613. *Organic Fluorine Compounds. Part IV.* Some Reactions of Difluoromalonyl Chloride, and the Action of Iodine on Disilver Difluoromalonate.*

By E. J. P. Fear, J. Thrower, and J. Veitch.

Reactions of difluoromalonyl chloride with lithium aluminium hydride, benzene (Friedel–Crafts), diethyl sodiomalonate, and trifluoroethanol are described.

Tetrafluorosuccinyl chloride has been shown to be a product of the action of phosphorus oxychloride on tetrafluorosuccinic acid.

Interaction of disilver difluoromalonate with iodine gave a complex mixture of products, including carbon monoxide and carbonyl fluoride. A mechanism is advanced to explain this reaction.

Earlier studies have shown that the vapour-phase fluorination of benzene with manganic fluoride gives a mixture of polyfluoro*cyclo*hexenes [1] which on alkaline, oxidative degradation affords difluoromalonic and tetrafluorosuccinic acid, estimated to be in the ratio 3 : 2 by weight.[2] Separation of these acids was facilitated by treatment with phosphorus oxychloride and fractional distillation of the resultant difluoromalonyl chloride and tetrafluorosuccinic anhydride. These reactions thus provided a most attractive route to difluoromalonic acid.

Previously, the amount of phosphorus oxychloride used was based on the assumption that the only reaction would be that of cyclodehydration of tetrafluorosuccinic acid. We now report a more detailed investigation using an increased amount of phosphorus oxychloride, and describe reactions of difluoromalonyl chloride and the interaction of disilver difluoromalonate with iodine.

This re-examination has led to the isolation of the hitherto unknown tetrafluorosuccinyl chloride, characterised as the derived diamide and dianilide, and by hydrolysis: Padbury and Kropa [3] obtained tetrafluorosuccinic anhydride by the action of phosphorus oxychloride on tetrafluorosuccinic acid but did not report the formation of the diacyl chloride.

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* Part III, *J. Appl. Chem.*, 1956, **6**, 45.

[1] Fear and Thrower, *J. Appl. Chem.*, 1955, **5**, 353.

[2] Fear, Thrower, and Veitch, *ibid.*, p. 589.

[3] Padbury and Kropa, U.S.P. 2,502,478; *Chem. Abs.*, 1950, **44**, 6431.

Hauptschein, Stokes, and Nodiff[4] stated that hexafluoroglutaryl chloride could be obtained only in extremely small yield by the action of phosphorus pentachloride or thionyl chloride on hexafluoroglutaric acid, the reaction resulting primarily in cleavage products due to loss of carbon dioxide;. no properties of the diacyl chloride were given. Treatment of hexafluoroglutaric acid with phosphorus oxychloride afforded a 76·5% yield of the anhydride.[4] In the case of 3*H*-heptafluoroadipic acid, phosphorus pentachloride, though not thionyl chloride, gave the diacyl chloride in 50% yield.[5]

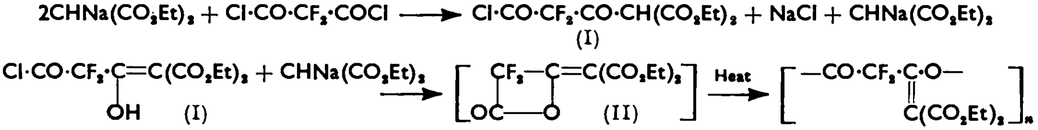
It is evident, therefore, that with the exception of the first member of the series, other methods of synthesis of perfluorodiacyl chlorides should be investigated. It is worthy of note that reaction of perfluoromonobasic acids with phosphorus pentachloride yields the perfluoroacyl chloride in high yield.[4, 6]

The residue from our phosphorus oxychloride reaction was shown to contain difluoromalonic acid and octafluoroadipic acid. The latter comprised approximately 1% of the original acid mixture and, as yet, its precursor(s) in the polyfluoro*cyclo*hexene mixture has not been identified.

Reduction of difluoromalonyl chloride with lithium aluminium hydride gave 2 : 2-difluoropropane-1 : 3-diol, characterised as its di-*p*-nitrobenzoate. However, dimethyl difluoromalonate,[2] on reduction with the same reagent, fails to give the diol.[7]

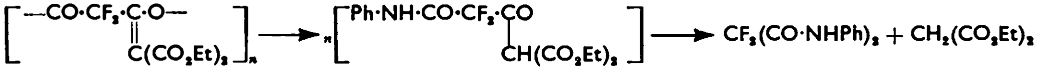
Condensation of difluoromalonyl chloride with benzene, in the presence of aluminium chloride, gave the 1 : 3-diketone, dibenzoyldifluoromethane. This gave only a mono-oxime, and no 2 : 4-dinitrophenylhydrazone (conditions used by Simons, Black, and Clark[8]).

