277. *Organic Fluorine Compounds. Part X.* Reaction of Organic Compounds with Iodine in the Presence of Silver Fluoride or Trifluoroacetate.*

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A mixture of iodine and silver fluoride causes iodine substitution of aromatic compounds and allylic positions; it can also lead to the dehydrogenation of activated aromatic compounds, such as phenol ethers and dialkylarylamines. An analogous behaviour was observed for the system silver trifluoroacetate–iodine. This system also converts primary alcohols into aldehydes and secondary alcohols into the corresponding ketones and α-dicarbonyl compounds.

The experiments reported were undertaken in the hope of obtaining fluorine-containing organic compounds by the reaction between iodine and silver fluoride in the presence of olefins and acetylenes. It had been expected that a substance such as IF might form and add to the double or triple bonds, but this was not so, although some noteworthy observations were made.

The mixture of iodine and silver fluoride, applied to an excess of the substance tested, substitutes aromatic rings and allylic positions; positive iodine is thus formed as an intermediate.[1] The *inorganic* product is a red compound of silver iodide and silver fluoride;[2] the latter must, therefore, be used in excess and the reactions can be formulated as follows:

$$(1)\ AgF + I_2 \longrightarrow AgI + I^+ + F^-;\ (2)\ I^+ + RH \longrightarrow RI + H^+;\ (3)\ AgI + AgF \longrightarrow AgI,AgF$$

Benzene gave iodobenzene in 10% yield, toluene *p*-iodotoluene in 15% yield, anisole *p*-iodoanisole in 51% yield, and 1-ethoxynaphthalene a 40% yield of the 4-iodo-derivative. From 2-methoxy- and 2-ethoxy-naphthalene, the 1-iodo-derivatives were obtained in 47 and 50% yield, respectively, accompanied by 30% of 2 : 2′-dimethoxy- and 2 : 2′-diethoxy-1 : 1′-dinaphthyl. The system silver fluoride–iodine exerts, therefore, also an oxidising action. This effect became predominant for *NN*-dialkyl aromatic amines (dimethyl-aniline, -*p*-toluidine, and -α- and -β-naphthylamine); it was observed even when silver fluoride *alone* was brought into contact with substances which produced metallic silver and compounds of the Methyl Violet type. Other silver salts which behaved analogously are the nitrate, trifluoroacetate, and (less violently) the sulphate; silver chloride, bromide, and iodide were ineffective. From dimethylaniline and silver trifluoroacetate, for example, the crystalline trifluoroacetate of Methyl Violet was obtained analytically pure; it was identified by its absorption spectrum.[3]

As to olefinic and acetylenic compounds, ethyl cinnamate, ethyl phenylpropiolate, and phenylpropiolic acid proved refractory, but ethyl crotonate, *cyclo*hexene, α-methylstyrene, propenylbenzene, 4-phenylbut-1-ene, and allylbenzene reacted smoothly. Owing to the sensitivity of the allyl-type iodides formed, only ethyl β-iodocrotonate could be isolated as such. 4-Phenylbut-1-ene gave (probably) 3-iodo-4-phenylbut-1-ene which was isolated, after reaction with benzylamine, as 3-benzylamino-4-phenylbut-1-ene hydriodide. Analogously, ethyl γ-iodocrotonate was converted into the hydriodide of ethyl γ-benzylamino-crotonate. With *cyclo*hexene, the product (3-iodo*cyclo*hexene) was identified by dehydrohalogenation to *cyclo*hexa-1 : 3-diene, isolated as its adduct with maleic anhydride.

In the same way as the system silver fluoride–iodine, iodine–silver trifluoroacetate, according to Haszeldine.[4] iodinates aromatic compounds in good yield; it has been

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* Part IX, Bergmann and Cohen, *J.*, 1958, 2259.

[1] Kikindai, *Ann. Chim.* (*France*), 1956, **1**, 273.

[2] Simons, " Fluorine Chemistry," Academic Press Inc., New York, 1950, Vol. I, p. 526.

[3] Holmes, *Ind. Eng. Chem.*, 1924, **16**, 35; 1925, **17**, 918.

[4] Haszeldine, *J.*, 1952, 993; cf. Henne and Zimmer, *J. Amer. Chem. Soc.*, 1951, **73**, 1362.

assumed that the reactive species is trifluoroacetyl hypoiodite $CF_3\cdot CO_2I$. The analogy between the two systems is demonstrated by the fact that ethyl crotonate is converted into ethyl γ-iodocrotonate also under Haszeldine's conditions.

