

Studies of Fluorinated β -Diketones and Related Compounds. Part II.¹ Synthetic and Infrared Spectral Studies of 1,3-Diketonatochromium Derivatives, and their Substitution Reactions

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Seventeen 1,3-diketonatochromium derivatives have been prepared from fluorinated β -diketones, and their electrophilic substitution reactions have been studied. Chloro-, bromo-, and nitro-substituents have been introduced at the central carbon atom of the ligand under controlled conditions. The effect of these groups on C=O and C=C stretching frequencies is discussed.

THE chemistry of the metal 1,3-diketonates has aroused much recent interest. The metal 1,3-diketonate system behaves as a sensitive heterocycle possessing at least some aromatic character. Holm and Cotton² have expressed doubts over such aromaticity in these compounds, but Collman *et al.*,³⁻⁵ supported by other workers,^{6,7} recognise their quasi-aromatic character and have reported electrophilic substitution reactions.

More recently, metal complexes of some fluorinated β -diketones have been prepared and have found promising use in laser devices^{8,9} and in analytical chemistry.^{10,11} We now report the preparation of seventeen new 1,3-diketonatochromium(III) derivatives, a study of some of their electrophilic substitution reactions, and their i.r. spectra. The results support the quasi-aromatic character of these compounds.

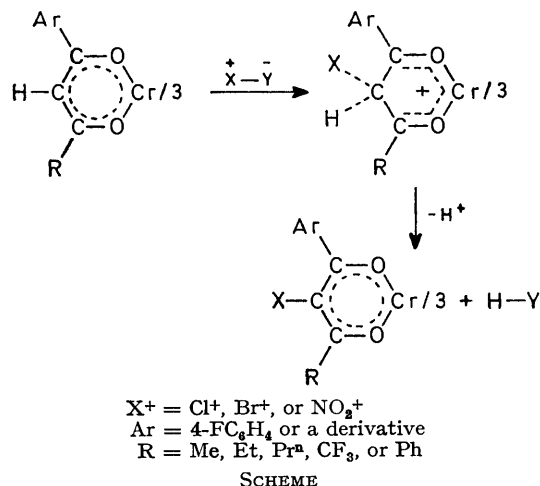
RESULTS AND DISCUSSION

Electrophilic Substitutions.—Electrophilic substitution reactions at the central carbon atom of the ligand are illustrated in the Scheme.

Substitution in the phenyl rings is not expected, as these rings are deactivated owing to the predominating electron-release resonance effect in these systems.¹² In general, reactions of methyl-substituted metal 1,3-diketonates are faster than those of their phenyl-substituted analogues.^{12,13} Thus in the case of compounds (4) and (14) (see Table) we were able to obtain good yields only after doubling the usual reaction time.

It appeared, as expected, that the methyl substituents in the 1,3-diketonates enhanced the reactivity of the chelate rings and simultaneously shielded the donor oxygen atoms from attack by the electrophile. We also obtained good yields of electrophilic substitution products from compounds (2) and (3) (Table) in which the methyl group was replaced by ethyl or n-propyl. On the other hand, compounds (9)—(11), (15), and

(16) underwent electrophilic substitution very slowly under forcing conditions owing to the strong positive inductive effect of the trifluoromethyl group.^{12,14}



The halogenation of the diketonates was performed with *N*-halogenosuccinimide in polar solvents (chloroform and methanol) without an acid catalyst.¹⁵ The reaction was faster in methanol owing to its high dielectric constant and consequent increased production of electrophiles.¹⁶ The halogenation of those diketonates containing a trifluoromethyl group was effected only by refluxing in methanol for 8–10 h, giving moderate yields. In some cases [compounds (1)—(3), (6)—(8), (12), and (14)] halogenated products were obtained by refluxing with *N*-halogenosuccinimide in carbon tetrachloride for 4–6 h, reaction taking place by a free-radical mechanism.¹⁶

For nitration, copper(II) nitrate trihydrate was more effective and gave higher yields than aluminium(III) nitrate nonahydrate, suggesting that a copper

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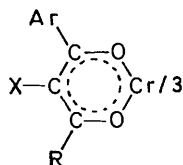
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1,3-Diketonatochromium derivatives *



