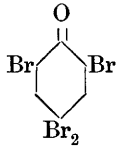


CXXV.—*Studies on the Origin of Colour. Derivatives of Fluorene.*

By IDA SMEDLEY.

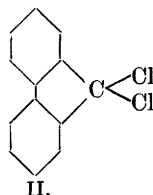
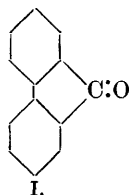
THE experiments to be described were undertaken with the object of ascertaining whether two halogen atoms can displace the carbonyl oxygen in coloured ketones without destroying the chromophoric nature of the group affected. The evidence on this point is at present somewhat conflicting. The keto-dichlorides of the naphthalene and hydrindonaphthene series appear to be colourless when pure (Zincke, *Ber.*, 1887, **20**, 2053; 1888, **21**, 1027, 3540); the naphthalene keto-dibromides are also colourless (Armstrong and Davis, *Brit. Assoc. Rep.*,

1903, 174); but tribromophenol bromide, , is always de-

scribed as yellow (Kastle, *Amer. Chem. J.*, 1902, **27**, 31; Lewis, *Trans.*, 1902, **31**, 1001). The last compound, however, is very unstable and it is doubtful if the colour be that of the pure substance.

The di-iodo-derivatives in which two iodine atoms are attached to a single carbon atom are few in number: the simplest of these, methylene iodide, is colourless, although it has an abnormally high refractive index. Iodoform, as is well known, is yellow in colour, but other substituents besides iodine appear to condition colour in conjunction with two atoms of iodine: thus di-iodo-acetic acid and its salts (Perkin and Duppa, *Journ. Chem. Soc.*, 1860, **13**, 1; Angeli, *Ber.*, 1893, **26**, 1, 595) and di-iodo-camphor (Brühl, *Ber.*, 1904, **37**, 2156) are described as yellow, and it appears probable that the colour is inherent in the pure substances.

The colour of the halides prepared from coloured ketones derived from colourless hydrocarbons was therefore of considerable interest. The substance chosen for investigation was fluorenone (I).



As prepared by oxidation of commercial fluorene, this ketone has a deep yellow colour; after purification it forms large, lemon-yellow

crystals. The dichloride (II) prepared from it by the action of phosphorus pentachloride proves to be colourless.

Numerous experiments were made without success to convert this chloride into a corresponding iodo-compound by the action of various iodides. When dissolved in benzene or carbon disulphide, it was at once acted on by aluminium iodide, an intense blue liquid being obtained, which was readily decolorised; but no well-characterised substance could be isolated from this product. Experiments made to convert the chloride from benzophenone into an iodide were equally unsuccessful.

Whereas the evidence is in agreement with the view that the displacement of the oxygen of the carbonyl group by two chlorine atoms destroys the power to act as a colour centre, the effect of the other halogen atoms requires further elucidation.

The derivatives of fluorene afford striking instances of the property of halochromism described by Baeyer, Kaufmann, and others (Baeyer and Villiger, *Ber.*, 1902, **35**, 1189, 1754, 3013; 1903, **36**, 2774; Kehrmann and Wentzel, *Ber.*, 1901, **34**, 3815; Kaufmann, *Ber.*, 1902, **35**, 1321; 1903, **36**, 561). When fluorenone is dissolved in concentrated sulphuric acid, deep violet or brownish-red solutions are formed; the solution of the dichloride in the cold acid has a deep green colour, which changes to violet on heating, fumes of hydrogen chloride being evolved; fluorenone is precipitated from both of these solutions on dilution. The condensation product obtained by heating together fluorenone chloride and phenol, represented by the formula $(C_6H_4)_2C(C_6H_4 \cdot OH)_2$, although itself colourless, gives an intensely crimson solution when dissolved in concentrated sulphuric acid; the original substance is precipitated unchanged on diluting the liquid with water. Sulphuric acid has more tendency to form such coloured salts than hydrogen chloride; in fact, I was not able to obtain evidence that any of the fluorene derivatives studied afford coloured hydrochlorides. Solutions of fluorenone in anhydrous ether, glacial acetic and glacial phosphoric acids were saturated with dry hydrogen chloride without showing any intensification of colour. The fact that fluorenone and the corresponding dichloride give differently coloured solutions in cold sulphuric acid may possibly be due to the formation in the latter case of a hydrochloride which is decomposed by warming and converted into the violet sulphate; on the other hand, the green solution of fluorenone chloride in sulphuric acid closely resembles in colour that obtained on adding aluminium chloride to a solution of fluorenone chloride in carbon disulphide, so that most probably the colour is due to the presence of some salt-like compound of the chloride.

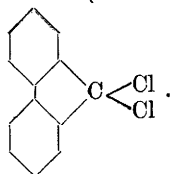
The cause of the phenomenon of halochromism is generally supposed to be the change from bivalent to quadrivalent oxygen, consequent on an oxonium sulphate being produced. Without assuming further

change in the structure of the molecule, it is difficult to understand that this should account for the development of colour. The difficulty of isolating these coloured salt-like compounds is, however, so great that the evidence as to their constitution remains far from satisfactory.