Haszeldine's results have been supplemented by a study of the behaviour of 1- and 2-naphthol, 1- and 2-methoxynaphthalene, and alizarin. Whilst 1-naphthol gave only an intractable product, a yield of 20% of 1-iodo-2-naphthol was obtained from 2-naphthol. The two methyl ethers differed, though only quantitatively, in their behaviour, 1-iodo-2-methoxynaphthalene being formed in 70%, 4-iodo-1-methoxynaphthalene in 15% yield. 4-Iodoalizarin was obtained in 60% yield. No oxidative effect on 2-methoxynaphthalene was observed in this case.

Primary alcohols are dehydrogenated smoothly by silver trifluoroacetate and iodine to the corresponding aldehydes; the yields were: for *n*-butanol 25%, allyl alcohol 25%, crotyl alcohol 50%, benzyl alcohol 75%, and cinnamyl alcohol 80%. The reaction with secondary alcohols is more complex. Treatment of the product formed from propan-2-ol with 2 : 4-dinitrophenylhydrazine gave a mixture of the dinitrophenylhydrazones of acetone and methylglyoxal; the latter was also obtained by the analogous reaction with acetone. Equally, from ethyl methyl ketone we obtained diacetyl (yield, 50%), from *iso*butyl methyl ketone acetyl*iso*butyryl (yield, 33%), and from acetophenone phenylglyoxal. 1-Styrylethanol gave a 40% yield of benzylideneacetone, together with polymer. These reactions are similar to those of ketones with selenium dioxide.[5] Quantitative studies have shown that the oxidation of secondary alcohols to ketones requires 2 mol. of silver trifluoroacetate and 1 mol. of iodine; the latter is recovered quantitatively as silver iodide. One can, therefore, assume the following mechanism, involving the formation of trifluoroacetyl hypoiodite:

$$\begin{array}{c}
CF_3\cdot CO_2Ag + I_2 \longrightarrow CF_3\cdot CO_2I + AgI \\
CF_3\cdot CO_2I + R^1R^2CH\cdot OH \longrightarrow CF_3\cdot CO_2H + HI + R^1R^2C\colon O \\
CF_3\cdot CO_2Ag + HI \longrightarrow AgI + CF_3\cdot CO_2H \\
\hline
2CF_3\cdot CO_2Ag + I_2 + R^1R^2CH\cdot OH \longrightarrow R^1R^2C\colon O + 2CF_3\cdot CO_2H + 2AgI
\end{array}$$

The transformation of ketones into 1 : 2-dicarbonyl compounds is more complicated. It often occurs only after an induction period of 5—15 min. and requires 1 mol. of iodine and 2 mol. of the silver salt. The silver iodide separates quantitatively from the organic solution, but the dicarbonyl compound can be isolated from it only after treatment with water. The overall equation is, therefore:

$$R^1\cdot CO\cdot CH_2R^2 + 2CF_3\cdot CO_2Ag + I_2 + H_2O \longrightarrow R^1\cdot CO\cdot COR^2 + 2AgI + 2CF_3\cdot CO_2H$$

Ketones form fairly stable azeotropes with trifluoroacetic acid; they boil at a higher temperature than either the ketone or the acid (b. p. 71°) and have no strictly stoicheiometric composition: the azeotrope with acetone, b. p. 108°, contains 60·2% of trifluoroacetic acid (calc., 65·0% for a 1 : 1-compound); the azeotrope with *iso*butyl methyl ketone, b. p. 132°, contains 54·0% of trifluoroacetic acid (calc., 51·9%); the azeotrope with *cyclo*hexanone, b. p. 163°, contains 44% of trifluoroacetic acid (calc., 52·4%).

When the azeotrope with *iso*butyl methyl ketone was distilled *in vacuo* (b. p. 48°/35 mm.) the distillate contained 42% of trifluoroacetic acid.

EXPERIMENTAL

Silver fluoride was prepared in the dark. To 25% hydrofluoric acid (80 ml.) in a Polythene beaker, silver oxide (80 g.) was added in small portions. After 30 min., the neutral mixture was filtered and evaporated in a porcelain dish. The residue was dried at 150° and kept in a desiccator. The yellowish product is very sensitive to light; it contained 0·1—0·3% of insoluble silver and 85% of total silver (calc., 85·1%). It is reduced to metallic silver by aliphatic

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[5] Riley, Morley, and Friend, *J.*, 1932, 1875.

alcohols, diethyl ether, and dioxan. Reactions with silver fluoride were carried out with an excess of the substrate as solvent.