An attempt was made to prepare 1-acetyl-1 : 1-difluoroacetone by the condensation of difluoromalonyl chloride and diethyl sodiomalonate (molar ratio 1 : 2). The reaction did not proceed as expected, but gave an extremely viscous product which degraded on attempted high-vacuum distillation and was cleaved to its components on treatment with water. The following reaction scheme is proposed to explain the formation of this polymeric material :



$$2CHNa(CO_2Et)_2 + Cl{\cdot}CO{\cdot}CF_2{\cdot}COCl \longrightarrow \underset{(I)}{Cl{\cdot}CO{\cdot}CF_2{\cdot}CO{\cdot}CH(CO_2Et)_2} + NaCl + CHNa(CO_2Et)_2$$

This mechanism accounts for the amounts of sodium chloride (2 moles) and diethyl malonate (1 mole) recovered from the reaction, and for the formation of difluoromalondianilide by treatment of the reaction product with aniline. Ruggli and Maeder[9] have shown that preferential enol-lactone formation takes place in reactions expected to give *cyclo*pentane-1 : 3-diones and straight-chain diketones. Thus, the condensation of succinyl chloride and diethyl sodiomalonate (molar ratio 1 : 2) gave a 45% yield of an enol-lactone isomeric with the expected, but unknown, succinylmalonic ester. These workers isolated, in addition, small amounts of the 1 : 4-diketone, succinylbismalonic ester, and its enol-anhydride. Treatment of their enol-lactone with aniline gave succindianilide. It should be noted that Scheiber[10] claimed to have prepared succinyl- and adipyl-malonic esters, but the properties of these compounds, apart from certain derivatives, are not given. Enolisation



$$\left[-CO{\cdot}CF_2{\cdot}\underset{\underset{C(CO_2Et)_2}{\|}}{C}{\cdot}O-\right]_n \longrightarrow n\left[Ph{\cdot}NH{\cdot}CO{\cdot}CF_2{\cdot}\underset{\underset{CH(CO_2Et)_2}{|}}{CO}\right] \longrightarrow CF_2(CO{\cdot}NHPh)_2 + CH_2(CO_2Et)_2$$

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[4] Hauptschein, Stokes, and Nodiff, *J. Amer. Chem. Soc.*, 1952, **74**, 4005.

[5] Barbour, Mackenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341.

[6] (*a*) Hauptschein, O'Brien, Stokes, and Filler, *J. Amer. Chem. Soc.*, 1953, **75**, 87; (*b*) Haszeldine, *J.*, 1950, 2789.

[7] Fear, Thrower, and Veitch, unpublished work.

[8] Simons, Black, and Clark, *J. Amer. Chem. Soc.*, 1953, **75**, 5621.

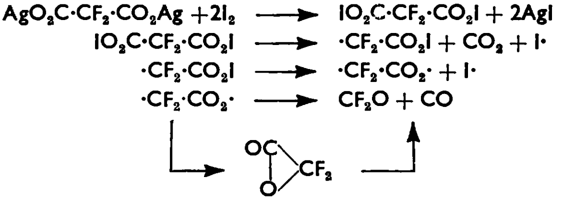
[9] Ruggli and Maeder, *Helv. Chim. Acta*, (*a*) 1943, **26**, 1476; (*b*) 1944, **27**, 436.

[10] Scheiber, *Ber.*, 1909, **42**, 1318.

of the ester (I) should be facilitated by the presence of a flanking difluoromethylene group (cf. $CF_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2H$, 66% enolic at 22°),[11] but it is likely that the highly strained four-membered, enol-lactone ring in (II) would rearrange spontaneously to a linear polyester.

