Journal of Fluorine Chemistry, 17 (1981) 555–560

Received: October 22, 1980

Studies in Fluorinated 1,3-Diketones and related compounds Part XII[a]. Synthesis and spectroscopic studies of Some new polyfluorinated 1,3-diketones, and their copper 1,3-diketonates

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SUMMARY

New polyfluorinated 1,3-diketones have been prepared from polyfluorinated acetophenones and appropriate esters in the presence of sodamide. The corresponding copper 1,3-diketonates have been obtained by treating a methanolic solution of polyfluorinated 1,3-diketone with methanolic solution of copper acetate. The polyfluorinated 1,3-diketones have been characterized by elemental as well as by spectral studies, viz: I.R., ^{1}H N.M.R.and ^{19}F N.M.R. In I.R., characteristic absorptions observed are: C-F stretching bands (1300 - 1000) cm^{-1}, C-F deformation modes (900 - 700 cm^{-1}) and intramolecular hydrogen bonding (3000 - 2500 cm^{-1}). In ^{1}H N.M.R. methine (= CH) signal is observed at δ 6.2 - 6.8 ppm and enolic proton resonance signal at δ 13 - 15 ppm indicating the presence of strong hydrogen bonding in such polyfluorinated 1,3-diketones.

INTRODUCTION

In connection with our comprehensive study of polyfluorinated 1,3-diketones and related compounds, we have already reported the synthesis of some new polyfluorinated 1,3-diketones [1] along with electrophilic substitution reactions of the corresponding europium 1,3-diketonates [2] and spectral studies of some new tris lanthanide 1,3-diketonates [3]. We now report the synthesis and characterisation of six more new polyfluorinated 1,3-diketones $ArCOCH_2COR'$ (where Ar = Fluoroaryl and R' = alkyl or fluoroalkyl) and their copper chelates.

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a Part XI. K.C. Joshi, V.N. Pathak and V. Grover, J. Fluorine Chem., 15 (1980) 527.

RESULTS

The spectral characterization of these compounds yielded data which was in agreement with earlier observations [4,5] viz: intramolecular hydrogen bonding (3000 - 2500 cm^{-1}), absence of the carbonyl band which would arise from the diketo form (1750 - 1725 cm^{-1}), C-F stretching bands (1300 - 1000 cm^{-1}) and C-F deformation modes (900 - 700 cm^{-1}). Similarly, in ^{1}H n.m.r., a methine signal (=C<u>H</u>) was observed at δ (6.2 - 6.8) ppm and the proton of the enolic hydroxyl group at δ (13 - 15) ppm. There was no signal for methylene protons. The ^{19}F n.m.r. spectra are recorded in Table 1. The appearance of only one signal for aromatic fluorines may probably be due to the spectra being recorded at 56.4 MHz and inadequate resolution.

EXPERIMENTAL

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 analytical data are expressed relative to $CFCl_3$. Melting/boiling points are uncorrected.

<u>Materials</u>

3,4-Difluoroacetophenone and 2,4,6-trifluoroacetophenone were prepared according to the method of Buu-Hoi <u>et al</u>.[6].

<u>Synthesis of polyfluorinated 1,3-diketones</u>

These were prepared according to the method of Adams and Hauser [7]. To a stirred suspension of sodamide (2 mole) in ether (50 ml), was added a solution of polyfluoroacetophenone in dry ether (1 mole in 50 ml). After 1 hr., the calculated amount of ester (1 mole in 20 ml dry ether) was added and refluxing continued. with stirring for 10-20 hrs. depending upon the nature of the ester. The ether was removed and the residual mixture, containing polyfluorinated 1,3-diketone was poured into water (300 ml) and 1,3-diketone precipitated in the form of its copper 1,3-diketonates The free 1,3-diketone was regenerated by treatment with 10% sulphuric acid and extracted with ether. On removal of the solvent, the product was distilled under reduced pressure.

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

TABLE 1

^{19}F n.m.r. data* for polyfluorinated 1,3-diketones at 32°C in CCl_4 (5-10%) solution (shifts 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.	2,4,6 Tri-F	CH_3	106.0	-	-	-
2.	2,4,6 Tri-F	C_2H_5	105.7	-	-	-
3.	2,4,6 Tri-F	C_2F_5	106.4	-	124.8	79.6
4.	2,4,6 Tri-F	n-C_3F_7	106.5	128.4	124.3	80.0
5.	3,4 Di-F	CH_3	105.9	-	-	-
6.	3,4 Di-F	C_2H_5	105.4	-	-	-

* ppm upfield of $CFCl_3$

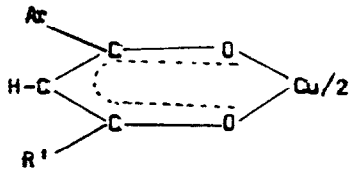
TABLE 2

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

S. No.	Substituent in Ar	R'	B.p. °C	Yield %	C% Cal.	C% Found	H% Cal.	H% Found	F% Cal.	F% Found
1.	2,4,6 Tri-F	CH_3	134/6.5 mm	80	55.55	55.49	3.24	3.20	26.38	26.37
2.	2,4,6 Tri-F	C_2H_5	113/5.5 mm	76	57.39	57.35	3.91	3.89	24.78	24.72
3.	2,4,6 Tri-F	C_2F_5	78/0.8 mm	72	41.25	41.20	1.25	1.22	47.50	47.47
4.	2,4,6 Tri-F	n C_3F_7	95/1.0 mm	70	38.92	38.88	1.08	1.00	51.35	51.33
5.	3,4 Di-F	CH_3	124/0.7 mm	74	60.60	60.58	4.04	4.00	19.19	19.10
6.	3,4 Di-F	C_2H_5	101/0.6 mm	75	62.26	62.19	4.72	4.70	17.92	17.88

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
1.	2,4,6 Tri-F	CH_3	268	80	48.63	48.60	2.43	2.39
2.	2,4,6 Tri-F	C_2H_5	257	75	50.62	50.60	3.06	3.00
3.	2,4,6 Tri-F	C_2F_5	238	88	37.63	37.58	0.85	0.75
4.	2,4,6 Tri-F	$\underline{n}\ C_3F_7$	242	86	35.05	35.00	0.74	0.68
5.	3,4 Di-F	CH_3	246	80	52.46	52.42	3.06	3.00
6.	3,4 Di-F	C_2H_5	252	82	54.60	54.55	3.30	3.25

ACKNOWLEDGEMENT

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

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