414. *Acylation of Metal Chelates. Part I. The Influence of the Metal Ion and a β-Diketone Ligand on the Point of Reaction.*

By H. D. MURDOCH and D. C. NONHEBEL.

Metal chelates of β-diketones with benzoyl chloride give mixtures of the *C*- and *O*-benzoylated products. The reactions of the sodium, barium, copper, nickel, and zinc chelates of di-isobutyrylmethane, di-n-butyrylmethane, benzoylisobutyrylmethane, benzoyl-n-butyrylmethane, and dibenzoylmethane have been examined. In all cases the zinc chelates give less of the *C*-benzoylated products than do the chelates of the other metals. Phenyl and bulky alkyl groups in the terminal positions of the β-diketone ligand respectively decrease and increase the amount of *C*-benzoylation. The mechanism of the reactions is discussed and reasons are given for the observed effects.

REACTION of metal chelates of β-diketones (I) (and β-keto-esters) with acyl halides has long been used [1] to afford triacylmethanes (II); enol esters of the β-diketone (III) are

R·CO·CH_2·COR′ (I) R·CO·CH(COR″)·COR′ (II) R·C(O·COR″):CH·COR′ (III)

frequently formed as by-products, and one such ester was the major product.[2,3] Brändström [4] has reviewed the acylation and alkylation of alkali-metal complexes of β-dicarbonyl compounds for conditions which lead to extensive (or complete) complex-formation between the enol and the metal. There are only a few reports of acylation and alkylation of chelates involving other than alkali metals,[5-7] but these suffice to indicate that the metal ion can exert a significant control on the point of reaction.

Nesmeyanov and Kabachnik [8] have discussed the effect of the metal ion on the products in an empirical way for reactions of ambidentate anions but without considering steric or electronic characteristics of these ions, although both these factors have been shown [9] to be relevant in determining the product ratios in the alkylation of phenoxides and β-naphthyl oxides. Less is known of their importance in reactions of derivatives of β-diketones, but preliminary results again indicate that steric hindrance affects *O*- more than *C*-acylation since chelates of dipivaloylmethane [6] (I; R = R′ = Bu^t) with benzoyl chloride give predominantly the triacylmethane, whereas chelates of acetylacetone [2,3] and dibenzoylmethane [6] give a mixture of both products.

[1] Claisen, *Ber.*, 1893, **26**, 1893; Perkin and Stenhouse, *J.*, 1891, **59**, 996; Curtin and Russell, *J. Amer. Chem. Soc.*, 1951, **73**, 5162; Guthrie and Rabjohn, *J. Org. Chem.*, 1957, **22**, 460.
[2] Nef, *Annalen*, 1893, **277**, 59.
[3] Claisen, *Annalen*, 1893, **277**, 162.
[4] Brändström, *Arkiv Kemi*, 1953, **6**, 155.
[5] (*a*) Zagorevskii, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 3084; (*b*) 1959, **29**, 615; Michael and Carlson, *J. Amer. Chem. Soc.*, 1936, **58**, 353; Fear and Menzies, *J.*, 1926, 937; Zaugg, Dunningan, Michaels, Swett, Wang, Sommers, and DeNet, *J. Org. Chem.*, 1961, **26**, 644.
[6] Hammond and Nonhebel, unpublished work.
[7] Barry, *J.*, 1960, 670.
[8] Nesmeyanov and Kabachnik, *J. Gen. Chem.* (*U.S.S.R.*), 1955, **25**, 37.
[9] Curtin, Crawford, and Wilhelm, *J. Amer. Chem. Soc.*, 1958, **80**, 1391; Kornblum and Lurie, *ibid.*, 1959, **81**, 2705.

Previous work on acylation of β-diketone chelates has, at best, been only semi-quantitative and it was felt necessary to study the reactions quantitatively, the more so as the triacylmethanes are much more easily isolated than the enol esters. In the present study, the products were analysed by ultraviolet spectroscopy (Vierordt's method [10]). It was found that the *O*-compounds (enol esters) were very susceptible to hydrolysis to the parent β-diketone, making it necessary to determine the diketone as well as the *C*- and the *O*-compound. The method was found to be accurate within 5% for known mixtures of diketone and *C*- and *O*-compounds. By very careful experimentation hydrolysis of the *O*-compound could be virtually eliminated, as shown by the absence of diketone. The *C*-compound was stable under the conditions used. It is significant that in duplicate experiments the percentage of *C*-compound remained constant whereas the percentages of the *O*-compound and diketone sometimes varied considerably. In a number of experiments the products were separated chemically, and such results were always in broad agreement with the results from spectroscopic analysis (see Experimental section).

The effect of varying the metal ion on the product ratio was studied for a fairly small but representative range of metals, by using chelates of sodium, barium, copper(II), nickel, and zinc, representating alkali, alkaline-earth, transition, and Group IIB metals with " Lewis-acid " activity. Previous work [6] had indicated that chelates of zinc behaved differently from those of the other metals. Steric and electronic effects in the β-diketone were examined by using chelates of the above metals with di-isobutyrylmethane (I; R = R′ = Pr^i), di-n-butyrylmethane (I; R = R′ = Pr^n), benzoylisobutyrlylmethane (I; R = Ph, R′ = Pr^i), benzoyl-n-butyrylmethane (I; R = Ph, R′ = Pr^n), and dibenzoylmethane (I; R = R′ = Ph). From a comparison of the reactions of the chelates of di-iso- with those of di-n-butyrylmethane, and those of benzoyl-iso- with those of benzoyl-n-butyrylmethane, it is reasonable to attribute changes in product ratio to steric factors. The differences in product ratios from the reactions of (*a*) di-isobutyryl- and benzoylisobutyryl-methane, and (*b*) those of di-n-butyryl- and those of benzyl-n-butyryl-methane indicate the importance of electronic factors in the organic ligand.

