

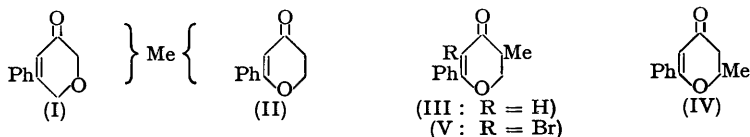
## NOTES.

*A Constituent of the Essential Oil of Myrtus bullata.*

By C. W. BRANDT, W. I. TAYLOR, and B. R. THOMAS.

[Reprint Order No. 5334.]

A READILY crystallised, optically inactive compound,  $C_{12}H_{12}O_2$ , was isolated from the essential oil of *Myrtus bullata* (Banks and Solander), a shrub endemic to New Zealand and common in the lowland forests of the North Island. The infra-red spectrum (solid film) showed a strong band at  $1681\text{ cm.}^{-1}$  in the carbonyl-stretching region suggestive of an  $\alpha\beta$ -unsaturated ketone group in a six-membered ring, and the ultra-violet absorption showed the presence of the chromophoric grouping  $\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot$  (cf. Wilds *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 1985). Presence of the unsaturated ketone grouping was confirmed by the preparation of a 2:4-dinitrophenylhydrazone, which showed a maximum, as expected, at  $412\text{ m}\mu$ . There was no hydroxyl-stretching absorption at *ca.*  $3000\text{ cm.}^{-1}$  and this was supported by negative results on attempted acylation. An ether linkage was therefore inferred and since Zeisel determinations were negative, the second oxygen atom must form part of the six-membered ring containing the ketonic system. This leads to the partial structures (I) and (II) as the only possibilities, with a methyl group, confirmed by *C*-methyl determination, as yet unplaced.



On hydrolysis in aqueous-alcoholic potassium hydroxide the compound yielded both acetophenone and benzoic acid which could only have arisen by fission of the potential 1:3-diketone in the 2:3-dihydro- $\delta$ -pyrone (II). The formation of acetophenone instead of propiophenone showed that the methyl group could not be at  $C_{(3)}$ ; thus the only structures available are (III) and (IV). A decision between them was readily made since the dihydropyrone was stable to selenium dioxide in boiling acetic acid, and therefore the compound must be (III) with no methylene group adjacent to the carbonyl group.

To provide further support, attempts were made to dehydrogenate or oxidise the dihydropyrone to the pyrone, but without success. Addition of one mol. of bromine in carbon tetrachloride followed by debromination afforded a compound,  $C_{12}H_{11}O_2\text{Br}$ , which from the bathochromic shift of the ultra-violet absorption maximum and the inertness of the bromine atom must have the constitution (V). The dihydropyrone also reacted very sluggishly with *N*-bromosuccinimide, to give, after debromination, the bromo-compound (V) in poor yield.

Synthesis of 2:3-dihydro-3-methyl-6-phenyl-4-pyrone is under investigation.

*Experimental.*—Ultra-violet absorption spectra were taken in 95% EtOH.

2:3-Dihydro-3-methyl-6-phenyl-4-pyrone (III).—The crude solid material which separated from the steam-distillate of the essential oil was purified by crystallisation from light petroleum





*Chemical Action of Ionising Radiations in Aqueous Solutions.*  
*Part XIII.\* Absolute Yield of the Ferrous Sulphate Dosimeter.*

By F. T. FARMER, T. RIGG, and J. WEISS.

[Reprint Order No. 5359.]

DILUTE ferrous sulphate in 0.8N-sulphuric acid has, in the last few years, become a standard dosimeter for ionising radiations. Much discussion has arisen as to the absolute yield of this system, usually expressed as the  $G$  value, *i.e.*, moles of ferric salt produced per 100 ev. Miller (*J. Chem. Phys.*, 1950, **18**, 79) and Hardwick (*Canad. J. Chem.*, 1952, **30**, 17) have reported values of about  $G(\text{Fe}^{\text{III}}) \approx 20$  for gamma-rays or hard X-rays, and Rigg, Stein, and Weiss (*Proc. Roy. Soc.*, 1952, *A*, **211**, 375) reported  $G = 19.7$  for X-rays (200 kv). On the other hand, Hochanadel and Ghormley (*J. Chem. Phys.*, 1953, **21**, 880) found  $G(\text{Fe}^{\text{III}}) = 15.6$  for  $^{60}\text{Co}$  gamma-rays, while other recent work [Lazo, Dewhurst, and Burton, 1953 Report Radiation Project, Contract AT (11-1) - 38, Univ. Notre Dame; Jerome Weiss, Bernstein, and Kuper, 1953, Brookhaven National Laboratory Report] has led to  $G(\text{Fe}^{\text{III}}) = 15.9$ .

