges may be distributed between two oxygen atoms and the formylbenzyl structure, may be regarded as simulating the resonance stabilisation in the symmetrical carbonate anion  $O{-}\underset{O}{\overset{|}{C}}{-}O$.

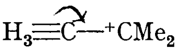
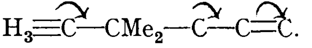
The resulting hyperconjugation of two H–C bonds is thus rendered approximately equivalent to that due of three such bonds in Me. In harmony with this view hyperconjugation is reduced in the group  $HO{-}\underset{O}{\overset{\|}{C}}{-}{}^-\overset{H^+}{C}H{-}Ar$, and still more by the further reduced symmetry in the ester  $EtO{-}\underset{O}{\overset{\|}{C}}{-}{}^-\overset{H^+}{C}H{-}Ar$, although differences are magnified by the decreasing $+I$ effect in the series $CH_2{\cdot}CO_2^-$ > $CH_2{\cdot}CO_2H$ > $CH_2{\cdot}CO_2Et$.

In the substituents CH_2Cl and $CH_2{\cdot}NEt_3^+$ the stabilisation of the negative charge must be assumed to arise from the strong electron-attracting effect of NEt_3^+ and, to a smaller extent, of Cl, an effect which is probably purely electrostatic, *viz.*, $^+NEt_3{\leftarrow}{}^-\overset{H^+}{C}H{-}Ar$. The prototropic mobility of propene systems activated solely by NR_3^+ groups is small but detectable,[18] and hence the group $CH_2{\cdot}NEt_3^+$ may possess weakly acidic character and some interaction between the basic catalyst and the positive hydrogens of the CH_2 group cannot be completely excluded, although it is regarded as negligible because of the high stoicheiometric ratio (~350 : 1) of aldehyde : tri-*n*-propylamine.

The marked hyperconjugative power of the group $CH_2{\cdot}NR_3^+$ might also be expected in an extended grouping of the type $^+NHR_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}$ and so provide a satisfactory explanation of the ready bromination [19] of the di-cation of di-*p*-alkylaminophenylmethane in the 2 : 2′-positions by Br$^+$. *meta*-Orientation of electrophilic substitution in an attached benzene ring by groups NR_3^+ is known to arise from marked *deactivation* of the benzene ring positions in the order *o*, *p* ≫ *m*, the electrophilic substituent entering the least deactivated position at a rate much slower than that in unsubstituted benzene. The ready bromination of di-*p*-alkylaminophenylmethanes with bromine–silver sulphate in concentrated sulphuric acid thus seems to result from re-activation of the 2 : 2′(*ortho*)-positions by the hyperconjugative ($+E$) effect of the CH_2 group (see *C*). That these positions are also the least deactivated by the $-I$ effect of the *m*-NR_2H^+ group we regard as incidental, rather than as the main reason for the observed orientation of bromination.



(*C*)

The suggestion that the main feature involved in the effect of the substituent X in increasing the hyperconjugation of the whole group CH_2X lies in its capacity for further stabilisation of the charge in one structure of the hyperconjugated hybrid is capable of logical extension to explain the postulated hyperconjugation of a Bu^t–C bond.[20] In such hyperconjugation, represented as Bu^t–C–C–X ⟷ $^+$Bu^{t}C=CX$^-$, the *positive* charge on $^+$Bu^t should be stabilised by ordinary H–C hyperconjugation from the methyl groups  $H_3{\equiv}C{-}{}^+CMe_2$ (9 structures), thus visualising an overall hyperconjugation of the type  $H_3{\equiv}C{-}CMe_2{-}C{-}C{=}C$.

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[17] D. P. Evans and Young, *J.*, 1954, 1310.

[18] Ingold and Rothstein, *J.*, 1931, 1666.

[19] Gorvin, *J.*, 1955, 83.

[20] Hughes, Ingold, and Shiner, jun., *J.*, 1953, 3830, and references there cited.

