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SHORT COMMUNICATION

# Studies in Fluorinated 1,3-Diketones and related compounds Part XI[a]. Synthetic and Spectral Studies of Fluorinated 1,3-Diketonatoeuropium chelates*

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The chemistry of the fluorinated metal 1,3-diketonates has aroused much recent interest in laser devices [1], as N.M.R. shift reagents [2] and in analytical chemistry [3]. The quasi-aromaticity of transition metal 1,3-diketonates is well established [4], but the quasiaromatic nature of the chelate rings of lanthanide 1,3-diketonates is yet to receive proper attention. In this paper, we report the quasiaromatic character of some lanthanide 1,3-diketonates to selective electrophilic substitution reactions. Like transition metal 1,3-diketonates, the lanthanide 1,3-diketonato system was also found to behave like a sensitive heterocycle possessing some aromatic character. All the synthesized compounds have been characterised by their i.r., $^{1}$H n.m.r., $^{19}$F n.m.r. spectral studies[4]

The methine proton at the central carbon atom of the chelate ring has been subjected to nitration, chlorination and bromination according to the schema.

Substitution in the phenyl rings is unlikely because of ring deactivation from electron release resonance effects.

Prominent absorption bands in the i.r. spectra occur at 1630-1550 and 1530-1500 cm$^{-1}$ and are attributed to the C=O and C=C stretching modes. The disappearance of the C-H in-plane bending vibration band (from region 1225-1180 cm$^{-1}$) provides strong evidence for halogen entering at the central carbon

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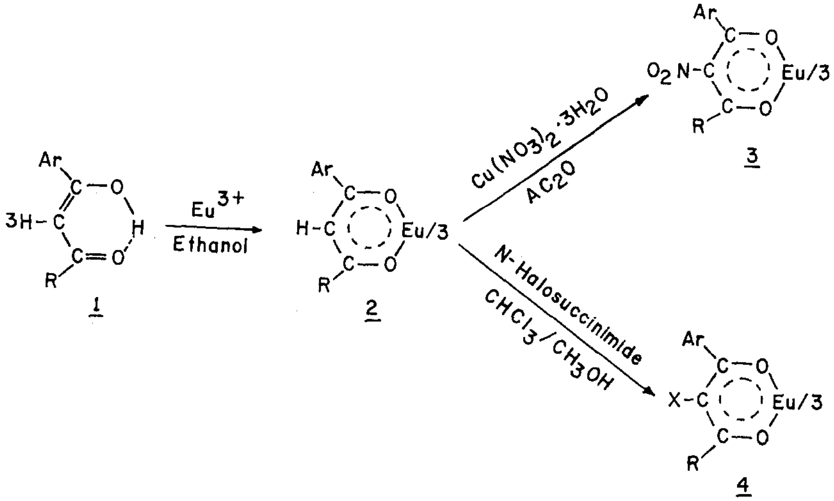


atom of the ligand. In the i.r. spectra of the nitrated 1,3-diketonates, three additional bands appear in the regions 1575-1552, 1362-1348 and 825-800 $cm^{-1}$ attributed to asymmetric and symmetric $NO_2$ stretching modes and to C-N or N-O vibrational modes respectively.

The disappearance of the methine resonance signal from the region $\delta$ 6.2 ppm in the $^1H$ n.m.r. spectra gives strong evidence for electrophilic substitution at the central carbon atom.

In the $^{19}F$ n.m.r. spectra, characteristic signals are observed in the regions - 73.5 to - 88.5 ($-CF_2-C\underline{F}_3$), - 118.5 to -128.5 ($-C\underline{F}_2-CF_3$), - 128.5 to - 38.5 ($-CO \cdot C\underline{F}_2 \cdot CF_2-$) aromatic fluorine is observed at -108.5 to - 118.5. All values are relative to $CFCl_3$.

EXPERIMENTAL

I.r. spectra were recorded using a Perkin-Elmer 337 spectrometer; $^1H$ n.m.r. spectra by a Perkin Elmer model R8-12 (60 MHz) in $CDCl_3$ solution with TMS as an internal standard. $^{19}F$ n.m.r. (56.4 MHz) spectra were recorded in $CHCl_3$ solution and data are expressed relative to $CFCl_3$. Melting points are uncorrected.

## Materials

4-Fluorobenzene, 4-methoxy-3-fluorobenzene [5], 4-fluoroacetophenone and 4-methoxy-3-fluoroacetophenone [6] were prepared by literature methods. The general method of the preparation of fluorinated 1,3-diketones and the fluorinated tris 1,3-diketonates have already been reported by us [7, 8].

