Journal of Fluorine Chemistry, 15 (1980) 245–252

Received: September 19, 1979

SHORT COMMUNICATION

Studies in Fluorinated 1,3-Diketones and related compounds Part X[a]. Synthesis of some New Polyfluorinated 1,3-diketones, their copper 1,3-diketonates and Spectral Studies

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It is well recognised that fluorinated 1,3-diketones serve as versatile intermediates for the synthesis of a large number of heterocyclic compounds such as pyrazoles [1], flavones [2], isoxazoles [3] and diazepines [4] in addition to forming metal 1,3-diketonates [5]. At present, fluorinated 1,3-diketones are indespensable reagents in synthetic organic/analytical chemistry and have found novel analytical uses like analysing lunar samples [6], cobalt in vitamin B_{12} [7] and in detection of trace elements in blood, serum and other essential biological materials [8].

In this communication, the synthesis and characterization of six new polyfluorinated 1,3-diketones; $R.CO.CH_2.CO.R'$ (where, R = polyfluoroaryl and R' = perfluoroalkyl) and their copper chelates are reported. Spectral studies have clearly shown the existence of intramolecular hydrogen bonding [9,10] (i.r. at 3000-2500 wb cm^{-1}). Other prominent absorption bands are at 1620-1600 cm^{-1} ($C \overset{....}{=} O$ stretching mode) and 1510-1500 cm^{-1} ($C \overset{....}{=} C$ stretching mode). The absence of absorption bands in the region 1750-1725 cm^{-1} excludes the possibility of the existence of 1,3-diketones in a typical diketo form. A number of strong absorption bands are observed between 1330-1000 cm^{-1} which are due to C-F or CF_3 stretching modes while CF_3 deformation modes are observed at 900-700 cm^{-1}. The following changes were noticed after the formation of copper 1,3-diketonates. Firstly, the intramolecular

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[a] Part IX. K.C. Joshi, V.N. Pathak and V. Grover, J. Fluorine Chem., 13 (1979) 261.

(O-H---O absorption band disappeared from the region 3000-2500 cm^{-1} secondly the C-H stretching band of the chelated ring hydrogen shifted to higher frequencies, and finally perturbed double bond character was observed for the $C \overset{-}{\text{--}} O$ group.

In the ^{1}H n.m.r. spectra, of all compounds, a sharp signal is observed at δ (6.2 - 6.8) ppm which is assigned to methine protons $(=C\underline{H}-)$ present at the α-position. The appearance of enolic O-H protons at very low applied fields indicates the presence of intramolecular hydrogen bonding in these compounds [11, 12]. The absence of methylene signals again disproves the existence of these compounds in the diketo form. Of the two α-hydrogen atoms, one is always associated with an enolic hydroxyl group $(-CH=\underset{OH}{\underset{|}{C}}-)$ resulting in 100% enolization of the 1,3-diketones.

The ^{19}F n.m.r. spectra are recorded in table - 1.

In the mass spectra, the molecular ion peaks were observed for all species except for 4,4,4-trifluoro-1(2,4,6-trifluorophenyl)butane-1,3-dione. Some of the general characteristics observed during mass degradation are: (i) elimination of water; (ii) stepwise decomposition of perfluoroalkyl groups; (iii) presence of $Ar.C\equiv O^{+}$ groups; (iv) characteristic fragmentation of fluoroalkyl groups; (v) elimination of aromatic fluorine in the form of neutral H-F; and (vi) rearrangement leading to formation of tropylium cations

Experimental Section

I.r. spectra were recorded using a Perkin-Elmer-337 spectrometer; ^{1}H n.m.r. spectra by a Perkin Elmer model RB-12 (60 MHz) in CCl_4 solution with TMS as an internal standard. ^{19}F n.m.r. (56.4 MHz) spectra were recorded in CCl_4 solution and data are expressed relative to $CFCl_3$. Melting/boiling points are uncorrected.

Materials

4-Fluorobenzene [13], 4-fluoroacetophenone [14], ethyl trifluoroacetate [15], and ethyl pentafluoropropionate [16] were prepared by literature methods.