As already stated, these ideas in no sense neglect the importance of purely inductive effects of the groups CH_2X. Earlier results for *p*-alkylbenzaldehydes[1a] clearly reveal the superimposed operation of such effects since the apparent negative values of $\delta(\Delta F)$ per single hyperconjugated H–C bond (see Table) increase in the series Me (—1·3), Et (—1·7), Pr^i (—3·4), whilst the group value (—2·6) for the *p*-Bu^t compound must be mainly, if not exclusively, due to its relative stabilising $+I$ effect on the free aldehyde. For substituents CH_2X studied which possess a $-I$, destabilising effect on the free aldehyde, their hyperconjugative effects may, therefore, be underestimated.

The observed effects of $CH_2{\cdot}OH$ and $CH_2{\cdot}OMe$ are difficult to interpret since their K values are well spaced on opposite sides of the value for unsubstituted benzaldehyde. The closely similar values of K for *m*- and *p*-$MeO{\cdot}CH_2{\cdot}C_6H_4{\cdot}CHO$ imply that only an inductive effect is operative in both positions and, moreover, that it is a weak overall electron-attracting effect. The electron-attracting character of $CH_2{\cdot}OMe$ and, to a smaller extent, $CH_2{\cdot}OH$, is revealed in the accelerated rates of alkaline hydrolysis of the esters $RO{\cdot}CH_2{\cdot}CO_2Et$ (relative to $CH_3{\cdot}CO_2Et$) by the $B_{AC}2$ mechanism.[21] We can, however, offer no satisfactory explanation of the marked difference in behaviour of the groups $CH_2{\cdot}OMe$ and $CH_2{\cdot}OH$ or for the apparent absence of any hyperconjugation in the former group. The higher K value for *p*-$HO{\cdot}CH_2{\cdot}C_6H_4{\cdot}CHO$ suggests the operation of a weak hyperconjugative effect by $CH_2{\cdot}OH$. This could be explained, as for CH_2Cl, by stabilisation of the type $\overset{\text{H}^+}{\text{HO}}\!\leftarrow{}^{-}\text{CH–Ar}$, and it may be noted that the K values are in the order *p*-$^+NEt_3{\cdot}CH_2 > Cl{\cdot}CH_2 > HO{\cdot}CH_2$, *i.e.*, in the order of decreasing $-I$ effects $NEt_3^+ > Cl > OH$. In the case of $CH_2{\cdot}OH$ there are other possible complicating factors. One is the partial conversion into the anion $^-O{\cdot}CH_2{\cdot}C_6H_4{\cdot}CHO$, although the concentration (and total amount) of basic catalyst present is very small. Another is the possibility of self-condensation of a hemiacetal type between the aldehyde group of one molecule and the primary alcohol group of a second. No such self-condensation could be detected under equilibration conditions but viscous condensation by-products were often encountered in the preparation of some of these formylbenzyl compounds, particularly with the *p*-hydroxymethyl derivative.

We have not discussed our results on the basis of the conception of Baddeley *et al.*[6] regarding the geometrical requirements for hyperconjugation of a CH_2X group because the largest group $CH_2{\cdot}NEt_3^+$, which is the only one in which planarity with the benzene ring might be difficult, apparently exhibits the largest hyperconjugation. It therefore appears that this steric factor is not important in the examples we have studied.

EXPERIMENTAL

Microanalyses are partly by Mrs. Y. Richards, The University, Leeds.

Materials.—*m*-, b. p. 72·4°/10 mm., and *p*-Tolualdehyde, b. p. 85—86°/15 mm., were purchased samples, purified through their bisulphite derivatives and semicarbazones as previously described.

