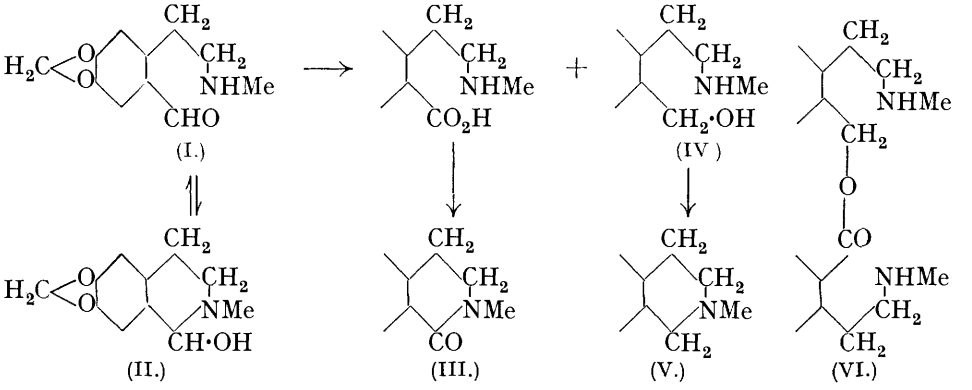
NOTES.

The "Cannizzaro Reaction" of Hydrastinine. By (MISS) SARAH N. MCGEOCH and THOMAS S. STEVENS.

THE conversion by alkali, of hydrastinine (I or II) into oxy- (III) and hydro-hydrastinine (V) (Freund and Will, *Ber.*, 1887, **20**, 2400), is usually represented by the scheme (I—V). Such a ring closure of the amino-alcohol (IV) appeared improbable, and we therefore prepared this substance with a view to study its stability towards caustic alkali.



Tiffeneau and Fuhrer (*Bull. Soc. chim.*, 1914, **15**, 172) have shown that fission on heating with acetic anhydride is a specific reaction of tertiary benzylamines, not shared by β-phenylethylamines (*e.g.*, $CH_2Ph{\cdot}NMe_2 \longrightarrow CH_2Ph{\cdot}OAc + NMe_2Ac$). Hydrohydrastinine was similarly converted into the *diacetyl* derivative of (IV), and when this substance was hydrolysed by alkali under conditions similar to those used by Freund and Will, the product was the free amino-alcohol (IV) and not hydrohydrastinine.

This observation does not, however, prove that hydrastinine reacts in the form (II) in Freund and Will's experiment, the *iso*quinoline ring remaining intact throughout, for if Tischtschenko's interpretation (*J. pr. Chem.*, 1912, **86**, 322) of the Cannizzaro reaction be correct (*e.g.*, $2Ph{\cdot}CHO \longrightarrow Ph{\cdot}CO_2{\cdot}CH_2Ph \longrightarrow Ph{\cdot}CO_2K + CH_2Ph{\cdot}OH$), hydrastinine (I) would yield, as intermediate product, the ester (VI), which then might undergo ring closure to hydrohydrastinine. A successful synthesis of this ester is unlikely, on account of the tendency of *O*-acyl derivatives of amino-alcohols to pass into their *N*-acyl isomerides. Such a difficulty would not arise in a study of the Cannizzaro dismutation in an *O*-pseudo-base (lactole). Hessert's method (*Ber.*, 1877, **10**, 1445) for the preparation of "hydrophthalide" [VII; $CH_2(OH){\cdot}C_6H_4{\cdot}CHO \rightleftharpoons \overline{O{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH{\cdot}OH}$], a most suitable example, yielded in our hands a product which agreed with his description, but was essentially impure phthalide. Attempts to prepare the methyl ether of (VII) from *o*-bromobenzyl methyl ether or from *o*-methoxymethylbenzoic acid failed, as the former substance did not react with magnesium, and the latter gave only phthalide even with cold thionyl chloride.

It would be easy to test the possible intermediate formation of an ester if this type of dismutation could be effected in an amino-alcohol in which the reactive group did not form part of a ring, *e.g.*, $C_5H_{10}{>}N{\cdot}CH_2{\cdot}OH \rightleftharpoons C_5H_{10}NH + CH_2O \longrightarrow H{\cdot}CO_2Me + HN{<}C_5H_{10} \longrightarrow MeN{<}C_5H_{10}$—but this was not achieved in any of several cases, including the above example.