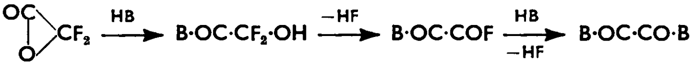
The ester, di-(2 : 2 : 2-trifluoroethyl) difluoromalonate, was obtained in fair yield by treating difluoromalonyl chloride with 2 : 2 : 2-trifluoroethanol. It was completely hydrolysed by an equal weight of water at 100° in 5 hr. There are few references to the preparation of diesters of perfluoro-dibasic acids (or their derivatives) and 1 : 1-H_2-perfluoro-alcohols. Hauptschein and his co-workers [6a] synthesised di-(1 : 1-H_2-perfluorobutyl) perfluoroglutarate by use of perfluoroglutaric anhydride, because of their difficulty in producing satisfactory yields of perfluorodiacyl chlorides. Their ester was only slightly hydrolysed in 10% potassium carbonate solution, but easily so in 10% potassium hydroxide solution.

Disilver difluoromalonate reacted extremely vigorously with iodine in the absence of solvent. No difluorodi-iodomethane was isolated, but silver iodide, carbon dioxide, carbon monoxide, and carbonyl fluoride were detected in the reaction products. The stoicheiometry of this complex reaction has not been determined. The formation of these compounds can best be accounted for by a free-radical mechanism :



$$AgO_2C{\cdot}CF_2{\cdot}CO_2Ag + 2I_2 \longrightarrow IO_2C{\cdot}CF_2{\cdot}CO_2I + 2AgI$$
$$IO_2C{\cdot}CF_2{\cdot}CO_2I \longrightarrow {\cdot}CF_2{\cdot}CO_2I + CO_2 + I{\cdot}$$
$${\cdot}CF_2{\cdot}CO_2I \longrightarrow {\cdot}CF_2{\cdot}CO_2{\cdot} + I{\cdot}$$
$${\cdot}CF_2{\cdot}CO_2{\cdot} \longrightarrow CF_2O + CO$$

Thus, carbonyl fluoride and carbon monoxide can be conceived as stabilisation products of the diradical $\cdot CF_2{\cdot}CO_2\cdot$. Alternatively, the latter could be stabilised by lactone formation, with subsequent fission to carbonyl fluoride and carbon monoxide. Carbonyl fluoride was identified by its reaction with aniline to give *s*-diphenylurea and anilinium fluoride. Evidence has been obtained for the formation of difluoroacetolactone by the identification of small amounts of its base-cleavage products, oxalic acid and oxanilide.



(where B = OH, NHPh)

A similar scheme has been proposed by Haszeldine,[12] and by Hauptschein, Stokes, and Grosse [13] for base-cleavage of perfluoro-lactones. Oxalic acid and oxanilide can also be considered as derivatives of oxalyl fluoride. However, the formation of this fluoride is unlikely, since it would involve fission of a C–F bond.

In addition to the above products, a small amount of tetrafluorosuccinic acid was detected, which could have resulted by dimerisation of the radical $\cdot CF_2{\cdot}CO_2I$, followed presumably by hydrolysis. No tetrafluoro-1 : 2-di-iodoethane, the decarboxylation product of $IO_2C{\cdot}[CF_2]_2{\cdot}CO_2I$, was detected. In view of the recent suggestion by Stewart and Cady that the thermal decomposition of trifluoroacetyl hypofluorite proceeds by a $\cdot CF_3$ radical mechanism,[14] the breakdown of $\cdot CF_2{\cdot}CO_2I$ to give $\cdot CF_2\cdot$, and hence tetrafluoroethylene, may be possible. However, further work will be necessary to establish this point.

Haszeldine [12] proposed the initial formation of hypoiodites in silver salt reactions with iodine and made use of a free-radical mechanism, similar to the above, to explain lactone formation with disilver hexafluoroglutarate and octafluoroadipate. However, Hauptschein and his co-workers [13] reported that the thermal degradation of the latter with iodine failed

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[11] Haszeldine and Sharpe, " Fluorine and its Compounds," Methuen and Co., Ltd., London, 1951, p. 94.

[12] Haszeldine, *Nature*, 1951, **168**, 1028.

[13] Hauptschein, Stokes, and Grosse, *J. Amer. Chem. Soc.*, 1952, **74**, 1974.