The measurements by Miller, by Hardwick, and by Jerome Weiss *et al.* (*loc. cit.*) were based on ionisation measurements in air, with the values  $W(\text{air}) = 32.5, 31.9$ , and  $34.3$  ev, respectively, where  $W(\text{air})$  is the energy required to form an ion pair. Hochanadel and Ghormley's value was obtained calorimetrically, and that of Rigg *et al.* was based on the ionisation method described by Farmer, Stein, and Weiss (*J.*, 1949, **3241**) who also used  $W(\text{air}) = 32.5$  ev.

Recently, we have become aware that two corrections must be made to our previously reported value: (i) In the case of 200-kv X-rays, allowance must be made for photo-electric absorption processes in the 0.8N-sulphuric acid. (ii) Several recent investigations have shown that the  $W$  values previously used are too low; according to Valentine (*Proc. Roy. Soc.*, 1952, *A*, **211**, 75)  $W(\text{air}) = 35.0 \pm 0.5$  ev.

The former correction can be made from measurements of the apparent  $G(\text{Fe}^{\text{III}})$  value at different acid concentrations. The results given in the Table show that the yield of ferric salt in 0.8N- is appreciably greater than that in 0.01N-sulphuric acid (these experiments were carried out by the method described by Rigg *et al.*, *loc. cit.*). It is clear that for the present purpose, the *initial yields* have to be considered. Thus, while it is well known that in the strongly acid solutions the yield-dose relation is linear, this is no longer true at the lower acidities, on account of the pH-dependent back-reaction,  $\text{Fe}^{3+} + \text{O}_2^- \longrightarrow \text{Fe}^{2+} + \text{O}_2$ , which tends to lower the yield of ferric salt (*cf.* Rigg *et al.*, *loc. cit.*). According to the last-named workers, there is no obvious chemical reason for an increase in the initial yield of ferric salt in the more concentrated acid solutions and it is therefore suggested that the true  $G$  value should be very close to the (initial)  $G$  value at low acidities, *e.g.*, in 0.01N-acid which is sufficiently close to pure water from the point of view of energy absorption. The increase of the yield with sulphuric acid concentration is therefore attributable to the photo-electric effect, so that the original  $G$  value is decreased from 19.7 to 18.0 (see Table).

*Variation of the initial yield of ferric salt with sulphuric acid concentration for  $3.1 \times 10^{-4}\text{M}$ -  
 $\text{FeSO}_4$ , in air-saturated solution irradiated with X-rays (200 kv).*

Concn. of $\text{H}_2\text{SO}_4$ (N) .....	0.80	0.10	0.01
Apparent yield ( $\text{Fe}^{\text{III}}/100$ ev), calc. with $W(\text{air}) = 32.5$ ev .....	19.7	18.2	18.0

The magnitude of the correction made here for 200-kv X-rays is also compatible with calculations based on the energy distribution in the radiation produced by the X-ray tube and with the geometry of the experimental arrangement. For 0.8N-sulphuric acid, even with X- or gamma-rays of energy greater than 1 Mev, a correction of about 2.5% must be

\* Part XII, *J.*, 1954, 66.

made for the increased electron density. By using the recently established value  $W(\text{air}) = 35.0$  ev (Valentine, *loc. cit.*), the lower  $G$  value of 18.0 obtained after correction for photoelectric absorption is further lowered to  $18.0(32.5/35.0) = 16.7$ . Very recently, moreover, it has been discovered that a further correction must be made for geometrical factors in the standard air chamber used at the National Physical Laboratory, against which the dosimeter employed in this work was calibrated (Kemp and Hall, *Brit. J. Radiol.*, 1954, **27**, 219). This reduces the value of  $G$  by a further 3%. Taking account of the various experimental errors, which are estimated to be not more than  $\pm 5\%$ , we arrive, therefore, at a final value of  $G(\text{Fe}^{\text{III}}) = 16.2 \pm 0.8$ .