β-(6-*Hydroxymethylpiperonyl*)*ethylmethylamine* (IV).—Hydrohydrastinine (4 g.) was boiled for 4 hours with acetic anhydride (30 c.c.), the excess of anhydride removed in a vacuum, and the residue boiled with charcoal in benzene. From the filtered and concentrated solution,

ligroin precipitated the *diacetyl* derivative as a resin, which crystallised from the same solvent in needles, m. p. 77—78° (Found : N, 4·8. $C_{15}H_{19}O_5N$ requires N, 4·8%). This was boiled with excess of 15% sodium hydroxide solution for an hour, the solution extracted with benzene, and the base precipitated as *picrate*, which formed long, deep yellow laminæ from alcohol, m. p. 195—197°, and depressed the m. p., 174—176°, of hydrohydrastinine picrate (Found : C, 46·5; H, 4·1. $C_{11}H_{15}O_3N,C_6H_3O_7N_3$ requires C, 46·6; H, 4·1%). The free base could not be obtained crystalline.

o-*Methoxymethylbenzoic Acid.*—Methyl sulphate (15 g.) was gradually added to phthalide (5 g.) dissolved in sodium hydroxide solution (70 c.c. of 10%) at 40° with stirring, which was continued for ½ hour at 70°. The cooled mixture was extracted with ether, acidified with sulphuric acid, and again extracted. The second extract was washed with sodium carbonate solution, from which the acid was precipitated by sulphuric acid. It formed needles, m. p. 116—118°, from chloroform, and depressed the m. p., 118°, of *o*-hydroxymethylbenzoic acid (Found : *M*, by titration, 167. $C_9H_{10}O_3$ requires *M*, 166). The acid dissolved sparingly in water or alcohol, readily in chloroform, benzene, or ether, and slowly reverted to phthalide on keeping.—The University, Glasgow. [*Received, July 18th*, 1934.]

The Preparation of Some Fluoro-aromatic Acids. By J. Frederick J. Dippy and Frank R. Williams.

The introduction of fluorine into the aromatic nucleus has been greatly facilitated by Balz and Schiemann's method (*Ber.*, 1927, **60**, 1186); ethyl *p*-fluorobenzoate has thus been obtained from ethyl *p*-aminobenzoate by Schiemann and Winkelmüller ("Organic Syntheses," Vol. 13, p. 52), who describe the product as a liquid. This preparation has now been repeated, and the ester obtained as a solid, crystallising at 0° from light petroleum (b. p. 40—60°) (Found : C, 64·1; H, 5·4. Calc. for $C_9H_9O_2F$: C, 64·3; H, 5·4%), m. p. 26°, in agreement with that recorded by Holleman and Slothouwer (*Chem. Zentr.*, 1911, i, 74).

An attempt to prepare *p*-fluorobenzoic acid directly from *p*-aminobenzoic acid was unsuccessful, but *o*- and *m*-fluorobenzoic acids have been obtained from the corresponding amino-acids.

o-*Fluorobenzoic Acid.*—Hydrochloric acid (60 c.c.; 10%) was added to *o*-aminobenzoic acid (15 g.) in warm water (50 c.c.), and the solution cooled and filtered. Sodium nitrite (7·5 g.) in water was slowly stirred in at 0°, followed after 5 minutes by 40% aqueous hydrofluoboric acid (24 g.; 1 mol.; excess caused poorer yields); the bulky precipitate of diazonium borofluoride which was deposited after a few minutes was washed with a little cold water, dried (10 g.), and decomposed at 125°; a sublimate and violet vapour arose, which disappeared after prolonged heating. The product was extracted with sodium carbonate solution, and the extract filtered and acidified, whereupon *o*-fluorobenzoic acid was deposited, m. p. 126·5° (1·1 g.) on recrystallisation from water (charcoal) (Kuhn and Wassermann, *Helv. Chim. Acta*, 1928, **11**, 31, give m. p. 125·5°, uncorr.).

m-*Fluorobenzoic Acid.*—By a similar procedure, 15 g. of *m*-aminobenzoic acid yielded 8·5 g. of diazonium borofluoride, which decomposed at 155° to give 0·8 g. of *m*-fluorobenzoic acid, m. p. 124° (Holleman, *Rec. trav. chim.*, 1906, **25**, 330, gives m. p. 124°).

Notwithstanding the thorough drying of both diazonium borofluorides, much tarry matter was produced in their thermal decomposition.

Similar attempts to prepare *p*-fluorophenylacetic acid and its ethyl ester failed; in each case a brown amorphous solid was produced, containing a negligible amount of diazonium borofluoride. This acid was, however, obtained as follows. Sodium cyanide (1 g.) in water (1 g.) was refluxed with *p*-fluorobenzyl chloride (2 g.) in alcohol (3 c.c.) for 3 hours, and then heated with water on the steam-bath; the oil which separated was washed, and then boiled with 10 c.c. of 10% hydrochloric acid. The p-*fluorophenylacetic acid* (*ca.* 1 g.) obtained on cooling crystallised from water (charcoal) in colourless diamond-shaped leaves, m. p. 86° (Found : C, 61·7; H, 4·55. $C_8H_7O_2F$ requires C, 62·3; H, 4·5%).

