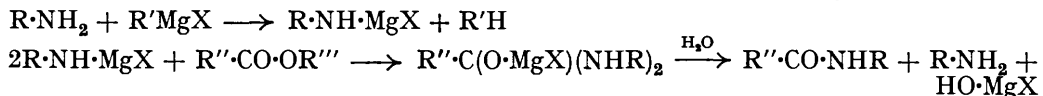


NOTES.

Identification of Acids and Esters. By DOUGLAS V. N. HARDY.

ESTERS may be directly converted into the corresponding anilides by treatment with anilino-magnesium bromide (Bodroux, *Compt. rend.*, 1904, 138, 1427; 1906, 142, 401; *Bull. Soc. chim.*, 1905, 33, 832), which is readily obtained from any simple Grignard reagent and aniline. By replacement of the latter with other aromatic amines, substituted anilides may also be obtained :



This process for identifying the acidic component of an ester is speedy, economical, and employs materials which are generally available. It is particularly valuable when used in conjunction with the separation of acid mixtures by fractional distillation of the corresponding methyl or other ester (cf. Hardy, this vol., pp. 362, 364). Even when small, the individual fractions may be readily converted into anilides in order to identify the original acids. If necessary, an identification may be confirmed by a similar preparation of a substituted anilide. The experimental procedure is as follows : Aniline (4 g.) is slowly dropped into a cold solution of ethylmagnesium bromide prepared from magnesium (1 g.), ethyl bromide (5 g.), and pure dry ether (30 c.c.). When the vigorous evolution of ethane has ceased, the ester (0.02 mol.) is added, the mixture warmed on a water-bath for 10 minutes and cooled, and dilute hydrochloric acid added to dissolve magnesium compounds and the excess of aniline. After removal of ether the anilide, which is obtained in almost calculated amount, remains as a solid crust above the aqueous solution.

Thanks are due to Professor G. T. Morgan, Director of Chemical Research, for permission to publish this note.—CHEMICAL RESEARCH LABORATORY, TEDDINGTON. [Received, February 5th, 1936.]

A Minimum Estimate of the Dipole Moments of Two Oxonium Salts. By (Mrs.) C. G. LE FÈVRE and R. J. W. LE FÈVRE.

THE pyrylium, flavylium, and xanthylium salts have been considered by Robinson to be oxonium salts with the positive charge distributed over the C—O—C atoms of the kation. Direct physical proof of this has been difficult owing to the limited solubilities of these substances in suitable solvents. The following compounds have been found to dissolve in dimethylaniline : 2-Phenyl- and 2-phenyl-3-methylbenzopyrylium perchlorates, 2-phenyl-, 6-chloro-2-phenyl-, and 6:8-dichloro-2-phenyl-benzopyrylium ferrichlorides, and 4-phenyl-2:6-di-*p*-tolylpyrylium ferrichloride. Of these, the polarisations of only the first two were successfully determined, because the others gave solutions having such high conductivities that the measurement of their dielectric constants by the resonance method was impossible.

Observations.—The symbols in the following tables have already been defined (J., 1935, 959)

2-Phenylbenzopyrylium perchlorate in dimethylaniline at 25°.

| | | | | | |
|------------------------|---------|---------|---------|---------|---------|
| $f_1 \cdot 10^6$ | 0 | 833.0 | 1399.9 | 1603.9 | 2113.1 |
| ϵ | 4.8435 | 4.9589 | 5.0397 | 5.0455 | 5.1090 |
| d | 0.95198 | 0.95280 | 0.95336 | 0.95357 | 0.95409 |
| P_1 | — | 1216.7 | 1226.8 | 1103.1 | 1091.7 |
| n | 1.55971 | — | — | — | 1.56023 |
| R_1 | — | — | — | — | 75.9 |

Whence P_1 for $f_1 = 0$ is ca. 1250, and $\mu = ca. 8$.

2-Phenyl-3-methylbenzopyrylium perchlorate in dimethylaniline at 25°.

| | | | | | |
|------------------------|---------|---------|---------|---------|---------|
| $f_1 \cdot 10^6$ | 0 | 1500.1 | 2066.9 | 2998.7 | 3802.5 |
| ϵ | 4.8435 | 5.0135 | 5.0866 | 5.1828 | 5.2651 |
| d | 0.95198 | 0.95350 | 0.95394 | 0.95500 | 0.95558 |
| P_1 | — | 1014.2 | 1042.4 | 992.7 | 970.4 |

Whence P_1 for $f_1 = 0$ is ca. 1100, and $\mu = ca. 7$.