In the case of 200-kv  $X$ -rays, this new  $G$  value leads to the value 3.80 for the yield  $G(\text{R})$  of free radical pairs ( $\text{H} + \text{OH}$ ) from water, and to 0.54 for the yield of the "molecular" decomposition  $G(\text{M})$  of water. This is based on recent measurements of Rigg and Weiss (unpublished work) which are also in agreement with the previous measurements by Allen (*Discuss. Faraday Soc.*, 1952, **12**, 79; Johnson and Allen, *J. Amer. Chem. Soc.*, 1952, **74**, 4147). Similar experiments with radium gamma-rays have shown that the ratio  $G(\text{M})/G(\text{R})$  is about 20% less than with 200-kv  $X$ -rays; the  $G(\text{Fe}^{\text{III}})$  is probably within the experimental limits given above for the  $X$ -rays, on account of the relatively small contribution of  $G(\text{M})$  to this yield.

CHEMISTRY DEPARTMENT, KING'S COLLEGE,  
UNIVERSITY OF DURHAM, NEWCASTLE-ON-TYNE, 1.

[Received, May 5th, 1954.]

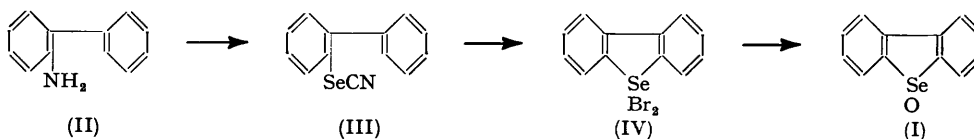
### A Modified Synthesis of Dibenzoselenophen Oxide.

By L. CHERICI and R. PASSERINI.

[Reprint Order No. 5254.]

DIBENZOSELENOPHEN OXIDE (I) has been prepared by treating dibenzoselenophen dibromide or dichloride with 3% aqueous sodium hydroxide (Courtot and Montamedi, *Compt. rend.*, 1934, **199**, 531; Behaghel and Hofmann, *Ber.*, 1939, **72**, 582). Recently McCullough and his associates (*J. Amer. Chem. Soc.*, 1950, **72**, 5753) described a new synthesis of dibenzoselenophen, and obtained the oxide by oxidation with 40% peracetic acid in glacial acetic acid.

Since a convenient supply of peracetic acid was not readily available, and every attempted oxidation with hydrogen peroxide in glacial acetic acid failed, we modified the methods already reported. As stated by McCullough and his co-workers the direct bromination of bis-2-diphenyl diselenide by Behaghel and Hofmann's method leads to a mixture of dibenzoselenophen dibromide and bromodibenzoselenophen dibromide. We found that addition of bromine to a chloroform solution of 2-selenocyanatodiphenyl gives a good yield of dibenzoselenophen dibromide. From the latter, dibenzoselenophen oxide can be easily obtained as indicated by Courtot and Montamedi (*loc. cit.*).



The present synthesis is more convenient than those already recorded, and appears to be particularly suitable for the preparation of dibenzoselenophen oxide from 2-aminodiphenyl.

*Experimental.*—2-Selenocyanatodiphenyl (III). 2-Aminodiphenyl (80 g.) was diazotised in dilute hydrochloric acid, and cold aqueous potassium selenocyanate (80 g.) added to the neutralised (Congo red) solution. Vigorous stirring was continued for 1 hr., then the mixture was

allowed to decompose for 6 hr. The reddish oil was extracted with ether, the ether extract dried ( $\text{Na}_2\text{SO}_4$ ), the excess of ether removed, and the oil distilled at reduced pressure. An orange-coloured product (70 g.), b. p. 193—195/10 mm., was obtained.

*Dibenzoselenophen dibromide* (IV). To a solution of 2-selenocyanatodiphenyl (51 g.) in chloroform (275 c.c.), bromine (20 c.c.) was added dropwise during 3 hr., and external cooling (running water) was then continued for another 3 hr. The mixture was then set aside at room temperature for 12 hr. and finally heated at 70° for 24 hr. Evolution of hydrogen bromide having then ceased the mixture was filtered and the precipitate washed with little chloroform. Dibenzoselenophen dibromide formed red needles (80%), m. p. 122° (Found: Se, 20.35. Calc. for  $\text{C}_{12}\text{H}_8\text{SeBr}_2$ : Se, 20.2%).

