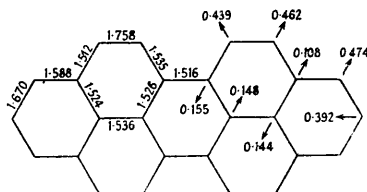## Bond Orders in Dibenzo[cd,lm]perylene.*

By E. Theal Stewart.

CALCULATION of the bond orders and the free valences in dibenzo[*cd,lm*]perylene by the method of molecular orbitals (Coulson, " Valence," Oxford University Press, 1952, Ch. 9) gives the results shown in the molecular diagram, bond order being shown on the left and free valences on the right.

In the ground state the highest occupied and the lowest vacant orbitals have the binding energies $\varepsilon = 0.285\beta = 0.266\gamma$ (b_{1g}), and $\varepsilon = -0.285\beta = -0.307\gamma$ (b_{3u}), the overlap integral between adjacent carbon atoms being taken as 0.25. [β, γ, and the symmetry notation are as defined by Coulson (*Proc. Phys. Soc.*, 1948, **60**, 257). The X-axis is normal to the molecular plane; the Y-axis and the Z-axis are respectively the long and the short axes of the molecule.] Dibenzo[*cd,lm*]perylene may be assumed to have the symmetry $V_h \equiv D_{2h}$, and the electronic transition $b_{1g} \leftrightarrow b_{3u}$ ($A_{1g} \leftrightarrow B_{2u}$) is thus allowed with y polarization.

On the basis of the empirical relation $\gamma = -2.3 \times 10^4$ cm.$^{-1}$ (Platt, *J. Chem. Phys.*, 1950, **18**, 1168), this transition should correspond to a first absorption band (*i.e.*, lowest-energy band) at about 750 mμ. However, the first absorption band of peropyrene, which Clar (*Ber.*, 1943, **76**, 458) has formulated as dibenzo[*cd,lm*]perylene, is at about 440 mμ. The simple molecular-orbital method gives notably inexact results in the calculation of the absolute values of transition energies; but the discrepancy between theory and experiment in the present case seems surprisingly large. There is little reason for supposing that peropyrene has a structure other than that which Clar proposed; but it is as well to note that the evidence for his formulation consists solely of (*a*) the one-stage synthesis of peropyrene from perinaphthenone [or from perinaphthane-4-carboxylic acid (Alder and Wolff, *Annalen*, 1952, **576**, 182)]; and (*b*) an indecisive combustion analysis.

It is perhaps significant that peropyrene is exceptional in giving an exceedingly poor result (624 mμ) in the normally successful perturbation method which Dewar (*J.*, 1952, 3532) introduced for calculating the wave-length of the first absorption band of condensed polynuclear aromatic hydrocarbons. In Dewar's method the molecule is supposed to be dissected into two odd-membered radicals; the non-bonding molecular orbital of each radical is expressed in the usual way as a linear combination of atomic orbitals; and the transition energy is then obtained as a function of the coefficients of the atomic orbitals at the points of dissection. Dewar suggested that the failure of his calculation in the case of peropyrene was due to the assumption of a uniform value for the various resonance integrals, the value for the " lateral " bonds probably being abnormally high (the bond order is in fact shown to be 1·758 in the present calculation). On repeating his calculations using the arbitrary values $\sqrt[8]{2}\,\beta$ for the lateral bonds, $\beta/\sqrt[8]{2}$ for the bonds adjacent to the lateral bonds, and β for all other bonds, he obtained the value 457 mμ for the wave-length of the first absorption band, in remarkable agreement with the experimental result, quoted as 458 mμ. It would seem, however, that this agreement is purely fortuitous; for a further refinement of Dewar's calculations, in which *all* the resonance integrals are adjusted in accordance with the calculated bond orders, gives the value 573 mμ. More-

* Ring Index No. 3841.

over, on applying Dewar's method to other molecules containing individual bonds of high order, again adjusting all the resonance integrals to correspond with the bond orders, one obtains results which are in general in poorer agreement with experiment than those Dewar obtained by using the uniform value β. For example :

	Observed	Calc. (uniform value for resonance integrals)	Calc. (values of resonance integrals adjusted)
	mμ	mμ	mμ
Phenanthrene	293	328	277
3 : 4-Benzophenanthrene ...	317	284	274
Pyrene	364	360	337

The relative values (β′) of the various resonance integrals used in calculating the co-efficients of the atomic orbitals in the non-bonding molecular orbitals were obtained from the bond orders by first calculating the bond lengths (Coulson, *Proc. Roy. Soc.*, 1951, *A*, **207**, 91), and then using the Lennard-Jones relation,

$$2 \, \beta' = W_d - W_s + \tfrac{1}{2}K_d(r - r_d)^2 - \tfrac{1}{2}K_s(r - r_s)^2,$$

with $W_d - W_s = -54\cdot4$ kcal., $K_d = 9\cdot57 \times 10^5$ dyne/cm., and $K_s = 4\cdot50 \times 10^5$ dyne/cm. (Coulson and Altmann, *Trans. Faraday Soc.*, 1952, **48**, 293). In calculating the transition energies, Dewar's value of β (determined empirically from the absorption spectrum of benzene) was taken to be equal to the value of β′ corresponding to a bond order of 1·667 (the bond order in benzene).

