130. *Organic Fluorides. Part VII. Co-ordination Compounds of Fluoroacetylacetones.*

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Mono-, tri-, and hexa-fluoro-derivatives of acetylacetone have been prepared by a Claisen type of condensation. Only the hexafluoro-derivative, where two CH_3 groups have been replaced by CF_3 groups, show properties which differ greatly from those of the parent acetylacetone.

Certain co-ordination compounds have been made and their absorption spectra determined. The uranous complexes with trifluoroacetylacetone and hexafluoroacetylacetone can be sublimed *in vacuo* without decomposition.

THE acetylacetone complexes of many metals are volatile (Morgan and Moss, *J.*, 1914, **105**, 189) and certain of the acetylacetone derivatives of bivalent metals can be distilled without decomposition. The uranyl acetylacetone complex is stable but cannot be sublimed or distilled without decomposition, and although the uranous derivative is more volatile it slowly decomposes when heated. Since greater volatility and increased stability result from the introduction of several fluorine atoms into an organic molecule, the fluoroacetylacetone derivatives of uranium were examined in the hope that these might prove to be stable and volatile without decomposition.

Monofluoroacetylacetone was made by condensing ethyl monofluoroacetate with acetone in the presence of sodium. Similarly ethyl trifluoroacetate with acetone yielded trifluoroacetylacetone, and with trifluoroacetone (Swarts, *Bull. Acad. Roy. Belg.*, 1927, **13**, 175) gave hexafluoroacetylacetone (Miss L. M. Turton, Thesis, Birmingham, 1945). Since this work was completed, the synthesis of tri- and hexa-fluoroacetylacetone by a similar method has been described (Henne, Newman, Quill, and Staniforth, *J. Amer. Chem. Soc.*, 1947, **69**, 1819; Reid and Calvin, *ibid.*, 1950, **72**, 2948). The condensation proceeded most vigorously between ethyl trifluoroacetate and acetone, and with ethyl monofluoroacetate was comparable in vigour to that with ethyl acetate. That of trifluoroacetone with ethyl trifluoroacetate was much less vigorous.

There is a marked difference between mono- and tri-fluoroacetylacetone on the one hand and hexafluoroacetylacetone on the other. It was expected that the monofluoroacetylacetone would not differ very much from acetylacetone but it seemed likely that the trifluoroacetylacetone would show some of the peculiarities of the hexafluoroacetylacetone. In fact the trifluoro-compound behaved more like the unsubstituted acetylacetone.

Mono- and tri-fluoroacetylacetone boil at about the same temperature (105° approx.). This is rather surprising since, by analogy with the hydrofluorocarbons (Grosse and Cady, *Ind. Eng. Chem.*, 1947, **39**, 367; Fowler *et al.*, *ibid.*, p. 375), the introduction of one fluorine atom might be expected to increase the boiling point above that of acetylacetone (137°). Since hexafluoroacetylacetone boils at about 64° (cf. Henne *et al.*, *loc. cit.*) it appears that although the intermolecular forces are modified by replacing hydrogen by fluorine in each methyl group the factor influencing the boiling point is whether one or both methyl groups are involved.

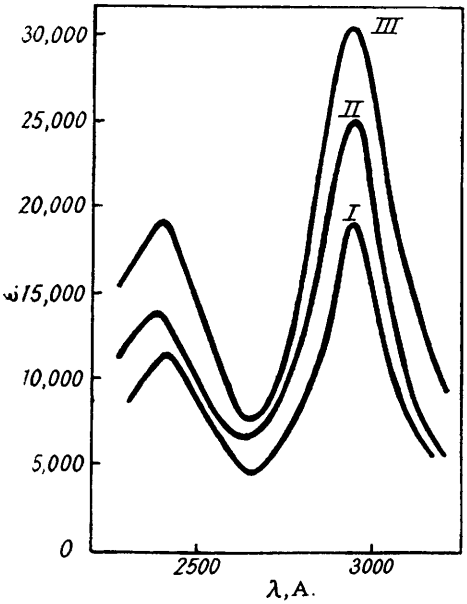
The tendency of the fluoroacetylacetones to form hydrates increases as the number of fluorine atoms increases. Thus the more highly fluorinated hexafluoroacetylacetone crystallised as a hydrate even on exposure to air, and co-ordination of it with metals could be effected only in anhydrous media. Further, while acetylacetone is soluble in eight parts of water, hexafluoroacetylacetone is miscible with water in all proportions.