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The Vector Analysis of Dipole Moments. By FRANK R. GOSS.

IT has been supposed that the dipole moment of a sufficiently complex molecule should be capable of resolution by the method of vector analysis into two or more link moments, each associated with a special electric doublet within the molecule. The dipole moments hitherto employed for liquids, however, are entirely dependent on the assumed validity of the Clausius–Mosotti expression, which makes no allowance for the effect of anisotropy and requires modification accordingly (Goss, this vol., p. 696). As the modified formula for the liquid state has provided a method by which accurate dipole moment values can be calculated, it is of interest to re-examine the validity of the method of vector analysis. A series of compounds has been chosen, whose dipole moments can be resolved into the link moments of electric doublets separated by valency angles, already measured by other physical methods. The angles between the C–Cl bonds of the chlorinated methanes have been measured by Bewilogua (*Physikal. Z.*, 1931, **32**, 265) by *X*-ray diffraction experiments on the vapours, and the moments of methyl chloride and chloroform have been recalculated (Goss, this vol., p. 698) by using the temperature variation of the true polarisation ($_TP$) from recorded values of the observed polarisation in the liquid state (P_2). The data for methylene chloride have now been similarly recalculated from the recorded observations of Morgan and Lowry (*J. Physical Chem.*, 1930, **34**, 2385), and are given below, p being the volume polarisation of the solvent, *i.e.*, $(\epsilon - 1)/(\epsilon - 2)$.

Methylene chloride.

	In carbon tetrachloride.			In methylene chloride.				
T.	P_∞.	ϵ.	p.	P.	ϵ.	p.	$_TP$.	$_TP - {}_TK$.
263°	73·4	2·303	0·3028	46·7	10·51	0·7602	91·1	32·7
283	70·0	2·262	0·2961	46·8	9·58	0·7410	85·4	33·3
303	67·3	2·221	0·2893	46·7	8·71	0·7199	81·1	33·3

$\mu = 1{\cdot}78$ D; $P_{E+A} = 16{\cdot}7$ c.c.; $P_E = 15{\cdot}8$ c.c.

If it is assumed, with Bewilogua (*loc. cit.*), that the moment due to the electric doublet associated with the C–Cl link is the same for all the chlorinated methanes, it is possible, by using Bewilogua's valency angles, to calculate by the vector-analysis method the moments of chloroform and methylene chloride. The following table shows that the values so obtained are identical with those now recalculated by the author's method from polarisation data :

	CH_3Cl.	CH_2Cl_2.	$CHCl_3$.	CCl_4.
Valency angle (Bewilogua [1])	—	124° ± 6°	116° ± 3°	109·5°
μ, calculated (Bewilogua [1])	(1·85)	1·74 ± 0·17	1·2 ± 0·4	0
μ, accepted value (Debye [2])	1·86	1·56	1·11	0
μ, true value (Goss [3])	1·85	1·78	1·20	0

[1] *Loc. cit.* [2] "Polare Molekeln," 1929, appendix and supplements.
[3] This vol., p. 696; and this paper.

The new values may have to be modified slightly when more accurate data become available from a wider temperature range.—THE UNIVERSITY, LEEDS. [*Received, June 20th*, 1934.]

Correction to "The Synthesis of Substances analogous to Bile Acid Degradation Products. Part II." By JOHN W. BAKER.

IN the removal of hydrogen bromide from methyl α-bromo-*n*-propane-ααβ-tricarboxylate by means of pyridine (Baker, J., 1933, 811), it has now been found that the reagent evidently catalyses a three-carbon prototropic change in the Δ^α-propene ester (which must be the initial product), and the resulting unsaturated ester consists mainly of the Δ^β-ester. Hence the solid bromo-ester, m. p. 68°, obtained by the subsequent addition of hydrogen bromide, is not the β-bromo-compound, as previously supposed, but *methyl γ-bromo*-n-*propane-ααβ-tricarboxylate*. The experimental data have suggested that further study of the isomerisation of the propene ester would be of interest, and hence fuller discussion is reserved. Meanwhile, it should be noted that the new structure of the bromo-ester affects the constitutions assigned to all the compounds which were derived from it.—THE UNIVERSITY, LEEDS. [*Received, August 3rd*, 1934.]