Table 1 lists the chelates of these diketones which have been prepared. They were fairly readily soluble in organic solvents, but markedly less so when phenyl groups were present in the β-diketone. Their infrared spectra are very similar, showing chelate-carbonyl absorption in the 1575—1600 $cm.^{-1}$ region.

The ultraviolet absorption spectra of metal chelates have been correlated with the bonding present, ionic chelates having spectra similar to the chelating agent whereas in covalent chelates the absorption maxima are shifted to longer wavelengths.[11] The sodium, barium, and zinc chelates have spectra similar to those of the parent diketones, indicating that they have essentially ionic bonding (see Table 1). The copper and nickel chelates exhibit appreciable bathochromic shifts, indicating a higher degree of covalency. The bathochromic shifts observed for the spectra of the copper and nickel chelates are least for the chelates of dibenzoylmethane and greatest for those of di-isobutyrylmethane and di-n-butyrylmethane, suggesting that the dibenzoylmethane chelates are most ionic and that the di-isobutyrylmethane and di-n-butyrylmethane chelates are most covalent.

The *O*-benzoylated β-diketones were identified by comparison with authentic specimens synthesized by a modification of Claisen's method [12] from the appropriate acid chloride and β-diketone. Their infrared spectra (Table 2) show absorption characteristic of an ester-carbonyl (1750 $cm.^{-1}$) and an αβ-unsaturated carbonyl group (1680—1700 $cm.^{-1}$), and a double bond (1610 $cm.^{-1}$), consistently with their structure.

The structure of *O*-acylated β-diketones can be determined by reduction of the carbonyl

[10] See Gillam and Stern, " Electronic Absorption Spectroscopy," Arnold, London, 1954, p. 186.
[11] McKenzie, Mellor, Mills, and Short, *J. Proc. Roy. Soc., New South Wales*, 1944, **78**, 70; Sone, *J. Amer. Chem. Soc.*, 1953, **75**, 5207.
[12] Claisen, *Ber.*, 1903, **36**, 3674.

TABLE 1.

Metal chelate	Recryst. from †	Physical prop.	M. p.	$\lambda_{max.}$ (mμ) * in EtOH		Metal (%) Reqd.	Formulæ	Found
DIBM	(Di-isobutyrylmethane)		—	220 (7200)	272 (11,700)	—	—	—
Na(DIBM)	Et_2O	White needles	200—201°	218 (3500)	275 (4500)	12·9	$C_9H_{15}NaO_2$	12·55
Ba(DIBM)$_2$	Et_2O–Pet	White rhomboids	194		278 (15,500)	30·6	$C_{18}H_{30}BaO_4$	30·5
Cu(DIBM)$_2$	Pet	Blue rhomboids	124 (lit.,[a] 127—129°)	248 (15,500)	296 (21,500)	17·0	$C_{18}H_{30}CuO_4$	16·7
Ni(DIBM)$_2$	PhMe	Green needles	172 (lit., 155°)[b]		298 (3200)	16·0	$C_{18}H_{30}NiO_4$	16·35
Zn(DIBM)$_2$	PhMe–MeOH	White needles	152		272 (22,400)	17·3	$C_{18}H_{30}O_4Zn$	17·3
BIBM	(Benzoylisobutyrylmethane)		—	243 (6300)	306 (18,500)	—	—	—
Na (BIBM)	Et_2O	White powder	230—232	248 (11,200)	308 (31,800)	10·85	$C_{12}H_{13}NaO_2$	10·8
Ba(BIBM)$_2$	Et_2O–Pet	White powder	242	248 (12,300)	308 (32,600)	26·6	$C_{24}H_{26}BaO_4$	26·6
Cu(BIBM)$_2$	Pet	Green-grey needles	168 (lit.,[c] 168)	256 (19,900)	322 (25,900)	14·4	$C_{24}H_{26}CuO_4$	14·6
Ni(BIBM)$_2$	PhMe–Pet	Green plates	168	242 (20,200)	328 (26,300)	13·4	$C_{24}H_{26}NiO_4$	13·35
Zn(BIBM)$_2$	$CHCl_3$–MeOH	White needles	114	246 (14,000)	316 (33,700)	14·75	$C_{24}H_{26}O_4Zn$	14·5
DBM	(Dibenzoylmethane)		—	251 (9000)	344 (27,000)	—	—	—
Na(DBM)	¶	White powder	350	251 (7600)	340 (21,000)	9·35	$C_{15}H_{11}NaO_2$	9·35
Ba(DBM)$_2$	PhMe	Yellow powder	350	250 (12,500)	343 (36,000)	23·5	$C_{30}H_{22}BaO_4$	23·6
Cu(DBM)$_2$	PhMe	Green needles	296—300 (lit.,[d] 297)	261 (1900)	350 (3800)	12·5	$C_{30}H_{22}CuO_4$	12·8
Ni(DBM)$_2$	PhMe	Brown powder	282	250 (2700)	350 (4500)	11·4	$C_{30}H_{22}NiO_4$	11·4
Zn(DBM)$_2$	C_6H_6	White needles	220	253 (16,500)	340 (52,000)	12·8	$C_{30}H_{22}O_4Zn$	13·1
BNBM	(Benzoyl-n-butyrylmethane)		—	244 (6000)	307 (12,000)	—	—	—
Na(BNBM)	Et_2O	White powder	292—293	246 (2800) ‡	308 (7200)	10·85	$C_{12}H_{13}NaO_2$	10·9
Ba(BNBM)$_2$	Et_2O	White powder	192—194	244 (12,000)	315 (25,600)	26·6	$C_{24}H_{26}BaO_4$	26·5
Cu(BNBM)$_2$	MeOH	Green needles	134 (lit.,[e] 134)	256 (27,000)	324 (33,500)	14·4	$C_{24}H_{26}CuO_4$	14·9
Ni(BNBM)$_2$	$PhMe_2$	Green needles	163—164	240 (19,300)	326 (24,000)	13·4	$C_{24}H_{26}NiO_4$	13·5
Zn(BNBM)$_2$	MeOH	White needles	120	244 (14,700)	316 (31,300)	14·75	$C_{24}H_{26}O_4Zn$	14·6
DNBM	(Di-n-butyrylmethane)		—	—	272 (6200)	—	—	—
Na(DNBM)	Et_2O	White powder	350		272 (9000)	12·9	$C_9H_{15}NaO_2$	13·1
Ba(DNBM)$_2$	Et_2O	White powder	161—163		277 (19,000)	30·6	$C_{18}H_{30}BaO_4$	30·1
Cu(DNBM)$_2$	MeOH	Blue needles	158 (lit.,[f] 158)	248 (15,500)	298 (23,000)			
Ni(DNBM)$_2$	PhMe	Green plates	liq.	260 (6300)	298 (18,500)	16·0	$C_{18}H_{30}NiO_4$	16·2
Zn(DNBM)$_2$	Et_2O	White powder	148		273 (11,000)	17·3	$C_{18}H_{30}O_4Zn$	17·5