p-*Chloromethylbenzaldehyde.*—*p*-Toluidine was converted[22] into *p*-tolunitrile, m. p. 28°, which was chlorinated in the side chain (with illumination by a 500 w Nernst lamp) at its b. p. until 95% of the theoretical amount of chlorine had been absorbed, to give p-*cyanobenzyl chloride*, m. p. 81° after crystallisation from ligroin (b. p. 60—80°) (Found : Cl, 23·8. C_8H_6NCl requires Cl, 23·4%). After examination of the by-product formed when Stephen's reaction[3] was applied to this compound, the following technique for its conversion into the aldehyde was used. The important modifications are italicised. Anhydrous stannous chloride (80 g.) in 1400 ml. of dry ether was saturated with dry hydrogen chloride, through a *wide-bore delivery tube, at* 0° *until the oily complex which initially separated had passed into homogeneous solution.*[23] A solution of the nitrile (50 g.) in dry ether (400 ml.) was then added and the mixture was *completely* re-saturated with hydrogen chloride at 0°. Mechanical stirring was maintained

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[21] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, London, 1954, p. 758, Table 47-2.

[22] *Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 514.

[23] Cf. King, L'Ecuyer, and Openshaw, *J.*, 1936, 353; Evans and Walker, *J.*, 1947, 1572.

throughout. The mixture was then allowed to rise to room temperature and was *kept for* 3 *days*, with occasional stirring, to ensure complete separation of the aldimine stannichloride. The supernatant ether was then decanted and the washed precipitate was hydrolysed with water at 60—70° and, after the remaining ether had evaporated, the aqueous liquors were *immediately cooled* to minimise hydrolysis of the side-chain chlorine. The separated *p*-chloromethylbenzaldehyde solidified and was *filtered* off, and dissolved in ether. The supernatant aqueous solution was extracted with ether, the ethereal solution was washed with aqueous sodium carbonate and the combined ether solutions were dried (Na_2SO_4) and concentrated. This technique prevents the formation of emulsions which are obtained if the whole product is extracted with ether. When cooled, p-*chloromethylbenzaldehyde* crystallised and had m. p. 73°, after recrystallisation from ligroin (b. p. 40—60°) (Found : C, 61·9; H, 4·5; Cl, 23·1. C_8H_7OCl requires C, 62·15; H, 4·6; Cl, 22·9%) (yield, 38 g., 72·5%). Although this aldehyde combines with sodium hydrogen sulphite no crystalline derivative separates and regeneration affords a water-soluble aldehyde, probably *p*-hydroxymethylbenzaldehyde. Analysis of its semicarbazone, m. p. 205° (decomp.) after crystallisation from aqueous alcohol, indicates some reaction with side-chain chlorine (Found : C, 50·7; H, 5·1; Cl, 15·5. Calc. for $C_9H_{10}ON_3Cl$: C, 51·1; H, 4·8; Cl, 16·75%). Regeneration from the semicarbazone caused some hydrolysis of the side-chain chlorine. The aldehyde forms a 2 : 4-dinitrophenylhydrazone, m. p. 246° after crystallisation from acetic acid. With acetic anhydride and one drop of concentrated sulphuric acid at 40—50° for 0·75 hr. it gave *p*-chloromethylbenzylidene diacetate, m. p. 73° (mixed m. p. with original aldehyde, 57—60°) after crystallisation from ligroin (b. p. 40—60°) (Found: C, 56·9; H, 5·2; Cl, 13·35. Calc. for $C_{12}H_{13}O_4Cl$: C, 56·15; H, 5·1; Cl, 13·8%). Again some reaction with side-chain chlorine seems to have taken place. The aldehyde was oxidised with potassium permanganate to *p*-chloromethylbenzoic acid, m. p. 199°, after crystallisation from water.

