CCLXXXVII.—*The Action of Bromine on Dimethylpyrone.*

By JOHN NORMAN COLLIE and LOUIS KLEIN.

THE constitution of the pyrone nucleus is of importance in that many interesting compounds are derived from it. Bromine reacts with it at once, but does not give ordinary addition products, and similarly there is no indication that any ethylenic linkages are present in dimethylpyrone.

10 G. of dimethylpyrone (1 mol.) and 13 g. of bromine (1 mol.) were allowed to react in chloroform solution, and the mixture became orange-coloured and slightly warm. The solvent was evaporated at the ordinary temperature, and the resulting bright orange-coloured, crystalline solid was washed with water, which removed dimethylpyrone hydrobromide, together with a small quantity of some pyrone compound containing bromine—this was probably the bromodimethylpyrone, but owing to its high solubility it could not be separated from the hydrobromide.

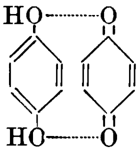
The orange compound (yield, 10 g.) was best recrystallised from acetic acid or chloroform; m. p. 136° (Found: C, 34·1; H, 3·8; Br, 49·5; *M*, cryoscopic in naphthalene, 456, 479. Calc. for $C_{14}H_{17}O_4Br_3$: C, 34·4; H, 3·5; Br, 49·1%; *M*, 489).

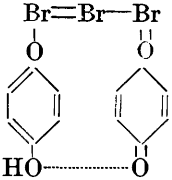
This compound has also been obtained by Hantzsch and Denstorff (*Annalen*, 1906, **349**, 39), who only gave a bromine determination, by the action of bromine on dimethylpyrone hydrobromide. They recognised it as a perbromide, and we have confirmed this by obtaining several characteristic reactions for perbromides, some of which were carried out quantitatively, although in the reaction with ammonia only about two-thirds of the theoretical amount of nitrogen were evolved.

On being warmed with water, the compound loses its colour and dissolves, except for a small quantity of a yellow oil (Found: ionisable Br, 37·0%). On standing with water for 3 days, however, only a trace of the yellow oil remained, and the ionisable bromine was then 46·9%. The yellow *oil* does not crystallise on keeping and cannot be distilled (Found: Br, 58·1. $C_7H_6O_2Br_2$ requires Br, 56·7%). Aqueous potassium hydroxide behaves in a similar manner to water (Found: ionisable Br, 46·1%).

The action of heat on the orange compound is complex. If kept just at its m. p. it loses colour, and then solidifies on cooling. If more strongly heated, it chars and gives off hydrogen bromide, the product being almost entirely soluble in water, and consisting chiefly of dimethylpyrone hydrobromide, mixed with a small quantity of (probably) the bromodimethylpyrone, which, however, could not be separated. The small amount of insoluble *substance* was a yellow, non-crystallisable oil (Found : Br, 61·4%).

The orange compound resembles quinhydrone in some respects, *e.g.*, reaction with water and possession of colour, and this suggests a similarity in molecular constitution :





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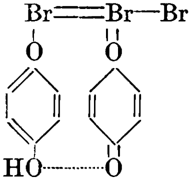

The action of a larger amount of bromine on dimethylpyrone was tried : 10 g. of the pyrone and 26 g. of bromine in chloroform solution. After evaporation of the chloroform, the residue was treated with water, and the insoluble portion recrystallised from dilute alcohol. A colourless compound resulted; m. p. 163° (Found : C, 29·8; H, 2·6; Br, 56·3. Calc. for $C_7H_6O_2Br_2$: C, 29·8; H, 2·1; Br, 56·7%). This compound had been previously obtained by Feist and Baum (*Ber.*, 1905, **38**, 3562). On being boiled with water it gives bromoacetone. It does not form salts with acids, and its solution in alcohol does not give an immediate precipitate with silver nitrate. On being heated with sodium ethoxide solution, it turns deep red in colour.

If excess of bromine is allowed to react with dimethylpyrone in the absence of a solvent, the mixture becomes warm, and on boiling it evolves hydrogen bromide and eventually becomes solid. Extraction with alcohol leaves a crystalline residue, which is almost insoluble in most solvents. From hot acetic anhydride, however, a *substance* separates in bunches of needles, m. p. 229° (darkening at 227°) (Found : C, 19·3; H, 1·2; Br, 71·5. $C_7H_4O_2Br_4$ requires C, 19·1; H, 0·9; Br, 72·7%). This compound is very stable, being unaffected by metallic sodium in boiling benzene solution, or by warm concentrated sulphuric or nitric acids, from solutions in which it is precipitated unchanged on the addition of water. Heating with ammonia in a sealed tube at 140° or boiling with sodium hydroxide solution, however, effect decomposition, which is very far-reaching in the former case.

A curious iodine compound was obtained by one of the authors (J., 1900, **77**, 1116; 1921, **119**, 1550) by the action of iodine on the barium salt of diacetylacetone. Bromine has now been found to give a similar compound; it was added slowly with shaking to an aqueous suspension of the barium salt (45 g.), and dilute hydrochloric acid then precipitated 9 g. of the *substance*, which was recrystallised from dilute alcohol; m. p. 106°; b. p. *ca.* 310° (decomp.) (Found: C, 38·6; H, 3·4; Br, 36·6. *M*, microcryoscopic in camphor, 236. $C_7H_7O_3Br$ requires C, 38·4; H, 3·2; Br, 36·5%; *M*, 219). In all its reactions it resembles the iodine compound. It can be boiled with the strongest sodium hydroxide, or with sodium ethoxide, without decomposition, and is reprecipitated on adding an acid. Cold concentrated sulphuric acid does not decompose it, and although it does not react with cold sodium carbonate solution, on warming, carbon dioxide is evolved. With bleaching-powder solution, it gives a precipitate of calcium carbonate. With ferric chloride, it gives a red precipitate. It can also be made by the action of bromine on the sodium salt of diacetylacetone. It forms a *monobenzoyl* derivative, m. p. 112° (Found: C, 51·8; H, 3·7; Br, 24·5. $C_{14}H_{11}O_4Br$ requires C, 52·0; H, 3·4; Br, 24·8%); and with phenylhydrazine it yields a *compound*, m. p. 142° (decomp.) (Found: N, 8·8; Br, 26·3. $C_{13}H_{13}O_2N_2Br$ requires N, 9·1; Br, 25·9%).

An unsuccessful attempt was made to produce a corresponding chlorine compound by the action of chlorine on the barium salt of dimethyl pyrone.

THE RALPH FORSTER LABORATORIES OF ORGANIC CHEMISTRY,
UNIVERSITY COLLEGE, LONDON. [*Received, June 30th*, 1927.]