These are probably only minimum estimates, since if it were possible to effect measurements at higher dilutions than those employed, the polarisations at infinite dilution would undoubtedly appear to be much larger. Nevertheless, the order obtained is that to be expected if an electron is transferred in a molecule through a distance of 1.5 Å. For comparison, it is recorded that Wrede (*Z. Physik*, 1927, **44**, 261), using the molecular-beam method, found $\mu = ca. 10$ for certain alkali halides, Malone and Ferguson (*J. Chem. Physics*, 1934, **2**, 99) reported 7.84 for lithium perchlorate in dioxan, and Williams (*J. Amer. Chem. Soc.*, 1928, **50**, 2350) 4.7 for silver perchlorate in benzene solution at 25°. The last determination was repeated by Kraus and Hopper (*ibid.*, 1934, **56**, 2265), using much lower concentrations, and a limiting molecular polarisation of the order 2,000 c.c. was found, corresponding to a moment considerably higher than that reported by Williams.—UNIVERSITY COLLEGE (UNIVERSITY OF LONDON). [Received, November 28th, 1935.]

Telfairic Acid. By GEORGE D. GOODALL and ROBERT D. HAWORTH.

THOMS (*Arch. Pharm.*, 1900, **233**, 48) isolated an isomeride of linoleic acid, which he named telfairic acid, from the seeds (Koeme seeds) of *Telfairia pedata*. A re-examination of this acid, rendered possible in 1930 by the kindness of Dr. R. S. Morrell, to whom our thanks are due for a supply of seeds, has shown that telfairic acid is identical with linoleic acid.

The kernels of the seeds on extraction with light petroleum (b. p. 40–60°) gave a 60% yield of a pale yellow oil (iodine value, 89.0; saponification value, 192.5). This oil (50 g.) was saponified with 10% methyl-alcoholic potassium hydroxide (200 c.c.), and the acids, liberated with 10% sulphuric acid, were isolated with ether. The unsaturated acids (35 g.), separated by the lead salt-ether method and subjected to Rollett's bromination process (*Z. physiol. Chem.*, 1909, **62**, 410), yielded tetrabromostearic acid (15 g.), m. p. 114° after crystallisation from light petroleum (b. p. 60–80°), which gave no depression in m. p. with an authentic specimen. Methyl tetrabromostearate, m. p. 58°, and tetrahydroxystearic acid, m. p. 174°, were prepared and identified by comparison with authentic specimens obtained from poppy-seed oil.—UNIVERSITY OF DURHAM, ARMSTRONG COLLEGE, NEWCASTLE-UPON-TYNE. [Received, January 21st, 1936.]

Velocity of the Reaction between *o*-Nitrobenzyl Bromide and Pyridine. Addendum to Mechanism of Aromatic Side-chain Reactions, etc. Part IV. By JOHN W. BAKER.

It was suggested by Bennett (*Chem. and Ind.*, 1935, **54**, 1008) that the increased velocity of reaction of 2 : 4-dinitrobenzyl bromide with pyridine (in dry acetone) (J., 1935, 1840) might be due to the electron repulsion by the negatively charged oxygen of the *o*-nitro-group acting directly, through the medium, on the side-chain bromine. *o*-Nitrobenzyl bromide has now been investigated, and the velocity is compared below with those observed for benzyl bromide and its *p*-nitro- and 2 : 4-dinitro-derivative.

Interaction of $R \cdot C_6H_4 \cdot CH_2Br$ and Pyridine in Dry Acetone at 40° (0.025M).

| | R = | H. | <i>o</i> -NO ₂ . | <i>p</i> -NO ₂ . | 2 : 4-(NO ₂) ₂ . |
|--|-----|-------|-----------------------------|-----------------------------|---|
| $k \times 10^4$, sec. ⁻¹ | | 4.817 | 5.47 | 4.333 | 8.960 |

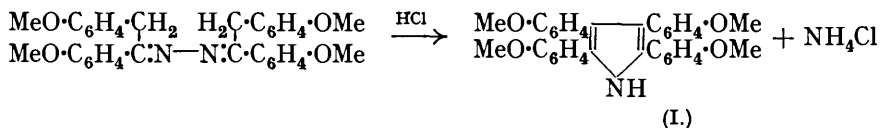
The slight acceleration produced by the *o*-nitro-substituent indicates that a small direct effect in the above sense must be recognised. Since a *p*-nitro-group has a small retarding influence, the much greater velocity increase observed in the 2 : 4-dinitro-compound cannot, however, be

accounted for on this basis. As suggested (*loc. cit.*), the latter increase must result from the greatly increased electron attraction due to the presence of two nitro-groups appropriately oriented to the side chain.