m-*Chloromethylbenzaldehyde*. A similar technique was used with *m*-chloromethylbenzonitrile, m. p. 68°; the supernatant ether was removed from the precipitated aldimine stannichloride through an inverted sintered-glass filter. After being twice washed *in situ* with dry ether the stannichloride was freed from ether and hydrogen chloride in a vacuum-desiccator and decomposed with warm water, and the aldehyde was repeatedly extracted with ether. The combined ether extracts were repeatedly washed with sodium hydrogen carbonate, and the residue from the dried (Na_2SO_4) ether solution was distilled (N_2 stream) (b. p. 76—77°/0·3 mm.). Redistillation (N_2) just before use gave the aldehyde, b. p. 64·5°/0·13 mm., which was collected in a previously degassed receiver and sealed under nitrogen. In spite of all precautions this aldehyde is very rapidly oxidised to *m*-chloromethylbenzoic acid, m. p. 135° after crystallisation from water (Reinglass [24] gives m. p. 135°) and hence is difficult to analyse (Found : C, 63·0; H, 4·4; Cl, 23·35. Calc. for C_8H_7OCl : C, 62·15; H, 4·6; Cl, 22·9%). It was characterised as its *semicarbazone*, m. p. 213° (from ethanol) (Found : Cl, 17·1; N, 19·8. $C_9H_{10}ON_3Cl$ requires Cl, 16·75; N, 19·85%). The extreme ease of oxidation of this aldehyde made it difficult to manipulate and generally unsuitable as an intermediate for the preparation of other required aldehydes. It was, however, converted into the *m*-methoxymethyl compound.

p-*Hydroxymethylbenzaldehyde*. Attempted hydrolysis of the *p*-chloromethylaldehyde with moist silver oxide caused simultaneous oxidation to *p*-hydroxymethylbenzoic acid, m. p. 178° (raised to 179° by admixture with a genuine specimen, m. p. 180°) after crystallisation from water. A suspension of *p*-chloromethylbenzaldehyde (11 g.) in ~0·005N-barium hydroxide (25 ml.) was refluxed in an atmosphere of nitrogen for 3 hr. After saturation with salt the solution was extracted with ether. The residue from the dried ethereal solution crystallised at 0° to give a white solid, m. p. 39—42° (63%). Attempted distillation of this (N_2) at 160—180°/1·5 mm. gave a glassy polymer which reverted to the original monomeric aldehyde during 6 months. Purification was best effected by crystallisation (repeated Soxhlet extraction) from ligroin (b. p. 40—60°) in which it is only slightly soluble and thus was obtained p-*hydroxymethylbenzaldehyde*, m. p. 47° (Found : C, 70·7; H, 6·0. $C_8H_8O_2$ requires C, 70·6; H, 5·9%). Löw [25] and le Canu [26] describe this compound, prepared from *p*-$CH_2Br{\cdot}C_6H_4{\cdot}CHBr_2$, as a liquid. The same aldehyde was isolated (from the ethereal solution obtained by continuous ether-extraction of the combined aqueous liquors of the Stephen reaction on *p*-chloromethylbenzonitrile) as its (?) cis-2 : 4-*dinitrophenylhydrazone*, m. p. 164° (from alcohol) (Found : C, 52·4; H, 4·1%) and (?) trans-2 : 4-*dinitrophenylhydrazone*, m. p. 232° (mixed m. p. with *cis*-, 182—185°) (Found :

[24] Reinglass, *Ber.*, 1891, **24**, 2418.
[25] Löw, *Annalen*, 1885, **231**, 363.
[26] Le Canu, *Compt. rend.*, 1894, **118**, 535.

C, 52·0; H, 3·9; N, 15·8. $C_{14}H_{12}O_5N_4$ requires C, 53·2; H, 3·8; N, 17·7%), and not depressing the m. p. of the same derivative prepared from the genuine aldehyde.

