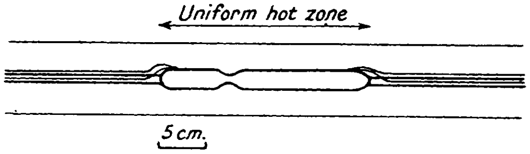
NOTES.

The Preparation of Pure Arsenic. G. A. GEACH, R. A. JEFFERY, and R. J. SHELTON.

THE best recorded method for the preparation of pure arsenic is the reduction of pure antimony-free ammonium arsenate in ammonia (A. de Passile, *Compt. rend.*, 1934, **198**, 178). It is difficult by this process to obtain the volatile metal completely free from the more volatile arsenious oxide. We have found that such oxide-free arsenic can be obtained by reducing pure arsenious oxide with zirconium in a sealed tube. The reaction is violently exothermic, but can be moderated if the zirconium is mixed with some inert material, and is controlled by the rate at which arsenious oxide is sublimed from a cooler part of the tube into the reduction zone.

Experimental.—Purchased zirconium powder contains quantities of gases which are removed by heating the powder at 600° in a vacuum furnace until most of the gas is given off (this is judged by the pressure in the continuously pumped furnace), and then at 1000° for one hour. The powder is then mixed with 15% (by weight) of zirconium oxide, and the mixture fritted to 1100° in a vacuum ($<10^{-3}$ mm.). Sufficient of this material, in the form of small lumps, to contain 20 g. of zirconium is placed at one end of a transparent silica reaction tube of the form shown in the figure; the constriction retains the zirconium in the shorter part of the tube Pure arsenious oxide is pelleted and 93·5% of the theoretical quantity placed at the other end of the tube, which is then evacuated roughly (10^{-2} mm.) and sealed. The overall length of this tube is the same as the uniform-temperature zone of the furnace to be used. Thermocouples are attached to each end of the reaction tube which is held so that it can be moved axially into the furnace whilst carefully separated from the furnace walls. The temperature of the zirconium end is gradually raised (300° per hour) to 930—950° while the end containing arsenious oxide remains cool (about 40°). The tube is then slowly advanced into the hot zone of the furnace so that the cooler end heats to 950° in 90 minutes; during this time the reaction takes place. The end originally containing the zirconium is then pushed slightly out of the hot zone so that the part of the tube in which the arsenious oxide had been placed is about 50° hotter than any other part for ten minutes. The tube is next returned to its initial position and is then allowed to cool with the furnace. With this arrangement the absolutely clean end of the tube which originally contained the arsenious oxide is always its coolest part and the volatile arsenic condenses there as a crystalline mass. When the tube is quite cold it may be cut open and the metal removed; it should, however, be stored in a sealed tube. The yield is 90% (based on the arsenious oxide).



Attempted reduction with aluminium, calcium, and magnesium. Although it was doubtful on theoretical grounds whether these metals might be suitable reducing agents, information was vague and small-scale (1 g.) experiments were carried out. Aluminium: the reduction occurred at 950°; the yield was only 16%. The tube became filled with voluminous aluminium oxide and there appeared to be some attack of the silica tube. Calcium: the reaction occurred at 1050°; the yield was 37%. *X*-Ray diffraction examination of the residue of the tube showed calcium arsenite to be present. Magnesium: reduction occurred at 1050°, but at this temperature the magnesium metal is itself sufficiently volatile to contaminate the product.

The estimation of arsenious oxide in arsenic metal. Roughly 1 g. of the metal was digested for 15 minutes in 100 ml. of warm (*ca.* 60°) 0·1M-sodium carbonate. This was filtered, and the filtrate acidified with hydrochloric acid and titrated with 0·02N-potassium permanganate.

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Hydrolysis Products of p-*Bromobenzylthiuronium Bromide.* By H. M. E. CARDWELL.

DAVEY and SHASKY (*J. Amer. Chem. Soc.*, 1941, **63**, 3526) have reported that *p*-bromobenzylthiuronium bromide is to be preferred to benzylthiuronium bromide as a reagent for the characterisation of carboxylic acids, as it is less readily hydrolysed and hence may be used in slightly alkaline aqueous solutions. This statement has been confirmed, but in the example described below the two possible hydrolysis products, S-p-*bromobenzyl*iso*thiourea* and p-*bromotoluene-ω-thiol* were also isolated. They are described here because they may be encountered by other workers and, as they are solids, may possibly be confused with thiuronium salts, particularly where the reagent is being used to facilitate the fractionation of mixtures of carboxylic acids.

