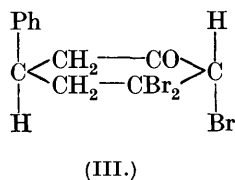
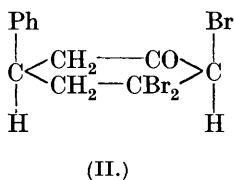
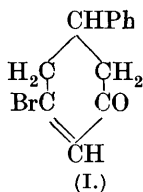


CLII.—*Conversion of Hydroaromatic into Aromatic Compounds. Part II. Action of Bromine on 5-Chloro- and 5-Bromo-1-phenyl- Δ^4 -cyclohexen-3-one.*

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WHEN chlorine acts on 5-chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one, chlorinated hydroaromatic compounds result which can readily be transformed into aromatic compounds by simple means (Hinkel, J., 1924, **125**, 1847). The present investigation was undertaken not only to obtain analogous halogen compounds of diphenyl, but also to study the influence of the phenyl group in substituted dihydroresorcinols and their derivatives.

As in the case mentioned above, bromine is rapidly absorbed by 5-bromo-1-phenyl- Δ^4 -cyclohexen-3-one (I), but, in marked contrast with the behaviour of 5-chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one, 4:5:5-tribromo-1-phenylcyclohexan-3-one can be readily isolated in the solid state. This tribromo-ketone exists in two crystalline forms, which probably have the *cis*- and *trans*-configurations (II) and (III); one form is much less stable than the other and from a study of its decomposition would seem to have the structure (III).



The two forms are readily interconvertible by crystallisation from either absolute alcohol or ether, the latter solvent giving rise to the unstable form. This form loses hydrogen bromide at room temperature when kept for a few days (especially in ethereal solution); the more stable form requires several weeks before showing any appreciable decomposition. The same decomposition can be readily accomplished by heating the tribromo-ketone, either alone or with alcoholic potash. In every case the product of the decomposition

consists of a mixture containing 5-bromo-3-hydroxydiphenyl, 4:5-dibromo-3-hydroxydiphenyl, and a small quantity of phenyldihydroresorcinol. Since the positions occupied by the bromine atoms in the tribromo-ketone are known, there can be little doubt that the diphenyl derivatives obtained from it have the structures assigned to them. Experiments are, however, in progress with the object of preparing these compounds synthetically.

The removal of hydrogen bromide from 4:5:5-tribromo-1-phenylcyclohexan-3-one can occur in one of two ways to form the dibromohexenone (IV) or (V). Unlike the corresponding chloro-derivatives



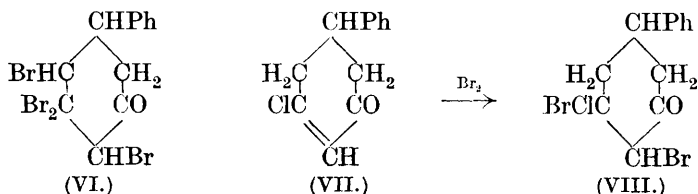
of dimethyldihydroresorcinol (Hinkel, *loc. cit.*), the intermediate dihalogen compound (V) cannot be isolated, it being immediately transformed into 5-bromo-3-hydroxydiphenyl, nor can the dibromohexenone (IV) be obtained from 4-bromo-1-phenyldihydroresorcinol (compare Crossley and Le Sueur, J., 1903, **83**, 110). As the compound (IV) could not give rise to 5-bromo-3-hydroxydiphenyl without undergoing an exceptionally drastic internal rearrangement, it seems probable that the loss of hydrogen bromide occurs at carbon atoms 5 and 6 of the tribromo-ketone, giving the compound (V) (compare Hinkel, *loc. cit.*), from which, by loss of hydrogen bromide from carbon atoms 1 and 4, 5-bromo-3-hydroxydiphenyl can readily be formed.