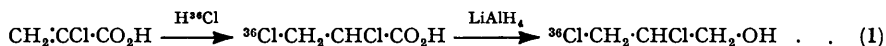The author is grateful to Professor C. A. Coulson, F.R.S., and Dr. L. E. Orgel for helpful discussion.

Some Experiments Relating to the Chemistry of the Dichlorohydrins.

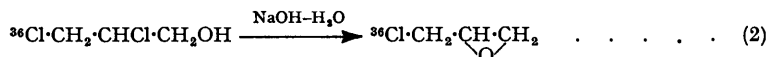### By P. B. D. DE LA MARE and J. G. PRITCHARD.

CHARACTERISATION of the isomeric dichlorohydrins, 2 : 3-dichloropropan-1-ol and 1 : 3-dichloropropan-2-ol, was difficult until Lennart Smith (*Z. physikal. Chem.*, 1917, **92**, 740) showed that the two isomers can best be distinguished by their rates of reaction with alkali. In a current investigation, it was desired to prepare 2 : 3-dichloropropan-1-ol labelled with ^{36}Cl in one of the two possible positions. The route adopted was the following, in which the second stage is, so far as we are aware, a new example of a well-known reaction :

$$CH_2{:}CCl{\cdot}CO_2H \xrightarrow{H^{36}Cl} {}^{36}Cl{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2H \xrightarrow{LiAlH_4} {}^{36}Cl{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2{\cdot}OH \quad . \quad . \quad (1)$$

It was considered unlikely that rearrangement would occur in either stage, and this was confirmed by treating the [3-^{36}Cl]-2 : 3-dichloropropan-1-ol with aqueous alkali. Pure epichlorohydrin was isolated from the product, and contained, within 3%, all of the ^{36}Cl :

$$^{36}Cl{\cdot}CH_2{\cdot}CHCl{\cdot}CH_2OH \xrightarrow{NaOH-H_2O} {}^{36}Cl{\cdot}CH_2{\cdot}\underset{O}{CH{\cdot}CH_2} \quad . \quad . \quad . \quad . \quad (2)$$

Activity, 48·3 ± 1·0 counts l. mole^{-1} min.$^{-1}$ Activity, 46·8 ± 1·2 counts l. mole^{-1} min.$^{-1}$

In preliminary experiments, it was shown that if 2 : 3-dichloropropan-1-ol is allowed to react to completion with one equivalent of alkali at 0° the sodium chloride produced in the reaction does not all come from the central carbon atom. This would be difficult to understand if epichlorohydrin were the sole organic product of reaction ; and, in fact, when the reaction is carried out on a preparative scale, epichlorohydrin can be obtained only in about 50% yield   It seems likely, from its known reactions (*e.g.*, with phenols in alkaline

solution, to give ethers of the type $CH_2{\cdot}CH{\cdot}CH_2{\cdot}OR$; cf. Boyd and Marle, *J.*, 1908, **93**,
839; 1909, **95**, 1807; 1910, **97**, 1788) that epichlorohydrin would condense with any alcohols present in alkaline solution. Consistently, there was isolated from the products of the reaction of 2 : 3-dichloropropan-1-ol with alkali a fraction containing complex high-boiling products.

After reaction of 2 : 3-dichloropropan-1-ol with Li^{36}Cl in anhydrous acetone at 65° for four days, 76% of the introduced ^{36}Cl was in the 3-, and the remainder in the 2-position, as is consistent with the expectation that the 2-position would be considerably hindered sterically for bimolecular substitution. The difference in rate of bimolecular attack at the two positions is not, however, sufficiently great for the reaction to be useful for the specific labelling of the 3-position.

Experimental.—Radioactive hydrochloric acid and lithium chloride were obtained from potassium chloride which had been irradiated by a high flux of neutrons at the Atomic Energy Research Establishment, Harwell, Didcot, Berks. We are indebted to this organisation for their co-operation in providing this specimen. Radioactivity was measured with the conventional type of liquid counter made by Twentieth Century Electronics Ltd., most of whose counters were found to have walls sufficiently thin to allow the passage of the weak β-radiation from ^{36}Cl. Amplifying, scaling, and recording units were commercial models. All counts recorded here are corrected for a background of about 10 counts min.$^{-1}$.

Pure 2 : 3-dichloropropan-1-ol was prepared by fractionation of commercial dichloro-hydrin; it had b. p., 182°/760 mm., 71·7—72·2°/10 mm., n_D^{25} 1·4822. Its reaction with sodium hydroxide (both reactants 0·05N) had $k_2 = 0{\cdot}0100$ l. mole^{-1} min.$^{-1}$ at 0·0°, and 0·32 l. mole^{-1} min.$^{-1}$ at 25·0°; no systematic trend in the rate-coefficients was observed, and the absence of any appreciable rapid initial reaction showed the absence of the isomeric dichlorohydrin.

Pure 1 : 3-dichloropropan-2-ol was prepared by the reaction of hydrochloric acid with epichlorohydrin (cf. Hill and Fisher, *J. Amer. Chem. Soc.*, 1922, **44**, 2586). Fractionation gave a product of b. p. 172°/760 mm., n_D^{25} 1·4810. Its reaction at 0·0° with sodium hydroxide (both reactants 0·05N) had $k_2 = 2{\cdot}12$ l. mole^{-1} min.$^{-1}$, constant within experimental error over the 68% reaction followed.

