NOTES

Co-ordination Compounds of Beryllium and m- *and* p-*Nitrobenzoylacetone.* By HENRY BURGESS.

THE mutarotation of beryllium benzoylcamphor was attributed to an asymmetric arrangement around the beryllium atom by Lowry and Burgess (J., 1924, **125**, 2082), but owing to the occurrence of two asymmetric carbon atoms in the camphor nucleus, rigorous proof of the suggestion could not be obtained. It was proposed to confirm it by using an unsymmetrical β-diketone or β-ketonic ester which contained no asymmetric carbon atom and the basic or acidic group necessary for the resolution. *p*- and *m*-Aminobenzoylacetone and ethyl *p*-nitrobenzylacetoacetate appeared to fulfil these conditions. Owing to the resolution of beryllium benzoylpyruvate by Mills and Gotts (J., 1926, 3121), it was decided to place on record the results already obtained.

p-*Nitrobenzoylacetone.*—Freshly powdered sodamide (10·5 g.) was slowly added to ethyl *p*-nitrobenzoate (50 g.) and acetone (19·8 c.c.) in dry ether (150 c.c.), cooled to −17°. The mixture immediately became greenish-black and ammonia was evolved. After being kept for 2 hours in the freezing mixture and for 20 hours at room temperature, the product was poured into ice-water, the ether separated, and the aqueous layer extracted twice with chloroform. (From these extractions, 16 g. of ethyl *p*-nitrobenzoate were recovered.) The aqueous layer was filtered through charcoal and acidified, and the resulting precipitate was filtered off and dried. This solid was extracted several times with ether, the ethereal solution was evaporated, and the resulting yellowish-brown crystals were recrystallised from methyl alcohol (yield, 1·5 g.), p-*nitrobenzoylacetone* being obtained in golden-yellow needles, m. p. 112—113·5° (Found : C, 58·1; H, 4·5; N, 6·8. $C_{10}H_9O_4N$ requires C, 57·95; H, 4·4; N, 6·8%). It is readily soluble in ordinary organic solvents except the cold alcohols and is insoluble in water. With caustic soda, it gives a bright yellow solution, and with copper acetate it produces a green precipitate, which is soluble in chloroform.

Beryllium p-*nitrobenzoylacetone* was obtained in nearly theoretical yield by the method described for beryllium benzoylcamphor (*loc. cit.*) (Found : C, 57·6*; H, 3·9*; Be, 2·2*. $C_{20}H_{16}O_8N_2Be$ requires C, 57·0; H, 3·8; Be, 2·1%). It is readily soluble in chloroform and hot benzene, from which it separates in brownish-yellow, compact crystals, m. p. 243—244°. It is sparingly soluble in alcohol and insoluble in water.

m-*Nitrobenzoylacetone.*—Preliminary experiments having shown that benzoylacetone can be recovered quantitatively from concentrated sulphuric acid at room temperature, the following nitration was carried out : A mixture of nitric acid (*d* 1·42; 7 c.c.) and sulphuric acid (*d* 1·84; 24 c.c.) was slowly added to benzoylacetone (15 g.) in sulphuric acid (100 c.c.), mechanically stirred and kept at −11° to −9°. After 15 minutes, the product was poured on ice; the precipitate obtained crystallised from hot methyl alcohol in very pale yellow needles, m. p. 114—115° (*p*-nitrobenzoylacetone depresses the m. p. by 20°) (yield, 47%) (Found : C, 58·1; H, 4·6%). m-*Nitrobenzoylacetone* is easily soluble in ordinary organic solvents except the cold alcohols and ligroin. The yellow coloration with alkalis is less intense than that of the *p*-nitro-derivative. With alcoholic ferric chloride, it gives a wine-red colour.

Beryllium m-*nitrobenzoylacetone*, prepared by the usual method, crystallised from acetone–alcohol in orange-yellow, square plates, m. p. 207—208° (Found : C, 57·3*; H, 3·9*; Be, 2·1%). It is

---

* Values so marked are the results of micro-estimations carried out by Siegmund Weil, Tübingen.

readily soluble in chloroform and benzene, less soluble in acetone, and slightly soluble in alcohol.

Ethyl Bis-p-*nitrobenzylacetoacetate.*—*p*-Nitrobenzyl bromide was slowly added to an equivalent quantity of ethyl sodioacetoacetate in absolute alcohol, sodium bromide being precipitated. After heating for 2 hours, the alcohol was evaporated, water added, and the precipitate crystallised from acetone–methylated spirit, *ethyl bis*-p-*nitrobenzylacetoacetate* separating in colourless flakes, m. p. 137—139° (Found: C, 60·5, 60·0; H, 5·0, 4·6; N, 6·8, 6·7. $C_{20}H_{20}O_7N_2$ requires C, 60·0; H, 5·0; N, 7·0%). It is readily soluble in acetone, ether, chloroform, and hot benzene, and sparingly soluble in cold alcohol. It gives a coloration neither with caustic soda nor with ferric chloride.