*Dibenzoselenophen oxide* (I). A suspension of the dibromide (20 g.) in aqueous sodium hydroxide (3%; 150 c.c.) was then thoroughly stirred at room temperature. The red solution became practically colourless during 1½ hr. and was then heated on a water-bath for 2—3 min. The cooled suspension was filtered and the precipitate crystallized from aqueous ethanol; it had m. p. 207—208° (Found: Se, 32.05. Calc. for  $\text{C}_{12}\text{H}_8\text{OSe}$ : Se, 32.0%).

ISTITUTO CHIMICA INDUSTRIALE, BOLOGNA.  
ISTITUTO CHIMICA FARMACEUTICA, PARMA.

[Received, March 29th, 1954.]

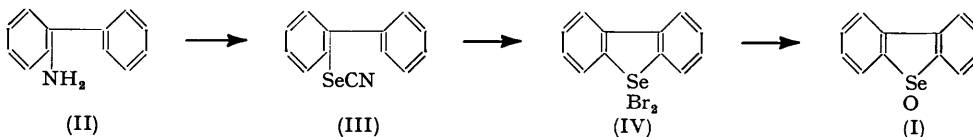
### A Modified Synthesis of Dibenzoselenophen Oxide.

By L. CHERICI and R. PASSERINI.

[Reprint Order No. 5254.]

DIBENZOSELENOPHEN OXIDE (I) has been prepared by treating dibenzoselenophen dibromide or dichloride with 3% aqueous sodium hydroxide (Courtot and Montamedi, *Compt. rend.*, 1934, **199**, 531; Behaghel and Hofmann, *Ber.*, 1939, **72**, 582). Recently McCullough and his associates (*J. Amer. Chem. Soc.*, 1950, **72**, 5753) described a new synthesis of dibenzoselenophen, and obtained the oxide by oxidation with 40% peracetic acid in glacial acetic acid.

Since a convenient supply of peracetic acid was not readily available, and every attempted oxidation with hydrogen peroxide in glacial acetic acid failed, we modified the methods already reported. As stated by McCullough and his co-workers the direct bromination of bis-2-diphenyl diselenide by Behaghel and Hofmann's method leads to a mixture of dibenzoselenophen dibromide and bromodibenzoselenophen dibromide. We found that addition of bromine to a chloroform solution of 2-selenocyanatodiphenyl gives a good yield of dibenzoselenophen dibromide. From the latter, dibenzoselenophen oxide can be easily obtained as indicated by Courtot and Montamedi (*loc. cit.*).



The present synthesis is more convenient than those already recorded, and appears to be particularly suitable for the preparation of dibenzoselenophen oxide from 2-aminodiphenyl.

*Experimental.*—2-Selenocyanatodiphenyl (III). 2-Aminodiphenyl (80 g.) was diazotised in dilute hydrochloric acid, and cold aqueous potassium selenocyanate (80 g.) added to the neutralised (Congo red) solution. Vigorous stirring was continued for 1 hr., then the mixture was

Since the atomic number of silver is roughly half that of mercury, there are some grounds for believing (cf. Woodward and Long, *Trans. Faraday Soc.*, 1949, **45**, 1131) that on this account the Raman intensity of  $\text{Ag}_2^{++}$  would be somewhat lower (perhaps by a factor of about 4) than that of  $\text{Hg}_2^{++}$ . Even so it is improbable that as much as 1% of the silver could have been present in the form of double ions, despite the high concentration of the solution investigated.

If, on the contrary, we assume that a high proportion of the silver was indeed present as  $\text{Ag}_2^{++}$ , then it follows conversely that the intrinsic Raman intensity of this species must be at least 1000 times smaller than that of  $\text{Hg}_2^{++}$ . It is true that the type of covalent bonding in  $\text{Ag}_2^{++}$  cannot be the same as in  $\text{Hg}_2^{++}$ ; for whereas  $\text{Hg}^+$  possesses a single *s*-electron, the pairing of which with a similar *s*-electron belonging to a second  $\text{Hg}^+$  doubtless gives rise to the bond in  $(\text{Hg}-\text{Hg}^{++})$ , the  $\text{Ag}^+$  ion possesses no such *s*-electron. The nature of the covalent bond in the hypothetical  $\text{Ag}_2^{++}$  is not clear, and it is possible that the species might have an unusually low Raman intensity; but a value 1000 or more times less than for  $\text{Hg}_2^{++}$  appears improbable. The non-appearance of a Raman effect therefore throws considerable doubt on the hypothesis of the existence of the double argentous ion in appreciable concentration.