[14] Stewart and Cady, *ibid.*, 1955, **77**, 6110.

to yield perfluorovalerolactone; their main product was octafluoro-1 : 4-di-iodobutane. It is of interest that carbon monoxide has been reported as a product of the reaction of certain disilver salts of unfluorinated dibasic acids with iodine.[15]

EXPERIMENTAL

Treatment of Fluoro-dibasic Acid Mixture with Phosphorus Oxychloride.—Freshly distilled phosphorus oxychloride (422 g.) was added to the acid mixture (279 g.), prepared as described previously,[2] and the mixture was heated under reflux at 105—110° for 4½ hr. Distillation through a 1 ft. Dufton column gave a liquid (A) (353 g.), b. p. 32—93°, and a residue (B). Fractionation of (A) through a 3 ft. vacuum-jacketed column (Dixon gauze cylinders, 1/16 × 1/16 in.) afforded the fractions: (i) tetrafluorosuccinic anhydride (39·5 g.), b. p. 54—55·5°; (ii) (12 g.), b. p. 55·5—66·8°; (iii) difluoromalonyl chloride (85·8 g.), b. p. 66·8—68·1°; (iv) (23·9 g.), b. p. 68·1—86·1°; (v) *tetrafluorosuccinyl chloride* (6·7 g.), b. p. 86·1—86·3° [Found: Cl, 32·3%; equiv. (by titration of total acid after hydrolysis), 55·6. $C_4O_2Cl_2F_4$ requires Cl, 31·3%; equiv., 56·75]; (vi) (18·8 g.), b. p. 86·3—106·2°; and (vii), a residue (126 g.).

Characterisation of Tetrafluorosuccinyl Chloride.—(*a*) Hydrolysis of the acid chloride with an excess of water, followed by continuous ether-extraction of the aqueous solution and addition of aniline to the ether concentrate, gave dianilinium tetrafluorosuccinate, m. p. 224° (from ethanol–chloroform) (Found: equiv., 185. Calc. for $C_{16}H_{16}O_4N_2F_4$: equiv., 188).

(*b*) Anhydrous ammonia was passed into an ethereal solution of the acid chloride until precipitation was complete. The solid was filtered off, washed with ether, triturated with water, and then recrystallised from water to give tetrafluorosuccinamide, m. p. 261°.

(*c*) Similarly, aniline gave tetrafluorosuccindianilide, m. p. 227·5—228° (from aqueous acetone) (Found: C, 56·7; H, 3·8. Calc. for $C_{16}H_{12}O_2N_2F_4$: C, 56·5; H, 3·6%). Padbury and Kropa [3] reported m. p. 220—225°.

Detection of Octafluoroadipic Acid.—Water (1 l.) was added carefully to residue B (see above), and the solution was extracted continuously with ether for 65 hr. Evaporation of the ether *in vacuo* gave an acidic solid (41 g.) which was treated with phosphorus oxychloride (60 g.) as above, to give a liquid (42 g.), b. p. 75—116°. Fractionation through a 2 ft. column gave difluoromalonyl chloride (13·8 g.). No derivatives of tetrafluorosuccinic acid were detected.

When the residue from this reaction was hydrolysed with water and the solution extracted continuously with ether, a solid (16·7 g.) was obtained which, sublimed at 117—140°/0·15—0·2 mm., gave a dense, white acid (13·6 g.), a part of which (6 g.) was converted into its aniline salt (10·5 g.). This was recrystallised from ethanol, to give dianilinium difluoromalonate (52%), m. p. 164—165° (Found: equiv., 162. Calc. for $C_{15}H_{16}O_4N_2F_2$: equiv., 163). The mother-liquor was evaporated at room temperature and the recovered solid (46%) recrystallised once from ethanol–chloroform and twice from acetone–chloroform, to give dianilinium octafluoroadipate (11%), m. p. 212—212·5° (Found: C, 45·2; H, 3·5%; equiv., 236. Calc. for $C_{18}H_{16}O_4N_2F_8$: C, 45·4; H, 3·4%; equiv., 238). Tatlow and Worthington [16] reported m. p. 212°.

2 : 2-*Difluoropropane*-1 : 3-*diol.*—A solution of difluoromalonyl chloride (12·2 g.) in ether (35 ml.) was added slowly to a stirred suspension of lithium aluminium hydride (4·3 g.) in ether (75 ml.). The mixture was then heated under reflux, with continued stirring, for 30 min., and cooled, water (50 ml.) added dropwise, and the mixture poured into 6N-sulphuric acid (250 ml.). The ether layer was separated, the aqueous phase (no detectable fluorine in ionic form) extracted continuously with ether for 48 hr., and the combined ether solutions dried ($CaSO_4$), filtered, and evaporated to give the crude diol (7·2 g., 93%). Sublimation at 120—125°/16 mm. gave 2 : 2-difluoropropane-1 : 3-diol, m. p. 51—52° (Found: F, 33·9. Calc. for $C_3H_6O_2F_2$: F, 33·9%).