* $\varepsilon_{max.}$ in parentheses. † Pet = light petroleum (b. p. 60—80°). ‡ In chloroform. ¶ Eluted with ether.
Refs.: (*a*) Hammond, Borduin, and Gutter, *J. Amer. Chem. Soc.*, 1959, **81**, 4682. (*b*) Cotton and Fackler, *J. Amer. Chem. Soc.*, 1961, **83**, 2818. (*c*) Stylos, *Ber.*, 1887, **20**, 2181. (*d*) Wislicenus, *Annalen*, 1898, **308**, 228. (*e*) Swamer and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 1352. (*f*) Zellars and Levine, *J. Org. Chem.*, 1948, **13**, 160.

TABLE 2.

Infrared spectra of *O*-benzoylated diketones, R·CO·CH:CR′·O·COPh.

R	R′	ν_{max} (cm.$^{-1}$)			R	R′	ν_{max} (cm.$^{-1}$)		
Pr^i	Pr^i	1750	1700	1610	Ph	Pr^n	1750	1700	1610
Ph	Pr^i	1750	1700	1610	Pr^n	Pr^n	1750	1700	1610
Ph	Ph	1745	1670	1610					

to a secondary alcohol group (cf. IV) by sodium borohydride in methanol. Subsequent acid hydrolysis affords a β-keto-alcohol (V) which is spontaneously dehydrated to the αβ-unsaturated ketone (VI). Such treatment of the *O*-benzoyl derivative of benzoylisobutyrylmethane above gave isopropyl styryl ketone (VI; R = Ph, R′ = Pr^i), showing

$$\text{R·CO·CH:CR′·O·COPh} \longrightarrow \underset{\text{(IV)}}{\text{R·CH(OH)·CH:CR′·O·COPh}}$$

$$\underset{\text{(V)}}{\text{R′·CH(OH)·CH}_2\text{·COR′}} \longrightarrow \underset{\text{(VI)}}{\text{R·CH:CH·COR′}}$$

that its structure is 3-benzoyloxy-4-methyl-1-phenylpent-2-en-1-one (III; R = R″ = Ph, R′ = Pr^i); *i.e.*, the benzoyl group is attached to the carbonyl-oxygen atom adjacent to the alkyl group. This structure was confirmed by hydrogenation and subsequent hydrogenolysis of the *O*-benzoyl derivative to isopentyl phenyl ketone.

Among the infrared bands listed in Table 2, the only differences are for the tribenzoyl compound. This is consistent with the benzoyl group's being attached to the carbonyl-oxygen atom adjacent to the alkyl group in each case, a conclusion supported by the

similarity of the ultraviolet spectra of the *O*-benzoyl derivatives of benzoyl-iso- and -n-butyrylmethane. The *O*-acetate of benzoyl-n-butyrylmethane has also been shown to have the acetyl group attached to the oxygen atom adjacent to the propyl group.[13]

The *C*-benzoylated β-diketones were isolated from the reactions of the sodium, copper, or nickel chelates of the diketones with benzoyl chloride. Their infrared spectra were similar to each other, but different from those of the *O*-compounds, in particular in that they had no ester-carbonyl or double-bond absorption. Unlike the *O*-benzoates they formed copper chelates and gave colours with ferric chloride solution. Benzoyldi-isobutyrylmethane on alkaline hydrolysis gave benzylisobutyrylmethane, which could not be obtained from the *O*-benzoyl derivative.

