Acylation of Metal Chelates. Part V.[1] The Influence of Electronic Effects in the β-Diketone Ligand

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The effect of substituents in metal chelates of *para*-substituted dibenzoylmethanes in their reactions with benzoyl chloride have been examined. Electron-releasing substituents have been shown to increase the amount of *C*-benzoylation and electron-attracting substituents to increase the amount of *O*-benzoylation. A mechanistic interpretation of these results is proposed.

THE nature of the metal ion,[2] electronic effects in the acylating agent,[1] and steric effects in the β-diketone ligand [3] have all been shown to influence the ratio of *C*- to *O*-acylated products obtained in the reactions of metal chelates of β-diketones with acyl chlorides. In particular it had been concluded that factors which favour attack by an intermediate carbonium ion result in preferential attack at the oxygen in the ambidentate anion of the β-diketone.[1,2]

Electronic effects in the β-diketone ligand, which would influence the ionic character of the metal–oxygen bond would also be expected to affect the relative proportions of the *C*- and *O*-acylated diketone. The difference in product ratios obtained in the reactions of chelates of (*a*) di-isobutyrylmethane and benzoylisobutyrylmethane, and (*b*) di-n-butyrylmethane and benzoyl-n-butyrylmethane were taken to indicate the importance of electronic effects in the ligand.[2] This was examined more systematically in the present work

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[1] Part IV, H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.* (*C*), 1968, 2298.

[2] H. D. Murdoch and D. C. Nonhebel, *J. Chem. Soc.*, 1962, 2153.

[3] D. C. Nonhebel and J. Smith, *J. Chem. Soc.* (*C*), 1967, 1919.

by studying the benzoylation with benzoyl chloride of metal chelates of several *para*-substituted dibenzoylmethanes. Chelates of *para*-substituted dibenzoylmethanes were chosen to enable the influence of electronic effects to be examined without the interference of steric factors.

TABLE 1

Amounts (%) of *C*-benzoylated product in reactions of metal chelates of substituted dibenzoylmethanes with benzoyl chloride.

Metal	Subst. *p*-NO$_2$	*p*-Br	*p*-Cl	H	*p*-MeO	*p*-Me
Cu	20 *			23 *	22 *	60 *
Ni	2·5 *	26	29	36 *	41	63
Na	21 *			33 *	29 *	58
Ba	35 *			30 *		
Zn	11			9	13	

* Heterogeneous reaction mixtures.

Table 1 gives the amounts of *C*-benzoylated products (triketones) obtained in the reactions of chelates of several substituted dibenzoylmethanes with benzoyl chloride. The reactions of the nickel chelates were studied in greater detail because of their greater solubility in the reaction medium. Heterogeneity has been shown to result in an increased amount of *C*-alkylation in the reactions of alkali-metal phenoxides.[4] The results obtained show that *C*-benzoylation is favoured in reaction of nickel chelates of *para*-substituted dibenzoylmethanes containing electron-attracting substitutents. The results also suggest that heterogeneity can increase the amount of *C*-benzoylation.

β-Diketones containing electron-donating substituents have been shown by n.m.r. spectroscopy to have stronger hydrogen bonds.[5] It may well be that metal chelates of these diketones would be stronger and more covalent if the enolic diketone is considered to be essentially a hydrogen chelate. Diketones forming strong intramolecular hydrogen bonds do not necessarily form strong metal chelates because of the complication of π-electron interaction between the ligand and the transition metal. The correlation was supported by the u.v. spectra of the copper and nickel chelates of *para*-substituted dibenzoylmethanes (Table 2). The u.v. absorption spectra have been correlated with the bonding present; more ionic chelates have spectra similar to the chelating agent whereas the covalent chelates have absorption maxima which are shifted to longer wavelengths.[6,7] That the bathochromic shift is greatest for chelates of diketones containing electron-releasing groups is consistent with their being more covalent.