Silver trifluoroacetate was prepared by Haszeldine's method;[6] its reactions were best carried out in carbon tetrachloride or tetrachloroethylene, which are not attacked by the mixture of the salt with iodine.

Iodination of Ethyl Crotonate.—(*a*) To ethyl crotonate (40 ml.) and silver fluoride (13 g.; 0·1 mole), iodine (12·5 g.; 0·05 mole) was added in small portions and the mixture gently heated in a water-bath. After the solution had become colourless, the red precipitate was filtered off and washed with dry ether (20 ml.), and the filtrate distilled. Ethyl γ-iodocrotonate distilled at 83—85/(1 mm. (lit.,[7] 90°/2 mm.) (yield, 2·4 g.; 20%) (Found: C, 30·9; H, 3·2. Calc. for $C_6H_9O_2I$: C, 30·0; H, 3·8%). When the filtrate was heated with benzylamine (10 g.; 0·1 mole) at 50° for some minutes, a crystalline precipitate of *ethyl α-benzylaminocrotonate hydriodide* was obtained, m. p. 175° after recrystallization from propyl alcohol (Found: C, 44·5; H, 5·7; N, 4·1. $C_{13}H_{18}O_2NI$ requires C, 44·9; H, 5·2; N, 4·0%).

(*b*) A mixture of iodine (12·5 g.; 0·05 mole) and carbon tetrachloride (50 ml.) was heated to the b. p. and quickly chilled, and silver trifluoroacetate (13 g.; 0·058 mole) and (slowly and with efficient agitation) ethyl crotonate (5·7 g.; 0·057 mole) were added. Within 10 min., the colour of the iodine disappeared; the silver iodide was filtered off and washed with carbon tetrachloride. Distillation gave ethyl γ-iodocrotonate, b. p. 83—85°/1 mm. (95 g.; 80%), identified by transformation into γ-hydroxycrotonic acid, m. p. 108°, by Glattfeld and Lee's method.[8] The amount of dry silver iodide isolated was 12·0 g. (0·05 mole); *i.e.*, half of the iodine was recovered as silver salt.

Iodination of cyclo*Hexene.*—The solution obtained from *cyclo*hexene (50 ml.), silver fluoride (13 g.), and iodine (12·5 g.) at 20—30° was diluted with light petroleum (b. p. 40—60°; 20 ml.) and refluxed with pyridine (15 ml.) for 2 hr. The product was washed with dilute hydrochloric acid, dried ($MgSO_4$), and refluxed with maleic anhydride (10 g.) for 2 hr. Upon cooling, 3 : 6-*endo*ethylene-1 : 2 : 3 : 6-tetrahydrophthalic anhydride (1·8 g.; 10%) crystallized, m. p. 147° (lit.,[9] 147°). It was identified by hydrolysis to the free dicarboxylic acid, m. p. 152° (lit.,[9] 152°).

Iodination of 4-*Phenylbut*-1-*ene.*—The product from 4-phenylbut-1-ene[10] (20 g.), silver fluoride (8·25 g.), and iodine (6·25 g.) at 20—30° was filtered and the solid phase washed with light petroleum (b. p. 40—60°; 20 ml.). To the filtrate, benzylamine (2·7 g.) was added; the precipitate of 3-*benzylamino*-4-*phenylbut*-1-*ene hydrodide*, recrystallized from water, had m. p. 221° (Found: C, 55·7; H, 5·3; N, 3·8. $C_{17}H_{20}NI$ requires C, 56·0; H, 5·5; N, 3·8%). Allylbenzene,[11] propenylbenzene,[12] and α-methylstyrene[13] decolorized iodine in the presence of silver fluoride, but no definite product was isolated.

Iodination of Benzene.—The reaction between benzene (40 ml.), silver fluoride (13 g.), and iodine (12·5 g.) was carried out as above at room temperature and completed by a short heating on the water-bath. The solid was filtered off and washed with benzene (10 ml.). Distillation gave iodobenzene (2 g.; 10%), b. p. 185—186°, n_D^{20} 1·6220. In the same way, toluene gave a 15% yield of *p*-iodotoluene, b. p. 207—208°, m. p. 35°, and anisole a 57% yield of *p*-iodoanisole, b. p. 127° (20 mm.), m. p. 52°.