The diol, with *p*-nitrobenzoyl chloride in pyridine gave the *di*-p-*nitrobenzoate*, m. p. 107—108°, plates from ethanol (Found: C, 49·5; H, 3·1; N, 6·6; F, 9·5. $C_{17}H_{12}O_8N_2F_2$ requires C, 49·8; H, 2·95; N, 6·8; F, 9·3%).

Dibenzoyldifluoromethane.—Difluoromalonyl chloride (8·6 g., 0·049 mole) in anhydrous benzene (25 ml.) was added dropwise to a stirred suspension of powdered aluminium chloride (14·7 g., 0·11 mole) in benzene (100 ml.) at 10°. The mixture was stirred for 30 min. at room temperature, and then poured on crushed ice (100 g.) and concentrated hydrochloric acid (10 ml.). After separation, the aqueous phase was extracted with benzene, and the combined benzene solutions were washed with dilute hydrochloric acid, water, dilute sodium hydroxide,

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[15] Kleinberg, *Chem. Rev.*, 1947, **40**, 381.
[16] Tatlow and Worthington, *J.*, 1952, 1251.

and water, and dried ($CaSO_4$). Removal of benzene afforded *dibenzoyldifluoromethane* (9·0 g., 68%). After two sublimations at 85—90°/0·25 mm. and recrystallisation from ethanol (lustrous plates), the diketone had m. p. 59—59·5° (Found: C, 69·3; H, 4·2; F, 14·4. $C_{15}H_{10}O_2F_2$ requires C, 69·3; H, 3·9; F, 14·6%).

Treatment of dibenzoyldifluoromethane with hydroxylamine hydrochloride in pyridine at *ca.* 80° for 4 hr. gave, after isolation in the usual manner, a *monoxime*, m. p. 111—112° (colourless plates from light petroleum) (Found: C, 65·6; H, 4·1; N, 4·7. $C_{15}H_{11}O_2NF_2$ requires C, 65·5; H, 4·0; N, 5·1%). No dioxime was isolated after a five-fold increase in reaction time.

Condensation of Difluoromalonyl Chloride and Diethyl Sodiomalonate.—Difluoromalonyl chloride (17·7 g., 0·1 mole) was added dropwise to a stirred suspension of diethyl sodiomalonate (0·2 mole) in dry ether (350 ml.). The orange-yellow mixture was stirred and heated under reflux for 30 min., set aside overnight, and filtered with suction to remove sodium chloride (11·5 g., after ether-extraction and air-drying. Note: removal of sodium chloride as an aqueous solution results in cleavage of the reaction product to diethyl malonate and difluoromalonic acid). The combined filtrate and extract were dried ($CaSO_4$), and after removal of the ether the resultant yellow fluid was distilled *in vacuo*, to give diethyl malonate (13 g., 0·08 mole), b. p. 85—88°/11 mm., n_D^{24} 1·4118, and an oily residue (30·1 g.) [Found: F, 13·7%; *M* (cryoscopically in benzene), 688. $(C_{10}H_{10}O_6F_2)_n$ requires F, 14·4%]. Attempted distillation of a portion of the latter at 5×10^{-3} mm. (bath-temp. 150—180°) resulted in a marked increase in viscosity, with some degradation of the distilland as shown by darkening, a slow increase of pressure, and slight evolution of hydrogen fluoride. Addition of aniline (0·70 g.) to the above oily residue (1·0 g.) in ether (20 ml.) gave a minute precipitate, which was filtered off and identified as dianilinium difluoromalonate, m. p. 163·5—164° (from ethanol). The filtrate, on being kept overnight, deposited difluoromalondianilide (0·42 g.), m. p. 197° (from aqueous ethanol), undepressed in admixture with an authentic sample.[2] Evaporation of the ethereal mother-liquor gave a viscous residue, containing diethyl malonate, from which there was isolated a further crop (0·35 g.) of the dianilide. Thus, the total yield of difluoromalondianilide, based on $(C_{10}H_{10}O_6F_2)_n$, was 70%.