Experiments were also carried out with the object of preparing thiofluorenone, the colour of the thio-ketones being of much interest; the only sulphur-containing compound which could be isolated, however, is the colourless disulphide, $(C_6H_4)_2 \begin{matrix} S \\ \diagdown \\ \diagup \\ S \end{matrix} (C_6H_4)_2$.

EXPERIMENTAL.

9:9-Dichlorofluorene (*Fluorenone Chloride*),



Fluorenone chloride is prepared by heating fluorenone with slightly more than the theoretical quantity of phosphorus pentachloride on a water-bath. When cool, the product is poured on to ice to remove phosphorus oxychloride; a white solid remains which is usually coloured yellow by the presence of fluorenone. When recrystallised from benzene, it forms large, colourless, orthorhombic prisms melting at 103° .

0.3556 gave 0.4386 AgCl. Cl = 30.51.

$C_{13}H_8Cl_2$ requires Cl = 30.21 per cent.

This substance resembles the corresponding chloro-derivatives of aceto- and benzo-phenone in its behaviour: it is rapidly acted on by hot water, slowly by cold; it is therefore decomposed at the ordinary temperature by a solution of silver nitrate. When warmed with aniline, it is vigorously acted on; it is converted by dimethylaniline and a trace of zinc chloride into a deep blue product, which dissolves readily in spirit, forming a pink solution.

It dissolves in cold concentrated sulphuric acid giving a green solution; on warming this liquid, fumes of hydrogen chloride are evolved, the colour changing to a deep violet. On diluting the liquid with water, fluorenone is precipitated.

On warming the chloride with a solution of hydroxylamine hydrochloride, pale yellow needles of fluorenoneoxime melting at $193\text{--}194^\circ$ are formed; by the action of phenylhydrazine, fluorenonehydrazone (m. p. 149°) is obtained.

Diethoxyfluorene.—To prepare this compound, a solution of five grams of fluorene chloride in benzene was mixed with 50 c.c. of a 10 per cent. solution of alcoholic potash. The liquid was then heated during eight hours in a reflux apparatus on a water-bath. The colour of the solution became yellow and gradually deepened to a very dark red, potassium chloride being precipitated; this was filtered off and the filtrate concentrated: brown plates then separated, which, when recrystallised from absolute alcohol, were obtained as red prisms melting at 82° . These appeared to be evenly coloured and remained red when recrystallised from benzene or alcohol. By recrystallisation from a mixture of alcohol and water, however, they were obtained as white plates, a small amount of a red colouring substance, probably Graebe's red hydrocarbon, being first precipitated. The analytical numbers agreed with those required by the formula $(C_6H_4)_2C(O \cdot C_2H_5)_2$, and the substance is therefore 9:9-diethoxyfluorene.

0.0410 gave 0.122 CO_2 and 0.0266 H_2O . C = 81.14; H = 7.21.

$C_{17}H_{15}O_2$ requires C = 80.31; H = 7.09 per cent.

The red crystals originally obtained were converted by the action of glacial acetic or mineral acids into fluorenone (m. p. 84°), a small amount of red substance remaining unattacked.

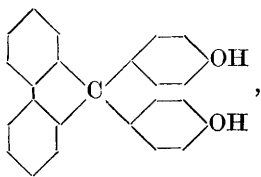
Diphenoxyfluorene.—On heating fluorene chloride with two molecular proportions of phenol, a viscous product is formed, which is converted by repeated crystallisation from alcohol into a mass of white needles efflorescing on exposure to air. The crystals lose their transparent appearance when heated above 100° and melt sharply at 223 — 224° . Analysis gave the following results:

(1) C = 79.24; H = 5.73. (2) C = 78.92; H = 6.21; after drying at 100° , C = 85.28; H = 5.14.

$(C_6H_4)_2C(C_6H_4OH)_2$ requires C = 85.71; H = 5.16 per cent.

$(C_6H_4)_2C(C_6H_4OH)_2, 2EtOH$ „ C = 78.73; H = 6.78 „ „

It is a matter of interest that a compound represented by the formula



derived from so highly coloured a ketone as fluorenone, should be colourless. It dissolves in caustic alkali and also in concentrated sulphuric acid, forming, in the latter case, an intensely crimson liquid

which becomes colourless on dilution with water, the original substance being then precipitated unchanged. The basic properties of the oxygen are indicated not only by the formation of a coloured salt with sulphuric acid but also by the power the compound exhibits of combining with alcohol.

Action of Aluminium Iodide.

The action of aluminium iodide on a solution of fluorene chloride in benzene or carbon disulphide is vigorous, iodine being at once liberated ; no organic iodide could be detected in the product.

The action of aluminium iodide on a solution of the chloride from benzophenone in carbon disulphide produced a black mud from which eventually a white substance free from halogen was isolated. When recrystallised from benzene this melted at 221° , agreeing in solubility, melting point, and appearance with the description given of tetraphenylethylene.

The action of aluminium chloride on fluorene chloride dissolved either in benzene or in carbon disulphide produces an intense bluish-black substance, which is rapidly decolorised by the addition of solvents containing oxygen or on exposure to air, from which amorphous products containing chlorine may be separated ; the nature of these is still under investigation.

