NOTES.

The Determination of Hypophosphites by Potassium Permanganate. By JAMES R. POUND.

THE usual methods for the determination of hypophosphites suffer from various disadvantages. Oxidation of the hypophosphite is slow both by hypobromite and by bromate–bromide in slightly acid solution, there is danger of loss of bromine, and the solutions must be standardised frequently and under the same conditions as the test; potassium permanganate may be used instead of the bromate; and all three methods are completed by addition of potassium iodide and titration by sodium thiosulphate. In our experiments the hypobromite method tends to give higher results than the other two, but, carefully used, all three methods agree with the well-known mercuric chloride method, in which the resulting mercurous chloride is weighed, the last method requires about 4 hours' treatment on the water-bath or a longer time in the cold. Oxidation of hypophosphite to phosphate by repeated evaporation with nitric acid is slow but is accurate if the phosphate is subsequently weighed as magnesium ammonium phosphate hexahydrate.

Oxidation of hypophosphite by potassium permanganate in neutral or acid solution is slow, and direct titration is impossible. Even after several days' standing, oxidation in acid solution does not exceed 96%; however, a *small* amount of potassium bromide has a catalytic effect, possibly due to the formation of free bromine, and oxidation is complete in a few hours at room temperature. To 5 ml. of (approx.) N/10-hypophosphite, in a glass-stoppered flask, there are added (in order) 10 ml. of N/10-permanganate, 0·5—1 ml. of 10N-sulphuric acid, and 0·1 ml. of M-potassium bromide; after 2—3 hours' standing, 10 ml. of N/10-ferrous sulphate (freshly standardised) are added and the flask is immediately closed and shaken; the brown oxides of manganese are soon dissolved and the small amount of bromine vapour is fixed; then the excess of ferrous sulphate is titrated by the permanganate solution. The errors involved in thiosulphate–iodine work are certainly not less than in this process. As the potassium bromide and bromine concentrations in the solution are always low, there is little bromine in the flask at any time and therefore little tendency to loss of bromine; however, the stoppers of the flasks should be lightly vaselined. According to the equation for this action 10 ml. of N/10-potassium permanganate require 0·2 ml. of 10N-acid and 1 ml. of M-potassium bromide, so the smaller volume of bromide used indicates its catalytic effect. Excess of acid should be avoided, as decomposition of the potassium permanganate and loss of oxygen may then occur, especially in the presence of the manganese oxides produced.

In one series of experiments the above method gave the normality of the hypophosphite solution as 0·1172 (the same value being found by the phosphate method), and the error was ± 1·4% (six determinations over periods of 2—70 hours); in another series of seven experiments, with 3 hours' to 3 days' standing, the error was ± 1%. It is difficult to obtain this accuracy with any of the other volumetric methods, even working with careful " blanks ".

Preparation of Some p-*Alkyl-substituted Benzoic Acids.* By A. ZAKI and H. FAHIM.

A SOLUTION of the *n*-alkylbenzene (prepared from bromobenzene by the Fittig reaction) and acetyl chloride in light petroleum (b. p. 60—70°) at 0° was treated with aluminium chloride, stirred for 1 hour at room temperature, heated on the water-bath for ¼ hour, and decomposed by ice-cold water. Oxidation of the resulting

p-alkylphenyl methyl ketone to the acid was effected by alkaline sodium hypobromite solution (sodium hydroxide, 25 g.; water, 70 c.c.; ice, 60 g.; bromine, 10 c.c.). The yields of the acids were nearly quantitative.

On oxidation with potassium permanganate, the *p*-alkylbenzoic acids gave terephthalic acid (methyl ester, m. p. 140°).

p-n-Butylphenyl methyl ketone, obtained in 55% yield by the action of acetyl chloride (32 g.) and aluminium chloride (32 g.) on *n*-butylbenzene (Braun and Deutsch, *Ber.*, 1912, **45**, 2181) (20 g.) in light petroleum (50 c.c.), was a slightly yellow liquid, b. p. 268—270°/766 mm. The *oxime* separated from dilute methyl alcohol in white crystals, m. p. 43—44° (Found : C, 75·5; H, 8·9; N, 7·3. $C_{12}H_{17}ON$ requires C, 75·4; H, 8·9; N, 7·3%), the *semicarbazone* from alcohol in white star-like crystals, m. p. 182—183° (Found : C, 67·1; H, 8·2; N, 18·05. $C_{13}H_{19}ON_3$ requires C, 66·95; H, 8·15; N, 18·0%), and the p-*nitrophenylhydrazone* from alcohol in tiny orange-yellow crystals, m. p. 151—152° (Found : C, 69·8; H, 7·1; N, 13·9. $C_{18}H_{21}O_2N_3$ requires C, 69·45; H, 6·75; N, 13·5%).

p-n-*Butylbenzoic acid* was obtained by shaking *p-n*-butylphenyl methyl ketone (3·5 g.) with warm sodium hypobromite solution (87 c.c.) for ½ hour. The product was diluted with water, and the acid precipitated with sulphur dioxide. It crystallised from dilute alcohol in white needles, m. p. 101° (Found : C, 74·1; H, 7·8. $C_{11}H_{14}O_2$ requires C, 74·15; H, 7·85%).

