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STUDIES IN FLUORINATED 1,3-DIKETONES AND RELATED COMPOUNDS PART XV[a]. SYNTHESIS AND SPECTROSCOPIC STUDIES OF SOME NEW FLUORINATED MONOTHIO-1,3-DIKETONES

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SUMMARY

Six new polyfluorinated monothio-1,3-diketones have been synthesized from the corresponding fluorinated acetophenones and appropriate O-alkyl thioesters in the presence of sodamide. All these monothio-1,3-diketones are characterized by I.R. and ^{1}H N.M.R. spectral studies.

INTRODUCTION

The chemistry of fluorinated 1,3-diketones and related monothio-1,3-diketones is well recognised. Monothio-1,3-diketones like monothioacetylacetone and thiothenoyltrifluoroacetone have received considerable attention in analytical

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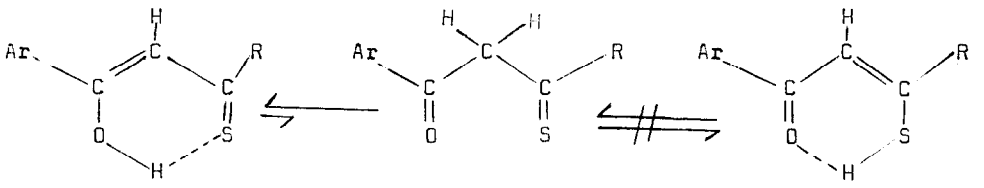
chemistry as superior chelating agents [1]. These are particularly useful in solvent extraction of trace metals and it has been noticed that the volatility of metal chelates increases with the degree of fluorination of the ligand [2] and on replacing oxygen with sulphur [3]. In continuation of our comprehensive programme of developing new fluorinated 1,3-diketones, monothio-1,3-diketones and related compounds [4-8], we now report the synthesis and characterisation of some new fluorinated monothio-1,3-diketones.

Viz: 4-(3,4-Difluorophenyl)butan-4-one-2-thione; 3-(3,4-Difluorophenyl)-1-phenylpropan-1-one-3-thione; 4-(2,4,6-Trifluorophenyl)butan-4-one-2-thione; 3-(2,4,6-Trifluorophenyl)-1-phenylpropan-1-one-3-thione; 4-(2,3,4,5,6-Pentafluorophenyl)butan-4-one-2-thione; 3-(2,3,4,5,6-Pentafluorophenyl)-1-phenylpropan-1-one-3-thione.

The monothio-1,3-diketones could exist in any of the forms:



(B) (A) (C)

The i.r. spectra of our fluorinated monothio-1,3-diketones show weak bands in the region 3655-3540 cm^{-1} which are attributed to intermolecularly hydrogen-bonded O-H stretching vibrations. Bands which are present in the region 2700-2100 cm^{-1} are designated to chelated enol groups (C=S.....H-O-C=). C-O and C-C stretching vibrations are observed in the regions 1630-1595 cm^{-1} and 1565-1550 cm^{-1}. The absence of absorption bands in the region 1725-1700 cm^{-1} indicates that these compounds exist entirely in the hydrogen-bonded enol form. A very strong band due to overlapping of C-S and C-F stretching absorptions is observed in the region 1265-1220 cm^{-1}. In addition, very strong bands due to C-F stretching vibrations are observed in the region 1180-1011 cm^{-1}. ^1H n.m.r. data support the above observations. The compounds show =CH signals in the region δ 6.8-7.4 ppm and

=C-O-H...S=C- signals in the δ 13-15.8 ppm region. The absence of methylene signals (in the δ 3.0-3.2 ppm) and non-appearance of enethiol (=C-S-H) proton signals in the region δ 4.8-6.8 ppm are strong evidence for the absence of form (C).

TABLE 1

Analytical and characteristic data of fluorinated monothio-1,3-diketones, $ArCOCH_2CSR$

Sl No.	Subst. in Ar	R	Dist. Temp. °C/P	Mol. Formula	C% Calc. (Found)	H% Calc. (Found)	F% Calc. (Found)	S% Calc. (Found)
1	3,4-DiF	CH_3	130/ 1mm.	$C_{10}H_8F_2OS$	56.07 (56.01)	3.74 (3.72)	17.76 (17.72)	14.95 (14.89)
2	3,4-DiF	C_6H_5	160/ 2mm.	$C_{15}H_{10}F_2OS$	65.22 (65.20)	3.62 (3.58)	13.77 (13.70)	11.59 (11.55)
3	2,4,6-Tri F	CH_3	120/ 1mm.	$C_{10}H_7F_3OS$	51.72 (51.68)	3.02 (3.00)	24.57 (24.52)	13.79 (13.78)
4	2,4,6-Tri F	C_6H_5	140/ 2mm.	$C_{15}H_9F_3OS$	61.22 (61.17)	3.06 (3.00)	19.39 (19.38)	10.88 (10.87)
5	2,3,4,5,6-Penta F	CH_3	100/ 0.5 mm.	$C_{10}H_5F_5OS$	44.78 (44.75)	1.87 (1.82)	35.45 (35.40)	11.94 (11.93)
6	2,3,4,5,6-Penta F	C_6H_5	110/ 0.5 mm.	$C_{15}H_7F_5OS$	54.54 (54.54)	-	28.79 (28.75)	-

In the ^1H n.m.r. spectra, the enolic proton (O-H...S) signals are sharp and at low field (δ 13-15.8 ppm) indicating strong intramolecular and weak intermolecular hydrogen bonding.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 337 spectrometer in Nujol mull; ^1H n.m.r. spectra by a Perkin-Elmer RB-12 spectrometer in $COCl_3$ solution with TMS as an internal standard.

Synthesis of fluorinated acetophenones

3,4-Difluoro- and 2,4,6-trifluoro-acetophenones were prepared according to the method of Joshi et al. [4].

Synthesis of O-ethyl thioesters

The thioesters R(CS)OEt were prepared from corresponding imidic esters by the action of hydrogen sulphide [7].

Synthesis of monothio-1,3-diketones

These were prepared by the method reported by us earlier [7] by the Claisen condensation. All the fluorinated monothio-1,3-diketones gave single spots on t.l.c., and are recorded along with their analytical data in Table 1.

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