Effect of the Metal Ion.—The metal chelates of the β-diketones were treated with a slight excess of benzoyl chloride in refluxing cyclohexane. The inorganic products

TABLE 3.

Amounts (%) * of *C*-benzoylated product $R{\cdot}CO{\cdot}CH\langle^{COPh}_{COR'}$ in reactions of metal chelates with benzoyl chloride.

Metal	R: Pr^i R′: Pr^i	Ph Pr^i	Ph Ph	Ph Pr^n	Ph^n Pr^n
Na	79·5	68·0	47·0	39·5	42·0
Ba	86·0	42·0	36·0	32·5	35·5
Cu	99·0	47·5	31·5	30·5	34·5
Ni	83·5	43·0	31·0	44·5	35·5
Zn	18·0	28·5	22·0	12·5	0·0

* Mean of two experiments, max. difference 5%.

were the corresponding metal chlorides, except that the copper(II) chelates gave cuprous chloride. The organic product was analysed by ultraviolet spectroscopy. Table 3 shows the percentages of *C*-benzoylated product formed in each reaction. The percentage of *O*-benzoyl compound is obtained by difference and is the sum of the percentages of *O*-benzoyl compound and the β-diketone, the latter resulting from hydrolysis of the former. Clearly differentiated is the low yield of *C*-benzoyl product obtained from all the zinc chelates, as was observed [6] also for dipivaloylmethane. The sodium, barium, copper, and nickel chelates do not, however, give exclusively *C*-benzoyl products, as is implied in the literature. The results also contrast with those of Barry [7] who found higher yields of triacylmethanes from copper than from sodium chelates.

Previous work indicated that the reaction involves co-ordination of the acyl halide with the metal ion.[4,6] This is substantiated by the greater reactivity of chelates of di-n- than of di-isobutyrylmethane (see Table 4) and similarly of chelates of benzoyl-n- than of benzoyliso-butyrylmethane. The reaction is faster the less well shielded the metal ion is by the organic ligand.

TABLE 4.

Times (hr.) for complete reaction of benzoyl chloride with diketones $R{\cdot}CO{\cdot}CH_2{\cdot}COR'$.

Metal	R: Pr^i R′: Pr^i	Ph Pr^i	Ph Ph	Ph Pr^i	Pr^n Pr^n
Na	1	0·7	3 *	0·3	0·1
Ba	0·15	0·25	2 *	0·25	Instantaneous
Cu	18	16	24 *	8	2
Ni	4	0·75	2	0·3	0·1
Zn	4	1	4	0·5	3·5

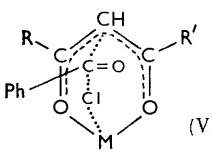
* Reaction mixtures initially partly heterogeneous.

The chelates of sodium, barium, copper, and nickel, where the metal can increase its co-ordination number above that required for chelation, are considered to react through a co-ordination intermediate in which the acyl halide is co-ordinated to the metal ion. This is substantiated by the reactivity of chelates of these metals which was generally

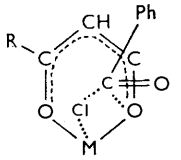
[13] Roll and Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 5469.

in the order: barium > sodium, nickel ≫ copper. The barium chelates would be expected to be the most reactive since the barium ion is considerably larger than the other metal ions. The low reactivity of the copper chelates is explicable since copper has only a weak fifth co-ordination whereas barium, sodium, and nickel can readily increase their co-ordination numbers above that required for chelation. That reaction occurs through a co-ordinated complex is supported by the inability of benzoyl chloride to react with either the copper or the nickel complex with di-isobutyrylmethane in pyridine: copper and nickel chelates of β-diketones are known to form strong solvates with pyridine,[14] thereby preventing co-ordination of the benzoyl chloride.

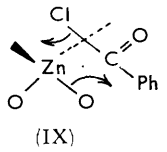
This co-ordination of the acylating agent to the metal increases the polarization of the carbon–chlorine bond of the acylating agent, giving the carbon atom a partial positive charge as suggested by Brändström [4] for the reactions of sodium chelates. This charged carbon atom will then be attracted by the π-electrons in the chelate ring, eventually reacting through the transition states (VII and VIII) to give respectively *C*- and *O*-benzoyl derivatives. This differs from Brändström's mechanism in which *O*-benzoylation occurs solely by reaction of an acyl cation with the enolate ion of the diketone. No explanation can be given at this stage for the variation in the yield of *C*-benzoyl product in the reactions of sodium, barium, copper, and nickel chelates.