We are grateful to Mr. R. P. Bell for having suggested these experiments and to Prof. C. W. Davies for his interest and for permission to refer to his forthcoming paper.

INORGANIC CHEMISTRY LABORATORY, OXFORD.

[Received, May 24th, 1954.]

### *Complex Fluorides. Part III.\* Lattice Constants of Some Complex Fluorides of Lithium or Sodium and Quadrivalent Elements.*

By B. Cox.

[Reprint Order No. 5331.]

WHEREAS many partial and several complete structure determinations have been made on complex fluorides of formula  $\text{A}_2\text{MF}_6$ , where  $\text{A} = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_2$ , or  $\text{Tl}$ , no information is available at present on analogous lithium and sodium salts. In the course of investigations on complexes of quadrivalent elements, it has been found by *X*-ray powder photography that sodium fluorosilicate, fluorotitanate, fluorogermanate, fluoromanganate, and fluoroplatinate form an isomorphous series. Lattice constants for the hexagonal unit cells are:  $\text{Na}_2\text{SiF}_6$ ,  $a = 8.86$ ,  $c = 5.02$ ;  $\text{Na}_2\text{TiF}_6$ ,  $a = 9.21$ ,  $c = 5.15$ ;  $\text{Na}_2\text{GeF}_6$ ,  $a = 9.10$ ,  $c = 5.13$ ;  $\text{Na}_2\text{MnF}_6$ ,  $a = 9.03$ ,  $c = 5.13$ ;  $\text{Na}_2\text{PtF}_6$ ,  $a = 9.41$ ,  $c = 5.16$  Å. Lithium fluorosilicate is isomorphous with the sodium salts, with  $a = 8.22$ ,  $c = 4.56$  Å; lithium fluorogermanate gives a powder pattern which, though similar in appearance to that of the fluorosilicate, cannot be indexed completely on the basis of a hexagonal unit cell; and the same applies, though to a greater degree, to lithium fluorotitanate. It is hoped to publish later a full determination of the structure of sodium fluorosilicate.

*Experimental.*—Sodium hexafluoromanganate(IV) was prepared by electrolytic oxidation of manganous fluoride and sodium fluoride in 40% hydrofluoric acid, as described in Part II for the ammonium salt. The solubility of the sodium salt in 40% hydrofluoric acid precluded the use of the acid for washing out any sodium fluoride present (Found: Mn, 23.3.  $\text{Na}_2\text{MnF}_6$  requires Mn, 25.6%).

The fluoroplatinate was obtained by fluorination of sodium chloroplatinate with bromine trifluoride (see Sharpe, *J.*, 1950, 3444, for a description of the method); the product of the reaction was heated at 200° for 30 min., dissolved in cold water, and precipitated by addition of alcohol (Found: Pt, 54.1.  $\text{Na}_2\text{PtF}_6$  requires Pt, 54.9%). Sodium fluorotitanate (Hunter, *J. Amer. Chem. Soc.*, 1910, **32**, 330) and fluorogermanate (Muller, *Proc. Amer. Phil. Soc.*, Suppl.

\* Part II, *J.*, 1954, 1798.

5, 1926, 65, 44; *Chem. Abs.*, 1927, 21, 3171) were prepared from the dioxides, hydrofluoric acid, and sodium fluoride (Found, for the fluorotitanate: Ti, 23.0; Calc. for  $\text{Na}_2\text{TiF}_6$ : Ti, 23.1. Found, for the fluorogermanate: Ge, 29.8; Na, 20.3; Calc. for  $\text{Na}_2\text{GeF}_6$ : Ge, 31.2; Na, 19.8%). The sodium fluorosilicate used was a pure commercial product. Lithium salts were prepared from the dioxides, hydrofluoric acid, and lithium carbonate (Found, for the fluorosilicate: Li, 8.9. Calc. for  $\text{Li}_2\text{SiF}_6$ : Li, 8.9. Found, for the fluorogermanate: Li, 6.9. Calc. for  $\text{Li}_2\text{GeF}_6$ : Li, 6.9. Found, for the fluorotitanate: Ti, 27.6. Calc. for  $\text{Li}_2\text{TiF}_6$ : Ti, 27.2%).

X-Ray powder photographs were taken and interpreted as described in Part II. The calculated density of sodium fluorosilicate, on the assumption of 3 mols. per unit cell, is 2.73; this compares with a value of 2.75 found by Stolba (*Z. anal. Chem.*, 1872, 11, 199).

Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a Maintenance Grant.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[Received, April 26th, 1954.]

### *8-Amino-6-methoxyquinoline, and Some Derivatives of 5 : 5'-Diquinolyl.*

By W. V. FARRAR.

[Reprint Order No. 5337.]

8-AMINO-6-METHOXYQUINOLINE is reported to melt at 40—41° (*inter al.*, B.P. 267,169; Altman, *Rec. Trav. chim.*, 1938, 57, 941; Crum and Robinson, *J.*, 1943, 561). Chichibabin and Hoffmann, however (*Compt. rend.*, 1939, 208, 535), report m. p. 52°, alleging that the lower-melting products were contaminated with 6-methoxyquinoline. The amine is in fact dimorphic.

In the reduction of 6-methoxy-8-nitroquinoline with iron and ferrous chloride in ethanol, considerable quantities of a high-melting crystalline by-product were observed which was shown to be 8 : 8'-diamino-6 : 6'-dimethoxy-5 : 5'-diquinolyl. Its formation is probably due to the oxidation of the aminoquinoline by ferric salts, a reaction which was found to give the diquinolyl derivative in 45—50% yield. A similar oxidation of  $\alpha$ -naphthylamine gives naphthidine (Reverdin and de la Harpe, *Chem. Ztg.*, 1892, 16, 1687; Sah and Yuin, *Rec. Trav. chim.*, 1939, 58, 751), but the reaction is not very general. 5- and 6-Aminoquinolines do not react; 8-amino-6-hydroxyquinoline, 1-aminoacridine, and 8-nitro-1-naphthylamine gave complex and unidentifiable products. From 8-aminoquinoline, however, 8 : 8'-diamino-5 : 5'-diquinolyl was obtained in *ca.* 5% yield. The structure of this substance was confirmed by hydrolysis with hydrochloric acid, which gave a small yield of the known 8 : 8'-dihydroxy-5 : 5'-diquinolyl (Bratz and Niementowski, *Ber.*, 1919, 52, 189). The 5 : 5'-orientation of this compound is known from its synthesis by an unambiguous Skrap reaction.

*Experimental.*—8 : 8'-Diamino-6 : 6'-dimethoxy-5 : 5'-diquinolyl. (a) Iron borings (260 g.), ethanol (500 g.), water (150 g.), and ferrous chloride (10 g.) were stirred together at 65° in an iron vessel fitted with a glass reflux condenser. 6-Methoxy-8-nitroquinoline (95% pure, 215 g.) was added during 1.5 hr. without external heating. During the addition, hydrochloric acid (10 c.c.) had to be added to keep iron in solution (sodium sulphide test). The mixture, after refluxing for 2 hr., was basified with sodium carbonate and filtered, and the filter-cake was washed with hot ethanol. The filtrate and washings were freed from solvent and finally distilled *in vacuo*, giving 8-amino-6-methoxyquinoline, b. p. 169—171°/3 mm. (104 g.). The first two of a series of preparations gave distilled material, m. p. 38—40°; the molten product was poured into glass bottles and allowed to solidify. After three weeks, both bottles had cracked, owing to expansion of their contents, which now had m. p. 49—51°. All subsequent preparations had this higher m. p.



The non-volatile residue was broken up and extracted with acetone; the extracts, on standing, gave brownish crystals (26 g.) of crude diquinolyl compound.

(b) 8-Amino-6-methoxyquinoline (5 g.), hydrated ferric chloride (15 g.), hydrochloric acid (10 c.c.), and water (100 c.c.) were refluxed for 1 hr., basified with aqueous sodium hydroxide, and filtered, and the solid product was washed and dried. Extraction with acetone (Soxhlet) gave the almost pure diquinolyl derivative (2.25 g., 45%).

Recrystallisation of diquinolyl products from (a) or (b) from acetone gave large yellow-brown prisms of a *solvate*, which lost acetone at 60° (loss, 24.7.  $C_{20}H_{18}O_2N_2 \cdot 2C_3H_6O$  requires loss 25.1%); the material became opaque and sulphur-yellow and then had m. p. 252° (decomp.) [Found: C, 69.6; H, 5.2; N, 16.3; OMe, 16.8%; *M* (Rast), 326, (nitrite titration, 2NH<sub>2</sub>-groups) 348.  $C_{20}H_{18}O_2N_4$  requires C, 69.4; H, 5.2; N, 16.2; OMe, 17.9%; *M*, 346]. The compound is sparingly soluble in the common solvents; like other derivatives of 8-aminoquinoline, it forms orange salts. The *diacetyl* derivative formed colourless needles, m. p. 289—290°, from acetone (Found: C, 66.55; H, 5.35.  $C_{24}H_{22}O_4N_4$  requires C, 66.9; H, 5.15%).

