288. β-*Diketones and Their Metal Complexes. Part II.*[1] *Acetylation of Fluoroacetone to* 1-*Fluoropentane*-2,4-*dione.*

By J. P. FACKLER, JUN., and F. A. COTTON.

1-Fluoropentane-2,4-dione has been prepared by reaction of fluoroacetone with acetic anhydride in the presence of the acetic acid–boron trifluoride complex. The copper(II) salt was isolated in about 57% yield and on acid hydrolysis gave the diketone. The proton and fluorine nuclear resonance spectra of the β-diketone have been obtained; they afford proof of structure and indicate 87 ± 4% enolization of the pure liquid at ~25°.

DURING spectroscopic and other investigations of β-diketone complexes[1] synthetic procedures for new substituted acetylacetones are being developed.* In this paper we describe the acetylation of fluoroacetone with acetic anhydride in the presence of boron trifluoride. This acid technique was used in preference to the more common basic Claisen condensation since α-halogeno-ketones are susceptible to basic cleavage of the carbon–halogen bond.[2] To our knowledge, there is no prior report of any acylation of an α-fluoroketone.

The Condensation.—The normal procedure, passing boron trifluoride into a mixture of fluoroacetone and acetic anhydride at —70°, gave no β-diketone.* At 0° this procedure gave a deep red solution which, after being refluxed with aqueous sodium acetate, yielded with cupric acetate a blue precipitate whose analyses indicated that the ligands consisted of ~53% of fluoroacetylacetone and ~47% of acetylacetone; steam-distillation of the refluxed solution led to nearly pure di(acetylacetonate)copper(II) (acetylacetone is a normal by-product of the boron trifluoride condensation of acetic anhydride with a ketone [2]). By using the inverse addition procedure and eliminating the treatment with sodium acetate di-(1-fluoropentane-2,4-dione)copper(II) was prepared in 30—60% yield. Since one recrystallization sufficed to purify the copper complex, little if any acetylacetone is formed during the inverse addition procedure.

Haszeldine *et al.*[3] claim to have obtained monofluoroacetylacetone by condensing ethyl fluoroacetate with acetone by means of sodium. After considerable purification their product gave the copper and ferric salts; their copper salt gave an ultraviolet spectrum substantially identical with that of our salt. However, a middle cut of the crude product obtained when we repeated their work gave a proton resonance spectrum which appeared very complicated in the high-field region and we think that their material contained some 1-fluoropentane-2,4-dione.

It is likely that any di-(3-fluoropentane-2,4-dione)copper(II) formed in our synthesis would have been precipitated or extracted into benzene by the procedure used. The copper complex was blue (not blue-grey as might be expected for a 3-substituted β-diketone complex of copper) and an ether extract of the ligand obtained after decomposition by ice-cold 3N-sulphuric acid gave only the fluorine nuclear magnetic resonance spectrum expected for 1-fluoropentane-2,4-dione. While the mechanism of condensations catalyzed by boron trifluoride has not been established in detail, the schemes (1) and (2) discussed by Hauser, Swamer, and Adams [2] are probably correct in essentials. For either path, the β-diketone produced from an unsymmetrical ketone depends on the mode of enolization under the influence of the acid (BF_3 or H^+). In the present case it was considered likely that enolization of the starting ketone would be predominantly from the CH_2F side, so that

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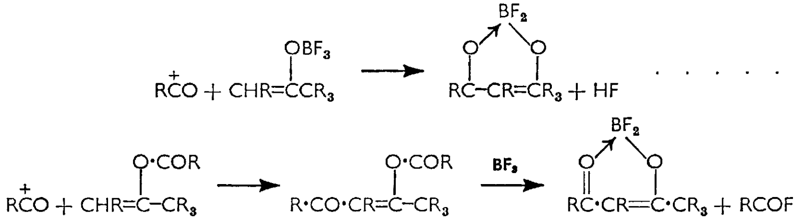
* *Note added in proof*: Bergman, Cohen, and Shahak (*J*, 1959, 3279) have condensed fluoroacetone with acetic anhydride, in the presence of boron trifluoride, and obtained an impure β-diketone, b. p. 49—51°/30 mm., which they believed to be 3-fluoropentane-2,4-dione.

