LXXVI.—*Investigations on the Bivalency of Carbon. Part III. Some Experiments on Xanthhydrol, Dixanthhydryl Ether, and Xanthhydryl Chloride.*

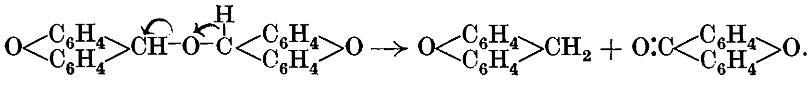
By Frederic Goronwy Kny-Jones and Allan Miles Ward.

Xanthhydrol and benzhydrol being very similar in their properties, an attempt was made to study quantitatively the rate of displacement of chlorine from xanthhydryl chloride as in the case of diphenylchloromethane (Ward, J., 1927, 2285). In lime-dried ethyl alcohol at room temperature, however, the chloride lost its halogen immediately and completely as hydrogen chloride, the reactivity appearing to be exactly comparable with that of triphenylmethyl chloride.

Xanthhydryl chloride reacted readily with water at room temperature, giving xanthone and xanthen in approximately equal quantities, together with some xanthhydrol. As was to be expected in view of this result, xanthhydrol was readily decomposed by hydrochloric acid, being changed completely to equal quantities of xanthone and xanthen after 5 minutes' boiling with $N/100$-acid : it was, however, not attacked by boiling $N/10$-sodium hydroxide. Dibenzhydryl ether (Ward, *loc. cit.*) was formed from benzhydrol by boiling with dilute acids, but it was stable to boiling *N*/100-acid : such acid converted dixanthhydryl ether into xanthone and xanthen (equal quantities) in ½ hour.

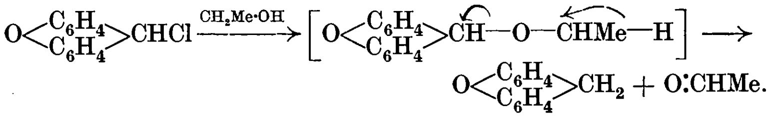
The reactions with alcohol are analogous. Xanthhydryl chloride and ethyl alcohol yielded xanthen as the main product, and some xanthone. (The alcoholic solution restored the colour to Schiff's reagent, but responded to no other test for acetaldehyde : compare Fosse, *Compt. rend.*, 1901, **133**, 880; *Bull. Soc. chim.*, 1906, **35**, 1005.) Xanthhydrol also was completely converted into xanthen (main product) and xanthone on being boiled with *N*/20-ethyl-alcoholic hydrogen chloride for 1 hour. The change was incomplete after shorter times of heating. Xanthhydrol, therefore, is much more stable in the presence of alcoholic than of aqueous hydrogen chloride. Dixanthhydryl ether, which is insoluble in ethyl alcohol, dissolved readily on being boiled with ethyl-alcoholic hydrogen chloride (*N*/20) for a few minutes : the solution remained homogeneous when cooled to room temperature and the product was xanthhydrol (yield, at least 89% of the theoretical).

Xanthhydrol, dixanthhydryl ether, and xanthhydryl chloride, therefore, are far more reactive than benzhydrol, dibenzhydryl ether, and diphenylchloromethane. Although, however, diphenylmethane and benzophenone are not produced from the last three compounds under the conditions under which xanthen and xanthone are produced from the first three, they can be obtained by reactions at higher temperatures (see, *e.g.*, Nef, *Annalen*, 1897, **298**, 234; also in the thio-series, Schönberg, Schütz, Bruckner, and Peter, *Ber.*, 1929, **62**, 2550). In connexion with the preceding transformations in ethyl alcohol, the observations of Bacon (*Amer. Chem. J.*, 1905, **33**, 92), Goldthwaite (*ibid.*, 1903, **30**, 461), and Norris and Young (*J. Amer. Chem. Soc.*, 1924, **46**, 2580) on the pyrogenic decomposition of arylalkyl alkyl ethers are of interest. Kauffmann and Pannwitz (*Ber.*, 1912, **45**, 766) have shown that triarylcarbinols in general are reduced to the corresponding triarylmethanes by alcoholic hydrogen chloride or by formic acid, and triphenylmethyl chloride in pure ethereal solution in the presence of zinc chloride (Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 204) or aluminium chloride (Norris and Young, *loc. cit.*) decomposes into triphenylmethane and acetaldehyde, doubtless by a similar mechanism (see also Hardy, J., 1929, 1000). The scheme which has been used to explain these decompositions would in the case of dixanthhydryl ether be as follows :



$$O{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}CH{-}O{-}\overset{H}{C}{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}O \longrightarrow O{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}CH_2 + O{:}C{<}\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}{>}O.$$