α-Chloroacrylic acid was prepared by the following method (Imperial Chemical Industries Ltd., Fr.P. 845,230/1939; cf. *Chem. Abs.*, 1941, **35**, 1070, 7975). Trichloroethylene was condensed with paraformaldehyde in the presence of concentrated sulphuric acid and copper bronze. Steam-distillation gave a lower layer of an oil, which was dissolved in ether. When the ether was allowed to evaporate *in vacuo*, the oil solidified to a material, m. p. 63—65° (lit., 64°). The crude oil was found suitable for the preparation of αβ-dichloropropionic acid by the following method (cf. Werigo and Melikov, *Ber.*, 1877, **10**, 1499). Dry hydrogen chloride (9·8 g.), containing a suitable amount of H^{36}Cl, was dissolved in acetic acid (100 ml.), and to this was added α-chloroacrylic acid (22·4 g.). After reaction had proceeded for 64 hr. at 45°, the product was fractionated, giving 15 g. of material, b. p. 114—118°/14·5 mm., which solidified and on recrystallisation from light petroleum gave [β-^{36}Cl]-αβ-dichloropropionic acid, m. p. 51·5—53° (lit., 50°) (Found: C, 25·2; H, 2·8. Calc. for $C_3H_4O_2Cl_2$: C, 25·2; H, 2·8%). αβ-Dichloropropionic acid was reduced as follows. To the acid (17·5 g.) in dry ether (70 ml.) was added lithium aluminium hydride (4·5 g.) in dry ether (100 ml.). The mixture was refluxed for 15 min. and then treated with 2N-sulphuric acid (250 ml.). The ethereal layer was dried (K_2CO_3, then Na_2SO_4) and fractionated, giving [3-^{36}Cl]-2 : 3-dichloropropan-1-ol (7 g.), b. p. 78—79°/13 mm., n_D^{25} 1·4822 (Found: C, 27·7; H, 4·85. Calc. for $C_3H_6OCl_2$: C, 27·9; H, 4·7%). Its reaction with sodium hydroxide (both reactants 0·05N) had $k_2 = 0{\cdot}32$ l. mole^{-1} min.$^{-1}$ at 25·0°. No systematic trend in the rate-coefficients was observed, and the absence of any appreciable rapid initial reaction showed the absence of the isomeric dichlorohydrin.

To prepare epichlorohydrin from this material, it was first diluted by the addition of 8·08 g. of inactive 2 : 3-dichloropropan-1-ol to 4·57 g. of the active material. The diluted sample was treated with N-sodium hydroxide (99 ml.) for 18 hr. at 0°. The product was extracted with ether, and the extract was dried (Na_2SO_4) and fractionated, giving 2 ml., b. p. 117—118°/760 mm., n_D^{25} 1·4358 (Found: C, 38·9; H, 5·6. Calc. for C_3H_5OCl: C, 38·9; H, 5·4%). A specimen of this material (1·483 g., in 10 ml. of alcohol) had a count of 75·1 per min. The undiluted 2 : 3-dichloropropan-1-ol (1·176 g., in 10 ml. of alcohol) had a count of 121·6 per min. From these values can be calculated the activities recorded in connection with equation (2);

they are arbitrary, since they depend on the thickness of the wall of the counter; and are the actual number of counts per minute given by a molar solution.

When inactive 2 : 3-dichloropropan-1-ol (50 g.) was allowed to react with 1·00N-sodium hydroxide (390 ml.) at 0° for 23 hr., there were obtained (*a*) epichlorohydrin (17 g.), b. p. 117—122°, n_D^{25} 1·4365, (*b*) *ca.* 0·2 g., b. p. 122—170°, n_D^{25} 1·4498, and (*c*) *ca.* 7 g., b. p. 90—100°/18 mm., n_D^{25} 1·4778. This relatively high-boiling material (*c*) was a complex mixture, and was not investigated further. The smallness of fraction (*b*) excludes the formation in this reaction of any substantial amount of β-epichlorohydrin, b. p. 135°, or of the possible products of dehydrochlorination, 3-hydroxy-1- or -2-chloroprop-1-ene, b. p. 149° and 136° respectively. A separate experiment showed that some of the sodium chloride released in the reaction came from the 3-carbon atom. [3-³⁶Cl]-2 : 3-Dichloropropan-1-ol (1·200 g., activity 98·5 counts per min.) was allowed to react to completion with 1·00N-sodium hydroxide (9·4 ml.). The organic material and solvent were removed *in vacuo*, and the remaining salt had an activity of 22·5 counts per min.

The dehydrochlorination by aqueous alkali of [β-³⁶Cl]-αβ-dichloropropionic acid was also investigated. The acid (1·07 g.) was heated for 44 hr. at 18° and for 15 min. at 50° with 15·0 ml. (2 equivs.) of 1·00N-alkali. The product was neutralised with 1·25 ml. of 6·0N-hydrochloric acid. The water and organic acid were removed under a high vacuum. The remaining sodium chloride, dissolved in 10 ml. of water, had a count of 99·3 per min.; it was shown (Volhard) to contain 1·47N-chloride. Reaction with acidified silver nitrate for 22 hr. at 90° released no additional chloride ion, and hence the sodium chloride retained no organic chlorine compounds. The aqueous solution of the organic acid which had been removed *in vacuo* (38 ml.) had a count of 1·3 per min. It contained almost no chloride. Such a small activity is almost indistinguishable above the background, and determines an upper limit (5 ± 4%) to the extent to which dehydrochlorination of αβ-dichloropropionic acid yields β-chloroacrylic acid; the α-isomer has long been known to be the major product of this reaction (cf. Werigo and Werner, *Annalen*, 1873, **170**, 168).