(VII)



(VIII)



(IX)

In the reactions of the zinc chelates, in which the maximum co-ordination number of the metal is exactly that required for chelation, initial attack at the metal ion must result in cleavage of the metal–oxygen bond with the formation of a new metal–halogen bond and a benzoyl cation. The benzoyl ion will then attack the enolate anion at the point of highest electronegativity, *i.e.*, at the oxygen atom, to give predominantly the *O*-benzoyl product.[15] Alternatively, the reaction can be considered as a " concerted four-centre process," going through the transition state (IX), in which case *O*-benzoylation would again occur though here no free carbonium ion would be formed. The actual mechanism probably lies somewhere between these two extremes. The high Lewis-acid activity of zinc will enhance the polarization of the carbon–chlorine bond in the acylating agent, thereby facilitating the reaction. In this respect the zinc chelates behave like silver chelates, which are known to undergo predominantly *O*-acylation.[2] It is also significant that tetra-alkylammonium derivatives of β-dicarbonyl compounds, in which co-ordination of the acyl halide to the cation is impossible, give exclusively *O*-benzoyl products.[5a]

Steric Factors in the Ligand.—The sodium, barium, copper, and nickel chelates of di-isobutyrylmethane give much more of the *C*-benzoyl product than do the chelates of di-n-butyrylmethane (see Table 3). Similarly, though the difference is less striking, chelates of benzoylisobutyrylmethane give more of the *C*-benzoyl product than do those of benzoyl-n-butyrylmethane. The transition states (VII and VIII), formed in reactions of chelates in which the metal ion has a co-ordination number greater than that required for chelation, involve interaction of the carbon atom of the acylating agent with respectively the central carbon and the carbonyl-oxygen atom of the chelate ring. Models show that in the first case there is only slight interaction between the phenyl group and the bulky alkyl groups on the diketone, while in the second case there is very appreciable steric interaction between these groups.

[14] Bradley and Robinson, *J.*, 1926, 2356; Martell and Calvin, " Chemistry of the Metal Chelate Compounds," Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1952, p. 216.

[15] See Gould, " Mechanism and Structure in Organic Chemistry," Holt, Reinhart, and Winston Inc., New York, 1960, p. 298.

The same situation holds for the chelates of benzoyliso- and -n-butyrylmethane, since benzoylation has been shown to occur in each case at the carbonyl-oxygen atom adjacent to the alkyl group, and hence this oxygen atom is in a different steric environment in the chelates of these diketones.

Chelates of metals whose co-ordination number is that required for chelation, and which therefore react through an incipient carbonium ion rather than through co-ordination intermediates involving cyclic transition states, show less dependence on the steric requirements of the diketone, as would be expected.

Electronic Factors in the Ligand.—The effect of electronic changes in the diketone can be deduced by comparing the reactions of chelates of di-isobutyrylmethane with those of benzoylisobutyrylmethane, and also of the chelates of di-n-butyrylmethane and benzoyl-n-butyrylmethane. These comparisons are valid in that benzoylation occurs at the carbonyl-oxygen atom adjacent to the alkyl group, so that there should be little difference in steric effects. Replacement of an alkyl by a phenyl group in the terminal position of the β-diketone ligand leads to less *C*-benzoylation (see Table 3). The phenyl group has an electron-attracting effect, tending to make the carbonyl-oxygen atom adjacent to the phenyl group less negative, and hence to increase the residual positive charge on the metal relative to chelates of di-isobutyrylmethane and di-n-butyrylmethane. Therefore, on co-ordination of the benzoyl chloride, the polarization of the carbon–chlorine bond would be increased, giving a greater charge on the carbon atom of the carbonyl group of the acylating agent. This will increase the carbonium-ion character of the reaction and so increase the amount of *O*-benzoylation. That phenyl substituents do increase the positive charge on the metal and hence increase the ionic character of the chelate is borne out by the ultraviolet spectra of the copper and nickel chelates of benzoyl-iso- and -n-butyrylmethane. Further, this is consistent with *O*-benzoylation on the carbonyl-oxygen atom adjacent to the alkyl group, which would be the more negative of the two oxygen atoms.

Replacement of the second isopropyl group by a phenyl group, as in the chelates of dibenzoylmethane, further increases the amount of *O*-benzoylation. These results are less significant in that benzoylation occurs at the oxygen atom adjacent to the phenyl group with consequent alternation of steric factors.

This trend is not observable for the zinc chelates, where the reaction occurs essentially by a carbonium ion mechanism, and in fact rather more *C*-benzoylation is observed with the zinc chelates of benzoyliso- and -n-butyrylmethane and dibenzoylmethane. The chelates of these diketones would be rather more ionic and hence the reaction could be considered as proceeding more through an ambidentate anion, leading to a mixture of *C*- and *O*-benzoyl products, and less by a " concerted four-centre " process.

Experimental

Infrared spectra were determined for Nujol mulls and ultraviolet spectra for ethanol solutions unless otherwise stated. Identities were confirmed by mixed m. p. determinations and infrared comparison.

Preparations of β-Diketones.—Dibenzoylmethane was Light's reagent grade, redistilled, m. p. 78°.

Di-n-butyrylmethane was prepared by the method of Zellars and Levine,[16] b. p. 128—132°/65—70 mm. (lit.,[16] 101—102°/20 mm.).

Di-isobutyrylmethane.—Isopropyl methyl ketone (2 moles) in ether (100 ml.) was added to a stirred suspension of lithium amide, prepared *in situ* from lithium (2·5 g.-atoms), in ether (1 l.) at such a rate that the ether refluxed. Phenyl isobutyrate (1 mole) in ether (150 ml.) was then added in 15 min. to the stirred mixture which was refluxed for a further 4½ hr. The thick sludge was hydrolysed by shaking it with 10% hydrochloric acid. The ether layer

[16] Zellars and Levine, *J. Org. Chem.*, 1948, **13**, 160.

was washed with saturated sodium carbonate solution to remove any phenol, dried, and distilled, giving the diketone, b. p. 81°/17 mm. (lit.,[17] 62—63°/3 mm.) (74%; lit.,[17] 28%).