p-*Bromomethylbenzaldehyde.* Attempts at direct conversion of *p*-chloromethylbenzaldehyde by potassium bromide in hot aqueous alcohol resulted in only partial halogen replacement and some hydrolysis. Introduction of dry bromine (208 g.) under the surface of *p*-tolunitrile (143 g.) at 180° (not at its b. p.) with illumination, afforded *p*-cyanobenzyl bromide (119 g., 50%), m. p. 115—117° after crystallisation from ligroin (b. p. 60—80°). Application of the modified Stephen method to this nitrile was accompanied by complications similar to those observed in the corresponding chloromethyl compound and, in addition, hydrolysis of the aldimine stannichloride yielded a solid, m. p. 82°, which appears to be mixed crystals of the required aldehyde, *p*-hydroxymethylbenzaldehyde, and the original nitrile. Repeated crystallisation from ligroin (b. p. 60—80°) raised the m. p. to 92—94°; subsequent fractional sublimation at 50 mm. gave (*a*) at 70° *p*-hydroxymethylbenzaldehyde, m. p. 38—40° and (*b*) at 100—120° slightly impure *p*-bromomethylbenzaldehyde, m. p. 94—95°. The action of thionyl bromide on *p*-hydroxymethylbenzaldehyde under reflux caused oxidation, giving *p*-bromomethylbenzoic acid, m. p. and mixed m. p. 223°, and, at 30—40°, a solid, m. p. 117—118°, which is probably impure ωωω′-tribromo-*p*-xylene (le Canu [26] gives m. p. 116°) (Found: C, 28·7; H, 3·3; Br, 68·9. Calc. for $C_8H_7Br_3$: C, 28·0; H, 2·0; Br, 70·0%). The best method for preparation of the required aldehyde is to warm *p*-hydroxymethylbenzaldehyde and phosphorus tribromide in dry benzene at 45° for 10 min. After 2 hr. at room temperature the mixture was poured into water, and the separated solid was washed with aqueous sodium hydrogen carbonate and water and dried. Crystallisation fron ligroin (b. p. 40—60°) gave p-*bromomethylbenzaldehyde*, m. p. 96° (Found: C, 48·5; H, 4·0; Br, 40·0. C_8H_7OBr requires C, 48·3; H, 3·55; Br, 40·15%).

p-*Iodomethylbenzaldehyde.* The *p*-chloromethyl-aldehyde was heated under reflux with potassium iodide in dry acetone for 30 hr.; the solvent was distilled off and the residue was extracted with ether. Concentration of this solution gave p-*iodomethylbenzaldehyde* as yellow flakes, m. p. 118° (63%), identical with a specimen prepared by the action of an excess of phosphorus tri-iodide on *p*-hydroxymethylbenzaldehyde in benzene at 50° for 1 hr. (Found: C, 38·8; H, 2·6; I, 51·2. C_8H_7OI requires C, 39·05; H, 2·9; I, 51·6%). Preparation of this aldehyde by the Stephen method from *p*-cyanobenzyl iodide, m. p. 144° (from the chloro-compound and potassium iodide in dry acetone), failed.

p-*Methoxymethylbenzaldehyde.* This has previously [27] been prepared by methods different from that used by us. A solution of sodium (1·197 g.) in dry methyl alcohol (50 ml.) was added in small portions during 6—8 hr. to a solution of *p*-chloromethylbenzaldehyde (8·065 g.) in the same solvent (100 ml.) heated in nitrogen under reflux. The mixture was allowed to regain neutrality (phenolphthalein) after each addition of sodium methoxide. Then the solution was concentrated and poured into a 4-fold excess of semicarbazide hydrochloride in saturated sodium acetate solution. The purified semicarbazone, m. p. 184° (from alcohol) (Sabetay [27b] gives m. p. 186°) (Found: C, 57·8; H, 6·2; N, 20·4. Calc. for $C_{10}H_{13}O_2N_3$: C, 57·95; H, 6·3; N, 20·3%), was steam-distilled (CO_2 stream) with oxalic acid solution. The distillate was saturated with salt and extracted with ether. Distillation (N_2) of the residue from the dried ethereal solution gave the required aldehyde, b. p. 129°/18 mm. (overall yield, 52%) (Found: C, 71·6; H, 6·9. Calc. for $C_9H_{10}O_2$: C, 72·0; H, 6·7%). Oxidation with cold, neutral potassium permanganate converted it into *p*-methoxymethylbenzoic acid, m. p. 120—122° (Quelet [27a] gives m. p. 123°).