Iodination of 2-*Methoxynaphthalene.*—(*a*) At 80—90° iodine (12·5 g.) was added to a mixture of 2-methoxynaphthalene (40 g.) and silver fluoride (12 g.). After 30 min., the colour had disappeared and the liberation of hydrogen fluoride ceased. After addition of boiling benzene (150 ml.), the solid was filtered off and the liquid distilled *in vacuo*. At 95—96°/2 mm. the excess of 2-methoxynaphthalene distilled; at 141—142°/2 mm., 1-iodo-2-methoxynaphthalene [m. p. 88° after recrystallization from ethanol (lit.[14] 88°) (yield 13·5 g.; 47%) (Found: C, 46·4; H, 3·4. Calc. for $C_{11}H_9OI$: C, 46·5; H, 3·2%)]; and at 220°/2 mm., 2 : 2′-dimethoxy-1 : 1′-dinaphthyl [m. p. 190° after recrystallization from butanol (lit.[15] 190°) (yield 4·7 g.; 30%) (Found: C, 83·7; H, 6·1. Calc. for $C_{22}H_{18}O_2$: C, 84·1; H, 5·7%)].

[6] Haszeldine, *J.*, 1951, 584.
[7] Braun, *J. Amer. Chem. Soc.*, 1930, **52**, 3174.
[8] Glattfeld and Lee, *J. Amer. Chem. Soc.*, 1940, **62**, 354.
[9] Diels and Alder, *Annalen*, 1928, **460**, 98.
[10] Gilman and McGlumphy, *Rec. Trav. chim.*, 1928, **47**, 418.
[11] Hershberg, *Helv. Chim. Acta*, 1934, **17**, 351.
[12] Levy and Dvoleitzka-Gombinska, *Bull. Soc. chim. France*, 1931, **49**, 1765.
[13] Staudinger and Breusch, *Ber.*, 1929, **62**, 442.
[14] Meldola, *J.*, 1884, **45**, 156; Ray and Moomaw, *J. Amer. Chem. Soc.*, 1933, **55**, 3833.
[15] Pummerer, Prell, and Rieche, *Ber.*, 1926, **59**, 2159.

(*b*) A mixture of iodine (12·5 g.) and carbon tetrachloride (40 ml.) was heated to the b. p. and chilled very quickly. Silver trifluoroacetate (13 g.) and 2-methoxynaphthalene (7·9 g.) were added and the mixture refluxed until the colour of the iodine had disappeared. The precipitate was filtered off and washed with ether and the filtrate washed with water, dried, and concentrated. The residue, recrystallized from ethanol, had m. p. 88° (yield, 19·9 g.; 70%).

Iodination of 2-*Ethoxynaphthalene*.—As for the 2-methoxy-compound, but at 40—50°, the reaction gave 2-ethoxy-1-iodonaphthalene, yield 50%, b. p. 145—146°/0·2 mm.; from ethanol, m. p. 95° (lit.,[14] 95°) (Found: C, 48·5; H, 4·0. Calc. for $C_{12}H_{11}OI$: C, 48·3; H, 3·7%), and 2 : 2′-diethoxy-1 : 1′-dinaphthyl, yield 30%, b. p. 220°/0·2 mm.; from butanol, m. p. 90° (lit.[15] 90°) (Found: C, 84·5; H, 6·8. Calc. for $C_{24}H_{22}O_2$: C, 84·2; H, 6·4%).

Iodination of 1-*Ethoxynaphthalene*.—The reaction was carried out as for the 2-isomer. 4-Iodo-1-ethoxynaphthalene had b. p. 180°/0·2 mm., m. p. 44° after recrystallization from ethanol (lit.,[16] m. p. 43·5°) (yield, 40%), and decomposed quickly on standing.

Iodination of 1-*Methoxynaphthalene*.—The reaction of 1-methoxynaphthalene with silver trifluoroacetate and iodine was carried out as described for the 2-compound. 4-Iodo-1-methoxynaphthalene had m. p. 52° (lit.,[16] 52°) after recrystallization from ethanol (yield, 15%).