Table 1

^{19}F Spectral data* of polyfluorinated 1,3-diketones at 32^{o}C in CCl_4 (5-10%) solution relative to $CFCl_3$

$ArCOCH_2COR'$

S. No.	Substituent in Ar	R'	Aromatic fluorine	Aliphatic fluorines		
				$COC\underline{F}_2CF_2CF_3$	$CF_2C\underline{F}_2CF_3$	$C\underline{F}_3$
1.	4-F	$\underline{n}C_3F_7$	105.8	130.3	125.2	84.2
2.	3,4 Di-F	CF_3	105.9	-	-	79.5
3.	3,4 Di-F	C_2F_5	105.7	127.2	-	85.9
4.	3,4 Di-F	$\underline{n}C_3F_7$	105.7	129.3	124.3	84.9
5.	2,4,6 Tri-F	CF_3	105.7	-	-	79.6
6.	2,3,4,5,6 Penta-F	CF_3	147.2(2-$\underline{o}$-F) 150.1(1-$\underline{p}$-F) 152.5(2-$\underline{m}$-F)	-	-	76.0

* ppm upfield of $CFCl_3$

Preparation of 3,4-difluoroacetophenone

In a three necked flask (500 ml) fitted with a dropping funnel, mercury sealed stirrer and a reflux condenser, was taken a mixture of 1,2-difluorobenzene (25 g, 0.22 mole) and anhydrous aluminium chloride (61.2 g, 0.46 mole). Acetyl chloride (15.6 g, 0.22 mole) was gradually added with stirring. The reaction mixture was refluxed for 10 hrs. The residue was decomposed with ice cold hydrochloric acid (150 ml) and extracted with ether (3 x 50 ml). The solvent was removed and 3,4-difluoroacetophenone was dried over magnesium sulphate and distilled. B.P. 170° C, yield 20 g (80%). Found: F, 24.4%, Required: 24.4%.

The ketone and 2,4-dinitrophenylhydrazine were dissolved in ethanol and refluxed with a few drops of conc. hydrochloric acid. The precipitate was recrystallized from ethanol to give the corresponding 2,4-dinitrophenyl hydrazone. M.P. 186° C. Elemental analysis: Found: C, 49.9; H, 3.0; F, 11.3%. Required: C, 50.0; H, 2.9; F, 11.3%.

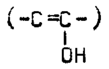
Preparation of 2,4,6-trifluoroacetophenone

2,4,6-Trifluoroacetophenone was prepared in a similar manner. B.P. 190°C, Yield (80%). Found: C, 55.2; H, 2.9; F, 32.8%; Required: C, 55.2; H, 2.9; F, 32.8%.

Synthesis of polyfluorinated 1,3-diketones

Polyfluorinated 1,3-diketones were prepared by reacting a polyfluoroacetophenone and a polyfluorinated ester [17] in the presence of sodamide.

Synthesis of 4,4,4-trifluoro-1-(2,3,4,5,6-pentafluorophenyl) butane-1,3-dione

Previously reported by Chappelow and Engel [18] (U.S. Pat. 3, 742, 062) without details of the synthetic procedure and physical data. This compound exists in 100% enolic form and shows $=\underline{\mathrm{CH}}$ at δ 6.6 ppm and  $(-\mathrm{C}{=}\underset{\substack{|\\ \mathrm{OH}}}{\underline{\mathrm{C}}}-)$ at δ 13.0 ppm.

Sodium hydride (1 g, 0.4 mole) was placed in a 100 ml three necked flask, fitted with a reflux condenser attached to a drying tube, a dropping funnel and a thermometer. The flask was cooled in an ice bath and 20 ml of dimethyl sulfoxide was

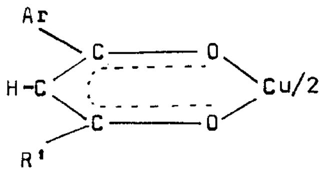
Table 2

Analytical and characteristic data of polyfluorinated 1,3-diketones $ArCOCH_2COR'$

S. No.	Substituent in Ar	R'	M.P./ B.P. °C	Yield %	C%		H%		F%	
					Cal.	Found	Cal.	Found	Cal.	Found
1.	4-F	$\underline{n}C_3F_7$	41	79	43.1	43.1	1.8	1.8	45.5	45.5
2.	3,4 Di-F	CF_3	124/0.5 mm	78	47.6	47.6	2.0	2.0	37.7	37.7
3.	3,4 Di-F	C_2F_5	112/6.5 mm	82	43.7	43.7	1.6	1.6	44.0	44.0
4.	3,4 Di-F	$\underline{n}C_3F_7$	72/1.0 mm	75	40.9	40.9	1.4	1.4	48.6	48.6
5.	2,4,6 Tri-F	CF_3	72/0.4 mm	80	44.4	44.4	1.5	1.5	42.2	42.2
6.	2,3,4,5,6 Penta-F	CF_3	48	60	39.2	39.2	0.6	0.6	49.7	49.7

