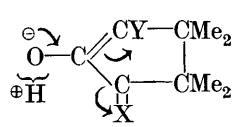
CCCXI.—*On the Possibility of Ring-chain Valency Tautomerism and of a Type of Mobile-hydrogen Tautomerism analogous to the Wagner–Meerwein Rearrangement. Part IV. Substitution Reactions of some Cyclic Derivatives of Phorone.*

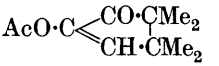
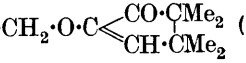
By CHARLES WILLIAM SHOPPEE.

IN the course of previous investigations (Francis and Willson, J., 1913, **103**, 2238; Ingold and Shoppee, this vol., p. 365) on the cyclic phorone derivatives represented by the formulæ (I) and (II), numerous observations have been made which indicate that the 5-carbon nucleus possesses remarkable stability such as is sometimes found to be associated with tautomeric complexes. Reference may be made to the smooth formation of bromohydroxyphorone (X = O, Y = Br) by the action of concentrated sulphuric acid on dibromophorone and by the action of bromine and water on 3 : 3 : 4 : 4-tetramethyl*cyclo*pentanone; to the conversion of hydroxyphorone (Y = H) into the bromohydroxy-compound by direct bromination without detectable intermediate addition; to the direct reduction of derivatives of bromohydroxyphorone to corresponding derivatives of hydroxyphorone without loss of the unsaturation on which tautomeric character depends; and finally to the stability towards brominating, reducing, and certain oxidising agents of some of the derivatives of hydroxy- and bromohydroxy-phorone. These observations call to mind the properties of the *gem*-dialkyl*cyclo*pentadiene nucleus investigated by Farmer, Ingold, and Thorpe (J., 1922, **121**, 128), and the analogy between compounds containing this nucleus and aromatic substances (Ingold, Seeley, and Thorpe, J., 1923, **123**, 852); it was therefore decided to study the action of substituting agents on hydroxyphorone and its derivatives in order

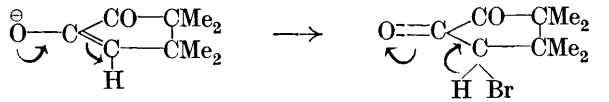
to determine the conditions under which the nuclear type is preserved.

(I.)  (II.)

By the action of bromine in chloroform upon the acetoxy-compound (III) and the methoxy- and *p*-bromobenzyloxy-compounds represented by (IV), bromohydroxyphorone was produced. Hydrogen bromide was evolved from the commencement of the reaction and no evidence was obtained of intervening bromine

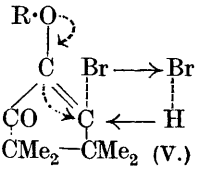
(III.)   (IV.)

addition. The fact that the alkyl and acyl groups are eliminated in the course of these reactions places difficulties in the way of their interpretation, since it is not known whether the eliminations are antecedent or subsequent to the nuclear substitution; if they are antecedent, substitution might occur through the ion of hydroxyphorone with the formation of a tautomeride of the product isolated (compare Part I, p. 383):

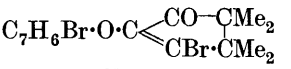


The facility with which this reaction would be expected to occur is such that, assuming the elimination of the *O*-substituent to be brought about by hydrogen bromide, a very small amount of fission at the commencement of the reaction would suffice to cause the whole of the subsequcnt process to pursue the course indicated. This mechanism is not analogous to the general case of substitution in the aromatic series, and the behaviour of other halogenating agents was therefore investigated. Quinolinium perbromide also causes the elimination of the acetyl group from the acetoxy-compound (III) and yields the same bromination product as that obtained by means of bromine. In the case of the *p*-bromobenzyloxy-compound (IV), however, fission did not take place and simple nuclear substitution was observed, the product being (VI). A similar result was achieved in the formation of (VII) from the acetoxy-compound (III) by brominating with quinolinium perbromide in the presence of a quantity of quinoline sufficient to prevent the formation of free hydrogen bromide during the process. These substitutions cannot involve prior ionisation of the organic

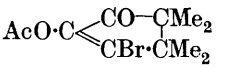
molecule and are regarded as taking the course indicated in formula (V).