We are indebted to Professor E. D. Hughes, D.Sc., F.R.S., and Professor C. K. Ingold, D.Sc., F.R.S., for their interest in this work.

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A Note on the Dipole Moment of Benzyl Alcohol.

By A. D. BUCKINGHAM, H. G. HOLLAND, and R. J. W. LE FÈVRE.

THE measurements now recorded were started about the same time as those on sulphur dioxide, methylene dichloride, chloroform, paraldehyde, and ethylene oxide (cf. *J.*, 1950, 283, 556, 3370), and for the same reason, that benzyl alcohol, having a *negative* Kerr constant (Leiser, " Abhandlungen der Deutschen Bunsen-Gesellschaft," 1910, Nr. 4), might display a *larger* apparent dipole moment in benzene solution than the true value determined for the gaseous solute. The work was part of a programme outlined in *Trans. Faraday Soc.*, 1947, **43**, 392; its background is explained in the references just cited, and also in *J.*, 1950, 290. Benzyl alcohol was of special interest since in Leiser's list it was only surpassed by paraldehyde in the negative magnitude of its Kerr constant; Leiser's data, relatively to carbon disulphide as 100, were : paraldehyde, −713, benzyl alcohol, −477; by contrast methylene dichloride and chloroform were only −36 and −100, respectively.

The following observations have been made at widely spaced times; for each batch, benzyl alcohol was freshly fractionated and only that portion with b. p. 204·8°/760 mm. was used. General experimental details require no comment (cf. Le Fèvre, " Dipole Moments," Methuen, 3rd Edn., Chap. 2, the circuits shown as Figs. 11 and 17 being employed for the dielectric capacity measurements on the vapour and the solutions respectively) except to mention that the gas cell has been calibrated with benzene as a secondary standard, $P_{C_6H_6}$ being taken as 26·62 c.c., this being the value for liquid

benzene. Comparisons between benzene and carbon dioxide now being made here (by Mr. Narayana Rao) are yielding values of the polarisation very close to this for benzene vapour (cf. also Craven, *Proc. Phys. Soc.*, 1945, **57**, 97). A full temperature range with gaseous benzyl alcohol could not be secured owing to its decomposition (with production of coke-like material necessitating dismantlement of the cell) above about 200°. [Beilstein's " Handbuch " (Zweites Ergänzungswerk, Vol. VI, p. 406) notes the thermal breakdown of benzyl alcohol in hot glass tubes at 210—215° or over copper from 230—330° to such products as benzaldehyde, toluene, dibenzyl ether, etc.] Values of $P_{gas}^{benzyl\ alcohol}$ at 191° and at two lower temperatures are reported in Table 2. In the absence of a direct determination of the distortion polarisation the value 32·5 c.c. for the molecular refraction $[R_L]_D$ (Walden, *Z. physikal. Chem.*, 1907, **59**, 385) has been used to estimate both μ_{gas} and $\mu_{C_6H_6}$; this should not seriously affect their relative magnitudes. Dielectric constants, ε, and densities, d, now found for solutions containing weight fractions w_2, of benzyl alcohol in benzene at 25° are listed in Table 1.

TABLE 1. *Dielectric constants and densities of benzyl alcohol–benzene mixtures.*

$10^6 w_2$	0	4721	9079	9270	11,480	14,510
ε_{25}	2·2725	2·2863	2·2990	2·3006	2·3062	2·3166
$10^6 w_2$	15,020	27,250	45,280	96,850	149,900	203,840
ε_{25}	2·3182	2·3566	2·4197	2·6095	2·8321	3·1085

$10^6 w_2$	0	6130	8962	9057	12,350	12,460	14,840	15,020	31,440
d_4^{25}	0·87378	0·87463	0·87513	0·87504	0·87557	0·87555	0·87588	0·87578	0·87829
$10^6 w_2$	50,910	66,310	110,910	135,600	149,900	203,840	208,810	255,610	
d_4^{25}	0·88157	0·88394	0·89101	0·89396	0·89606	0·90343	0·90489	0·91445	

whence (cf. *J.*, 1953, 1622) : $\Delta\varepsilon = (2·90_2 \pm 0·01_3)w_2 + 5·81w_2{}^2$ and $\Delta d = (0·142_5 \pm 0·001_6)w_2 + 0·047w_2{}^2$.