Experimental.—In the preparation of the *p*-bromobenzylthiuronium salt of methyl 2-keto-1-methyl-3-carboxymethyl-4-(2-methylthioethyl)*cyclo*hex-3-ene-1-carboxylate (Cardwell, *J.*, 1949, **715**) the crude acid was dissolved in a slight excess of 2N-sodium hydroxide and added to an excess of *p*-bromobenzylthiuronium bromide in hot ethanol. On dilution with water and cooling the salt separated and was collected by filtration. The aqueous alcoholic mother liquor on further dilutions with water gave two crops of solid. The first consisted of S-p-*bromobenzyl*iso*thiourea* which crystallised from *iso*propanol in colourless, flattened, rods, melting partially at 125—127° and completely at 199° (Found : C, 39·2; H, 3·3; S, 13·4. $C_4H_9N_2BrS$ requires C, 39·2; H, 3·7; S, 13·1%). The second crop consisted of *p-bromotoluene-ω-thiol* which crystallised from aqueous methanol in slender rods, m. p. 80—81·5° (Found : C, 41·7; H, 3·6; N, nil; S, 15·8. C_7H_7BrS requires C, 41·4; H, 3·4; N, nil; S, 15·8%). (Analyses are by Mr. A. Bennett.)—CHEMICAL DIVISION, WELLCOME RESEARCH LABORATORIES, BECKENHAM, KENT. [*Received, January 20th,* 1950.]

Preparation of Ethynylcarbinols from the Bisulphite Compounds of Aldehydes and Ketones.

By J. CYMERMAN and K. J. WILKS.

ONLY one reference to the preparation of diethynylglycols is known; Milas, Brown, and Phillips (*J. Amer. Chem. Soc.*, 1948, **70**, 2862) have reported the preparation of the tertiary diethynylglycols from diacetyl and acetonylacetone. No dialdehyde has however been condensed with acetylene, and the expected secondary diethynylglycols are unknown.

Aliphatic dialdehydes in particular are difficultly accessible materials, often available only in aqueous solution or as polymers, and the alkaline conditions normally used for the preparation of ethynylcarbinols (cf. Johnson, " The Chemistry of the Acetylenic Compounds," London, 1946) would probably cause polymerisation, rather than allow the normal reaction to take place.

The fact that the sodium bisulphite compounds of aliphatic dialdehydes can often be obtained as crystalline solids of high purity prompted a preliminary investigation of the reaction between acetylene and the sodium bisulphite adducts of carbonyl compounds. It was found that reasonable yields of ethynylcarbinols could be obtained by reaction of the solid bisulphite compounds with sodium acetylide in liquid ammonia. The purity of the bisulphite compounds could be estimated readily by their conversion into 2 : 4-dinitrophenylhydrazones, and the following results were obtained by this method.

Bisulphite compound of	Purity, %.	Formula.	Bisulphite compound of	Purity, %.	Formula.
Acetone	92·8	$C_3H_7O_4SNa$ [1]	Cinnamaldehyde	87·4	$C_9H_9O_4SNa$ [4]
Butyraldehyde	100·0	$C_4H_9O_4SNa$ [2]	Furfuraldehyde	86·5	$C_5H_5O_5SNa$ [5]
Benzaldehyde	93·8	$C_7H_7O_4SNa,1H_2O$ [3]	Citral	91·6	$C_{10}H_{17}O_4SNa$ [6]

[1] Limpricht, *Annalen*, 1855, **93**, 238. [2] Kahn, *Ber.*, 1885, **18**, 3365. [3] Fromm and Erfurt, *Ber.*, 1909, **42**, 3815. [4] Knoevenagel and Morrisse, *Ber.*, 1904, **37**, 4044. [5] Schwanert, *Annalen*, 1860, **116**, 261. [6] Tiemann, *Ber.*, 1898, **31**, 3311.

The following ethynylcarbinols have been prepared in the yields stated (calculated on pure bisulphite compound); these yields are compared with those given in the literature for the preparation from the free carbonyl compounds themselves. Only in the case of cinnamaldehyde did the yield obtained exceed that quoted in the literature.

Compound.	Yield obtained, %.	Literature yield, %.
2-Methylbut-3-yn-2-ol	46	77 [1]
Hex-1-yn-3-ol	32	46 [2]
1-Phenylprop-2-yn-1-ol	48	82·5 [3] 58 [1]
5-Phenylpent-4-en-1-yn-3-ol	13·5	2 [3]
1-(2-Furyl)prop-2-yn-1-ol	21·5	65 [3] 30 [4]
5 : 9-Dimethyldeca-4 : 8-dien-1-yn-3-ol	37	70 [5]

[1] Hennion and Murray, *J. Amer. Chem. Soc.*, 1942, **64**, 1220. [2] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 45. [3] Jones and McCombie, *J.*, 1942, 734. [4] Macallum, U.S.P. 2,125,384, 1938. [5] Heilbron, Johnson, Jones and Spinks, *J.*, 1942, 733.

No evidence is available concerning the mechanism of the reaction which could obviously take place either by direct substitution of the $-SO_3Na$ group by $-C\equiv CH$, or by the intermediate formation of the free carbonyl compound through removal of sodium bisulphite by the liquid ammonia. The application of the method to dialdehydes is under investigation. An attempted Grignard reaction of phenylacetylenylmagnesium bromide and acetone bisulphite compound afforded an almost quantitative recovery of phenylacetylene even after 8 hours' refluxing.