m-*Methoxymethylbenzaldehyde.* (*a*) *m*-Chloromethylbenzonitrile (9·3 g.) in dry methyl alcohol (65 ml.) was heated under reflux with a solution of sodium (1·41 g.) in the same solvent (25 ml.) until neutral (3—4 hr.). Water (20 ml.) was added to dissolve the precipitated salt, most of the methyl alcohol was removed by distillation, and the residue was extracted with ether, whence distillation of the product gave *m*-methoxymethylbenzonitrile [28] (7·6 g.), b. p. 132°/14 mm. (Found: C, 73·3; H, 6·1; N, 9·9. Calc. for C_9H_9ON: C, 73·4; H, 6·1; N, 9·5%). By Stephen's method this gave a product, b. p. 85—86°/0·4 mm., which, by determination as the 2 : 4-dinitrophenylhydrazone, contained only ~35% of the aldehyde. This was isolated with aqueous sodium hydrogen sulphite from which was regenerated m-*methoxymethylbenzaldehyde*, b. p. 76·5°/0·35 mm. (Found: C, 72·4; H, 6·6. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%). Its *semicarbazone*, m. p. 184° (from methanol) (Found: C, 57·8; H, 6·5; N, 20·6.

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[27] (*a*) Quelet, *Bull. Soc. chim.* (*France*), 1933, **53**, 22; (*b*) Sabetay, *Compt. rend.*, 1931, **193**, 1194; (*c*) Arditti and Palfray, *ibid.*, 1946, **223**, 547.

[28] Cf. Mann and Stewart, *J.*, 1954, 2825.

$C_{10}H_{13}O_2N_3$ requires C, 57·95; H, 6·3; N, 20·3%), regenerated the aldehyde when steam-distilled (N_2) with oxalic acid from saturated brine. The aldehyde is very readily oxidised.

(*b*) *m*-Chloromethylbenzaldehyde, when treated with sodium methoxide as for the *p*-compound, gave the aldehyde, b. p. 68°/0·18 mm.; the m. p. (184°) of the semicarbazone was not depressed on admixture with the sample obtained as above, but admixture depressed the m. p. of the semicarbazone of the *p*-methoxymethylbenzaldehyde to 157—162°.

Ethyl p-*formylphenylacetate.* Some difficulty was experienced in the preparation of this compound. Various methods to replace the side-chain chlorine in the *p*-chloromethyl-aldehyde by the cyano-group failed, gave mainly the hydroxymethyl compound, or (with potassium cyanide) caused a benzoin condensation to give 4 : *4′-bisethoxymethylbenzoin*, b. p. 82°/1·5 mm. (Found: C, 73·1; H, 7·5. $C_{20}H_{24}O_4$ requires C, 73·1; H, 7·7%). Conditions for the partial hydrolysis of *p*-cyanobenzyl cyanide [29] proved too sensitive to provide a satisfactory method, *p*-carbamidophenylacetic acid, m. p. 229°, being the usual product. The route, *p*-aminophenylacetic acid ⟶ *p*-cyanophenylacetic acid and the application of Stephen's reaction to the ester of the latter was also unsatisfactory. The aldehyde was finally obtained by Sommelet's method [30] but the required experimental conditions for chloromethylation of ethyl phenylacetate with chloromethyl methyl ether and stannic chloride are stringent. At −10° no reaction occurs: at 60—70° or at 25—32° polymers are obtained. Ethyl phenylacetate (104 g.) was added slowly to a stirred mixture of chloromethyl methyl ether (54 g.) and stannic chloride (250 g.), the temperature being kept at 5—10°. The mixture was poured on crushed ice and extracted with ether. The ethereal solution, when washed with aqueous sodium carbonate and dried, gave a pale yellow oil, distillation of which gave unchanged ethyl phenylacetate and ethyl *p*-chloromethylphenylacetate, b. p. 99—110°/0·05 mm. (Found: Cl, 14·6. Calc. for $C_{11}H_{13}O_2Cl$: Cl, 16·7%), containing ethyl *p*-methoxymethylphenylacetate (12—20%). Hydrolysis of the crude product with sodium hydroxide afforded a polymer, m. p. 110—130°, probably a polyester of *p*-hydroxymethylphenylacetic acid. The crude product, b. p. 99—110°/0·05 mm. (121 g.), and hexamine (133 g.) were heated in 50% acetic acid (1200 ml.) at 90° for 4 hr. in an atmosphere of carbon dioxide.[31] The solution was neutralised with solid sodium carbonate (700 g.) and extracted with ether. The solution was shaken with sodium hydrogen sulphite (375 g. in 600 ml. of water), and the bisulphite compound was filtered off and washed with ether. A further quantity was obtained by re-saturation of the aqueous filtrate. The ethereal washings and extract of the filtrate gave *ethyl* p-*methoxymethylphenylacetate*, b. p. 104—108°/0·05 mm. (Found: C, 69·0; H, 8·2. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·75%). The aldehyde bisulphite compound was decomposed with cold, aqueous sodium carbonate and extracted with ether. Some polymerisation occurred when the residue from the dried ethereal extract was distilled but 65% distilled at 97—110°/0·06 mm. and, when kept sealed under nitrogen for 12 hr. at 0°, crystallised. Filtration at 4° and redistillation of the separated crystals at 104—108°/0·05 mm. gave the aldehyde, m. p. 34—36°. Various methods of purification, including regeneration from its semicarbazone, were unsuccessful and it was best purified by rapid distillation (N_2) at 105°/0·05 mm. The distillate solidified to give pure *ethyl* p-*formylphenylacetate*, m. p. 38° (Found: C, 69·1; H, 6·3. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·3%). The overall yield of pure compound was 12—14%. The aldehyde is readily oxidised and was kept sealed under nitrogen. It was characterised as its *semicarbazone*, m. p. 182° (from absolute alcohol) (Found: C, 57·5; H, 6·0; N, 16·8. $C_{12}H_{15}O_3N_3$ requires C, 57·8; H, 6·1; N, 16·9%), and 2 : 4-dinitrophenylhydrazone, m. p. 134—136°. Oxidation with boiling aqueous potassium permanganate afforded terephthalic acid, identified as its dimethyl ester, m. p. and mixed m. p. 139—140°.