Benzoylisobutyrylmethane, similarly prepared from isopropyl methyl ketone and phenyl benzoate, had b. p. 186°/45 mm. (lit.,[18] 170°/26 mm.) (83%; lit.,[19] 41%).

Benzoyl-n-butyrylmethane, obtained similarly from methyl propyl ketone and phenyl benzoate, had b. p. 198—200°/65 mm. (lit.,[20] 167—170°/20 mm.) (67%; lit.,[20] 61%).

Preparation of Metal Chelates.—These were prepared in the following ways and purified as shown in Table 1.

Sodium di-isobutyrylmethane was prepared by shaking the diketone with a 30% solution of sodium hydroxide. The chelate separated and was filtered off and washed sparingly with cold water.

Sodium benzoyliso- and *-n-butyrylmethane* were similarly obtained by using a 40% solution of sodium hydroxide.

Sodium dibenzoylmethane separated when an ethanol solution of dibenzoylmethane was added to a 40% solution of sodium hydroxide.

Sodium di-n-butyrylmethane could only be obtained by adding the ketone dropwise to a hot 40% solution of sodium hydroxide.

Barium chelates were prepared by adding the diketone to a hot stirred 10% solution of barium hydroxide. The chelate separated, and was filtered off, washed thoroughly with hot water, and dried before crystallization.

Copper(II) *chelates* were obtained by shaking an ethanol solution of the diketone with a saturated aqueous solution of copper acetate.

Nickel chelates were similarly obtained from a solution of nickel acetate. The nickel chelates separated as dihydrates, which were dried by refluxing them in toluene solution in a Dean and Stark apparatus. The anhydrous chelates were obtained by crystallization from toluene.

Zinc chelates were prepared by the addition of ammonia to a stirred solution of zinc acetate and the diketone in aqueous ethanol. Care was needed not to add the ammonia too rapidly (thereby precipitating zinc hydroxide). The chelates were filtered off, washed with ammonia and water, and dried.

Preparation of O-*Benzoyl Derivatives of* β-*Diketones* (cf. Claisen [12]).—Di-isobutyrylmethane (0·025 mole) and benzoyl chloride (0·0375 mole) in dry pyridine (15 ml.) were left at room temperature for 24 hr. A small amount of water was added and the mixture left for a further 24 hr. to hydrolyse the excess of benzoyl chloride. Ether was added and the ethereal layer was separated, washed with water, dilute hydrochloric acid, saturated sodium hydrogen carbonate solution, and water, dried, and evaporated. The gum obtained was dissolved in light petroleum and chromatographed on alumina. The initial fractions eluted with light petroleum were re-chromatographed on alumina. The initial fractions from the second chromatogram gave no colour with ferric chloride solution, showing the absence of diketone. The light petroleum was distilled off, giving *5-benzoyloxy-2,6-dimethylhept-4-en-3-one* as a colourless oil (Found: C, 74·3; H, 8·0. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%), $\lambda_{max.}$ (in cyclohexane) 232 mμ (ε 18,300).

6-Benzyloxynon-5-en-4-one was similarly obtained (Found: C, 73·4; H, 7·9%), $\lambda_{max.}$ (in cyclohexane) 234 mμ (ε 21,000).

3-Benzoyloxy-4-methyl-1-phenylpent-2-en-1-one, prepared similarly, crystallized from ether as prisms, m. p. 59—60° (Found: C, 77·4; H, 6·4. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%), $\lambda_{max.}$ (in cyclohexane) 228 (ε 16,000) and 278 mμ (ε 15,800).

3-Benzoyloxy-1-phenylhex-2-en-1-one, similarly prepared, crystallized from ether as light yellow needles, m. p. 49—50° (Found: C, 77·7; H, 6·0. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%), $\lambda_{max.}$ (in cyclohexane) 228 (ε 18,000) and 278 mμ (ε 17,000).

3-Benzoyloxy-1,3-diphenylprop-2-en-1-one was prepared by setting dibenzoylmethane (0·025 mole) and benzoyl chloride (0·0375 mole) in pyridine (5 ml.) aside for 18 hr. Water and ether were added, a yellow solid being precipitated. This was filtered off, washed with ether and water, dried, and crystallized from benzene as yellow needles, m. p. 108—109 (lit.,[12] 108—109°).

[17] Smith and King, *J. Amer. Chem. Soc.*, 1943, **65**, 441.
[18] Stylos, *Ber.*, 1887, **20**, 2181.
[19] Baumgarten and Hauser, quoted in *Org. Reactions*, 1954, **8**, 142.
[20] Swamer and Hauser, *J. Amer. Chem. Soc.*, 1950, **72**, 1352.

Determination of the Constitution of 3-*Benzoyloxy*-4-*methyl*-1-*phenylpent*-2-*en*-1-*one*.—(*a*) Sodium borohydride (0·57 g.) in methanol (3·25 ml.) was added dropwise to a stirred solution of the benzoate (1·14 g.) in methanol (6·5 ml.), and the mixture was left for 2 hr., then acidified (Congo Red) with dilute hydrochloric acid, heated on a steam-bath for 10 min., cooled, and made alkaline by addition of sodium hydroxide solution. The aqueous phase was extracted with ether; the ethereal layer was separated, washed with water, dried, and evaporated to a gum. This was examined by vapour-phase chromatography and shown to be isopropyl styryl ketone by comparison with an authentic sample prepared by the condensation of benzaldehyde with isopropyl methyl ketone.[21] The infrared and ultraviolet spectra of the gum were also identical with the spectra of the authentic material.