8 : 8'-Diamino-5 : 5'-diquinolyl was made from 8-aminoquinoline by method (b) in ca. 5% yield. It formed yellow crystals, m. p. 262° (decomp.) from acetone, or platelets from dioxan (Found: C, 75.3; H, 4.55; N, 19.35.  $C_{18}H_{14}N_4$  requires C, 75.5; H, 4.9; N, 19.6%). The *diacetyl* derivative, pale yellow platelets from *n*-butanol, had m. p. 318—320° (decomp.) (Found: N, 14.7.  $C_{22}H_{18}O_2N_4$  requires N, 15.1%).

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,  
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.

[Received, April 28th, 1954.]

### The Oxidation of Some Quinazoline Derivatives.

By W. V. FARRAR.

[Reprint Order No. 5338.]

THE reaction of *p*-fluoroaniline with formaldehyde in acid solution gives a substance  $C_{14}H_{10}N_2F_2$ , which by analogy with similar products from *p*-chloro- and *p*-bromo-aniline (Wagner and Eisner, *J. Amer. Chem. Soc.*, 1937, **59**, 479) is probably (I; R = F). The most remarkable property of this compound is its ready oxidation at its melting point to the quinazolone (II; R = F), more conveniently obtained from it by use of permanganate.



The corresponding chlorine compound (I; R = Cl) is similarly oxidised at its melting point, but not so rapidly. The bromine compound (II; R = Br) was found by Cairncross and Bogert (*Coll. Czech. Chem. Comm.*, 1935, **7**, 548) among the products of the reaction between *p*-bromoaniline and formaldehyde; it was not found by Wagner and Eisner (*loc. cit.*); it almost certainly arose by aerial oxidation of (I; R = Br) during the lengthy manipulations carried out by the former workers.

*Experimental.*—6-Fluoro-3-*p*-fluorophenyl-3 : 4-dihydroquinazoline (I; R = F). *p*-Fluoroaniline hydrochloride (5.5 g.) was dissolved in hydrochloric acid (5 c.c.) and water (45 c.c.), and 37% formaldehyde solution (10 c.c.) was added. After 4 days, the insoluble hydrochloride was collected, taken up in hot water, filtered, and basified. Recrystallisation from aqueous ethanol gave needles (1.65 g.), m. p. 137—138° with resolidification (Found: C, 68.5; H, 4.2; N, 11.0.  $C_{14}H_{10}N_2F_2$  requires C, 68.85; H, 4.1; N, 11.45%).

6-Fluoro-3-*p*-fluorophenylquinazol-4-one (II; R = F). (a) The quinazoline (0.5 g.) was fused for 2 min. Extraction with ethanol gave two products in approximately equal amounts, the soluble one being unchanged starting material. The other, very sparingly soluble, was the

quinazolone, forming hair-like needles, m. p. 260°, from much ethanol (Found : C, 64.8; H, 3.5; N, 10.7.  $C_{14}H_8ON_2F_2$  requires C, 65.1; H, 3.15; N, 10.85%).

(b) The quinazoline (0.6 g.) in acetone (50 c.c.) was treated with powdered potassium permanganate until the solution was permanently pink, then added to excess of sodium hydrogen sulphite solution. The precipitated quinazolone was recrystallised from much ethanol (0.43 g., 70% yield).

The chlorine *analogue* (II; R = Cl), made by method (b) in 85% yield, formed fine needles (from much ethanol), m. p. 225° (Found : C, 57.7; H, 2.9; Cl, 24.4.  $C_{14}H_8ON_2Cl_2$  requires C, 57.7; H, 2.75; Cl, 24.4%). This substance may be identical with an unanalysed compound, m. p. 225°, prepared by Bischoff and Reinfeld (*Ber.*, 1903, **36**, 41), but this part of these authors' work could not be repeated.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, DYESTUFFS DIVISION,  
HEXAGON HOUSE, BLACKLEY, MANCHESTER, 9.

[Received, April 28th, 1954.]