Discussion.—From Table 1 the total polarisation of benzyl alcohol at infinite dilution in benzene is found to be $89·9 \pm 0·3$ c.c., whence, if $[R_L]_D$ is taken as $_DP$, $\mu_{C_6H_6} = 1·67_5 \pm 0·00_5$ D. The three polarisations of Table 2 yield, if the same $_DP$ is used, values for μ_{gas} of 1·71, 1·70, and 1·72 D. respectively. The mean of these is 1·71 D. Evidently the

TABLE 2. *Dielectric polarisations of benzyl alcohol as a vapour.*

| Temp.	$(\Delta C/p)_{p=0}^{PhCH_2 \cdot OH}$	P (c.c.)	Pressure (cm.)	No. of obsns.
178·3°	41·83 *	72·00	3—5·5	11
183·3	40·74 *	70·99	3—6	7
191·0	40·13 *	71·39	3—7	7

$* \ (\Delta C/p)_{p=0}^{C_6H_6} = -1·798 + 7790·0/T.$

" solvent effect " (*i.e.* the algebraic sign of $\mu_{soln} - \mu_{gas}$) is slightly negative, in contrast to that found for paraldehyde (*J.*, 1950, 290) where the ratio $\mu_{C_6H_6}/\mu_{gas}$ was definitely greater than unity. Benzyl alcohol is evidently another substance—additional to sulphur dioxide (*J.*, 1950, 283), methylene dichloride (*J.*, 1950, 556), and ethylene oxide (*J.*, 1950, 3370)— which breaks the " Kerr constant rule " of Le Fèvre and Le Fèvre (*J.*, 1935, 1747). The case is remarkable because of the largeness of the negative Kerr constant involved. It is of course possible that this is a property of *liquid* benzyl alcohol only, and arises from the presence of association complexes or aggregates whose anisotropic polarisabilities are not the same as those of the separated molecules, with which one is dealing at infinite dilution. A similar suggestion has been made for aniline (*J.*, 1949, 902).

Previous estimates of the dipole moment of benzyl alcohol (by the refractivity method) have been as follow :

	Solvent	μ, D
Williams, *Physikal. Z.*, 1928, **29**, 204	Benzene	1·66
Bodenheimer and Wehage, *Z. physikal. Chem.*, 1932, *B*, **18**, 343	Benzene	1·75
Higasi, *Bull. Inst. Phys. Chem. Res. Tokyo*, 1932, **11**, 729	Benzene	1·69
Fairbrother, *Proc. Roy. Soc.*, 1933, *A*, **142**, 173	Decalin	1·7
Hückel and Wenzke, *Z. physikal. Chem.*, 1942, *B*, **51**, 144	Benzene	1·45—1·89
„ „ „ „	*cyclo*Hexane	1·76—2·03
„ „ „ „	Carbon tetrachloride	1·67—1·76

The first four values are in reasonable accord with the μ_{gas} and $\mu_{C_6H_6}$ now found.   In detail however the measurements of Table 1 present an interesting disagreement with those of Hückel and Wenzke.   These authors reported that the polarisation–concentration curves of benzyl alcohol in the three solvents named changed their forms with temperature, P_2 tending to increase as infinite dilution was approached at lower temperatures, and *vice versa* (hence the variations in the apparent moments listed above).   With benzene the change-over was stated to occur between 35° and 40°.   After transforming molar into
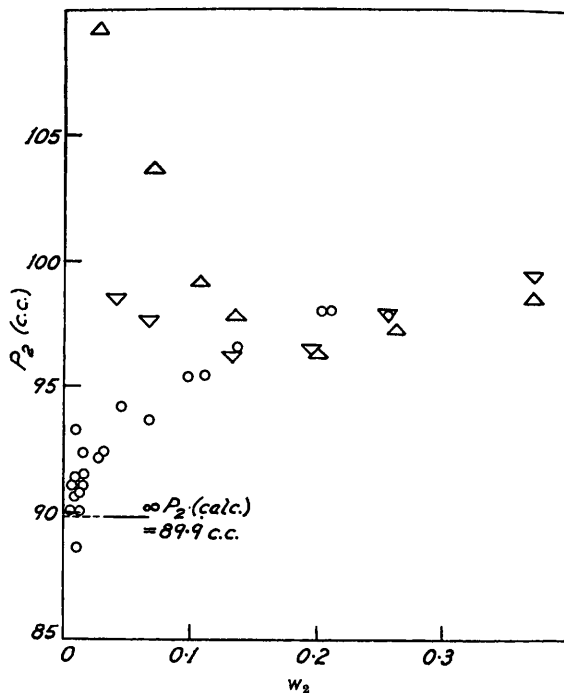
weight fractions, the values of P_2 of Hückel and Wenzke at 20° and 30° are shown as points $\triangle$ and $\triangledown$ respectively in the Figure : their increase as w_2 approaches zero can be seen.   By contrast, when the values of ε or d missing from Table 1 are provided by interpolation from smoothed graphs of these quantities against w_2, and the mixture formula of Sugden (*Trans. Faraday Soc.*, 1934, **30**, 720) is applied, the polarisations deduced (points $\bigcirc$) show diminution towards infinite dilution.   Beyond noting this apparent discrepancy with the observations by Hückel and Wenzke we withhold further comment pending studies in other media.

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The Dissociation Constant of Chlorous Acid.

By G. F. DAVIDSON.