Experimental.—Estimation of bisulphite compounds. An accurately weighed quantity of the freshly prepared bisulphite compound (0·1—1·0 g.), previously washed with alcohol and ether, and dried at 20° (P_2O_5), was warmed for 15 minutes with an excess of an aqueous-alcoholic solution of 2 : 4-dinitrophenylhydrazine sulphate, and the reaction mixture then cooled to 0° (ice). The precipitate was filtered off on a sintered-glass crucible and dried to constant weight either at 100° or, for the derivatives of cinnamaldehyde, citral, and furfuraldehyde, at 20°/20 mm. (P_2O_5).

2-*Methylbut*-3-*yn*-2-*ol.* A solution of sodium acetylide, prepared from sodium (11·5 g.) by Jones and McCombie's method (*J.*, 1942, 734), in liquid ammonia (500 c.c.) was treated gradually with acetone bisulphite compound (27·0 g., 0·16 mole) during one hour, with stirring and cooling. Cooling and stirring of the mixture were continued for a further 2 hours in a slow stream of acetylene, and the reaction was then terminated by the addition of powdered ammonium chloride (38 g.). The ammonia was allowed to evaporate and the residue was treated with the minimum of ice–water, acidified with dilute sulphuric acid (2N.) (Congo-red), and extracted with ether. Removal of the solvent from the washed and dried (Na_2SO_4) extracts afforded 2-methylbut-3-yn-2-ol (6·0 g., 46%) as a colourless liquid, b. p. 103—104°/760 mm., n_D^{20} 1·4201 (Hennion and Murray, *loc. cit.*, give b. p. 104°/760 mm., n_D^{20} 1·4211).

Hex-1-*yn*-3-*ol*. Prepared by the method described above from sodium (18 g.) in liquid ammonia (750 c.c.) and butyraldehyde bisulphite compound (44 g., 0·25 mole), hex-1-yn-3-ol was obtained as a colourless liquid (7·7 g., 32%), b. p. 140—141°/757 mm., n_D^{20} 1·4332 (Zalkind and Gverdsiteli, *J. Gen. Chem. Russia*, **1939**, **9**, 971, give b. p. 140—141°, n_D^{20} 1·4330).

1-*Phenylprop*-2-*yn*-1-*ol*. The above method was applied using sodium (30 g.) in liquid ammonia (1250 c.c.) and benzaldehyde bisulphite compound (105 g., 0·45 mole), and the mixture stirred for 5·5 hours. The ethereal extracts were washed with saturated sodium bisulphite solution in addition to the usual bicarbonate and water washings. The dried extract afforded 1-phenylprop-2-yn-1-ol (26·7 g., 48·0%) as a colourless oil, b. p. 61—62°/0·025 mm., n_D^{20} 1·5509, which solidified on storage to white needles, m. p. 22° (Hennion and Murray, *loc. cit.*, give b. p. 80°/4 mm., n_D^{20} 1·5505, and Jones and McCombie, *loc. cit.*, give m. p. 22°). The phenylurethane was obtained as white needles, m. p. 81—82°, from light petroleum (b. p. 60—80°) (Jones and McCombie, *loc. cit.*, give m. p. 81—82°).

5-*Phenylpent*-4-*en*-1-*yn*-3-*ol*. Application of the same method to sodium (55 g.) in liquid ammonia (1500 c.c.) and cinnamaldehyde bisulphite compound (254 g., 1 mole) gave a large quantity of polymeric material which was thoroughly extracted with ether. Removal of solvent left a residual oil which was distilled with steam from saturated sodium bisulphite solution. Extraction of the steam distillate with ether yielded a solid, m. p. 66° (18 g., 13·5%), which crystallised from light petroleum (b. p. 60—80°) in white needles, m. p. 66—67°. Light absorption: Maximum, 2510 A.; log ε = 4·2 (Jones and McCombie, *loc. cit.*, give m. p. 66—67°; maximum, 2510 A.; log ε = 4·31).

1-(2-*Furyl*)*prop*-2-*yn*-1-*ol*. Preparation by the above method from sodium (36 g.) in liquid ammonia (1500 c.c.) and furfuraldehyde bisulphite compound (100 g., 0·5 mole) during 4·5 hours gave the carbinol as a colourless oil (11·2 g., 21·5%), b. p. 69—70°/0·3 mm., n_D^{23} 1·5056 (Macallum, U.S.P. 2,125,384, 1938, gives b. p. 100—103°/25 mm., n_D^{20} 1·504).

5 : 9-*Dimethyldeca*-4 : 8-*dien*-1-*yn*-3-*ol*. Sodium (20 g.) in liquid ammonia (1500 c.c.) and citral bisulphite compound (64 g., 0·25 mole) gave (after washing the ethereal extract with saturated sodium bisulphite) the carbinol, b. p. 88—89°/0·02 mm., n_D^{22} 1·4872, as a colourless oil (15·0 g., 37%), giving an immediate white precipitate with Tollens's reagent (Heilbron, Johnson, Jones, and Spinks, *loc. cit.*, give b. p. 88°/0·02 mm., n_D^{20} 1·4875).

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