

NOTES.

A Reaction Adaptable to the Volumetric Estimation of Silver Chloride. By G. A. D. HASLEWOOD.

WHEN glacial acetic acid (4 c.c.) is added to a solution of silver chloride (2.5 mg.) in 0.2N-sodium thiosulphate (1 c.c.), there is formed an amorphous precipitate which rapidly crystallises in fine needles. The dried precipitate contains water [Found: Ag, 35.0; Na, 12.2; S₂O₃ (determined by treatment with iodine and back-titration with 0.005N-sodium thiosulphate), 48.0. Calc. for Na₅Ag₅(S₂O₃)₄.2H₂O (see Bassett and Lemon, J., 1933, 1423): Ag, 35.1; Na, 12.4; S₂O₃, 48.5%].

The mother-liquor contained a very small amount (approx. 0.3 mg./100 c.c. as AgCl) of silver. The crystalline precipitate (washed with glacial acetic acid) from known amounts of silver chloride gave good recovery figures as found by dissolution in 0.01N-iodine and back-titration with 0.005N-sodium thiosulphate. The reaction should be applicable to the volumetric estimation of silver chloride, alone or in mixtures.

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The Electric Dipole Moments of Nitrophenols. By H. O. JENKINS.

THIS note records a determination of the dipole moment of *o*-nitrophenol in benzene at 25°, with some remarks on the moments of substituted phenols in general. The usual procedure was used in the experimental work. In the following table, f_2 is the mol.-fraction of solute, ϵ_{25° the dielectric constant at 25°, $d_4^{25^\circ}$ the density, and P_2 the polarisation of nitrophenol.

f_2	$d_4^{25^\circ}$	ϵ_{25°	P_2	f_2	$d_4^{25^\circ}$	ϵ_{25°	P_2
0.00000	0.8736	2.2727	—	0.00656	0.8771	2.3687	237.9
0.00245	0.8750	2.3100	242.6	0.01023	0.8791	2.4194	232.8
0.00382	0.8756	2.3304	244.6	0.01476	0.8814	2.4830	229.6
0.00536	0.8766	2.3505	235.5	0.02910	0.8888	2.6839	220.9

$$\infty P_2 = 239 \text{ c.c.}; R = 33 \text{ c.c.}; \mu = 3.11 \text{ D.}$$

Only one previous determination is on record (Williams and Fogelberg, *J. Amer. Chem. Soc.*, 1930, **52**, 1356), viz., $\infty P_2 = 235 \text{ c.c.}$, which is in excellent agreement with the present one.

The electric moments of the substituted phenols increase in the direction $o < m < p$, which is contrary to expectation. This redetermination of the moment of the *o*-compound was made primarily to check the low value. Now Pauling (*ibid.*, 1936, **58**, 94) has drawn attention to the importance of double C=O structures in phenol and its derivatives as a means of interpreting the infra-red absorption. In the nitrophenols, resonance with structures having C=O and C=N bonds will also explain the approximate equality of the ionisation constants of the *o*- and *p*-compounds and the lower value of the *m*-compound. Also, it is clear that resonance with structures of this type participating will also explain the abnormally high electric moments of *p*-phenols such as *p*-nitro- and *p*-chloro-phenol (cf. Marsden and Sutton, this vol., p. 599). In the case of *o*-nitrophenol, resonance is also possible even if chelation occurs through hydrogen-bond formation, but on account of the uncertainty in the values of group moments and the relative contributions of the different structures, a calculation of the moment is difficult. There remains the possibility that the dipole-moment determination is seriously affected by the

solvent and possibly by association. Bury and Jenkins (J., 1934, 688) have shown that *o*-nitrophenol in benzene is not an ideal solute.

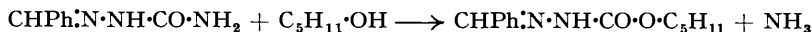
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The Rapid Detection of Silver Halide in Presence of Silver Cyanide. By ROBERT E. D. CLARK.