p-*Formylphenylacetic acid.* The ester (5 g.) was refluxed under carbon dioxide with a slight excess of a 1% solution of sodium hydrogen carbonate until dissolved (3 hr.). The acidified solution was extracted with ether. Concentration of the dried ether solution gave the *acid* as pale yellow needles, m. p. 131° (Found: C, 65·9; H, 5·1. $C_9H_8O_3$ requires C, 65·9; H, 4·9%) but in all subsequent crystallisations, as colourless prisms, m. p. and mixed m. p. 131° (Found: C, 65·65; H, 5·2%). In equilibration experiments the required potassium salt was prepared by neutralisation of the acid with a standard solution of potassium hydroxide in constant-boiling alcohol.

Methyl m-*formylphenylacetate.*—Many attempts to prepare this compound only produced sufficient product to characterise it as its *semicarbazone*, m. p. 195° (from methyl alcohol) (Found:

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[29] Mellinghoff, *Ber.*, 1889, **22**, 3209.
[30] Sommelet, *Compt. rend.*, 1913, **157**, 1443.
[31] Cf. Angyal and Rassack, *J.*, 1949, 2700; 1950, 2141.

C, 56·4; H, 5·6; N, 18·2. $C_{11}H_{13}O_3N_3$ requires C, 56·2; H, 5·6; N, 17·9%). *m*-Nitrobenzyl chloride was converted through the nitrile into *m*-nitrophenylacetic acid which was reduced [32] to *m*-aminophenylacetic acid. The unpurified acid, m. p. 164—148°, was converted by the Sandmeyer reaction into *m*-cyanophenylacetic acid, m. p. 114° (Found: C, 67·2; H, 4·5. Calc. for $C_9H_7O_2N$: C, 67·1; H, 4·35%), the *methyl ester*, b. p. 100·5°/0·15 mm. (Found: C, 68·5; H, 5·2; N, 8·3. $C_{10}H_9O_2N$ requires C, 68·5; H, 5·2; N, 8·0%), of which was prepared by the silver salt method. Erratic results were obtained when the Stephen method was applied to this ester but in one small-scale experiment a small amount of the aldehyde was obtained from which the semicarbazone was prepared. Attempts to convert *m*-cyanophenylacetic acid into the *m*-aldehyde by Stephen's method failed, and Beech's method [33] applied to *m*-aminophenylacetic acid gave only a trace of water-soluble aldehyde which, converted through its silver salt, gave the methyl ester, b. p. 104°/0·05 mm., the semicarbazone of which was identical with that prepared above.