The value of $k \times 10^4$ for the *o*-compound at 20° is 1.33, whence E (Arrhenius) is 12,870 cal., a value closely similar to those obtained for other members of the series.—THE UNIVERSITY, LEEDS. [Received, January 25th, 1936.]

Tetra-anisylpyrrole. By F. E. KING and G. D. PATERSON.

FOR the purposes of an investigation requiring an easily accessible hydroxyaryl derivative of pyrrole, the method introduced by G. M. and R. Robinson (J., 1918, 113, 639) for the preparation of tetraphenylpyrrole was extended to the synthesis of the *tetra-anisyl* compound (I). Cyclisation of the necessary intermediate, *viz.*, the *azine* of deoxyanisoin, occurred as follows:



When demethylated, the pyrrole (I) yielded tetra-*p*-hydroxyphenylpyrrole, which was characterised as an *acetate*. The free hydroxy-compound is readily attacked by air and all the usual oxidising agents, but no crystalline products were isolable.

Anisyl p-Methoxyphenyl Ketazine.—The requisite ketone was prepared by reducing anisoin with hydrochloric acid and stannous chloride in alcohol (Apitzsch and Metzger, *Ber.*, 1904, 37, 1676), a process which renders it more readily available than deoxybenzoin (see Apitzsch, *ibid.*, 1907, 40, 1803). When heated with phenylhydrazine at 120° until evolution of steam had ceased, it gave a *phenylhydrazone*, which slowly crystallised from a little methyl alcohol in needles, m. p. 79°, that subsequently darkened (Found: C, 76.5; H, 6.5. $\text{C}_{22}\text{H}_{22}\text{O}_2\text{N}_2$ requires C, 76.3; H, 6.3%).

Following the preparation of phenyl benzyl ketazine (G. M. and R. Robinson, *loc. cit.*), deoxyanisoin (4 g.) in alcohol (60 c.c.) was boiled under reflux with a solution of hydrazine sulphate (0.8 g.) and sodium acetate (5 g.) in water (40 c.c.). Precipitation of the *azine*, which began after 1 hour, was complete in 5 hours; the solution was then cooled, and the product (3.6 g.) collected. Crystallisation from large volumes of ethyl acetate gave orange-yellow needles, m. p. 155° (Found: N, 5.3. $\text{C}_{33}\text{H}_{32}\text{O}_4\text{N}_2$ requires N, 5.5%).

Tetra-anisylpyrrole.—Over the surface of the molten ketazine (15 g.), heated in an oil-bath at 170° and periodically shaken, a slow stream of hydrogen chloride was passed for 1 hour. The resulting *tetra-anisylpyrrole* (11 g.) was isolated by extracting the product with boiling acetic acid and filtering it from ammonium chloride. It was readily soluble in hot alcohol and ethyl acetate, but was best crystallised from acetic acid; although the solutions were usually green, by washing with a little methyl alcohol, colourless needles, m. p. 184°, were obtained (Found: C, 78.3; H, 5.9. $\text{C}_{32}\text{H}_{26}\text{O}_4\text{N}$ requires C, 78.2; H, 5.9%). The pyrrole dissolved in concentrated sulphuric acid to a red-brown solution with a dark green reflex, the colour eventually becoming olive-green.

Tetra-p-hydroxyphenylpyrrole.—When redistilled hydriodic acid (20 c.c.) was refluxed (oil-bath at 140°) with tetra-anisylpyrrole (3 g.) in a carbon dioxide atmosphere for 1½ hours, smooth and complete demethylation occurred. The insoluble product (2.5 g.) was collected, washed with water containing sulphur dioxide, and freed from iodine by shaking a solution in ethyl acetate with aqueous thiosulphate. By the addition of light petroleum to the dried solution, tetra-*p*-hydroxyphenylpyrrole was precipitated in minute colourless needles, m. p. 290° with previous decomposition, but owing to fairly ready atmospheric oxidation satisfactory analytical figures were unobtainable. It was therefore converted into the *acetyl* derivative by heating with anhydrous sodium acetate and excess of acetic anhydride under reflux (oil-bath at 160°) for 2 hours and isolated by pouring the solution into water. The product, which was insoluble in alcohol, crystallised from ethyl acetate in rosettes of colourless needles, m. p. 195° after softening at 150—160°. Drying in a vacuum at 130°, however, led to a slight loss in weight, and fusion then occurred at 195° without previous softening (Found, with dried material: C, 71.4; H, 4.9. $\text{C}_{36}\text{H}_{26}\text{O}_8\text{N}$ requires C, 71.6; H, 4.8%).

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