(V.)

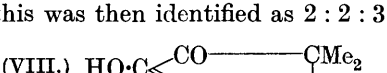


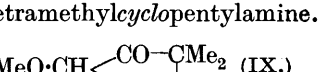
(VI.)



(VII.)

The acyl and alkyl derivatives mentioned above appear to show but little tendency to couple with diazonium salts, but hydroxyphorone readily does so, and it is therefore assumed that in this case the reaction occurs through the anion. Deep red dyes of the type (VIII) have been prepared from hydroxyphorone and several aromatic diazonium salts. The position of coupling was indicated in the first place by the fact that the reaction fails with bromohydroxyphorone, and was definitely proved by complete reduction of the dye given by *p*-carbethoxybenzenediazonium sulphate. Hydrolysis of the carbethoxy-group present in one of the pair of bases formed by reduction enabled the aliphatic constituent to be separated and this was then identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine.

(VIII.) 



(IX.)

In the above examples, the nuclear form originally present is preserved throughout the substitution, and it became of interest to ascertain whether, if the type were destroyed by previous reduction, it would be regenerated during halogenation. For this purpose, the saturated methoxy-compound (IX) was prepared, and when it was subjected to the action of bromine and chloroform, the tautomeric bromohydroxy-compound was produced.

EXPERIMENTAL.

Bromination with Free Bromine in Chloroform Solution.—*5-Acetoxy-2 : 2 : 3 : 3-tetramethyl-*Δ^4*-cyclopentenone.* The substance, b. p. 120—121°/10 mm., reacted readily at 35° with one molecular proportion of bromine, evolution of hydrogen bromide taking place. The residual oil, obtained after removal of the solvent on the steam-bath, readily solidified; it was pressed on porous tile and crystallised from ligroin (b. p. 80—100°), from which it separated in colourless needles, m. p. 116°, identified as bromohydroxyphorone by direct comparison and mixed melting point.

5-Methoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4*-cyclopentenone.* The pure methoxy-derivative, prepared by methylating the hydroxy-ketone, b. p. 110°/18 mm., was treated with 1 mol. of bromine; substitution

with evolution of hydrogen bromide occurred readily on gentle warming. The product, bromohydroxyphorone, m. p. 116°, was isolated and identified as above.

5-p-*Bromobenzyloxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*. The crystalline solid, m. p. 86°, was treated with 1·2 mols. of bromine in boiling chloroform, and substitution slowly took place. When evolution of hydrogen bromide had ceased, the solvent and the excess of bromine were removed on the steam-bath. The residual oil, which was lachrymatory and had the characteristic odour of *p*-bromobenzyl bromide, solidified on stirring, and was washed with a little hot ligroin (b. p. 40—60°) to remove this product. The solid was crystallised from ligroin (b. p. 80—100°) and then it had m. p. 116°; it was identified as before.

5-*Methoxy*-2 : 2 : 3 : 3-*tetramethyl*cyclo*pentanone*. The methoxy-compound was treated with excess of bromine in hot chloroform, substitution taking place with evolution of hydrogen bromide. The solvent, excess of bromine, and hydrogen bromide were removed on the steam-bath and the residual oil soon became solid. It was identified as bromohydroxyphorone. In another experiment, bromine (1 mol.) was added to the warm chloroform solution of the methoxy-compound. Substitution took place after a short induction period, and bromine was added until a permanent red colour was obtained. The residue remaining after evaporation partially crystallised, and the solid separated from ligroin (b. p. 60—80°) in colourless prisms, m. p. 99—100° The *dibromo*-compound gave no colour with aqueous-alcoholic ferric chloride, and was stable to bromine in acetic acid, and to alkaline permanganate; on keeping it decomposed with evolution of free bromine (Found: C, 37·1, 37·3; H, 5·6, 5·8. $C_{10}H_{16}O_2Br_2$ requires C, 36·6; H, 4·9%).

3 : 3 : 4 : 4-*Tetramethyl*cyclo*pentanone*. The ketone was treated with bromine (2 mols.), substitution taking place on gentle warming. The product obtained on evaporation crystallised from ligroin (b. p. 60—80°) in long needles, m. p. 93°, and depressed the m. p. (99—100°) of the substance described above (Found: C, 36·7, 37·2; H, 4·6, 4·4; Br, 53·8, 53·9. $C_9H_{14}OBr_2$ requires C, 36·2; H, 4·7; Br, 53·7%).