Triethyl-p-*formylbenzylammonium chloride*. Equimolar quantities of *p*-chloromethylbenzaldehyde (5·2 g.) and triethylamine (3·6 g.) with a few ml. of alcohol were sealed together and kept at 60° for 1 week. The separated salt was washed with 96% alcohol, the solution concentrated, and benzene was added. All water was removed by azeotropic distillation with fresh additions of dry benzene. The residual yellow oil crystallised and was kept sealed under dry benzene at 0° for 5 days. The crystals were drained on porous pot and the hygroscopic *salt* was dried and stored in a desiccator over phosphoric oxide (Found: C, 65·0; H, 9·0; N, 5·55; Cl, 13·8. $C_{14}H_{22}ONCl$ requires C, 65·7; H, 8·7; N, 5·5; Cl, 13·9%). The *styphnate* has m. p. 110° (from water) (Found: C, 50·7; H, 4·7; N, 11·65. $C_{20}H_{24}O_9N_4$ requires C, 51·7; H, 5·2; N, 12·1%).

Equilibrium Determinations.—Except where certain modifications were necessary (p. 405) the equilibrium constants were determined by the microtechnique described in previous Parts of this series, but, instead of removal of silver cyanide by filtration before back-titration of the excess of silver nitrate with standard ammonium thiocyanate, interference due to its solubility was prevented by addition of 5 ml. of pure nitrobenzene to the titration mixture. With all solid aldehydes, the absence of surface oxidation of the crystals was confirmed by examination under a high-power microscope both in ordinary and polarised light. The authors are indebted to Mr. P. Markey of the Department of Physical Chemistry for such examinations.

With *p*-chloromethylbenzaldehyde, under equilibration conditions, quaternary salt formation with the tri-*n*-propylamine catalyst corresponded to only 0·009 ml. of 0·0495N-silver nitrate, equivalent to the removal of only ~3% of the catalyst and well below the estimated titration error of 0·02 ml. The degree of interaction between side-chain chlorine and silver nitrate under the conditions of the determination of the excess of hydrogen cyanide varied slightly with the excess of silver nitrate present and was increased by precipitated silver cyanide. Under the standard conditions used (excess of silver nitrate equiv. to approx. 2·5 ml. of 0·05017N-ammonium thiocyanate; titration completed in 3 min. from the removal of the sample from the equilibrium mixture) a correction of 7·35% was needed, to be added to the back-titre of ammonium thiocyanate to compensate for the reaction of side-chain chlorine. Similar correction was made in determination of the equilibrium value for *m*-chloromethylbenzaldehyde.

Owing to removal of the catalyst, the slow equilibration of *p*-formylphenylacetic acid was followed by determination of the " equilibrium " value over a period of 13·5 weeks (duplicate blank titrations of the hydrogen cyanide solution being made for each reading) with the following results:

Time (weeks)	3	4	5	6	9	10	11	12	13·5
10^3K (mole l.$^{-1}$) (1)	9·22	7·12	7·02	6·30	6·44	4·17	4·03	3·40	—
(2)	—	7·72	7·16	6·81	6·79	5·93	5·92	4·44	2·34

The value of 10^3K was plotted against time and the portion of the curve (6—9 weeks) over which the value of K remained approximately constant was extrapolated to zero time to give the values: $10^3K = 6·43, 6·85$; mean, $6·64 \pm 0·2$ mole l.$^{-1}$.

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Department of Organic Chemistry,
The University, Leeds.

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[32] Cf. *Org. Synth.*, Coll. Vol. I, 2nd Edn., p. 52.

[33] Beech, *J.*, 1954, 1297.