p-n-Amylphenyl methyl ketone, obtained in 50% yield by the action of acetyl chloride (20 g.) and aluminium chloride (20 g.) on *n*-amylbenzene (Schramm, *Annalen*, 1883, **218**, 389) (15 g.) in light petroleum (50 c.c.), was a yellowish oil, b. p. 145°/11 mm. The *oxime* separated from dilute alcohol in tiny white needles, m. p. 62—63° (Found : C, 75·7; H, 9·2; N, 6·7. $C_{13}H_{19}ON$ requires C, 76·1; H, 9·3; N, 6·8%), the *semicarbazone* from alcohol in tiny white needles, m. p. 180—181° (Found : C, 68·0; H, 8·3; N, 17·3. $C_{14}H_{21}ON_3$ requires C, 68·0; H, 8·5; N, 17·0%), and the p-*nitrophenylhydrazone* from alcohol in orange needles, m. p. 149—150° (Found : C, 70·0; H, 7·0; N, 13·0. $C_{19}H_{23}O_2N_3$ requires C, 70·15; H, 7·1; N, 12·9%).

p-n-*Amylbenzoic acid*, obtained as above by shaking *p-n*-amylphenyl methyl ketone (4 g.) with sodium hypo-bromite solution (100 c.c.) for ½ hour, crystallised from dilute alcohol in white scales, m. p. 88° (Found : C, 74·95; H, 8·3. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%).

p-n-Hexylphenyl methyl ketone, obtained in 68% yield by the action of acetyl chloride (50 g.) and aluminium chloride (50 g.) on *n*-hexylbenzene (Braun and Deutsch, *loc. cit.*) (40 g.) in light petroleum (100 c.c.), was a· yellowish oil, b. p. 158°/12 mm. The *oxime* separated from dilute alcohol in white crystals, m. p. 45—46° (Found : C, 76·7; H, 9·5; N, 6·3. $C_{14}H_{21}ON$ requires C, 76·7; H, 9·6; N, 6·4%), the *semicarbazone* from alcohol in white crystals, m. p. 178° (Found : C, 69·1; H, 9·0; N, 16·2. $C_{15}H_{23}ON_3$ requires C, 69·0; H, 8·8; N, 16·1%), and the p-*nitrophenylhydrazone* from alcohol in orange feathery crystals, m. p. 135° (Found : C, 70·7; H, 7·4; N, 12·3. $C_{20}H_{25}O_2N_3$ requires C, 70·8; H, 7·4; N, 12·4%).

p-n-*Hexylbenzoic acid*, obtained by shaking *p-n*-hexylphenyl methyl ketone (4 g.) with sodium hypobromite solution (100 c.c.) for 1½ hours, separated from dilute alcohol in white crystals, m. p. 97° (Found : C, 75·9; H, 8·8. $C_{13}H_{18}O_2$ requires C, 75·7; H, 8·7%).

p-n-Heptylphenyl methyl ketone, obtained in 69% yield by the action of acetyl chloride (28 g.) and aluminium chloride (28 g.) on *n*-heptylbenzene (Sabatier and Mailhe, *Compt. rend.*, 1914, **158**, 834) (20 g.) in light petroleum (50 g.), was a yellowish oil which darkened on keeping, b. p. 160—163°/7 mm. The *oxime* separated from dilute alcohol in white crystals, m. p. 41—42° (Found : C, 77·2; H, 10·0; N, 5·8. $C_{15}H_{23}ON$ requires C, 77·25; H, 9·9; N, 6·0%), the *semicarbazone* from alcohol in white crystals, m. p. 176° (Found : C, 70·5; H, 9·1; N, 15·15. $C_{16}H_{25}ON_3$ requires C, 70·5; H, 8·9; N, 14·9%), and the p-*nitrophenylhydrazone* from alcohol in tiny orange needles, m. p. 140° (Found : C, 71·4; H, 7·6; N, 12·0. $C_{21}H_{27}O_2N_3$ requires C, 71·4; H, 7·65; N, 11·9%).

p-n-*Heptylbenzoic acid*, obtained by shaking *p-n*-heptylphenyl methyl ketone (15 g.) with sodium hypo-bromite solution (750 c.c.) for 3 hours, separated from dilute alcohol in white crystals, m. p. 101·5° (Found : C, 76·3; H, 9·1. $C_{14}H_{20}O_2$ requires C, 76·4; H, 9·1%).

p-n-Octylphenyl methyl ketone, obtained in 61% yield by the action of acetyl chloride (62 g.) and aluminium chloride (62 g.) on *n*-octylbenzene (von Schweinitz, *Ber.*, 1886, **19**, 641) (40 g.) in light petroleum (100 c.c.), was a yellowish oil, b. p. 165—168°/4 mm. (cf. Lipinski, *Ber.*, 1898, **31**, 938). The oxime separated from dilute alcohol in white crystals, m. p. 52—53° (Lipinski, *loc. cit.*, gives m. p. 43°) (Found : C, 77·7; H, 10·2; N, 5·9. Calc. for $C_{16}H_{25}ON$: C, 77·7; H, 10·1; N, 5·7%), the *semicarbazone* from alcohol in white needles, m. p. 174° (Found : C, 70·6; H, 9·3; N, 14·5. $C_{17}H_{27}ON_3$ requires C, 70·6; H, 9·3; N, 14·5%), and the p-*nitrophenylhydrazone* from alcohol in yellow needles, m. p. 127° (Found : C, 71·8; H, 8·0; N, 11·7. $C_{22}H_{29}O_2N_3$ requires C, 71·9; H, 7·9; N, 11·4%).

p-n-Octylbenzoic acid, prepared by shaking *p-n*-octylphenyl methyl ketone (8 g.) with sodium hypobromite solution (750 c.c.) for 2 hours, separated from dilute alcohol in white crystals, m. p. 99—100° (Beran, *Ber.*, 1885, **18**, 139, gives m. p. 139°) (Found : C, 76·8; H, 9·4. Calc. for $C_{15}H_{22}O_2$: C, 76·9; H, 9·4%).—FOUAD I UNIVERSITY, CAIRO, EGYPT. [*Received, October 24th*, 1941.]