## Nitration of europium 1,3-diketonates

The nitration of europium 1,3-diketonates was carried out by direct nitration of europium 1,3-diketonates under mildly acidic conditions. A cooled solution of europium 1,3-diketonate (0.001 mole) in acetic anhydride (5 ml) was added dropwise, with constant stirring, to ground copper nitrate trihydrate (0.003 mole) in acetic anhydride (5 ml) and kept at 0 to -5°C for 5 to 15 hrs. The reaction mixture was treated with ice-cold water and sodium acetate (0.1 mole) when a finely divided greenish precipitate separated.

The compounds were crystallized from a suitable solvent and gave single spots on t.l.c. plates in various solvent systems.

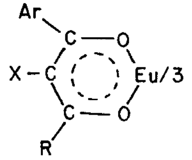
## Halogenation of europium 1,3-diketonates

To a solution of europium 1,3-diketonate (0.001 mole) in methanol was added N-chlorosuccinimide/N-bromosuccinimide (0.003 mole) and the solution refluxed for 4-7 hrs. The solvent was removed and the solid collected on a suction filter and washed several times with 95% ethanol (15 ml) followed by sodium hydrogen sulphite solution (10 ml), aqueous sodium hydroxide solution (15 ml), and finally with water (40 ml). The chlorinated/brominated europium 1,3-diketonates were recrystallized from benzene-hexane and found homogeneous as judged by single spots on t.l.c.

The nitro and halo derivatives of 1,3-diketonates are recorded in table - 1 along with their analytical data.

We are thankful to University of Rajasthan, Jaipur, for the award of University Research Fellowship to one of us (V.G).

Table I . Analytical and characteristic data of nitro and halo derivatives of fluorinated 1,3-Diketonatoeuropium chelates



| S. No. | Substituent in Ar | R | X | M.P. °C | Yield % | C% | | H% | | F% | | N% | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Calc. | Found | Calc. | Found | Calc. | Found | Calc. | Found |
| 1. | 4-F | $CH_3$ | $NO_2$ | 132 | 83 | - | - | - | - | - | - | 5.0 | 4.9 |
| 2. | 4-F | $CF_3$ | $NO_2$ | 140 | 78 | 36.5 | 36.5 | 1.2 | 1.1 | - | - | 4.3 | 4.3 |
| 3. | 4-F | $C_2H_5$ | $NO_2$ | 125 | 82 | 45.7 | 45.7 | 3.1 | 3.0 | - | - | 4.8 | 4.8 |
| 4. | 4-F | $C_2F_5$ | $NO_2$ | 135 | 80 | 34.9 | 34.8 | 1.0 | 1.0 | 30.1 | 30.0 | 3.7 | 3.7 |
| 5. | 4-F | $\underline{n}C_3F_7$ | $NO_2$ | 142 | 75 | 33.6 | 33.5 | 0.9 | 0.8 | 35.5 | 35.4 | 3.3 | 3.2 |
| 6. | 3-F, 4-OMe | $CH_3$ | $NO_2$ | 195 | 79 | - | - | - | - | - | - | 4.6 | 4.5 |
| 7. | 3-F, 4-OMe | $CF_3$ | $NO_2$ | 138 | 80 | 36.8 | 36.8 | 1.7 | 1.6 | 21.2 | 21.1 | 3.9 | 3.8 |
| 8. | 4-F | $CH_3$ | Cl | 128 | 80 | 45.4 | 45.4 | 2.7 | 2.6 | - | - | - | - |
| 9. | 4-F | $CF_3$ | Cl | 139 | 75 | 37.8 | 37.7 | 1.2 | 1.2 | - | - | - | - |
| 10. | 4-F | $C_2F_5$ | Cl | 147 | 75 | 35.9 | 35.8 | 1.0 | 1.0 | - | - | - | - |
| 11. | 4-F | $CH_3$ | Br | 135 | 78 | 38.8 | 38.7 | 2.3 | 2.2 | - | - | - | - |
| 12. | 4-F | $CF_3$ | Br | 144 | 75 | 33.0 | 33.0 | 1.1 | 1.0 | - | - | - | - |
| 13. | 4-F | $C_2F_5$ | Br | 139 | 76 | 31.9 | 31.9 | 0.9 | 1.0 | - | - | - | - |

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