The presence of 4:5-dibromo-3-hydroxydiphenyl among the products of the decomposition of the tribromo-ketone is explained in the following way. A constant product of the decomposition is phenyldihydroresorcinol, which must owe its origin to the presence of some 5-bromo-1-phenyl- Δ^4 -cyclohexen-3-one (I) (this is readily hydrolysed to phenyldihydroresorcinol even by the moisture of the air; compare Boyd, Clifford, and Probert, J., 1920, **117**, 1385). It would seem, therefore, that the tribromo-ketone decomposes to a small extent in yet a third manner, giving rise to 5-bromo-1-phenyl- Δ^4 -cyclohexen-3-one by loss of bromine. This bromine combines with (V), giving an unstable tetrabromo-compound (VI) (compare Hinkel, *loc. cit.*), which can give 4:5-dibromo-3-hydroxydiphenyl by loss of hydrogen bromide.

When the decomposition of the tribromo-ketone is effected by means of alcoholic potash, the yield of hydroxydiphenyl derivatives is diminished owing to the formation of a small quantity of 5-bromo-

3-ethoxydiphenyl (compare Crossley and Renouf, J., 1914, **105**, 167); 4:5-dibromo-3-ethoxydiphenyl is never produced under these conditions. (When a mixture of 5-bromo-3-hydroxydiphenyl and 4:5-dibromo-3-hydroxydiphenyl is treated with an alcoholic solution of hydrogen chloride, it is again only the monobromo-derivative which yields an ethoxy-compound.)

The action of bromine on 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one (VII) gives rise to 5-chloro-4:5-dibromo-1-phenylcyclohexan-3-one (VIII), which resembles the tribromo-analogue in existing in a stable and an unstable form. In its decomposition with alcoholic potash, however, it yields a monobromo- and a monochloro-hydroxy-



diphenyl in molecular proportion, in addition to a mixture of dihalogen derivatives. The monohalogen compounds were identified through their ethoxy-derivatives. This result is in marked contrast with the behaviour of other chlorobromo-hydroaromatic compounds, from which liberation of hydrogen bromide always precedes that of hydrogen chloride (compare Crossley, J., 1904, **85**, 264).

EXPERIMENTAL.

5-Bromo-1-phenyl- Δ^4 -cyclohexen-3-one (I).—30 G. of phenyldihydroresorcinol (2 mols.) were suspended in 100 c.c. of dry chloroform and heated at 70° for 3 hours with 25 g. of phosphorus tribromide (excess of 1 mol.); the chloroform was then evaporated. The residue was poured into water and extracted three times with ether. From the extracts, washed with 4% sodium hydroxide solution and with water and dried over calcium chloride, a substance was obtained which crystallised from alcohol in transparent, colourless plates, m. p. 81.5° (Found: Br, 31.6. $\text{C}_{12}\text{H}_{11}\text{OBr}$ requires Br, 31.9%). The ketone has an irritating effect on the skin, and when kept in a moist atmosphere gradually reverts to phenyldihydroresorcinol with liberation of hydrogen bromide.

4:5:5-Tribromo-1-phenylcyclohexan-3-one.—6.4 G. of bromine (1 mol.), dissolved in 22 c.c. of chloroform, were added to a well-cooled solution of 10 g. of 5-bromo-1-phenyl- Δ^4 -cyclohexen-3-one (1 mol.) in 30 c.c. of chloroform; rapid absorption of the bromine soon occurred, with rise in temperature. The chloroform was evaporated in a current of dry air at room temperature and the solid

residue was dissolved in warm alcohol, from which it crystallised in sheaves of large, white needles, m. p. 82° (decomp.) (Found : Br, 58.2. $C_{12}H_{11}OBr_3$ requires Br, 58.4%). The needles can be kept in a dry atmosphere for several weeks without suffering much decomposition. Crystallisation from ether gives transparent prisms, which also melt at 82° , and show appreciable decomposition with liberation of hydrogen bromide after being kept for 1 day.