The transition state, leading to the *O*-benzoylated product (enol benzoate) has been postulated to have a greater degree of ionic character than that leading to the *C*-benzoylated product.[1,2] Factors which increase the polarization of the oxygen–metal bond would thus be expected to give more of the *O*-benzoylated product; this is consistent with our experimental results. These results agree with those of Zagorevskii for reaction of enolate of ethyl acetoacetate with benzoyl chloride. He showed that the trimethylammonium enolate, in which chelation is clearly not possible, gave exclusively the enol benzoate.[8]

In reactions of benzoyl-*p*-nitrobenzoylmethane chelates, some dibenzoyl-*p*-nitrobenzoylmethane was obtained in part as its enol benzoate. Curtin and Russell had previously found that dibenzoyl-*p*-nitrobenzoylmethane and benzoyl-bis-*p*-nitrobenzoylmethane readily formed enol esters presumably because of the greater acidity of these triketones.[9] The chlorocupric chelate of *p*-nitrodibenzoylmethane was obtained in the reaction of copper benzoyl-*p*-nitrobenzoylmethane with benzoyl chloride. This when heated with water disproportionated to copper benzoyl-*p*-nitrobenzoylmethane and cupric chloride. Intermediates of this type have been postulated in reactions of copper chelates with acyl halides [10] *i.e.*, its isolation is undoubtedly due to its insolubility.

TABLE 2

U.v. spectra of *para*-substituted dibenzoylmethanes and their metal chelates *

	$\lambda_{max.}$ (nm) † in CHCl$_3$	
Benzoyl-*p*-nitrobenzoylmethane	262 (4·08)	358 (4·30)
Bis(benzoyl-*p*-nitrobenzoylmethanato)-copper	290	360
Bis(benzoyl-*p*-nitrobenzoylmethanato)-nickel	263	359
Dibenzoylmethane	254 (3·98)	344 (4·39)
Bis(dibenzoylmethanato)copper	261	350
Bis(dibenzoylmethanato)nickel	250	350
Benzoyl-*p*-methoxybenzoylmethane	293 (3·49)	357 (3·82)
Bis(benzoyl-*p*-methoxybenzoylmethanato)-copper	295	361
Bis(benzoyl-*p*-methoxybenzoylmethanato)-nickel	284	361
Benzoyl-*p*-methylbenzoylmethane	245 (3·89)	347 (4·42)
Bis(benzoyl-*p*-methylbenzoylmethanato)-copper	271	352
Bis(benzoyl-*p*-methylbenzoylmethanato) nickel	256	352

* Metal chelates too insoluble for quantitative u.v. data.
† Log ε in parentheses.

Consideration of these results together with those on the influence of substituents in the acylating agent on the ratio of *C*- to *O*-acylation clearly indicates that for the preparation of triacylmethanes containing more than one type of acyl group, best yields should be achieved by employing the metal chelate of the diketone containing the most electron-donating substituents and the acyl halide containing the most electron-withdrawing substituent.

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[5] D. C. Nonhebel, *Tetrahedron*, 1968, **24**, 1869.

[6] H. A. MacKenzie, D. P. Mellor, J. E. Mills, and L. N. Short, *J. Proc. Roy. Soc. New South Wales*, 1944, **78**, 70.

[7] K. Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207.

[8] V. A. Zagorevskii, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 3084.

[9] D. Y. Curtin and C. S. Russell, *J. Amer. Chem. Soc.*, 1951, **73**, 5162.

[10] D. C. Nonhebel, *J. Chem. Soc.*, 1962, 4628.

EXPERIMENTAL

I.r. spectra were determined for Nujol mulls and u.v. spectra for ethanol solutions. Identities were confirmed by mixed m.p. determinations and i.r. comparison. Light petroleum refers to the fraction b.p. 60—80°.

Preparation of β-*Diketones*.—These were prepared by methods previously described in the literature.

Copper(II) *Chelates of* p-*Substituted Dibenzoylmethanes*.—These compounds were obtained by addition of a hot aqueous solution of copper acetate to the diketone in refluxing ethanol. The precipitated chelate was filtered off, and purified by crystallisation (see Table 3).