ZAPPI and MANINI (*Anal. Asoc. Quim. Argentina*, 1934, **22**, 21) have replaced the Lassaigne (*Compt. rend.*, 1843, **16**, 387) test for cyanides by the addition of mercurous nitrate to the precipitate of silver halide and/or cyanide obtained by the addition of silver nitrate and nitric acid to the solution to be tested, the solid turning black if cyanide is present. It has now been observed that, on addition of excess of mercurous nitrate, the black precipitate at once dissolves in the cold, giving a clear colourless solution, whereas silver halides, if present, remain undissolved. Thus halides may be detected immediately in presence of cyanides by addition of nitric acid, silver nitrate, and mercurous nitrate (5%); after the black coloration has disappeared, a permanent precipitate indicates the presence of halide.—UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [Received, May 9th, 1936.]

The Reaction of Semicarbazones with Alcohols. By E. W. McCLELLAND and C. E. SALKELD.

WHEN benzaldehydesemicarbazone is heated with *isoamyl* alcohol, ammonia is eliminated and *isoamyl* benzylidenehydrazinecarboxylate formed :



The reaction, which is the reverse of the action of ammonia on an ester, appears to be of a general nature, as the semicarbazones of acetophenone, *o*-hydroxybenzaldehyde, piperonal and *o*-nitrobenzaldehyde give the corresponding *isoamyl* carboxylates. Since these substances are highly crystalline and have much lower and sharper melting points than the corresponding semicarbazones, they may be of value in characterising aldehydes and ketones which give sparingly soluble semicarbazones of indefinite melting point. The reaction described enables an aldehyde or ketone to be linked to an alcohol; hence the possibility of its use in resolution is evident.

The *isoamyl* carboxylates were prepared by the following general method. The semicarbazone (5 g.) was refluxed with *isoamyl* alcohol (150 c.c.) until ammonia was no longer evolved (11–36 hours). The solution was cooled and filtered, and the bulk of the *isoamyl* alcohol removed by distillation from an oil-bath at 170°. The product was finally freed from *isoamyl* alcohol by heating in an open dish at 100° and was purified by crystallisation. The rate of the reaction varies considerably with different semicarbazones; almost quantitative yields were obtained except with piperonal- and *o*-nitrobenzaldehyde-semicarbazones, where some unchanged semicarbazone was recovered even after prolonged refluxing.

isoAmyl benzylidenehydrazinecarboxylate, from benzaldehydesemicarbazone (11 hours' refluxing), crystallised from alcohol in white plates, m. p. 103° (Found : C, 66.6; H, 7.6; N, 12.6. $\text{C}_{13}\text{H}_{18}\text{O}_2\text{N}_2$ requires C, 66.6; H, 7.7; N, 12.0%).

isoAmyl α -phenylethylidenehydrazinecarboxylate, from acetophenonesemicarbazone (11 hours' refluxing), crystallised from light petroleum in white plates, m. p. 74° (Found : N, 11.6. $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N}_2$ requires N, 11.3%).

isoAmyl o-hydroxybenzylidenehydrazinecarboxylate, from *o*-hydroxybenzaldehydesemicarbazone (13 hours' refluxing), crystallised from alcohol in white plates, m. p. 140° (Found : C, 62.2; H, 6.9; N, 11.6. $\text{C}_{13}\text{H}_{18}\text{O}_3\text{N}_2$ requires C, 62.4; H, 7.2; N, 11.2%).

isoAmyl Piperonylidenehydrazinecarboxylate.—After piperonalsemicarbazone had been refluxed for 36 hours with *isoamyl* alcohol, ammonia was still being evolved. The solution was cooled, and the unchanged semicarbazone (1.1 g.) filtered off. The filtrate gave the required *isoamyl carboxylate*, which crystallised from benzene–ligroin in white needles, m. p. 83° (Found : N, 10.4. $\text{C}_{14}\text{H}_{18}\text{O}_4\text{N}_2$ requires N, 10.1%).

isoAmyl o-Nitrobenzylidenehydrazinecarboxylate.—*o*-Nitrobenzaldehydesemicarbazone and *isoamyl* alcohol, refluxed for 36 hours, gave unchanged semicarbazone (1.8 g.) and the required compound, which crystallised from benzene–ligroin as a buff-coloured micro-crystalline powder, m. p. 95° [Found : C, 55.4; H, 6.0; N, 15.7 (Schoeller). $\text{C}_{13}\text{H}_{17}\text{O}_4\text{N}_3$ requires C, 55.9; H, 6.1; N, 15.1%].—KING'S COLLEGE, LONDON. [Received, April 27th, 1936.]