(*b*) The benzoate (0·61 g.) in methanol (100 ml.) was hydrogenated at room temperature and pressure over a platinum catalyst. 250 ml. (2 mol.) of hydrogen were absorbed in 4 hr. The solution was filtered and evaporated to an oil, which was identified as isopentyl phenyl ketone by conversion into its semicarbazone, m. p. 150—152° (lit.,[22] 150—151°).

Reactions of Metal Chelates with Benzoyl Chloride.—(a) *Quantitative estimation of reaction products*. Benzoyl chloride (1 mol. for the sodium chelates and 2 mol. for the other chelates) was added to a 2% solution of the metal chelate in refluxing cyclohexane. The mixtures were refluxed until a drop of the supernatant liquid no longer gave the characteristic yellow colour of the 2,4,6-trinitrophenoxide ion with a cyclohexane solution of picric acid (unchanged chelate gives a yellow colour with picric acid). The metal chloride was filtered off and the solution concentrated. Pyridine, containing a small amount of water, was added and the mixture set aside for 16—24 hr. to hydrolyse the excess benzoyl chloride. Cyclohexane was then added (chloroform for the chelates of dibenzoylmethane), and the cyclohexane layer washed successively with water, dilute hydrochloric acid, saturated sodium hydrogen carbonate solution, and water. After drying, the solution was analysed by ultraviolet absorption spectroscopy; standard solutions of diketone and the *C*- and *O*-benzoyl products were used for calibration. All reactions were carried out in duplicate.

(b) *Isolation of reaction products*. (i) Chelates of di-isobutyrylmethane. The copper complex (0·61 g.) and benzoyl chloride (0·483 g.) in cyclohexane (30 ml.) were refluxed for 15 hr., then treated as above. Concentration of the final solution, after ultraviolet analysis, gave *benzoyldi-isobutyrylmethane* (0·82 g., 90%) as prisms (from light petroleum), m. p. 86° (Found: C, 73·4; H, 7·9. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%), $\nu_{max.}$ 1680 (C=O) and 1590 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ 252 (ε 18,500) and 282 mμ (ε 14,000). With saturated copper acetate solution this gave the *copper complex* as purple plates (from ether), m. p. 208—209° (Found: C, 66·2; H, 6·3. $C_{32}H_{38}CuO_6$ requires C, 66·0; H, 6·5%), $\nu_{max.}$ 1650 (C=O), and 1590 and 1560 cm.$^{-1}$ (chelate C=O), $\lambda_{max.}$ 250 (ε 26,600) and 300 mμ (ε 18,750).

Nickel di-isobutyrylmethane similarly gave an 80% yield of benzoyldi-isobutyrylmethane. The mother-liquors from this, on treatment with saturated copper acetate solution, gave copper di-isobutyrylmethane (8%), m. p. and mixed m. p. 123—124°.

Sodium and barium di-isobutyrylmethane on similar treatment both gave 80% yields of benzoyldi-isobutyrylmethane and a trace of diketone, identified as its copper chelate.

(ii) Chelates of benzoylisobutyrylmethane. Copper benzoylisobutyrylmethane (2·05 g.) in cyclohexane (100 ml.) was refluxed for 16 hr. with benzoyl chloride (1·08 ml.). The final solution, obtained as before, was concentrated, giving a yellow gum from which *dibenzoylisobutyrylmethane* (1 g., 40%) was obtained, after treatment with ether and light petroleum, with m. p. 136° (Found: C, 77·6; H, 6·4. $C_{19}H_{18}O_3$ requires C, 77·5; H, 6·2%), $\nu_{max.}$ 1718, 1680 (C=O), and 1590 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ 250 (ε 21,000) and 296 mμ (ε 8500).

The mother-liquors were chromatographed on alumina; light petroleum eluted a trace of 3-benzoyloxy-4-methyl-1-phenylpent-2-en-1-one, m. p. and mixed m. p. 59—60°, and ether eluted traces of benzoylisobutyrylmethane, identified as its copper chelate, m. p. and mixed m. p. 168°.

Sodium benzoylisobutyrylmethane similarly gave dibenzoylisobutyrylmethane (40%) and a trace of 3-benzoyloxy-4-methyl-1-phenylpent-2-en-1-one.

Barium benzoylisobutyrylmethane also gave dibenzylisobutyrylmethane (35%).

(iii) Chelates of dibenzoylmethane. Sodium dibenzoylmethane (0·83 g.) was suspended in cyclohexane (42 ml.) and refluxed for 2 hr. with benzoyl chloride (0·39 ml.). The mixture

[21] Lapworth, *J.*, 1902, **81**, 1489.
[22] Paterno and Traetta-Mosca, *Gazzetta*, 1909, **39**, I, 450.

was treated as above, and, on concentration of the final solution, tribenzoylmethane (0·45 g., 43%), m. p. 245° (lit.,[23] 241—244°), was obtained. Dibenzoylmethane was isolated from the mother-liquors as its copper chelate (0·2 g., 22%), m. p. and mixed m. p. 297°.

Nickel dibenzoylmethane on similar treatment gave tribenzoylmethane (35%), a trace of 3-benzoyloxy-1,3-diphenylprop-2-en-1-one, m. p. and mixed m. p. 105—108°, and dibenzoylmethane, identified as its copper chelate (20%), m. p. and mixed m. p. 297°.