Nickel Chelates of p-*Substituted Dibenzoylmethanes*.—These compounds were similarly obtained from a solution of nickel acetate. The nickel chelates separated as dihydrates, which were dried by refluxing them in toluene in a Dean–Stark apparatus, before crystallization (see Table 3).

TABLE 3

Copper and nickel chelates of *para*-substituted dibenzoylmethanes

Metal chelate $M(p\text{-}X{\cdot}C_6H_4{\cdot}CO{\cdot}CHBz)_2$					Metal (%)		
M	X	Form	Cryst. from	M.p.	Formulae	Reqd.	Found
Cu	NO_2	Green needles	DMF	290° (decomp.)	$C_{30}H_{20}CuN_2O_8$	10·6	10·6
Cu	MeO	Green needles	PhMe	239—244	$C_{32}H_{26}CuO_6$	11·1	11·2
Cu	Me	Green needles	PhH–Pet ether	241—245	$C_{32}H_{26}CuO_4$	11·85	11·8
Ni	NO_2	Yellow-brown powder	THF	290 (decomp.)	$C_{30}H_{20}N_2NiO_8$	9·6	9·9
Ni	MeO	Green powder	PhMe	256 (decomp.)	$C_{32}H_{26}NiO_6$	10·2	10·4
Ni	Me	Green powder	PhH–Pet ether	288—292	$C_{32}H_{26}NiO_4$	10·55	11·0
Ni	Br	Green powder	PhH	264—266 (decomp.)	$C_{30}H_{20}Br_2NiO_4$	8·6	8·8
Ni	Cl	Green powder	PhH	284—286 (decomp.)	$C_{30}H_{20}Cl_2NiO_4$	9·8	10·1

Benzoyl-p-*nitrobenzoylmethanatosodium*.—This compound was obtained by addition of methanol to a stirred mixture of sodium hydride (50% dispersion in oil) and a toluene solution of the diketone. The *orange-yellow precipitate* was filtered off, washed thoroughly with methanol and toluene, and dried, m.p. >340° (Found: Na, 7·9. $C_{15}H_{10}NNaO_4$ requires Na, 7·9%).

Benzoyl-p-*methoxybenzoylmethanatosodium*.—This compound was prepared by heating a solution of the diketone in refluxing toluene with powdered sodamide. The chelate was filtered off and dissolved in ethyl acetate to remove inorganic material. Evaporation of the ethyl acetate solution gave the chelate as a *yellow amorphous powder*, m.p. >340° (Found: Na, 8·4. $C_{16}H_{12}NaO_3$ requires Na, 8·3%).

Benzoyl-p-*toluoylmethanatosodium*.—This compound was similarly obtained as a *yellow amorphous powder*, m.p. >340° (Found: Na, 8·7; $C_{16}H_{12}NaO_2$ requires Na, 8·8%).

Bio(*benzoyl*-p-*nitrobenzoylmethyl*)*zinc*.—This compound was formed by the careful addition of dilute ammonia to a stirred solution of zinc acetate and the diketone in aqueous alcohol. The chelate was filtered off and crystallised from ethyl acetate–dimethylformamide as *orange needles*, m.p. 255—260° (Found: Zn, 10·7. $C_{30}H_{20}N_2O_8Zn$ requires Zn, 10·85%).

Bis-(*benzoyl*-p-*methoxybenzoylmethanato*)*zinc*.—This compound could only be obtained by reaction of the sodium chelate with zinc chloride in acetone. Addition of water precipitated the chelate, which was filtered off and dried *in vacuo* over phosphorus pentoxide. (The chelate was hydrolysed when heated in the presence of moisture). The dry chelate crystallised from toluene as *yellow prisms*, m.p. 192—194° (Found: Zn, 10·8. $C_{32}H_{26}O_6Zn$ requires Zn, 11·4%).