THE dissociation constant of chlorous acid is given by Latimer (" Oxidation Potentials," Prentice-Hall Inc., New York, 1938, p. 48) as 10^{-2}, a value which he deduces from the free energy of dissociation of the acid as evaluated in unpublished work by Barnett (Ph.D. Thesis, University of California, 1935). Fontana and Latimer (*J. Amer. Chem. Soc.*, 1947, **69**, 2598) quote Barnett's value for the free energy of dissociation at 25° as 2·67 kcal./mole, and this corresponds to a dissociation constant of $1·10 \times 10^{-2}$. From measurements of pH made with the glass electrode on solutions resulting from the addition of sulphuric acid to solutions of barium chlorite, Tachiki (*J. Chem. Soc. Japan*, 1944, **65**, 346; *Chem. Abs.*, 1947, **41**, 3347) found the dissociation constant of chlorous acid at 25° to be $4·9 \times 10^{-3}$. A third value, $1·01 \times 10^{-2}$ at 23°, has recently been reported by Lister (*Canad. J. Chem.*, 1952, **30**, 879), but no details of the method employed are given.

A new determination has now been made in connection with an investigation involving the use of acidified chlorite solutions as oxidants for aldehyde groups in oxidized celluloses. The method employed was the potentiometric titration of solutions of sodium chlorite with hydrochloric acid by means of the glass electrode at room temperature (19—20°). The sodium chlorite was obtained by two recrystallizations of the commercial salt and dehydration of the product; its purity, determined iodometrically, was 99·8%. The titrations were performed as rapidly as possible and were stopped when one-eighth of the amount of acid equivalent to the chlorite had been added. At this point the solutions were only faintly yellow, and it is therefore probable that decomposition of chlorous acid, which takes place with formation of chlorine dioxide, chloric acid, and hydrochloric acid (cf. White, Taylor, and Vincent, *Ind. Eng. Chem.*, 1942, **34**, 782), occurred to only a slight extent.

Two titrations were performed at each of four chlorite concentrations, and the dissociation function, defined by the equation $K_a' = a_{H^+} \cdot c_{ClO_2^-}/c_{HClO_2}$, was evaluated at about ten points in each titration. The mean values obtained for pK_a' are given in the Table.

Chlorite concn., M	0·01	0·02	0·05	0·1
pK_a'	⎰1·91	1·88	1·84	1·80
	⎱1·92	1·88	1·84	1·81

The data are not sufficiently accurate or extensive to yield an exact value for the thermodynamic dissociation constant K_a, but by plotting pK_a' against the square root of the ionic strength and extrapolating to infinite dilution the approximate value 1·97 is obtained for pK_a. The corresponding value of K_a is $1·07 \times 10^{-2}$, which agrees closely with that derived from Barnett's results.

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*The Oxidation of Phenylhydrazones. Part III.**

By B. M. LYNCH and K. H. PAUSACKER.

WITKOP and KISSMAN (*J. Amer. Chem. Soc.*, 1953, **75**, 1975) report that benzylazoxy-benzene ($C_{13}H_{12}ON_2$), the peracid oxidation product of benzaldehyde phenylhydrazone, is reduced by aluminium amalgam forming a compound, $C_{14}H_{14}N_2$, m. p. 155° but is reduced by lithium aluminium hydride to give benzaldehyde phenylhydrazone, m. p. 158° (*idem, loc. cit.*; Part I, *J.*, 1953, 2517).

We find that the product of aluminium amalgam reduction has the characteristics described by Witkop and Kissman, but different analytical results were obtained [Found : C, 79·2; H, 6·5; N, 14·2%; M (Rast), 190, 199. Calc. for $C_{13}H_{12}N_2$: C, 79·5; H, 6·2; N, 14·3%; M, 196. Calc. for $C_{14}H_{14}N_2$: C, 80·0; H, 6·7; N, 13·3%; M, 210].

The compound is, therefore, isomeric but not identical with benzaldehyde phenyl-hydrazone, their mixed m. p. being 20° lower. When the product obtained by aluminium amalgam reduction was heated at 160° for 15 min., it was converted into normal benzaldehyde phenylhydrazone, m. p. and mixed m. p. 158°.

It appears, therefore, that the compound is a stereoisomer of benzaldehyde phenyl-hydrazone. Definite assignment of configuration is not possible, but since it has been shown that the *trans*-configurations of benzylideneanilines (I; R = Ar) are the stable forms (De Gaouck and Le Fèvre, *J.*, 1938, 741), and as the reduction product is converted into a more stable compound when heated, it is probably the *cis*-form (II; R = NHPh), and normal benzaldehyde phenylhydrazone is then the *trans*-form (I; R = NHPh).

$$\text{(I)}\quad \begin{array}{c} \text{Ph} \\ \diagdown \\ \text{H} \diagup \end{array} \text{C=N} \diagdown_{\text{R}} \qquad\qquad \begin{array}{c} \text{Ph} \\ \diagdown \\ \text{H} \diagup \end{array} \text{C=N} \diagup^{\text{R}} \quad\text{(II)}$$

An isomer, m. p. 154°, of benzaldehyde phenylhydrazone was obtained by Bodforss (*Ber.*, 1926, **59**, 667) by fractional crystallisation of the product from benzaldehyde and phenylhydrazine.

Similar reduction of *p*-methoxybenzylazoxybenzene, *p*-benzylazoxychlorobenzene, and *p*-benzylazoxytoluene yielded the " normal " substituted benzaldehyde phenylhydrazones (identified by m. p. and mixed m. p.).

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* Part II, *J.*, 1954, 1131.

Reduction of Acids to Aldehydes with Formic Acid.

By ALLEN J. BARDUHN and KENNETH A. KOBE.

