

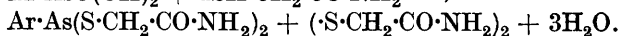
CXXXIII.—*Thiolacetamide as a Reagent for
identifying Arsinic Acids.*

By HARRY JAMES BARBER.

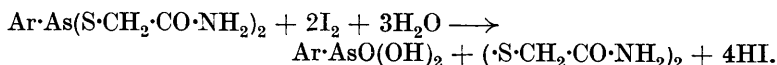
A DIFFICULTY frequently encountered in the chemistry of organic arsenic derivatives is that of establishing the identity of a product. It is the exception rather than the rule for an arsenic acid to have a true melting point. The comparison of the calcium, barium, and magnesium salts under standard conditions (King and Murch, J., 1924, **125**, 2601) is a useful but by no means decisive guide.

Arsinic acids are reduced by thiol compounds (see preceding paper) and it is shown here that the di(carbamylmethyl) arylthioarsinites which can be prepared by that method have, in general, definite melting points which are depressed by admixture with other di(carbamylmethyl) arylthioarsinites. It is suggested that these well-defined crystalline compounds may be a valuable additional means of identifying and characterising arsenic acids. The preparation is very simple and can be carried out with small amounts of material; moreover, the arsenic acid can be recovered by mild oxidation of the thioarsinite. The conditions for the preparation are varied somewhat according to the nature of the arsenic acid. In the normal case the arsenic acid is added to a hot aqueous solution of thiolacetamide (4 mols.); the arsenic acid dissolves, and the

thioarsinite crystallises on cooling. The reaction is represented by the equation $\text{Ar}\cdot\text{AsO}(\text{OH})_2 + 4\text{SH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2 \longrightarrow$



With sparingly soluble arsenic acids it is more convenient to use a solution of the sodium salt of the arsenic acid, and with nitro-compounds the reaction should be carried out in the cold to minimise the possibility of reduction of the nitro-group by the thiol compound. The thioarsinites can be recrystallised from hot water or from aqueous acetic acid and can be estimated rapidly by direct titration with standard iodine solution.



EXPERIMENTAL.

The following table, which gives the data for a number of typical arsenic acids, serves as an indication of the use of the method. The melting points are uncorrected figures. In the case of the higher-melting substances it is more satisfactory to heat the melting-point bath fairly rapidly so as to obtain sharper melting points. The molecular weights recorded were determined by dissolving 0.2 g. of thioarsinite in 50 c.c. of warm 2*N*-acetic acid, adding 50 c.c. of water, and titrating the warm solution (usually at about 40°) with *N*/10-iodine, with starch as indicator.

| Arsenic acid. | Thioarsinite. | | Molecular wt. | |
|--|---------------|---|---------------|--------|
| | M. p. | Formula. | Calc. | Found. |
| <i>a</i> Phenyl | 129—130° | $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}_2\text{S}_2\text{As}$ | 332 | 331 |
| <i>b</i> 2-Aminophenyl | 140 | $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_3\text{S}_2\text{As}$ | 347 | 351 |
| <i>c</i> 4-Aminophenyl | 145 | $\text{C}_{10}\text{H}_{14}\text{O}_2\text{N}_3\text{S}_2\text{As}$ | 347 | 347 |
| <i>d</i> 2-Hydroxyphenyl | 161—163 | $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_2\text{S}_2\text{As}$ | 348 | 348 |
| <i>e</i> 4-Hydroxyphenyl | 160—162 | $\text{C}_{10}\text{H}_{13}\text{O}_3\text{N}_2\text{S}_2\text{As}$ | 348 | 351 |
| <i>f</i> 3-Amino-4-hydroxy-phenyl | 132—133 | $\text{C}_{10}\text{H}_{14}\text{O}_3\text{N}_3\text{S}_2\text{As}$ | 363 | 363 |
| <i>g</i> 3-Acetamido-4-hydroxy-phenyl | 176 | $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_3\text{S}_2\text{As}$ | 405 | 405 |
| <i>h</i> 5-Acetamido-2-hydroxy-phenyl | 188 | $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_3\text{S}_2\text{As}$ | 405 | 408 |
| <i>i</i> 3-Amino-4-methylamino-phenyl | 141—143 | $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}_4\text{S}_2\text{As}$ | 382 | 376 |
| <i>j</i> 4-Chlorophenyl | 134—136 | $\text{C}_{10}\text{H}_{12}\text{O}_2\text{N}_2\text{ClS}_2\text{As}$ | 366.5 | 371 |
| <i>k</i> 4-Chloro-3-nitrophenyl | 142—143 | $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}_3\text{ClS}_2\text{As}$ | 411.5 | 418 |
| <i>l</i> 3 : 5-Diamino-4-hydroxy-phenyl | 159—161 | $\text{C}_{10}\text{H}_{15}\text{O}_3\text{N}_4\text{S}_2\text{As}$ | 378 | 381 |
| <i>m</i> 2 : 6-Diacetamidophen-oxycetic acid 4-arsinic acid | 157 | $\text{C}_{16}\text{H}_{21}\text{O}_7\text{N}_4\text{S}_2\text{As}$ | 520 | 532 |
| <i>n</i> 8-Acetamido-3-hydroxy-1 : 4-benzisooxazine-6-arsinic acid | 233—235 | $\text{C}_{14}\text{H}_{17}\text{O}_5\text{N}_4\text{S}_2\text{As}$ | 460 | 464 |

Mixtures of the preceding di(carbamylmethyl) arylthioarsinites

melt as follows: *b* and *c*, 124°; *d* and *e*, 142°; *a* and *f*, 110—115°; *g* and *h*, 150°; *c* and *f*, 125°.

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