Iodination of Alizarin.—Alizarin (1·2 g.), iodine (1·25 g.), and nitrobenzene (40 ml.) were heated at 120° and chilled quickly. Silver trifluoroacetate (2 g.) was added and the mass agitated for 4 hr. at room temperature and for 5 hr. at 100°. The solid was filtered off and washed with hot benzene (5 ml.). The filtrate was washed with water and after addition of light petroleum (b. p. 40—60°; 20 ml.) extracted with 15% potassium carbonate solution. The aqueous extract was acidified with hydrochloric acid and 4-iodoalizarin filtered off, after it had stood for 1 hr. at 0°, and recrystallized [m. p. 209—210° (lit.,[17] 209—210°) (yield, 1 g.; 60%)] from 90% acetic acid.

Reaction of Dimethylaniline with Silver Trifluoroacetate.—To a solution of dimethylaniline (6 g.) in methanol (15 ml.), silver trifluoroacetate (11 g.) in the same solvent (20 ml.) was added and the mixture cautiously heated until reaction set in. The black precipitate was filtered off and washed with boiling methanol (10 ml.), and the combined filtrates were concentrated to dryness. The residue was, according to the analysis and the spectrum ($\lambda_{max.}$ 550 mμ, in ethanol[3]) the *trifluoroacetate of Methyl Violet* (Found: C, 67·6; H, 6·7; N, 8·3; F, 11·9. $C_{26}H_{27}O_2F_3N_3$ requires C, 66·4; H, 6·0; N, 8·7; F, 12·1%). An analogous behaviour was observed with *NN*-dimethyl-*p*-toluidine [18] and -1- and -2-naphthylamine.[19]

Reaction of Alcohols with Silver Trifloroacetate and Iodine.—(a) n-*Butanol*. Butanol (40 g.), iodine (12·5 g.; 0·05 mole), and silver trifluoroacetate (24 g.; 0·4 mole) were stirred at room temperature until the colour of the iodine had disappeared. The silver iodide was filtered off (24 g.; 0·1 mole) and the solution fractionated. At 74—78°, 1 g. (25%) of butyraldehyde distilled (2 : 4-dinitrophenylhydrazone, m. p. 123°;[20] dimedone derivative, m. p. 134° [21]).

(b) *Allyl alcohol*. The reaction, carried out as above, gave acraldehyde, b. p. 50—54°, (yield, 25%) (2 : 4-dinitrophenylhydrazone, m. p. 165° [22]).

(c) *Crotyl alcohol*. The reaction between crotyl alcohol (36 g.), iodine (12·5 g.), and silver trifluoroacetate (24 g.) in carbon tetrachloride (50 ml.) at room temperature gave 23·5 g. of silver iodide and 1·75 g. (50%) of crotonaldehyde, b. p. 100—102° (2 : 4-dinitrophenylhydrazone, m. p. 191° [20]).

(d) *Benzyl alcohol*. From benzyl alcohol (5·5 g.), benzaldehyde (4 g.; 75%) was obtained in the same manner, b. p. 175—176° (2 : 4-dinitrophenylhydrazone, m. p. 236° [23]).

(e) *Cinnamyl alcohol*. From cinnamyl alcohol (6·6 g.), cinnamaldehyde (5·4 g.; 80%) was obtained analogously at 50—60°, b. p. 126—127/20 mm. (2 : 4-dinitrophenylhydrazone, m. p. 255° [24]).

(f) 1-*Styrylethanol*. The alcohol [25] (7·5 g.), iodine (12·5 g.), and silver trifluoroacetate

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[16] Tanaka, *Chem. News*, 1925, **131**, 49; *Chem. Abs.*, 1925, **19**, 2948.

[17] Joshi, Tilak, and Venkataraman, *Proc. Indian Acad. Sci.*, 1951, **34**, 304.

[18] Hodgson and Kershaw, *J.*, 1930, 277.

[19] Gokhlé and Mason, *J.*, 1930, 1757.

[20] Huntress and Mulliken, " Identification of Pure Organic Compounds," John Wiley and Sons, New York, 1941, p. 633.

[21] Kagan, Lyubarskii, and Fedorov, *J. Appl. Chem. U.S.S.R.*, 1934, **7**, 135.

[22] Bremner, Jones, and Beaumont, *J.*, 1946, 1018.

[23] Hinkel, Ayling, and Morgan, *J.*, 1932, 2793.