DAVIES and HODGSON (*J.*, 1943, 84) described the reduction of six acids to aldehydes by formic acid with titanium dioxide as catalyst, in yields, based on the acid consumed, of 80—90%, and with conversions of 20—40%, except for salicylic acid for which both the conversion and yield were 92%.

At least three other laboratories have failed to repeat this work. There undoubtedly is some critical factor, which neither the original authors nor we recognized, necessary for reaction. Correspondence with Davies and Hodgson eliminated some factors, but, although we tested a large variety of process conditions, possible contaminants to reactants, and various other catalysts, we have produced no trace of aldehydes. The original paper calls for heating the carboxylic acid, formic acid, and titanium dioxide catalyst in a sealed Carius tube at 250—260°. We have used a 300-c.c. stainless-steel autoclave controlled to $\pm0.5°$, also a Carius tube (cf. Davies and Hodgson), temperatures from 150° to 300°, and pressures from 275 to 1400 lb. in.$^{-2}$. The formic acid has been adulterated with many possible impurities.

It appears that the catalyst does not contain the missing factor, since some of the original catalyst of Davies and Hodgson was used without success. Rutile and anatase, oxides of manganese, thorium, vanadium, and cobalt precipitated on titanium dioxide were also tried unsuccessfully.

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Organic Fluoro-compounds. Part VIII. Some Indole Derivatives.†

By W. B. WHALLEY.

THE modified Hoesch reaction (Whalley, Part VII *) for the preparation of 2-trihalogeno-acetyl derivatives of αβ-unsubstituted coumarones has been applied to indole and several of its congeners with the production in good yield of the corresponding 3-trihalogenoacetyl-indoles. These derivatives, particularly the trichloro-ketones, are easily convertible into the appropriate acids, thus providing a useful addition to the limited number of methods available for the preparation of indole- and *N*-substituted indole-3-carboxylic acids in general, and to the hitherto unknown *N*-alkylindole-3-carboxylic acids unsubstituted in the 2-position, in particular. Moreover, the ease of alkylation of the acidic hydrogen attached to the nitrogen atom in 3-trifluoroacetylindoles affords a convenient alternative route to *N*-alkylindole-3-carboxylic acids.

Skatole gives 2-trifluoroacetylskatole under these conditions.

Experimental.—The Hoesch reactions with the appropriate indoles were carried out as described for αβ-unsubstituted coumarones (Part VII, *loc. cit.*).

1-*Methyl-3-trifluoroacetylindole.* (*a*) Prepared from indole (2 g.), 3-trifluoroacetylindole (1·5 g.)

* Part VII, *J.*, 1953, 3479. Enquiries concerning this paper should be addressed to the author at the Department of Organic Chemistry, The University, Liverpool, England.
† Patent applications pending.

separated from methanol in prisms, m. p. 214° (Found : C, 56·5; H, 3·0; N, 6·6. $C_{10}H_6ONF_3$ requires C, 56·3; H, 3·9; N, 6·6%); it was readily soluble, without decomposition, in 2N-sodium hydroxide, and on hydrolysis during $\frac{1}{2}$ hr. with boiling 25% aqueous potassium hydroxide gave indole-3-carboxylic acid (80%), m. p. and mixed m. p. 218° (decomp.). Ellinger (*Ber.*, 1906, **39**, 2519) records m. p. 218° (decomp.). Methylation by methyl iodide–acetone–potassium carbonate during 2 hr. furnished a quantitative yield of 1-*methyl-3-trifluoroacetyl-indole* as prisms, m. p. 105°, from methanol (Found : C, 58·5; H, 3·8; N, 6·3. $C_{11}H_8ONF_3$ requires C, 58·2; H, 3·6; N, 6·2%).

(*b*) The Hoesch reaction with 1-methylindole (2 g.) gave an identical product (2 g.); hydrolysis for 2 hr. with 40% sodium hydroxide gave 1-*methylindole-3-carboxylic acid* (1·5 g.), which separated from aqueous acetone in plates, m. p. 212° (decomp.) (Found : C, 68·7; H, 5·5; N, 7·7. $C_{10}H_9O_2N$ requires C, 68·6; H, 5·2; N, 8·0%).

3-*Trichloroacetylindole*, obtained in 50% yield, formed plates, m. p. 235—237° (decomp.) from methanol (Found : C, 45·9; H, 2·8; N, 5·6; Cl, 40·5. $C_{10}H_6ONCl_3$ requires C, 45·8; H, 2·3; N, 5·3; Cl, 40·5%). This ketone was converted quantitatively into methyl indole-3-carboxylate by the method described in Part IV (*J.*, 1951, 665), and into indole-3-carboxylic acid by dissolution in warm 2N-sodium hydroxide.

5 : 6-*Methylenedioxyindole-3-carboxylic acid.* 5 : 6-Methylenedioxyindole (Burton and Duffield, *J.*, 1949, 78) (1 g.) furnished 5 : 6-*methylenedioxy-3-trifluoroacetylindole* (0·6 g.) in yellow plates, m. p. 268°, from aqueous methanol (Found : N, 5·7. $C_{11}H_6O_3NF_3$ requires N, 5·5%). Hydrolysis of this ketone with boiling 10% aqueous potassium hydroxide during 1 hr. gave 5 : 6-*methylenedioxyindole-3-carboxylic acid* (75% yield); purified from benzene–acetone, it formed prisms, m. p. 239—240° (decomp.) (Found : N, 6·7. $C_{10}H_7O_4N$ requires N, 6·8%).