Di-(2 : 2 : 2-trifluoroethyl) Difluoromalonate.—Trifluoroethanol (9·91 g.) and difluoromalonyl chloride (8·76 g.) were heated together, under reflux, until the evolution of hydrogen chloride was complete (*ca.* 48 hr.), then poured into water (20 ml.), and the lower ester layer was washed with 1% sodium hydrogen carbonate solution and water, dried ($MgSO_4$), filtered, and distilled, to give the *ester* (8·6 g., 57%), b. p. 157—159°, d_{21}^{21} 1·525, n_D^{20} 1·326 (Found: F, 49·9. $C_7H_4O_4F_8$ requires F, 50·0%).

Disilver Difluoromalonate.—Water (14·4 g., 100% excess) was added to difluoromalonyl chloride (35·4 g.) under a condenser. Slow evolution of hydrogen chloride resulted and the rate of hydrolysis was increased by heating at 70° and finally at 90° to complete the reaction. Hydrogen chloride and excess of water were removed at 70—80°/15 mm. (7 hr.), to give crystalline difluoromalonic acid (25·6 g., 91·5%).

The acid (25·0 g.) was dissolved in water (500 ml.), and silver oxide (42·0 g.) added; the stirred mixture was then heated at 100° until reaction was complete. Excess of silver oxide was filtered off and the filtrate evaporated to give *disilver difluoromalonate* (59·0 g., 93·2%), as light grey crystals. This salt recrystallised from water or aqueous ethanol as white needles (Found: F, 10·8; Ag, 60·5. $C_3O_4F_2Ag_2$ requires F, 10·7; Ag, 61·0%).

Interaction of Disilver Difluoromalonate with Iodine.—The finely divided disilver salt (3·54 g.) was intimately mixed with powdered iodine (5·58 g.) in a flask fitted with a wide-bore condenser (surrounded by a Dewar flask containing solid carbon dioxide) connected to (i) a trap cooled at −80°, (ii) two traps, each containing aniline (3·72 g.) in dry ether (25 ml.), (iii) a trap cooled at −80°, (iv) a carbon monoxide indicator tube,[17] (v) a magnesium perchlorate drying tube, and (vi) a weighed carbon dioxide absorption tube containing soda-asbestos (5 g.) and magnesium perchlorate, protected by a calcium chloride tube. The apparatus was swept with pure dry nitrogen.

Momentary heating caused vigorous evolution of gas, lasting *ca.* 5 min.; the reaction could not be controlled. During this stage, a yellow solid was deposited in the first of the " aniline " traps, and the presence of carbon monoxide in the gaseous products was evident by the development of a brown stain in the yellow filling of the indicator tube. After the gas flow had subsided, the flask was heated strongly for 5 min. and passage of nitrogen was continued for a further 30 min.; solid was then deposited in the second " aniline " trap.

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[17] Ministry of Supply Aircraft Process Specification, D.T.D. 922A, H.M.S.O., London, February, 1948.

Carbon dioxide (0·45 g.) was absorbed by the soda-asbestos. No material was found in traps (i) and (iii). No organic liquids were recovered by heating the contents of the reaction flask, but silver iodide (4·47 g., 95%) was isolated. The precipitate in the first " aniline " trap was filtered off and washed with ether, to give anilinium fluoride (0·14 g.). Evaporation of the filtrate and treatment of the residue with dilute hydrochloric acid yielded *s*-diphenylurea (0·81 g.), m. p. and mixed m. p. 241—242° (after recrystallisation from aqueous ethanol) (Found: C, 73·5; H, 6·0; N, 12·9. Calc. for $C_{13}H_{12}ON_2$: C, 73·6; H, 5·7; N, 13·2%). Similarly, there was isolated from the second " aniline " trap, anilinium fluoride (0·01 g.), and oxanilide (0·1 g.), m. p. and mixed m. p. 252—253°.

On exposure of the condenser to air a white crystalline solid was formed on its walls. This was dissolved in ether (10 ml.) and aniline added dropwise until precipitation was complete. The salt formed (0·13 g.) was recrystallised from ethanol–chloroform [dianilinium tetrafluorosuccinate (13%), m. p. 220° (equiv., 187)]. Evaporation of the mother-liquor at room temperature afforded a white solid (after washing with chloroform), which on recrystallisation from ethanol–chloroform gave dianilinium oxalate (17%), m. p. and mixed m. p. 160° (Found: equiv., 139. Calc. for $C_{14}H_{16}O_4N_2$: equiv., 138).

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