(iv) Chelates of benzoyl-n-butyrylmethane. Sodium benzoyl-n-butyrylmethane (1·88 g.) in cyclohexane (100 ml.) was refluxed for 20 min. with benzoyl chloride (1·04 ml.), and the mixture was worked up in the usual way. Dibenzoyl-n-butyrylmethane (0·76 g., 29%), m. p. 110° (lit.,[24] 110°), was isolated on concentration of the final solution. Chromatography of the mother-liquors on alumina gave 3-benzoyloxy-1-phenylhex-2-en-1-one (0·45 g., 17%), m. p. and mixed m. p. 48—50°, eluted with light petroleum. Later fractions, eluted with ether, gave traces of benzoyl-n-butyrylmethane, identified as its copper chelate, m. p. and mixed m. p. 132—134°.

Copper benzoyl-n-butyrylmethane on similar treatment gave dibenzoyl-n-butyrylmethane (22%). Copper benzoyl-n-butyrylmethane (17%) was isolated by treatment of the mother-liquors with saturated copper acetate solution.

(v) Chelates of di-n-butyrylmethane. Copper di-n-butyrylmethane (6·3 g.) in cyclohexane (150 ml.) was refluxed for 3 hr. with benzoyl chloride (4·75 ml.). The cuprous chloride was filtered off and the filtrate treated in the usual manner. The gum obtained was chromatographed on alumina. The initial fractions, eluted with light petroleum, were rechromatographed on alumina, and the initial fractions from this second chromatogram gave 6-benzoylnon-5-en-4-one (0·49 g., 5·5%) as a colourless oil, identified by infrared comparison.

Elution of the first chromatogram with benzene gave a colourless oil. This, on treatment with aqueous alcoholic copper acetate, gave *copper benzoyldi-n-butyrylmethane* (1·2 g.), m. p. 172°, crystallizing from methanol as blue needles (Found: C, 65·9; H, 6·5. $C_{32}H_{38}CuO_6$ requires C, 66·0; H, 6·5%), $\nu_{max.}$ 1650 cm.$^{-1}$ (C=O) and $\lambda_{max.}$ 250 (ε 31,000) and 300 mμ (ε 24,000).

The copper chelate was dissolved in ether and shaken with dilute hydrochloric acid. The ether layer was washed with water, dried, and evaporated to dryness, giving *benzoyldi-n-butyrylmethane* (0·8 g., 9%) as a colourless oil (Found: C, 74·4; H, 7·7. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%), $\nu_{max.}$ 1680 (C=O) and 1595 cm.$^{-1}$ (aromatic), $\lambda_{max.}$ (in cyclohexane) 248 (ε 47,000) and 280 mμ (ε 34,000).

Reactions of Chelates of Di-isobutyrylmethane with Benzoyl Chloride in Presence of Pyridine.—(i) Copper di-isobutyrylmethane (2·1 g., 0·0056 mole) was refluxed for 50 hr. with benzoyl chloride (1·3 ml., 0·04 mole) in cyclohexane (100 ml.) containing pyridine (0·45 g., 0·006 mole). The mixture remained blue. The cyclohexane solution was washed very thoroughly with water to remove any pyridine, and with sodium hydrogen carbonate solution, and dried. On evaporation, blue crystals of copper di-isobutyrylmethane, m. p. and mixed m. p. 123—124°, were obtained.

(ii) Nickel di-isobutyrylmethane (2 g., 0·0055 mole) was refluxed for 48 hr. with benzoyl chloride (4 ml., 0·035 mole) in cyclohexane (100 ml.) containing pyridine (0·85 g., 0·012 mole). There was no indication of reaction and, on treatment as above, nickel di-isobutyrylmethane, m. p. and mixed m. p. 170—172°, was isolated.

Hydrolysis of Benzoyldi-isobutyrylmethane.—The triketone was refluxed for 45 min. in aqueous-methanolic potassium hydroxide. An excess of water was added, and the solution extracted with ether. The ether layer was dried, and after removal of the ether, benzoylisobutyrylmethane, identified as its copper chelate, m. p. and mixed m. p. 168°, was obtained.

Analysis of Metal Chelates.—The sodium chelates were decomposed with standard hydrochloric acid, and the excess of acid was determined by back-titration with sodium hydroxide solution.

The barium chelates were decomposed by warm 20% hydrochloric acid. The β-diketone generated was removed by ether-extraction and the barium determined as barium sulphate.

Analysis for copper was made by decomposition of the chelates with 20% sulphuric acid, followed by a standard potassium iodide–sodium thiosulphate titration to a starch indicator.

The nickel chelates were decomposed with 20% hydrochloric acid, the solution was extracted with ether, and the nickel determined as nickel dimethylglyoxime.

[23] Baeyer and Perkin, *Ber.*, 1883, **16**, 2133.
[24] Freer and Lachman, *Amer. Chem. J.*, 1897, **19**, 879.

The zinc chelates were decomposed with 20% hydrochloric acid, the solution was extracted with ether, neutralized with sodium hydroxide, and buffered with an aqueous ammonia–ammonium chloride buffer, and the zinc was estimated by titration with disodium dihydrogen ethylenediaminetetra-acetate to Erio T as indicator.

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CHEMISTRY DEPARTMENT, ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1. [*Received, September* 18*th*, 1961.]