5 : 6-*Dimethoxy-3-trifluoroacetylindole.* By Burton and Duffield's method (*loc. cit.*) condensation of veratraldehyde (14 g.) with nitromethane gave 3 : 4-*dimethoxy-ω-nitrostyrene* (10 g.) in yellow plates (from acetic acid), m. p. 142° (Found : C, 57·6; H, 5·4; N, 6·8. $C_{10}H_{11}O_4N$ requires C, 57·4; H, 5·3; N, 6·7%); this was converted by nitration into 4 : 5-*dimethoxy-ω* : 2-*dinitrostyrene* (7 g.), yellow prisms, m. p. 173° from acetic acid (Found : C, 47·6; H, 4·0; N, 11·0. $C_{10}H_{10}O_6N_2$ requires C, 47·3; H, 4·0; N, 11·0%). Simultaneous reduction and cyclisation of the latter styrene (6 g.) gave 5 : 6-dimethoxyindole (3 g.), m. p. 158° (Oxford and Raper, *J.*, 1927, 417, record m. p. 154—155°), which furnished 5 : 6-*dimethoxy-3-trifluoroacetylindole* (1·5 g.) in yellow flat needles, m. p. 207°, from methanol (Found : N, 5·5. $C_{12}H_{10}O_3NF_3$ requires N, 5·1%).

Derivatives of 7-methylindole. This indole (2 g.) gave 7-*methyl-3-trifluoroacetylindole* (1·2 g.) in yellow plates, m. p. 214°, from methanol (Found : C, 58·7; H, 3·7; N, 6·3. $C_{11}H_8ONF_3$ requires C, 58·2; H, 3·6; N, 6·2%). The ketone was easily soluble in 2N-sodium hydroxide without decomposition but when boiled with 5N-sodium hydroxide furnished 7-methylindole-3-carboxylic acid, m. p. 234° (decomp.). Kruber (*Ber.*, 1926, **59**, 2752) records m. p. 228° (decomp.). During 3 hr. in boiling acetone–potassium carbonate–benzyl bromide this ketone gave quantitatively 1-*benzyl-7-methyl-3-trifluoroacetylindole*, which separated from methanol in prisms, m. p. 140° (Found : C, 68·3; H, 4·5; N, 4·5. $C_{18}H_{14}ONF_3$ requires C, 68·1; H, 4·4; N, 4·4%). This was insoluble in 2N-sodium hydroxide but dissolved rapidly in warm 20% aqueous alcoholic potassium hydroxide, to furnish quantitatively 1-*benzyl-7-methylindole-3-carboxylic acid* as prisms, m. p. 241° (decomp.), from acetone (Found : C, 76·8; H, 5·7. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%).

7-*Methyl-3-trichloroacetylindole.* The addition during 20 min. of a solution of 7-methylindole (2 g.) in ether (25 ml.) to ether (100 ml.) containing zinc chloride (2 g.) and trichloromethyl cyanide (10 g.) previously saturated with hydrogen chloride at 0° gave an immediate yellow precipitate of the ketimine complex which, upon separation 24 hr. later and hydrolysis, furnished 7-*methyl-3-trichloroacetylindole* in plates, m. p. 202°, from methanol (Found : C, 48·9; H, 3·3; N, 5·0; Cl, 38·0. $C_{11}H_8ON_3Cl_3$ requires C, 48·0; H, 2·9; N, 5·1; Cl, 38·7%). This ketone was converted quantitatively into the corresponding acid and methyl ester.

1 : 2-*Dimethylindole-3-carboxylic acid.* 2-Methylindole (2 g.) gave 2-*methyl-3-trifluoroacetyl-indole* (1 g.) in prisms, m. p. 152°, from aqueous methanol (Found : C, 58·5; H, 3·9; N, 6·2. $C_{11}H_8ONF_3$ requires C, 58·2; H, 3·6; N, 6·2%). Methylation gave quantitatively 1 : 2-*di-methyl-3-trifluoroacetylindole* in plates, m. p. 115°, from methanol (Found : C, 60·1; H, 5·1. $C_{12}H_{10}ONF_3$ requires C, 60·0; H, 4·1%); this was hydrolysed to 1 : 2-dimethylindole-3-carboxylic acid, m. p. 220° (decomp.). King and L'Ecuyer (*J.*, 1934, 1901) record m. p. 217° (decomp.).

2-*Trifluoroacetylskatole.* Skatole (2 g.) gave this *ketone* (1·1 g.) in yellow prisms, m. p. 116°, from aqueous methanol (Found : C, 58·3; H, 3·5; N, 6·2. $C_{11}H_8ONF_3$ requires C, 58·2; H, 3·6; N, 6·2%); it was hydrolysed quantitatively to 3-methylindole-2-carboxylic acid, m. p. 166° (Found : C, 68·6; H, 5·2. Calc. for $C_{13}H_9O_2N$: C, 68·4; H, 5·2%).

Analyses of the fluorine-containing compounds were by the Clark Microanalytical Laboratories, Urbana, Illinois; the remainder were by Mrs. Rita Preis, Miss Doris Aitkin, and Miss Sally Haws.

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