Monofluoroacetylacetone readily afforded crystalline copper and iron co-ordination compounds. Trifluoroacetylacetone gave copper, iron and uranyl compounds by the usual procedure (cf. Biltz and Clinch, *Z. anorg. Chem.*, 1904, **40**, 220). While the uranous co-ordination compound could be made in aqueous solution the best yields were obtained under anhydrous conditions by allowing the trifluoroacetylacetone to react with uranium tetrachloride in an inert solvent in the presence of sodium. Hexafluoroacetylacetone failed to give co-ordination compounds in aqueous solution, no doubt because the compound reacts more readily with water than with metal ions. However, under the anhydrous conditions used for making the corresponding co-ordination compounds of trifluoroacetylacetone it readily formed a copper and a uranous compound (cf. Schultz and Larsen, *J. Amer. Chem. Soc.*, 1949, **71**, 3250).

Spectrophotometric examination showed that hexafluoroacetylacetone existed in the enolic modification to a much greater extent than was the case with either acetylacetone or hexabromoacetylacetone (cf. Reid and Calvin, *loc. cit.*).

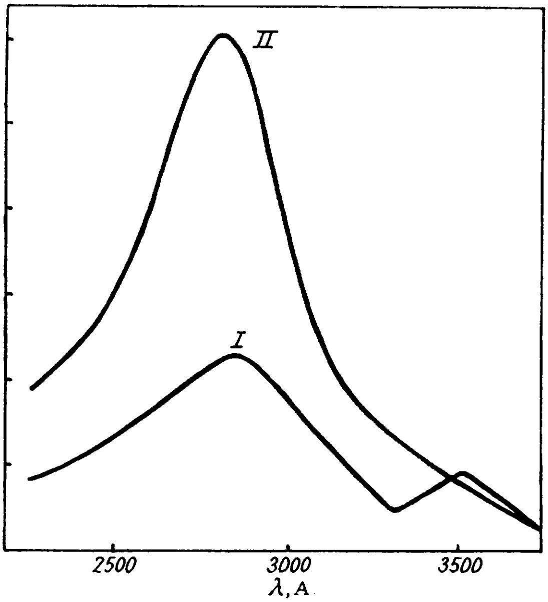
The ultra-violet absorption spectra of some co-ordination compounds of the fluoroacetylacetones, in ethanol, are shown in Figs. 1, 2, and 3, and the absorption maxima are recorded in the table.

FIG. 1.



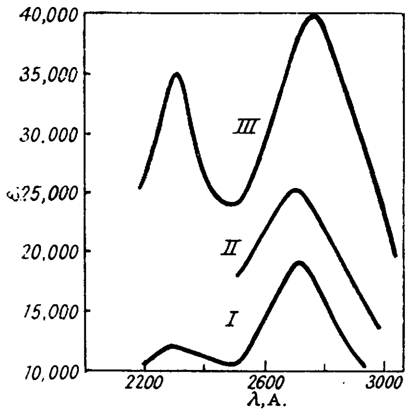
I. *Cupric derivative of acetylacetone.*
II. *Cupric derivative of monofluoroacetylacetone.*
III. *Cupric derivative of trifluoroacetylacetone.*

FIG. 2.



I. *Uranyl derivative of trifluoroacetylacetone.*
II. *Uranous derivative of trifluoroacetylacetone.*

FIG. 3.



I. *Ferric derivative of acetylacetone.*
II. *Ferric derivative of monofluoroacetylacetone.*
III. *Ferric derivative of trifluoroacetylacetone.*

Absorption maxima of co-ordination compounds.

	Cu.		Fe.		U.		UO_2.	
	λ.	ε.	λ.	ε.	λ.	ε.	λ.	ε.
Acetylacetone	2420	11,400	2290	12,000	—	—	—	—
	2950	19,000	2710	19,000	—	—	—	—
Fluoroacetylacetone	2400	14,000	2700	25,000	—	—	—	—
	2940	25,000	—	—	—	—	—	—
Trifluoroacetylacetone ...	2400	19,500	2300	30,000	2800	30,000	2860	11,500
	2940	31,000	2760	40,000	—	—	3520	4,500

EXPERIMENTAL.

Fluoroacetylacetone.—Dry acetone (25 c.c.) was added to fluoroacetic ester (20 g.) in the presence of sodium wire (5 g.), the mixture being cooled in an ice–salt bath. No apparent reaction occurred at this temperature but on removal of the cooling mixture the solution became red and after it had been kept overnight at room temperature all the sodium had dissolved. The usual methods failed to produce a copper derivative which would have facilitated purification, and hence the reaction mixture was diluted with water and the ethereal layer separated and washed once with water. The washings were combined with the aqueous layer and washed once with ether to remove any unchanged ester. On acidification of the aqueous solution with acetic acid, the colour changed from red to yellow. The solution now gave the typical red-purple colour with dilute ferric chloride but no insoluble copper derivative was produced (cf. Henne *et al.*, *loc. cit.*). The aqueous layer was acidified with dilute sulphuric acid and extracted with ether. The ethereal layer, which reacted acid after being washed with water, was dried and distilled, giving fluoroacetylacetone (5 g.), b. p. *ca.* 25°/15 mm. The diketone so obtained formed a blue-mauve cupric derivative which crystallised well from ethyl alcohol. The ferric derivative, prepared in the usual way, also crystallised from ethyl alcohol; it was readily soluble in ether.