The instability of dixanthhydryl ether in the presence of acids finds a parallel in the decomposition of bistriphenylmethyl ether (Gomberg, *loc. cit.*); the acids he used were, however, more concentrated and the product was triphenylcarbinol. The reaction between xanthhydryl chloride and ethyl alcohol may be assumed to proceed *via* the ethyl ether, which, however, has not been isolated :



$$O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CHCl \xrightarrow{CH_2Me\cdot OH} \left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH-O-CHMe-H\right] \longrightarrow O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH_2 + O{:}CHMe.$$

It appears highly probable, therefore, that the displacement mechanisms for systems CHR_1R_2X and $CR_1R_2R_3X$ are closely allied. The displacements of halogen which have been studied for some systems CHR_1R_2Cl may be interpreted as proceeding through a phase $R_1R_2C<$, but an hypothesis involving the ion $CR_1R_2H^{\cdot}$ will also provide an explanation (Ward, *loc. cit.*, p. 2287). The bivalent-carbon hypothesis is impossible for systems of the triphenylmethane type, and a larger range of reactions can be interpreted on the ionisation theory. Certain reactions which have been regarded as evidence of the formation of ions in the triphenylmethane series were observed in the xanthhydrol experiments. Conant and Evans (*J. Amer. Chem. Soc.*, 1929, **51**, 1934), for example, consider that the presence of free radicals is indicated by the precipitation of Prussian blue when a chloroform solution of the material under investigation is shaken with an aqueous solution of potassium ferricyanide and ferric chloride. Dixanthhydryl ether readily brings about this reaction. Further, Boyd and Hardy (J., 1928, 632) attribute to ionisation the red colour developed when triphenylcarbinol is dissolved in a mixture of sulphuric and acetic acids : $Ph_3C\cdot O\cdot SO_3H \rightleftharpoons Ph_3C^+ + SO_4H^-$. The colour may be due to a quinonoid tautomeride of this ion (see Gomberg and Sullivan, *J. Amer. Chem. Soc.*, 1922, **44**, 1810; Gomberg and Blicke, *ibid.*, 1923, **45**, 1765). The development and subsequent disappearance of a yellow-green colour in all the experiments in hydrochloric acid here described may therefore be evidence of the presence of the ion $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CH^+$. Conant and Sloan (*ibid.*, 1923, **45**, 2468) consider that they have obtained the free xanthyl radical in an impure state.

The accumulated evidence supports the ionisation theory rather than the theory of bivalent carbon. As applied to the problem of the Walden inversion (Ward, J., 1927, 445), the latter theory is now recognised to be untenable (see also the criticism of Ashworth and Burkhardt, J., 1928, 1795) : three groups, and not two, must be momentarily attached to the asymmetric carbon atom during the transformations, and evidence has been obtained that optical activity can persist under such conditions (McKenzie, Roger, and Wills, J., 1926, 779).

EXPERIMENTAL.

Preparation of Dixanthhydryl Ether.—When xanthhydrol was heated with petroleum for several days (Meyer and Saul, *Ber.*, 1893, **26**, 1276), the conversion into dixanthhydryl ether was incomplete. The preparation was therefore carried out by heating moist xanthhydrol, prepared from xanthone (25 g.), at 150—155°, and finally at 175° for 1¼ hours. The product was cooled, powdered, and extracted three times with methylated spirit. The residue (19·1 g.), m. p. 193—209°, was crystallised from 200 c.c. of xylene, washed with the same substance and with ether, and air-dried (yield, 17·8 g.); m. p. 205—211°. A sample of the dixanthhydryl ether, twice recrystallised from xylene, well washed with ether, and dried in a desiccator over paraffin wax, melted at 219° (Meyer and Saul, *loc. cit.*, give m. p. about 200°) (Found : C, 82·4; H, 5·0. Calc. : C, 82·5; H, 4·8%).

Preparation of Xanthhydryl Chloride.—(1) Thionyl chloride (2 c.c.), dissolved in 50 c.c. of light petroleum (b. p. 40—60°), reacted readily with dixanthhydryl ether (5 g.) suspended in the solution; as, however, needle-shaped crystals soon began to separate, the mixture was gently refluxed for 15 minutes until only a small amount of brown solid remained in suspension. The colourless solution was cooled in ether–solid carbon dioxide, and the crystals thus produced were collected and recrystallised repeatedly from 100 c.c. of the same solvent, long colourless needles being obtained. The solvent was removed as completely as possible in an atmosphere of nitrogen and the crystals were dried in a stream of the warmed gas (yield, 3—3·5 g.). The crystals became discoloured on drying and decomposition doubtless took place, but they could be kept unchanged for days in contact with light petroleum (Found, by titration of the hydrogen chloride liberated in alcoholic solution : Cl, 14·8, 15·0, 16·1, 13·8. Calc. : Cl, 16·4%).