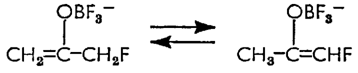
[1] Holm and Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 5658.
[2] Hauser, Swamer, and Adams, *Org. Reactions*, 1954, **8**, 98.
[3] Haszeldine, Musgrave, Smith, and Turton, *J.*, 1951, 609.

the 3-fluoropentanedione would be produced. Actually, failure to obtain this product does not conclusively vitiate this assumption; for, while the equilibrium (3) might lie to the right, the rate of reaction of the ion (I) with the carbonium ion could be much faster than that of (II).



$$\overset{+}{R}CO + CHR{=}\overset{OBF_3}{\overset{|}{C}}R_3 \longrightarrow RC(\text{–}O)\text{–}CR{=}CR_3(O\text{–})BF_2 + HF \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$\overset{+}{R}CO + CHR{=}\overset{O\cdot COR}{\overset{|}{C}}\text{–}CR_3 \longrightarrow R\cdot CO\cdot CR{=}\overset{O\cdot COR}{\overset{|}{C}}\text{–}CR_3 \xrightarrow{BF_3} RC\cdot CR{=}C\cdot CR_3(O,O\,BF_2) + RCOF \quad . \; . \quad (2)$$



$$CH_2{=}\overset{OBF_3^-}{\overset{|}{C}}\text{–}CH_2F \rightleftharpoons CH_3\text{–}\overset{OBF_3^-}{\overset{|}{C}}{=}CHF \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

(I) (II)

Nuclear Magnetic Resonance Spectra.—The fluorine nuclear resonance spectrum of 1-fluoropentane-2,4-dione in ether (consisting of two triplets, the stronger one showing fine structure) is interpreted as follows: The stronger triplet is due to fluorine in the enolic form of the compound. The primary components of the triplet are in the intensity ratio of 1 : 2 : 1 within experimental error, and the splitting is 46 ± 1 c.p.s.; the secondary splitting of each component into a doublet is attributed to coupling with the single hydrogen at position 3. The weaker triplet, which also has splittings of ~46 c.p.s. is assigned to fluorine in the keto-form; the secondary splitting of each component into a triplet by the methylene protons is not resolved owing to the weakness of the signals. The appearance of a triplet for the fluorine resonance in both the enol and the keto-form is as expected for the 1-fluoro-compound, but incompatible with the 3-fluoro-structure.

Proton nuclear magnetic resonance data for 1-*fluoropentane*-2,4-*dione* (*pure liquid at* 26° ± 3°).

Assignment	c.p.s. at 40 Mc[a]	δ (p.p.m.)	Relative intensities[c]	
(1) –OH (enol)	−380 ± 1·6	−9·50 ± 0·05	0·77	—
(2) =CH– (enol)	−24·3 ± 0·14[b]	−0·607 ± 0·004	0·78	—
(3) CH_2F (keto)	−12·1 ± 0·066	−0·302 ± 0·002	0·16	1·0[d]
(4) CH_2F (enol)	−8·69 ± 0·096	−0·217 ± 0·003	1·0[d]	—
(5) H_2O (ref.)	0·00	0·00	—	—
(6) CH_2F– (keto)	+35·0 ± 0·14	+0·875 ± 0·004	0·10	0·63
(7) CH_2F– (enol)	+37·9 ± 0·10	+0·948 ± 0·002	0·84	—
(8) –CH_2– (keto)	+59·4 ± 0·14	+1·48 ± 0·01	0·22	1·4
(9) CH_3– (keto)	+118·6 ± 0·37	+2·96 ± 0·01	0·89	5·5
(10) CH_3– (enol)	+124·3 ± 0·41	3·10 ± 0·02	5·3	—

Enol content[e] 87 ± 4%.

[a] Average values and deviations as calculated from six spectra. Centre of doublet, splitting ~3·5 c.p.s. [c] Visual approximation of areas (±10%). [d] Arbitrarily fixed intensities. [e] Average value from intensities, based on (9) and (10), (3) and (4), (6) and (7), (2) and (8).

For the proton resonance spectrum (see Table) the assignments are based on previous knowledge of chemical shifts in β-diketone complexes,[4,5] internal consistency, and consistency with the fluorine resonance spectrum, and to a limited extent on relative intensities. With respect to internal consistency, the agreement of the splitting of the resonance of the CH_2F protons, 46·6 ± 0·2 c.p.s, with the splitting in the fluorine triplet, 46 ± 1 c.p.s. and the agreement of the secondary splitting of each peak in the enol fluorine

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[4] Reeves, *Canad. J. Chem.*, 1957, **35**, 1351.
[5] Jarrett, Sadler, and Shoolery, *J. Chem. Phys.*, 1953, **21**, 2092.

resonance (~3 c.p.s.) with the splitting of peak (2) in the proton spectrum of the enol (~3·5), are good evidence of the correctness of the assignments.