Ethyl p-*Nitrobenzylacetoacetate.*—The mother-liquor from the above compound left an orange-coloured oil on evaporation. This solidified when cooled in the ice-chest, and crystallised from benzene–ligroin in very pale yellow needles, m. p. 43—45° (Found: C, 59·05; H, 5·8. $C_{13}H_{15}O_5N$ requires C, 58·8; H, 5·7%). It is very soluble in all organic solvents except ligroin, in which it is sparingly soluble. With caustic soda, it gives an intense yellowish-orange coloration, and with ferric chloride a deep reddish-purple colour slowly develops. Copper acetate precipitates a green copper derivative, which is soluble in chloroform.

I wish to take this opportunity of expressing my thanks to the Chemical Society for a grant towards the expenses of the research, and also to Professor C. S. Gibson for his helpful criticism and encouragement.—GUY'S HOSPITAL MEDICAL SCHOOL. [*Received, March* 21*st*, 1927.]

The Reduction of Arsenic Compounds in Acid and in Alkaline Solution by Sodium Hyposulphite (Hydrosulphite). Production of Sodium Arseno-hyposulphite. By WALTER FARMER and JAMES BRIERLEY FIRTH.

IN an investigation on the reduction of certain arsenic compounds by sodium hyposulphite, in which a product corresponding to arsenic subsulphide, As_3S, was isolated (J., 1926, 119), it was inferred from preliminary experiments (and existing literature) that two intermediate complex compounds are formed, one of which is a decomposition product of the other.

The Primary Intermediate Complex, Sodium Arseno-hyposulphite, $Na_3As(S_2O_4)_3$.—Preliminary experiments carried out in glass vessels indicated that, in the presence of alcohol, shaking of an alkaline solution of trisodium arsenite containing hyposulphite was followed by formation of two unstable precipitates, one of which was heavier than the other. Similar heavy precipitates were obtained when concentrated solutions of common sodium arsenate were used.

The products adhered to the walls of the vessel, and became viscous when treated with dilute alcoholic potash. In subsequent experiments, quartz containers were employed.

Sodium hyposulphite (2·75 g.) was introduced into a cold solution of 2·75 g. of common sodium arsenate in 3 c.c. of water to which a whirling motion had been imparted. The flask was closed, and the whirling maintained. Dissolution of the last traces of sodium hyposulphite was accompanied by formation of a heavy, granular solid, which settled in increasing quantity when the flask was kept at room temperature. The supernatant liquor was decanted off after 15 minutes, and the granular solid was washed five times by decantation with methylated alcohol and four times with benzene and kept in a quartz dish in a vacuum over sulphuric acid for 24 hours. A creamy-white powder was obtained (yield, 1 g.).

When a small quantity of the product was strongly heated in a Bunsen flame, a brown and a yellow sublimate formed and a garlic odour developed. If cautiously heated, the product first turned brown and, when more strongly heated, gave a brown and a yellow sublimate as before. When a small quantity of the product was treated with dilute hydrochloric acid, sulphur dioxide was evolved, and a brown product similar to that described in the previous paper (*loc. cit.*) formed.

Estimations of the arsenic content of the product, as magnesium pyroarsenate, gave: As, 14·1, 14·1, 14·1, 14·0%. Estimations of hyposulphite by Wilkes's method (*J. Soc. Chem. Ind.*, 1923, **42**, 356T) were based on the view that, in presence of hypoiodous acid, hydrolysis of 1 g.-mol. of arseno-hyposulphurous acid, $H_3As(S_2O_4)_3$, is attended by liberation of 4 g.-mols. of iodine according to the following equations:

(1) $H_3As(S_2O_4)_3 + 3H_2O = H_3AsO_3 + 3H_2S_2O_4$,
(2) $H_3AsO_3 + 2HIO + 3KOH = I_2 + K_3AsO_4 + 4H_2O$,
(3) $3H_2S_2O_4 + 9KIO + 6KOH = 6KHSO_4 + 9KI + 3H_2O$,
(4) $6KHSO_4 + 3KIO + 3KI = 3I_2 + 6K_2SO_4 + 3H_2O$.

Two samples gave: S_2O_4, 70·9, 70·5 [$Na_3As(S_2O_4)_3$ requires As, 14·2; S_2O_4, 72·7%].

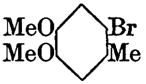
The Secondary Intermediate Complex, Sodium Arseno-thiosulphate, $Na_3As(S_2O_3)_3$.—Standard solutions of potassium hydroxide and hydrochloric acid of the same normality were prepared. 25 C.c. of the standard alkali in which 1 g. of sodium arseno-hyposulphite (1 mol.) and the calculated quantity of sodium sulphite (3 mols.)

had been dissolved were rapidly added to 25 c.c. of the standard acid containing 2·5 c.c. of concentrated acid. A turbidity developed, followed by precipitation of arsenious sulphide. Decomposition of sodium arseno-hyposulphite in presence of sodium sulphite by this neutralisation method is considered to lead to formation, and rapid decomposition, of sodium arseno-thiosulphate, arsenious sulphide being one of the products (compare Jellinek, *Z. physikal. Chem.*, 1911, **76**, 257; Szilàgyi, *Z. anorg. Chem.*, 1920, **113**, 69).—University College, Nottingham. [*Received, April 8th*, 1927.]