The product melted at 60—65° after softening at 50° : selected crystals melted above 70°, *e.g.*, 71—73°, 72—74·5° (Gomberg and Cone, *Annalen*, 1910, **376**, 188, give m. p. 73—75° after sintering at 71°). Colourless crystals when removed from the mother-liquor became yellow on drying in the air and then colourless again; they were unmelted at 100° and kept their needle shape.

(2) The same results were obtained by the interaction of xanthhydrol and thionyl chloride in boiling light petroleum.

Reaction between Xanthhydrol and Hydrochloric Acid.—(a) Xanthhydrol, prepared from xanthone (5 g.), was washed with water and refluxed for 1 hour with 75 c.c. of *N*/100-hydrochloric acid. The solid melted and needle-shaped crystals then separated. They were removed from the cooled solution, washed with water, and immediately heated to boiling with 30 c.c. of methylated spirit. The solution was cooled to room temperature, filtered from the crop of crystals, added to an equal bulk of glacial acetic acid containing 5 c.c. of a concentrated aqueous solution of urea, and poured after 2 hours into excess of water. The precipitate then formed was collected, washed with water, and added to the crop of crystals above. The whole was dried over calcium chloride (yield, 5·15 g.) and extracted four times with 40—50 c.c. of boiling light petroleum (b. p. 40—60°). The extracts were well cooled and filtered, and the combined filtrates evaporated to dryness, leaving 2·42 g. of colourless solid, m. p. 94—96°, mixed m. p. with xanthen (m. p. 100—101°) 96—97·5°. Two further similar extractions of the undissolved solid gave 0·09 g., m. p. 97—135°, and a seventh extraction gave 0·05 g., m. p. 142—158°. The remaining undissolved solid (2·46 g.) melted alone at 163—168°, and at 167—170° when mixed with xanthone (m. p. 174°).

This method of separating xanthen from xanthone, although not quantitative, since xanthone was slightly soluble in the light petroleum used, was the one that gave the best results. The steam-distillation method used by Heller and Kostanecki (*Ber.*, 1908, **41**, 1325) is unsatisfactory because xanthone is slightly volatile in steam.

(b) Xanthhydrol (0·5 g.) was boiled with *N*/100-hydrochloric acid (7·5 c.c.) for 5 minutes; the subsequent procedure was as described under (a). The alcoholic filtrate, after being added to the urea–glacial acetic acid, was still clear after 7 hours, whereas a portion of the same preparation of xanthhydrol, when dissolved in methylated spirit and added to the urea–acetic acid solution, was converted into a stiff paste after a few minutes.

(c) Similar experiments were carried out with hydrochloric acid, the strength being gradually increased to 5*N*; xanthen and xanthone were the only products isolated.

Xanthhydrol and Aqueous Sodium Hydroxide.—Xanthhydrol (0·5 g.) was boiled with 7·5 c.c. of *N*/10-aqueous sodium hydroxide for 1 hour. No yellow-green colour appeared and the xanthhydrol did not melt as in the hydrochloric acid reactions. The solid dissolved completely in about 10 c.c. of cold methylated spirit and the addition of this solution to the urea reagent gave a precipitate comparable in amount with that obtained on testing the xanthhydrol in (b).

Reaction between Dixanthhydryl Ether and Hydrochloric Acid.—(d) Dixanthhydryl ether (5 g.) was boiled with *N*/2-hydrochloric acid (75 c.c.) for 1 hour. The products were examined and separated as in (a); xanthhydrol was not present. The product (2·16 g.) obtained from the first four extractions melted at 97—98°, and at 98—99° when mixed with xanthen; the seventh extract (0·02 g.) had m. p. 163—166°. The remaining portion (2·35 g.), insoluble in the light petroleum, melted at 165—169°, and at 169—172° when mixed with xanthone.

(e) Finely powdered dixanthhydryl ether (0·5 g.) was boiled with *N*/100-hydrochloric acid (7·5 c.c.) for 15 minutes. The solution was cooled, and the product, which contained needle-shaped crystals, was collected, washed with water, and boiled with alcohol (15 c.c.). A part, doubtless unchanged ether, did not dissolve. The alcoholic solution did not give the urea reaction for xanthhydrol, but yielded a copious white precipitate on being poured into water.