Trifluoroacetylacetone.—To ethyl trifluoroacetate (74·5 g.) and sodium wire (10 g.) in ether (5 c.c.) at 0°, dry acetone (80 ml.) was added at such a rate as to maintain a steady reaction. After 2 hours at 0° the mixture was allowed to warm to room temperature. Ice-water (50 ml.) was added to the reddish-brown mixture. The aqueous layer was made slightly acid with acetic acid and the cupric trifluoroacetylacetone complex (see below) was precipitated by the addition of an excess of a warm saturated solution of cupric acetate. After being kept overnight at 0° the copper derivative was filtered off and dissolved in ether. The ethereal solution, after being shaken with 2N-sulphuric acid and then with water, was dried (Na_2SO_4) and distilled, giving trifluoroacetylacetone, b. p. 105°, n_D^{20} 1·379 (62%) (Found : C, 38·9; H, 3·0; F, 36·7. Calc. for $C_5H_5O_2F_3$: C, 39·0; H, 3·2; F, 37·0%). Henne *et al.* (*loc. cit.*) and Reid and Calvin (*loc. cit.*) record b. p. 107°.

When trifluoroacetylacetone was shaken with a saturated solution of copper acetate a light-blue precipitate of the cupric derivative was obtained which crystallised from alcohol as long blue needles (Found : F, 30·5; Cu, 16·9. Calc. for $C_{10}H_8O_4F_6Cu$: F, 30·8; Cu, 17·2%).

Trifluoroacetylacetone, shaken with concentrated ferric chloride in the presence of sodium acetate, gave the *ferric* compound as red crystals which separated well from alcohol (Found : F, 32·7; Fe, 10·7. $C_{15}H_{12}O_6F_9Fe$ requires F, 32·2; Fe, 10·9%).

Trifluoroacetylacetone was shaken with a solution of uranyl nitrate made slightly alkaline with aqueous sodium carbonate; the orange-yellow *uranyl* compound so formed recrystallised from dioxan, ether, or benzene (Found : C, 20·6; H, 1·6; F, 19·4; U, 40·7. $C_{10}H_8O_6F_6U$ requires C, 20·8; H, 1·4; F, 19·8; U, 41·3%). When heated at 160°/10^{-4} mm., the product decomposed with the production of trifluoroacetylacetone.

(*a*) To a solution of uranyl acetate (10 g.) in water (50 c.c.) sodium dithionite (7 g.) was added. The precipitate was dissolved in concentrated hydrochloric acid, kept for 24 hours, and filtered to remove a little sulphur. Dilute aqueous sodium hydroxide was then added to neutralize most of the acid and this was followed by trifluoroacetylacetone (10 g.) and more sodium hydroxide until vigorous shaking produced a khaki-green precipitate (5 g.) of the *uranous* compound (needles from alcohol, cubic crystals from benzene). These operations were carried out in an atmosphere of nitrogen. (*b*) The trifluoroacetylacetone (1 g.) in ether was added to uranium tetrachloride (2 g.) and sodium wire (2 g.). A reaction occurred and the solution became khaki-green. When the reaction subsided, the ethereal solution was decanted and concentrated in an atmosphere of nitrogen. The residual uranous compound (1 g.) was purified by sublimation or crystallisation. The crystals sublimed at 100—110°/10^{-4} mm. without decomposition and without leaving any residue (Found : C, 28·0; H, 2·0; F, 26·5; U, 26·5, 27·3. $C_{20}H_{16}O_8F_{12}U$ requires C, 28·0; H, 1·9; F, 26·8; U, 28·0%).

Hexafluoroacetylacetone.—Trifluoroacetone was prepared by Swarts's method (*Bull. Acad. Roy. Belg.*, 1927, **13**, 175) from ethyl trifluorosodioacetoacetate. [Ethyl trifluoroacetoacetate showed two bands in *cyclo*hexane : at 2380 (ε = 3000 approx.) and 2880 A. (ε = 400 approx.).] Its copper derivative showed bands at 2200 (ε = 11,000 approx.) and 2700 A. (ε = 21,000 approx.) (c = 3·0 mg.% in ethanol). Ethyl trifluorosodioacetoacetate was decomposed with hot (80—90°) dilute sulphuric acid in an all-glass apparatus, to give trifluoroacetone which was condensed in dry ether at −78°. The ethereal solution was dried ($MgSO_4$ or $CaCl_2$) and distilled, the trifluoroacetone being condensed in dry ether at −78°.