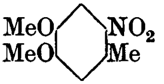
The Displacement of Bromine accompanying the Nitration of 6-*Bromohomoveratrole.*

By Tom Heap, Thomas G. H. Jones, and Robert Robinson.

Jones and Robinson (J., 1917, **111**, 919) described the conversion of 6-bromohomoveratrole (I) into a mononitro-derivative, m. p. 121°, by the action of a mixture of nitric acid and acetic anhydride.

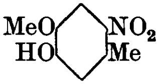


(I.)



(II.)

(III.)



(IV.)

We have, however, been unable to repeat the preparation of the nitro-derivative, since, on several occasions, following the description as closely as possible, the sole product of a sluggish reaction was 6-nitrohomoveratrole (II) (yield, 36%). Although it may be that some variation of the conditions is responsible for this divergence, we think it more likely that the observation of Jones and Robinson was erroneous as the result of contamination of the creosol employed with guaiacol and that the compound isolated was 4-bromo-5-nitroveratrole (III), m. p. 124° (or 121—122°, see below).

It is no longer necessary to employ beechwood tar as a source of creosol, since the pure phenol can be readily obtained from vanillin by Clemmensen's method.

6-*Bromohomoveratrole* (I).—The reduction of vanillin (100 g.) by means of amalgamated zinc and hydrochloric acid (Oberlin, *Arch. Pharm.*, 1925, **263**, 641) gave creosol (60 g.), b. p. 220—225°/760 mm., which was converted by known methods into homoveratrole, b. p. 218—220°, m. p. 22° (yield, 91%), and then into 6-bromohomoveratrole, b. p. 265—267°, m. p. 31° (yield, 94%). The latter crystallised in truncated octahedra, and, on oxidation with potassium permanganate and boiling dilute aqueous sodium hydroxide for 1½ hours, yielded 6-bromoveratric acid; this, alone or mixed with a specimen obtained by brominating methyl veratrate and hydrolysing the product, melted at 183—184°. When treated with a mixture of acetic anhydride and nitric acid under the conditions prescribed by Jones and Robinson (*loc. cit.*), bromohomoveratrole (20 g.) gave 6-nitrohomoveratrole (8·5 g.), which crystallised in yellow needles from methyl alcohol; m. p. 117—119°, alone or mixed with an authentic specimen (Found : C, 55·0; H, 5·8. Calc. for $C_9H_{11}O_4N$: C, 54·8; H, 5·6%).

6-*Nitro*iso*creosol* (IV).—Cardwell and Robinson (J., 1915, **107**, 256) commented on the fact that 6-nitrohomoveratrole is not readily hydrolysed by alkalis. It is certainly less readily attacked than nitroveratrole, but by following the procedure of Pollecoff and Robinson (J., 1918, **113**, 647) for the preparation of 4-nitroguaiacol an almost theoretical yield of the nitro*iso*creosol was obtained in 73 hours. The substance crystallised from aqueous alcohol in slender, pale yellow needles, m. p. 168—170° (Found : C, 52·6; H, 4·6; N, 7·6. $C_8H_9O_4N$ requires C, 52·5; H, 4·9; N, 7·7%). The *acetyl* derivative crystallised from alcohol in colourless, elongated, hexagonal plates, m. p. 100—101°. On methylation the phenol yielded 6-nitrohomoveratrole, m. p. 117—119°. The conditions applicable for its further nitration to 2 : 6-dinitro*iso*creosol were not ascertained, since the action of nitric acid led to the production of soluble orange-red substances.

6-*Bromoveratric Acid*.—When methyl veratrate is brominated in cold acetic acid solution and the product crystallised, the yield of pure methyl 6-bromoveratrate, m. p. 88—89°, is not satisfactory, and Professor Smiles has suggested to us that methyl 2-bromoveratrate may be produced in the reaction. On treatment with cold nitric acid (*d* 1·42) pure 6-bromoveratric acid, m. p. 183—184°, gave a 50% yield of 4-bromo-5-nitroveratrole, m. p. 121—122°, whilst the crude product gave a 36% yield of this substance under identical conditions. 4-Bromo-5-nitroveratrole, prepared from bromoveratrole, had m. p. 121—122°, and a mixture with the specimen from 6-bromoveratric acid had the same m. p. The matter will be further investigated, our chief concern at the moment being to confirm the recorded m. p.'s of 6-bromoveratric acid and its methyl ester.—THE UNIVERSITY, MANCHESTER. [*Received, July* 11*th*, 1927.]