(f) This experiment was carried out as in (e), but the mixture was boiled for ½ hour. The product dissolved completely in 5 c.c. of hot ethyl alcohol; the solution thus formed gave a crop of colourless needles on cooling, and the filtrate did not contain any xanthhydrol.

Reaction between Xanthhydryl Chloride and Water.—Xanthhydryl chloride (2 g.; Cl, 14·8%) was triturated with 30 c.c. of water at room temperature for ½ hour. The chloride, initially yellow-brown, rapidly became almost colourless. The products, collected and washed with water, were extracted with 30—40 c.c. of methylated spirit and the alcoholic solution was added to the urea reagent: a precipitate separated. Two more extractions of the residue were made and the precipitates were collected after some hours, washed with methylated spirit, and dried (total yield, 0·43 g., corresponding to 0·41 g. of xanthhydrol). The solutions and the remaining residue were worked up as in (a), the following yields being obtained: (i) 0·56 g., m. p. 94—96°, (ii) 0·05 g., m. p. 165—167°, (iii) 0·53 g., m. p. 168—170°.

Reaction between Xanthhydrol and Ethyl-alcoholic Hydrogen Chloride.—(g) Xanthhydrol (0·2 g.), dried over stick sodium hydroxide, was dissolved in ethyl-alcoholic hydrogen chloride (*N*/10 approx., prepared by passing hydrogen chloride into lime-dried ethyl alcohol) and boiled for 5 minutes. The cooled solution was tested for xanthhydrol and gave a copious precipitate. When the reaction mixture was boiled for 15 or for 30 minutes, there was also a positive test, but the amount of condensation product which separated in the latter case was small. Heating for 1 hour brought about complete decomposition of the xanthhydrol.

(h) Xanthhydrol (2·5 g.) was boiled with 20 c.c. of *N*/20-ethyl-alcoholic hydrogen chloride for 1 hour. The solvent was then distilled: it restored the colour to Schiff's reagent, but only slightly reduced ammoniacal silver nitrate. The solid residue was dried over calcium chloride (yield, 2·4 g.) and examined in the usual way. It gave: (i) 1·36 g., m. p. 93—95°, mixed m. p. with xanthen, 94—96°; (ii) 0·09 g., m. p. 142—164°; (iii) 0·80 g., m. p. 163—166°, mixed m. p. with xanthone, 168—171°.

Reaction between Dixanthhydryl Ether and Ethyl-alcoholic Hydrogen Chloride.—Dixanthhydryl ether (2 g.), when boiled with *N*/20-ethyl-alcoholic hydrogen chloride (20 c.c.), dissolved after 4 minutes, and solid did not separate when the solution was cooled. An equal volume of the urea reagent was added; a copious white precipitate, which separated after a few minutes, was collected after 14 hours and washed repeatedly with methylated spirit until the washings gave only a small precipitate on being poured into water. The product, after being dried over calcium chloride, weighed 1·98 g. (equivalent to 1·87 g. of xanthhydrol).

The alcoholic-acetic acid solution and washings did not give any precipitate on being further tested for xanthhydrol and were therefore poured into excess of water. The precipitate was collected and dissolved in about 30 c.c. of hot methylated spirit. Fine colourless needles (0·12 g.), which separated from the cooled solution, did not melt at 225°, and gave a copious evolution of ammonia on fusion with potash (this product is possibly formed from urea and xanthhydrol by the condensation of one molecule of each). When excess of water was added to the methylated spirit solution, a solid (0·26 g.) was obtained which began to melt at 90° but was not completely molten at 220°; it probably consisted mainly of xanthen and xanthone.

Reaction between Xanthhydryl Chloride and Ethyl Alcohol.—Lime-dried ethyl alcohol (about 50 c.c.) was added to a light petroleum solution of xanthhydryl chloride (prepared from 5 g. of xanthhydrol). The solution, which became successively brown and green, was shaken for a few minutes, and the solvent then distilled off. The green residue was dried in a current of air (yield, 4·1 g.). A portion of it (about 0·2 g.), tested for xanthhydrol, did not give a precipitate after 4 hours. The remainder was extracted four times with light petroleum. The soluble portion (3·05 g.) was yellow-brown and melted at 85—90°; it was dissolved in light petroleum and refluxed (charcoal) for $\frac{1}{2}$ hour. The pale yellow solution thus formed was filtered and evaporated; yield, 2·65 g., m. p. 91—93°; mixed m. p. with xanthen 97—99°. The green insoluble portion (0·58 g.) melted at 143—146°; it dissolved in acetone to a green solution, from which the colour was removed by means of charcoal. The purified product had m. p. 171—172° and mixed m. p. with xanthone 173—174°.

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Sir John Cass Technical Institute,
London, E.C. 3.

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