Action of heat. 12 G. of the tribromo-ketone were gently heated on the water-bath until the evolution of hydrogen bromide ceased. The dark semi-solid product was triturated with ether and the small quantity of phenyldihydroresorcinol which separated was removed by filtration. The filtrate on evaporation left a brown, oily residue, which was dissolved in light petroleum (b. p. $40-60^{\circ}$). After slow evaporation in the cold, the solution deposited white crystals. These were separated from the liquid (filtrate A), washed with light petroleum, and recrystallised from that solvent, 4 : 5-dibromo-3-hydroxydiphenyl separating in clusters of small, white needles, m. p. 81° (Found : Br, 48.7. $C_{12}H_8OBr_2$ requires Br, 48.8%). The benzoyl derivative, formed in the usual manner, crystallised from alcohol in small, white needles, m. p. 104° (Found : Br, 36.9. $C_{19}H_{12}O_2Br_2$ requires Br, 37.0%).

Filtrate A. The light petroleum was removed by evaporation, and the residual oil distilled in a vacuum, 5-bromo-3-hydroxydiphenyl being obtained as a colourless oil, b. p. $208-210^{\circ}/11$ mm. (Found : Br, 31.9. $C_{12}H_9OBr$ requires Br, 32.1%). The benzoyl derivative crystallised from alcohol in clusters of small needles, m. p. 108° (Found : Br, 22.85. $C_{19}H_{13}O_2Br$ requires Br, 22.7%).

Action of alcoholic potassium hydroxide. A 20% solution of potassium hydroxide was gradually added to an alcoholic solution of 20 g. of the tribromo-ketone, until the supernatant liquid remained alkaline after being gently warmed on the water-bath for a few minutes. Most of the alcohol was then removed by warming under diminished pressure, and the mixture was diluted with water, acidified, and shaken with ether, which extracted a dark liquid only partly soluble in aqueous sodium hydroxide. The insoluble portion was crystallised from alcohol, 5-bromo-3-ethoxydiphenyl separating in white clusters, m. p. $70-71^{\circ}$ (Found : Br, 28.7. $C_{14}H_{13}OBr$ requires Br, 28.9%). This compound can also be obtained by warming an alcoholic solution of 5-bromo-3-hydroxydiphenyl in presence of hydrogen chloride. As 4 : 5-dibromo-3-hydroxydiphenyl does not readily form an ethoxy-derivative under similar conditions, this serves as a convenient method for the separation of the two hydroxy-derivatives.

The alkaline filtrate from 5-bromo-3-ethoxydiphenyl was acidified,

and ether then extracted a brown viscous oil, which consisted of a mixture of 5-bromo-3-hydroxydiphenyl and 4:5-dibromo-3-hydroxydiphenyl, the separation of which was effected with light petroleum as described above.

5-Chloro-4:5-dibromo-1-phenylcyclohexan-3-one (VIII).—20 G. (1 mol.) of 5-chloro-1-phenyl- Δ^4 -cyclohexen-3-one (Boyd, Clifford, and Probert, J., 1920, **117**, 1383) in 40 c.c. of chloroform were brominated with 16 g. of bromine (1 mol.) in 50 c.c. of chloroform under the conditions described on p. 1202. The product crystallised from warm alcohol in semi-opaque, prismatic crystals, m. p. 98.5° (Found: Br, 43.5; Cl, 9.3. $C_{12}H_{11}OClBr_2$ requires Br, 43.7; Cl, 9.7%). When crystallised from alcohol, the compound is comparatively stable and can be kept for several weeks in a dry atmosphere. It crystallises from ether in transparent, rhombic crystals, m. p. 88.5° , which evolve hydrogen bromide gradually at room temperature and rapidly when warmed. They can be reconverted into the stable variety by crystallisation from alcohol.

Action of alcoholic potassium hydroxide. The reaction was carried out as described on p. 1203 and yielded a liquid product a portion of which was insoluble in aqueous sodium hydroxide. This portion crystallised from alcohol in clusters of small, white needles, m. p. $68-69^\circ$, and consisted of a mixture of 5-chloro- and 5-bromo-3-ethoxydiphenyl in molecular proportion (Found: Br, 15.7; Cl, 7.0. A molecular mixture of $C_{14}H_{13}OBr$ and $C_{14}H_{13}OCl$ requires Br, 15.7; Cl, 7.0%). The alkaline solution containing 5-chloro- and 5-bromo-3-hydroxydiphenyl, in addition to dihalogenohydroxydiphenyls, was not further examined.

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