Table 3

Analytical and characteristic data of copper (II) 1,3-diketonates



S. No.	Substituent in Ar	R'	M.P °C	Yield %	C% Cal.	C% Found	H% Cal.	H% Found	F% Cal.	F% Found
1.	4-F	$\underline{n}C_3F_7$	248	85	39.5	39.5	1.4	1.4	41.7	41.6
2.	3,4 Di-F	CF_3	210	82	42.4	42.4	1.4	1.4	33.6	33.6
3.	3,4 Di-F	C_2F_5	218	84	39.7	39.6	1.2	1.2	40.0	40.0
4.	3,4 Di-F	$\underline{n}C_3F_7$	222	86	37.6	37.6	1.0	1.0	44.7	44.7
5.	2,4,6 Tri-F	CF_3	254	85	39.9	39.9	1.0	1.0	37.9	37.9
6.	2,3,4,5,6 Penta-F	CF_3	253	83	35.6	35.6	0.3	0.3	45.1	45.1

added. The cooling bath was removed and the mixture was stirred with a magnetic stirrer for an hour. The temperature was then lowered to 15°C and ethyl trifluoroacetate (2.84 g, 0.2 mole) was added at the same temperature. The temperature was then lowered to 5°C and 2,3,4,5,6-pentafluoroacetophenone (2.1 g, 0.01 mole) was added very slowly during an hour. The temperature was then raised to 35°C and the mixture was stirred for 40 hrs. The dark reaction mixture was poured into crushed ice (50 g) containing 1 ml of 85% phosphoric acid with stirring. The organic layer was extracted with ether (3 x 50 ml) and the ether layer was washed with bromine water to remove free sulphur and sulphur compounds, followed by several washings with water. The extract was filtered and the crude solid was crystallized from petroleum ether-benzene mixture.

Analytical data of all polyfluorinated 1,3-diketones and their copper 1,3-diketonates are given in Table 2 and 3, respectively.

ACKNOWLEDGEMENT

We are thankful to C.S.I.R. (New Delhi) for the award of fellowship to one of us (V.G).

REFERENCES

1 K.C. Joshi and V.N. Pathak, Indian J. Chem., 11 (1973) 398.

2 M. Vijaya Lakshmi and N.V. Subba Rao, Curr. Sci., 36 (1967) 401.

3 K.C. Joshi, V.N. Pathak and V. Grover, Pharmazie, 34 (1979) 68.

4 D. Lloyd, R.H. McDougall and D.R. Marshall, J. Chem. Soc., (C), (1966) 780.

5 K.C. Joshi and V.N. Pathak, J. Chem. Soc. (Perkin Trans I), (1973) 57.

6. R.E. Sievers, K.J. Eisentraut, D.J. Griest, M.F. Richardson, W.R. Wolf, W.D. Ross, N.M. Frew and T.L. Isenhour, Second Lunar Science Conference, 2 (1971) 1451.

7 W.D. Ross, W.G. Scribner and R.E. Sievers, Eighth International Symposium on Gas Chromatography, 1970, 369.

8 P. Mushak, M.T. Glenn and J. Savory, Fluorine Chem. Rev., 6 (1973) 116.

9 J.D. Park, H.A. Brown and J.R. Lacher, J. Amer. Chem. Soc., 75 (1953) 4753.

10 R.S. Rasmussen, D.D. Tunicliff and R.R. Brattain, J. Amer. Chem.Soc., 71 (1949) 1068.

11 R.L. Lintvedt and H.F. Holtzclaw Jr., J. Inorg. Chem., 5 (1966) 239.

12 J.L. Burdett and M.T. Rogers, J. Amer. Chem. Soc., 86 (1964) 2105.

13 G. Balz and G. Schiemann, Ber., 60 (1927) 1186.

14 N. Buu Hoi and P. Jacquignon, Rec. Trav. Chim., 68 (1949) 781; Chem. Abstr., 44 (1950) 2509 g.

15 A.L. Henne, M.S. Newman, L.L. Quill and R.A. Staniforth, J.Amer.Chem. Soc., 69 (1947) 1819.

16 V. Grover, Ph.D. Thesis, University of Rajasthan, Jaipur, p 88 (1979).

17 K.C. Joshi, V.N. Pathak and S. Bhargava, J. Inorg. Nucl. Chem., 39 (1977) 803.

18 C.C. Chappelow Jr., and J.F. Engel, U.S. Patent, 3, 742, 062 (1973); Chem. Abstr., 79 (1973) 78395 h.