To sodium wire (7·8 g.) covered with dry ether, ethyl trifluoroacetate (37·8 g.) was added with cooling (0°). A dry ethereal solution of trifluoroacetone prepared by Swarts's method from 60 g. of ethyl trifluoroacetate was then added at −78°. The reaction mixture was allowed to warm to room temperature during 12 hours. Any trifluoroacetone which distilled during this time was condensed and returned to the reaction mixture which was kept overnight at room temperature until all the sodium had dissolved (cf. Henne *et al.*, *loc. cit.*). The reddish-brown mixture was treated with an excess of dilute sulphuric acid and extracted with ether. The combined ethereal extracts were dried (Na_2SO_4) and distilled, giving a liquid (20 g.) which boiled over the range 36—90° (Henne *et al.*, *loc. cit.*, give b. p. 63—64° for this compound). The material distilling between 54° and 85° underwent partial crystallisation which became complete on exposure to air. The portion of b. p. 85—90° crystallised immediately; it appeared to be the dihydrate of hexafluoroacetylacetone (cf. Schulz and Larsen, *loc. cit.*). The crystalline material reacted acid to litmus and Congo-red (Found : C, 24·8; H, 3·0. $C_5H_2O_2F_6,2H_2O$ requires C, 24·6; H, 2·5%).

A crystalline residue left after distilling the hexafluoroacetylacetone had m. p. 97° (after crystallisation from light petroleum). This product was soluble in ether and light petroleum and, unlike hexafluoroacetylacetone, it was insoluble in water. The nature and mode of formation of this crystalline compound will be the subject of a later communication.

The crystalline hydrate of hexafluoroacetylacetone showed a band at 3050 A. (ε = 80 approx.) (c = 116 mg.% in ether), moving to 2700 A. (ε = 100 approx.) after being kept over phosphoric oxide for 1 hour. When an ethereal solution of the hydrate was kept over sodium for 3 days the solution had a band at 3050 A. (ε = 4000 approx.) (c = 11·6 mg.%). It seems, therefore, that the anhydrous hexafluoroacetylacetone exists in the enolic modification to a much greater extent than either the parent acetylacetone (see Morton, *J.*, 1934, 898) or even the corresponding hexabromoacetylacetone which shows only an inflection in its absorption curve at 3000 A. (ε = 800 approx.) (c = 49·4 mg.% in *cyclo*hexane), whereas when it is enolised by dissolution in alcohol containing sodium ethoxide a band appears at 3640 A. (ε = 700 approx.) (c = 9·9 mg.%).

Hexafluoroacetylacetone failed to give the usual coloured compounds when treated with copper or iron salts in aqueous solution (cf. Henne *loc. cit.*) but when an ethereal solution of the hydrate was kept in contact with anhydrous copper sulphate the latter slowly became blue and the ethereal solution developed an emerald-green colour which showed an absorption band typical of the metallic acetylacetone compounds. Anhydrous hexafluoroacetylacetone gave a deep-red solution when treated in dry ether with anhydrous ferric chloride. The solution deposited red crystals which decomposed on removal of solvent, probably because of hydration of the diketone.

When the diketone reacted with uranium tetrachloride in ether solution in the presence of metallic sodium a brownish-khaki colour developed. Filtration in an inert atmosphere followed by evaporation gave a brownish crystalline residue of $(CF_3\cdot CO\cdot CH\cdot CO\cdot CF_3)_2U$ which was purified by sublimation at 40—50°/0·001 mm. The brown crystals, m. p. *ca.* 90°, b. p. 145° (decomp.), could be kept indefinitely in an atmosphere of carbon dioxide but underwent some decomposition when sublimed at 70—80°/0·2 mm.

Repeated attempts to prepare hexafluoroacetylacetone by classical methods (for example, by condensing trifluoroacetoacetic ester with trifluoroacetyl chloride) failed (W. K. R. Musgrave, Thesis, Birmingham, 1943; cf. Breslow *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 100, footnote 8).

The authors thank (the late) Professor Sir Norman Haworth, F.R.S., and Professor M. Stacey, F.R.S., for their interest in this work during 1940—46 and Dr. M. G. Webb for a specimen of hexabromoacetylacetone. They also thank the Director General for Scientific Research for permission to publish it.

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[*Received, October* 13*th*, 1950.]