No.	Substituents in Ar	R	X	M.p. (°C)	Yield (%)
(1)	4-F	Me	H	106—108	67.7
			Cl	245—246 †	65.0
			Br	110—112	45.4
(2)	4-F	Et	NO ₂	270—272	43.0
			H	148—150	71.3
			Cl	354—356 †	70.2
			Br	158	55.0
(3)	4-F	Pr ⁿ	NO ₂	295—300 †	67.7
			H	94—95	50.1
			Cl	160—161	59.6
			Br	178—180	64.4
(4)	4-F	Ph	NO ₂	135—136	54.0
			H	120—122	84.4
			Cl	207—210	51.1
			Br	295 †	66.0
(5)	4-F	CF ₃	NO ₂	266—267	66.6
			H	114—115	80.0
			Cl	208—210	76.1
			Br	116—118	56.4
(6)	4-F, 2-Me	Me	NO ₂	300 †	64.3
			H	125—127	70.3
			Cl	176—178	61.3
			Br	125—126	46.3
(7)	4-F, 3-Me	Me	NO ₂	145—148	64.5
			H	96—98	76.0
			Cl	175—177	61.2
			Br	350 †	46.7
(8)	2-F, 5-Me	Me	NO ₂	177—180	68.0
			H	127—130	81.2
			Cl	248—250	61.1
			Br	168—170	39.5
(9)	4-F, 2-Me	CF ₃	NO ₂	180—183	54.9
			H	120—122	43.0
			Cl	118—120	64.8
			Br	185	52.4
(10)	4-F, 3-Me	CF ₃	NO ₂	205—206	42.3
			H	77	65.7
			Br	152—154 †	52.7
			NO ₂	112—116	62.3
(11)	2-F, 5-Me	CF ₃	H	85.5	44.3
			Br	114	67.9
			NO ₂	174—175	43.3
			H	169—170	76.9
(12)	2-Cl, 4-F	Me	Cl	360 †	67.4
			Br	300 †	48.6
			NO ₂	197—200 †	72.2
			H	115—118	82.0
(13)	3-Cl, 4-F	Me	Cl	285—288 †	48.0
			Br	105—106	55.4
			NO ₂	124—127	62.6
			H	126—127	85.2
(14)	3-Cl, 4-F	Ph	Cl	203—206	50.4
			Br	208—210	63.6
			NO ₂	195—197	75.9
			H	91.5	54.1
(15)	2-Cl, 4-F	CF ₃	Cl	184—187	56.0
			Br	155—156	54.5
			NO ₂	182—185	58.9
			H	155—156	55.8
(16)	3-Cl, 4-F	CF ₃	Cl	178—181	50.0
			Br	161—162	48.4
			NO ₂	142—144	68.6
			H	142—145	65.9
(17)	5-F, 2-OH	Me	Cl	158—160	50.8
			Br	164—165	50.3
			NO ₂	135—136	57.3
			H	142—145	65.9

* Elemental analysis showed that the chromium 1,3-diketonates (1), (4), (5), (8), (9)—(11), and (14) contain one mol. equiv. of water. † Decomp.

complex may be involved.^{17,18} All nitrated 1,3-diketonatochromium derivatives in pyridine slowly developed a deep red colour, ascribed to formation of a charge-transfer complex.¹⁹

All attempted electrophilic substitution reactions (chlorination, bromination, and nitration), of analogous copper(II) chelates with appropriate electrophiles resulted in the destruction of the chelates. This instability seems to be associated with the unavailability of an inner orbital (in particular a *d* orbital) for complete saturation of the co-ordination sphere.^{4,20} Surprisingly, the 1,3-diketonatochromium derivatives (1), (4), (13), and (14) decomposed on treatment with bromine in methanol.

I.r. Band Assignments. †—Our assignments are in conformity with other recent observations.^{21–23} Prominent bands occur in the regions 1630—1550, 1530—1500, and 1225—1180 cm⁻¹ and are attributed to the C=O and C=C stretching modes and to the C-H in-plane bending vibration, respectively.

For all the chlorinated and brominated chromium 1,3-diketonates, the disappearance of the C-H in-plane bending vibration band provides strong evidence for the halogen entering at the central carbon atom of the ligand. Introduction of the halogen also affects the C=O and C=C stretching frequencies owing to its electro-negative character, the effect being much more pronounced on the C=C band. Partial overlapping of the C=O and C=C bands occurs in some cases [compounds (5), (6), (12), and (15) with X = Br], and in the case of the corresponding chloro-derivatives complete overlap is observed. This is in harmony with Dryden's²⁴ empirical rules.

In the spectra of the nitrated 1,3-diketonates, three additional bands appear in the regions 1575—1552, 1360—1348, and 825—800 cm⁻¹, and are attributed to asymmetric and symmetric NO₂ stretching modes, and to C-N or N-O vibrational modes, respectively. Here again the C-H in-plane bending vibration band has disappeared. Introduction of the nitro-group at the central carbon atom of the ligand weakens the C=C band much more than the C=O band owing to its negative inductive effect. When both Ar and R are phenyl groups, the asymmetric and symmetric NO₂

† Full details are deposited with the National Lending Library (see Experimental section).

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stretching frequencies are increased; it is probable that the nitro-group is forced out of the plane of the quasi-aromatic chelate ring by steric interaction with the adjacent phenyl rings.¹⁹

EXPERIMENTAL

Full details of analytical and i.r. spectral data are given in Supplementary Publication No. SUP 20563 (7 pp., 1 microfiche).*

The seventeen fluorinated 1,3-diketones were prepared as reported earlier.¹

1,3-Diketonatochromium Derivatives.—These were prepared ⁴ from chromium(III) chloride hexahydrate (0.027 mol), the appropriate β -diketone (0.08 mol), and urea (15 g) in dimethylformamide-water (24:1; 200 ml) at 100 °C.

Halogenation.—A mixture of *N*-halogenosuccinimide (0.023 mol) and 1,3-diketonate (0.0055 mol) in chloroform or methanol (150 ml) was refluxed for 15–30 min; the product, isolated as described in the literature,⁴ gave a single spot on t.l.c.

Nitration.—A cooled solution of 1,3-diketonate (0.0016

mol) in acetic anhydride (10 ml) was added dropwise with shaking to ground copper nitrate trihydrate (0.0060 mol) in acetate anhydride (10 ml) and the mixture was kept at 0 °C for 8 h. The nitrated chelates, isolated as described in the literature,¹³ gave single spots on t.l.c.

Diketonates containing either a trifluoromethyl group or two phenyl groups [compounds (4), (5), (9)–(11), (14), and (16)] were similarly nitrated by increasing the reaction time by nearly 12 h (first 4 h at 0 °C and later at room temperature).

Yields and m.p.s of 1,3-diketonates and their substitution products are recorded in the Table.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20.