[24] von Braun, Rudolph, Kroeper, and Pinkernelle, *Ber.*, 1934, **67**, 269.

[25] Meek, Lorenzi, and Cristol, *J. Amer. Chem. Soc.*, 1949, **71**, 1830.

(24 g.) in carbon tetrachloride (50 ml.) reacted at 60°; stirring was continued for 30 min. at room temperature. The filtered solution was washed with water, dried, and distilled. In addition to a dark resin, benzylideneacetone (3 g.; 40%) was obtained, b. p. 139°/25 mm. (2 : 4-dinitrophenylhydrazone, m. p. 227° [26]).

(g) *Propan-2-ol.* The reaction between propan-2-ol (40 ml.), iodine (12·5 g.), and silver trifluoroacetate (24 g.), which was added slowly at room temperature, was complete in 2 hr. The excess of the soluble silver salt was precipitated with 2 ml. of concentrated hydrochloric acid and the solution filtered and diluted with water to a total volume of 50 ml. Treatment with 2 : 4-dinitrophenylhydrazine gave a precipitate which was separated by fractional crystallization from alcohol into acetone 2 : 4-dinitrophenylhydrazone, m. p. 125°,[20] and methylglyoxal 2 : 4-dinitrophenylhydrazone, m. p. 130° [27] (Found: C, 43·6; H, 3·5; N, 22·5. Calc. for $C_9H_8O_5N_4$: C, 42·8; H, 3·2; N, 22·2%).

The structure of the second product was further proved by refluxing it (0·5 g.) with a solution of 2 : 4-dinitrophenylhydrazine (1 g.) in ethanol (100 ml.) and concentrated sulphuric acid (4 ml.), for 3 hr. Thus, the very difficultly soluble bis-2 : 4-dinitrophenylhydrazone of methylglyoxal was obtained, m. p. 300° [28] (from nitromethane) (Found: C, 41·5; H, 3·0; N, 25·7. Calc. for $C_{15}H_{12}O_8N_8$: C, 41·7; H, 2·8; N, 25·9%).

Reaction of Ketones with Silver Trifluoroacetate and Iodine.—(a) *Acetone.* To iodine (12·5 g.) suspended in carbon tetrachloride (40 ml.), silver trifluoroacetate (24 g.) and dry acetone (3 g.) were added, and the mixture was refluxed with agitation until, after about 10 min., reaction set in. When the colour had disappeared, the silver iodide (24·0 g.) was filtered off and the solution extracted three times with water (15 ml.). The combined aqueous extracts were acidified with hydrochloric acid, filtered, and heated briefly to evaporate the unchanged acetone. The methylglyoxal formed was then identified by conversion of aliquot portions of the solution into the osazone, m. p. 146°,[29] the bis-semicarbazone, m. p. 252°,[29] and the bis-2 : 4-dinitrophenylhydrazone, m. p. 300°.[28]

(b) *Ethyl methyl ketone.* The reaction was carried out, as described in the preceding paragraph, in tetrachloroethylene. Diacetyl was isolated by fractional distillation from the organic extract, b. p. 78—89° (yield, 50%); it was identified as the osazone, from nitromethane, m. p. 246° [30] (Found: C, 72·5; H, 7·0. Calc. for $C_{16}H_{18}N_4$: C, 72·2; H, 6·8%). Reaction did not occur in carbon tetrachloride.

iso*Butyl methyl ketone.* Treatment as above in carbon tetrachloride gave a 50% yield of *acetyl*iso*butyryl*, b. p. 116—118° (osazone, m. p. 115° [31]).

Acetophenone. Iodine (12·5 g.), silver trifluoroacetate, (24 g.), acetophenone (6 g.), and carbon tetrachloride (40 ml.) were heated and stirred until the colour disappeared. The filtered solution was washed with water, dried, and concentrated, and the residue dissolved in ethanol (10 ml.) and slowly poured into cold water (50 ml.). Thus, crystals of phenylglyoxal hydrate [5] were obtained, m. p. 89° [bis-semicarbazone, m. p. 220° [5] (Found: C, 48·4; H, 4·7. Calc. for $C_{10}H_{12}O_2N_6$: C, 48·4; H, 4·8%)].

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[27] Fischer and Taube, *Ber.*, 1924, **57**, 1506.
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[31] Pauly and Lieck, *Ber.* 1900, **33**, 503.