It is remarkable that the action of aluminium chloride on a mixture of fluorene chloride and ethyl iodide, a method by which the chlorine in chloroform may be displaced quantitatively by iodine (J. W. Walker, *Trans.*, 1904, **85**, 1090), leads to the formation of similar amorphous products free from iodine.

Thio-derivatives of Fluorene.

The thio-derivatives of fluorene do not appear to have been previously examined, although reference has been made to the red colour of the sulphur compounds produced by heating the hydrocarbons fluorene and acenaphthene with dry sodium thiosulphate ; fluorene is also stated to give a difluoryl compound (Hodgkinson, *Proc.*, 1896, **12**, 110) on heating it with sulphur.

On adding to fluorene chloride an alcoholic solution of potassium hydrosulphide prepared by saturating a 10 per cent. solution of caustic potash with sulphuretted hydrogen and allowing the mixture to stand for some hours, white needles begin to separate. These, when twice recrystallised from a mixture of benzene and petroleum, melt sharply at 167° to a pale yellow liquid which, on further heating, changes to a deep red.

From benzene, large, colourless crystals belonging to the mono-symmetric system were obtained.

On combustion with lead chromate,

0.1242 gave 0.3598 CO_2 and 0.0460 H_2O . $\text{C} = 79.01$; $\text{H} = 4.11$.

0.1680 ,, 0.4873 CO_2 ,, 0.0690 H_2O . $\text{C} = 79.11$; $\text{H} = 4.56$.

Two sulphur estimations gave $\text{S} = (1) 16.39$, (2) = 16.32.

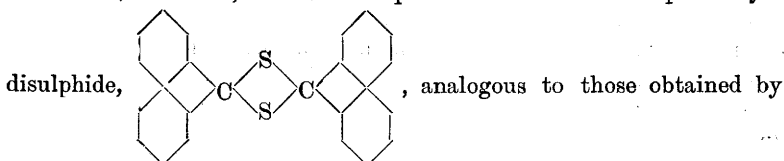
$\text{C}_{13}\text{H}_8\text{S}$ requires $\text{C} = 79.59$; $\text{H} = 4.06$; $\text{S} = 16.32$ per cent.

The molecular weight was determined by the lowering of the freezing point of a solution in benzene :

0.0908 in 12.84 benzene gave $\Delta t 0.095^\circ$. $\text{M. W.} = 372$.

The double formula, $\text{C}_{26}\text{H}_{16}\text{S}_2$, requires $\text{M. W.} = 360$.

The compound is not a simple thioketone ; neither is it readily oxidised by a neutral solution of potassium permanganate nor does it form a lead salt when treated with lead acetate in ethyl acetate solution ; it is, therefore, not a mercaptan. The substance is probably a



the action of an alcoholic solution of potassium hydrosulphide on acetophenone chloride and on benzophenone chloride (Behr, *Ber.*, 1872, 5, 970 ; Engler, *Ber.*, 1878, 11, 922). Since the action of alcoholic potash on fluorene chloride leads to the formation of a diethoxy-derivative, it is possible that a dimercaptan is at first formed but at once converted into the bimolecular compound.

If a solution of potassium sulphide, prepared by adding an equal volume of 10 per cent. caustic potash to the alcoholic potassium hydrosulphide solution previously used, be allowed to act on finely powdered fluorene chloride, the liquid gradually becomes yellow and, after standing for some days, deposits a bright red solid. To purify this substance, it is extracted with carbon disulphide, the solution evaporated to dryness, the residue dissolved in the least possible quantity of benzene and mixed with a concentrated solution of picric acid in benzene. The red crystals which separate are decomposed by ammonia and the red solid thus obtained is recrystallised from a mixture of chloroform and alcohol. Well-defined, shining, red needles melting at $187-188^\circ$ were thus obtained, which gave the following results on analysis :

0.9060 gave 0.0455 H_2O and 0.3352 CO_2 . $\text{C} = 95.20$; $\text{H} = 5.26$.

$(\text{C}_6\text{H}_4)_2\text{C}:\text{C}(\text{C}_6\text{H}_4)_2$ requires $\text{C} = 95.12$; $\text{H} = 4.88$ per cent.

This product is therefore identical with Graebe's red hydrocarbon,

bisdiphenylene-ethylene. The red needles may be obtained directly from the solution in carbon disulphide by adding light petroleum and leaving the solution to crystallise. The only other pure product isolated was fluorenone. It is remarkable that whilst the action of an alcoholic solution of potassium sulphide on benzophenone chloride is extremely rapid, a blue oil, thiobenzophenone, being at once formed, fluorenone chloride should be slowly reduced, the bimolecular hydrocarbon being formed.

Neither by the action of phosphorus pentasulphide on fluorenone nor by the distillation of the disulphide could any thioketone be isolated.

I desire to express my thanks to Professor Armstrong for the interest he has taken in this investigation and to acknowledge my indebtedness to the Research Fund Committee of the Chemical Society for a grant in aid of these experiments, which were begun at the Central Technical College and completed at the Davy-Faraday Research Laboratory.