General Procedure for Reactions of Metal Chelates with Benzoyl Chloride.—Benzoyl chloride (1·1 mol. for the sodium chelates and 2·2 mol. for the other chelates) was added to a refluxing 2% solution or suspension of the metal chelate (1 mol.) in benzene. Reactions were continued until all the chelate had reacted, *i.e.* when a drop of the supernatant liquid no longer gave the characteristic yellow colour of the 2,4,6-trinitrophenoxide ion with a benzene solution of picric acid. The metal chloride was filtered off from the hot solution. Pyridine, containing a few drops of water, was added to the cooled filtrate and the mixture set aside for 2 hr. in order to hydrolyse excess of benzoyl chloride. The mixture was then washed with water, dilute hydrochloric acid, water, sodium hydrogen carbonate solution, and water. The benzene solution was diluted with light petroleum and repeatedly extracted with a 2% sodium hydroxide solution until the alkaline extracts were no longer coloured. The organic layer was dried (Na_2SO_4) and evaporated to dryness. The residue was dissolved in methanol and a little dilute sodium hydroxide solution was added to it; the mixture was then heated on a water-bath for 5 min. Ethyl acetate was added to the mixture and the solution was again repeatedly extracted with a 2% sodium hydroxide solution. This whole procedure was repeated until the alkaline extracts were colourless showing that all the *C*-benzoylated compound had been extracted. The organic layer was dried (Na_2SO_4) and on evaporation yielded the parent diketone. The combined alkaline extracts were acidified with dilute hydrochloric acid and the resultant precipitate was extracted into methylene chloride. The methylene chloride layer was washed with water, sodium hydrogen carbonate solution, and water, and was then dried. Evaporation of the solvent gave the triketones.

Dibenzoyl-p-*toluoylmethane*.—This compound was obtained as colourless needles from methanol, m.p. 204—205° (Found: C, 81·2; H, 5·5. $C_{23}H_{18}O_3$ requires C, 80·7; H, 5·3%).

Dibenzoyl-p-*chlorobenzoylmethane*.—This compound was obtained as colourless needles from benzene–light petroleum, m.p. 190—220° (Found: C, 72·8; H, 4·4. $C_{22}H_{15}ClO_2$ requires C, 72·8; H, 4·4%).

With the chelates of benzoyl-*p*-nitrobenzoylmethane the enol benzoate of benzoyl-*p*-nitrobenzoylmethane separated from the benzene solution; it crystallized from benzene–light petroleum as white needles, m.p. 167—168° (Found: C, 73·45; H, 4·2; N, 2·8. $C_{29}H_{19}NO_6$ requires C, 72·95; H, 4·0; N, 2·9%). The filtrate, after crystallization of this compound, was treated as above except that extraction was effected with sodium carbonate solution since benzoyl-*p*-nitrobenzoylmethane was soluble in sodium hydroxide solution.

In separate experiments the benzene solution, after removal of excess benzoyl chloride, was concentrated and any triketone which had crystallized out was filtered off. The filtrate was diluted with an equal volume of light petroleum and chromatographed on alumina. Elution with this solvent gave the enol benzoate of the diketones, which were identical with those obtained from treatment of the diketone with benzoyl chloride in pyridine.[11]

All the reactions were carried out in duplicate. The yields of triketone in duplicate experiments were within 5% of each other. The method of extraction used was tested and found to be accurate to within ±5% for authentic mixtures of triketone and enol benzoate.

*Reaction Bis(benzoyl-*p*-nitrobenzoylmethanato)copper with Benzoyl Chloride.*—The reaction was carried out as above. Ethyl acetate was then added to the reaction mixture in order to dissolve any precipitated organic product; the mixture was then filtered. A portion of the yellowish residue (0·391 g.) was heated with aqueous methanolic sulphuric acid; the hydrolysis product benzoyl-*p*-nitrobenzoylmethane (0·284 g.) had m.p. and mixed m.p. 162° (Benzoyl-*p*-nitrobenzoylmethylcopper chloride would yield 0·286 g. of benzoyl-*p*-nitrobenzoylmethane). The inorganic residue was shown to contain copper. A second portion of the precipitate was treated with aqueous ammonium hydroxide but failed to give the cuprammonium blue colour. A third portion of the precipitate in water was heated under reflux for 20 hr. after which cupric chloride was detected in the solution.

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[11] J. L. Larkin, M. G. Murray, and D. C. Nonhebel, unpublished results.