Some of the intensity ratios (see Table) indicate that the spectra suffer from failure to achieve ideal slow passage: these intensity ratios were not unequivocally useful in making assignments, but they are never inconsistent. Similar anomalous intensity ratios may be seen in the spectra of acetylacetone and 3-methylacetylacetone published by Jarrett, Sadler, and Schoolery.[5] However, these authors apparently assumed that such anomalies, arising from differences in relaxation times, would not be too severe for certain comparisons (between =CH– and –CH_2– proton peaks) to be used in estimating the keto–enol ratio, and their estimate for acetylacetone agrees rather well with the result obtained classically by titration and with a more recent and probably more reliable nuclear magnetic resonance measurement by Reeves.[4] On the same basis, we estimate that pure liquid 1-fluoropentane-2,4-dione at 25° contains about 87% of the enolic form.

EXPERIMENTAL

Microanalyses by S. M. Nagy, M.I.T., and Schwarzkopf Microanalytical Laboratory, Long Island, New York.

Fluoroacetone.—This was prepared by Bergmann and Cohen's method[6] and had b. p. 78—80°/760 mm., n_D^{28} 1·3639 (Bergmann and Cohen gave b. p. 78—79°, n^{28} 1·3627).

The 2,4-dinitrophenylhydrazone (from ethanol–water) melted at 134—135° (lit.,[7] 134·2—135·4°) (Found: N, 21·5. Calc. for $C_9H_9FN_4O_4$: N, 21·9%).

Di-(1-*fluoropentane-*2,4-*dione*)*copper*(II).—Reaction of fluoroacetone with acetic anhydride was carried out essentially as described by Manyik *et al.*[8] in their inverse addition procedure. Acetic acid (48·0 g., 0·8 mole) at 0° was saturated with boron trifluoride (The Matheson Co.). A mixture of fluoroacetone (12·4 g., 0·163 mole) and acetic anhydride (Eastman White Label) (40·8 g., 0·4 mole) was then added during ~5 min. to the stirred powdery solid. After 30 min. the ice-bath was removed and stirring was continued for ~4 hr. as the flask warmed to room temperature. The mixture was poured into ice-cold sodium acetate solution (100 g. of trihydrate in 100 ml. of water). Excess (30 g.) of cupric acetate dihydrate in ice-water (~400 ml.) was added and the mixture kept near 0° for 30 min. The precipitated copper complex was filtered off, washed with water, then ether- and air-dried. The filtrate was extracted with warm benzene (5 × 200 ml.). After drying ($MgSO_4$), the benzene extracts were warmed and the solid complex was added and completely dissolved therein. Storing the solution at ~0° overnight, gave di-(1-fluoropentane-2,4-dione)copper(II) (13·9 g., 57% based on fluoroacetone). The complex may be recrystallized conveniently in small amounts from benzene or in larger amounts from dioxan–water (Found: Cu, 21·4; C, 40·3; H, 4·0; F, 12·7. Calc. for $C_{10}H_{12}CuF_2O_4$: Cu, 21·35; C, 40·3; H, 4·1; F, 12·8%).

1-*Fluoropentane-*2,4-*dione.*—The recrystallized copper complex (3 g.) was shaken with 3N-sulphuric acid (20 ml.). The β-diketone was extracted into ether, five 50-ml. portions being required. The extracts were dried ($MgSO_4$) and distilled: 1-*fluoropentane-*2,4-*dione* (1 g.), n^{25} 1·4501, was collected at 41—46°/18 mm. (Found: C, 51·0; H, 6·0; F, 16·0. $C_5H_7FO_2$ requires C, 50·8; H, 6·0; F, 16·1%).

Nuclear Magnetic Resonance Measurements.—Proton resonance spectra of the pure liquid diketone were observed at 26° ± 3° on a Varian Associates Model V-4300B high-resolution spectrometer at a frequency of 40 Mc. Chemical shifts were measured relative to water in a Pyrex capillary inserted in the sample tube. The 5 mm. Pyrex sample tubes were spun with the usual air-turbine device. Two independent measurements of the line separations were made by the audio beat method[9] in order to obtain a scale calibration. A line separation of 502 ± 5 c.p.s. was observed between the OH (enol) peak and the major methyl peak before the water capillary was inserted. A separation of 125 ± 1 c.p.s. was then determined between the

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[6] Bergmann and Cohen, *J.*, 1958, 2259.

[7] R. A. Wiles, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., U.S.A., 1958.

[8] Manyik, Frostick, Sanderson, and Hauser, *J. Amer. Chem. Soc.*, 1953, **75**, 5030.

[9] Roberts, "Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N.Y., 1959, p. 22.

water peak and the methyl peak after insertion of the capillary. These results provided the basis for the reported chemical shifts, δ (p.p.m.) [(freq. of peak-freq. of H_2O peak)/40] for all peaks in the spectrum.

The fluorine nuclear resonance spectra of ether solutions were also recorded at 40 Mc. The splittings in the observed triplet were found to be 46 ± 1 c.p.s. by the audio beat method, and those in the close doublets are estimated to be ~3 c.p.s.

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