5-*Benzoyloxy*-3 : 3 : 4 : 4-*tetramethyl*cyclo*pentanone*. The bromination of this substance (Part II, this vol., p. 1662) has been reinvestigated, but with little success. In addition to free benzoic acid, a bromine-free *substance* is formed, m. p. 100—101°, to which no formula has been assigned (Found: C, 71·3, 71·6; H, 7·4, 7·2%).

Bromination with Quinolinium Perbromide.—The reagent was prepared by the method of Rosenmund and Kühnhenn (*Ber.*, 1923,

56, 1264); alcohol, which these authors recommend for crystallisation, may be advantageously replaced by chloroform.

Acetoxy-derivative (III). (1) The compound was dissolved in glacial acetic acid, and the calculated quantity of quinolinium perbromide added. The whole was warmed on the steam-bath for ¼ hour, during which the red colour of the solution disappeared. On dilution with ice-water, a crystalline precipitate separated; this was filtered off, dried in a vacuum, crystallised from ligroin (b. p. 80—100°), and identified as bromohydroxyphorone (yield, 75%).

(2) The above experiment was repeated, but with the addition of quinoline (1 mol.). The product was isolated as described above, and when crystallised from dilute acetic acid had m. p. 73°. It was identified as 4-bromo-5-acetoxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone by direct comparison and by mixed m. p. (yield, 70%).

p-*Bromobenzyloxy-derivative* (IV). The same product was obtained with or without the presence of free quinoline. After crystallisation from ligroin (b. p. 60—80°), it had m. p. 64°, and did not depress the m. p. (64°) of 4-bromo-5-*p*-bromobenzyloxy-2 : 2 : 3 : 3-tetramethyl-Δ^4-*cyclo*pentenone on admixture (yield, 80%).

Coupling of the Hydroxy-ketone with Diazonium Salts.—With benzenediazonium sulphate the dye produced by coupling was amorphous, but with 2 : 4 : 6-tribromobenzenediazonium sulphate and with *p*-carbethoxybenzenediazonium sulphate, crystalline products were obtained. The diazonium sulphates were prepared according to the method of Knoevenagel (*Ber.*, 1895, **28**, 2049).

4-2′ : 4′ : 6′-*Tribromobenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone* separates in crimson needles when the theoretical quantity of dry 2 : 4 : 6-tribromobenzenediazonium sulphate, dissolved in aqueous methyl alcohol, is added to the aqueous methyl-alcoholic solution of the hydroxy-ketone. It is soluble in cold 2*N*-sodium hydroxide (Found : C, 36·2; H, 3·1. $C_{15}H_{15}O_2N_2Br_3$ requires C, 36·3; H, 3·0%).

4-p-*Carbethoxybenzeneazo*-5-*hydroxy*-2 : 2 : 3 : 3-*tetramethyl*-Δ^4-cyclo*pentenone*, obtained similarly, forms crimson needles, m. p. 160° (decomp.), and is soluble in cold 2*N*-sodium hydroxide (Found : C, 65·4; H, 6·7. $C_{18}H_{22}O_4N_2$ requires C, 65·4; H, 6·7%).

Reduction of the p-*Carbethoxy-dye.*—The substance (2·0 g.) was reduced in hot aqueous-alcoholic solution with successive small quantities of sodium hydrosulphite (5·0 g.). The product, which contained some substance readily oxidised by atmospheric oxygen, was extracted with ether, and the ethereal extract evaporated under a column. The residual oil was boiled with phosphorus and

hydriodic acid (*d* 1·7) for 2 hours to effect reduction of the phorone nucleus and hydrolysis of the *p*-carbethoxy-group. The liquid was then made strongly alkaline and steam-distilled, and the distillate extracted with ether. The ethereal extract was dried with anhydrous potassium carbonate and evaporated under a column. The product was identified as 2 : 2 : 3 : 3-tetramethyl*cyclo*pentylamine; it was accompanied by a trace of some other base yielding a picrate, m. p. 185° (decomp.).

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