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Metal-containing Polymers

I. The Preparation of Bis(1,2-dioximes)

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SUMMARY:

A series of diketones of formula $(p\text{-RCH}_2\text{COC}_6\text{H}_4)_2\text{X}$ (where R = H, Me, Et; X = O or $(\text{CH}_2)_n$ where n = 0, 1, 2, 3) has been prepared. The propionyl compounds (R = Et) have been converted by nitrosation to the bis(α-keto oximes) and thence, by oximation, into the corresponding bis(1,2-dioximes).

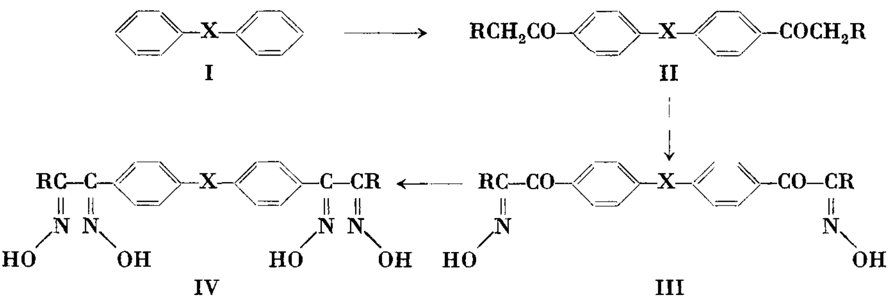
ZUSAMMENFASSUNG:

Eine Serie von Diketonen der Formel $(p\text{-RCH}_2\text{COC}_6\text{H}_4)_2\text{X}$ (worin R = H, CH_3, C_2H_5; X = O oder $(\text{CH}_2)_n$, worin n = 0, 1, 2, 3) wurde hergestellt. Die Propionylverbindungen ($R = C_2H_5$) wurden durch Nitrosierung in die Bis(α-ketoxime) überführt und danach durch Oximierung in die entsprechenden Bis(1,2-dioxime) verwandelt.

Introduction and Discussion

Currently, much interest is being displayed in polymeric materials which exhibit high thermal stability. This series of papers will report our attempts to contribute to this problem by the preparation of polymers in which metal atoms form an integral part of the macromolecule. The present paper outlines some preliminary experiments concerned with the production of a series of ligands containing 1,2-dioxime groups which were expected to yield polymeric chelates when treated with metal salts.

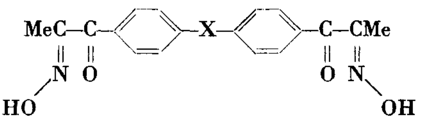
The synthetic route to the bis(1,2-dioximes) involved the bisacylation of the parent compounds (I; X = O or $(\text{CH}_2)_n$; n = 0,1,2,3); the nitrosation of the diketones (II) and finally, the conversion of the α-keto oximes (III) to the required bis(1,2-dioximes) (IV).



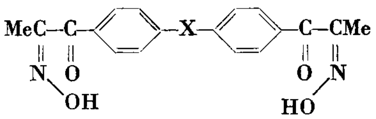
The acylation of the aromatic derivatives (I) was effected by a modification of the Friedel-Crafts reaction between acid chlorides and the parent compounds as described in the experimental section; it was observed that the yields of the bisketones (II) increased with increasing chain length in the chloride employed, as shown in Table I.

It is known that the nitrosation of acetophenone proceeds with difficulty whereas propiophenone gives a high yield of the ketoxime and that, in general, the methylene group of an alkyl methyl ketone is attacked in preference to the methyl group[1,2]. In agreement with this, difficulty was experienced in the nitrosation of the diacetyl compounds (II; R = H), whereas the dipropionyl compounds (II; R = Me) were smoothly converted to the α-keto oximes by use of a chloroform solution of *n*-butyl nitrite and hydrogen chloride. The dibutyryl compounds (II; R = Et) gave difficulties which may possibly be attributed to insufficient selectivity of the nitrosating agent for the α-methylene groups. In view of this, further work was based on the α-keto oximes derived from the dipropionyl derivatives; the properties of these α-keto oximes are given in Table II.

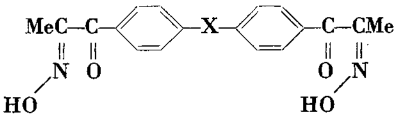
The geometric isomerism about the >C=N– bonds would lead one to anticipate the formation of three isomeric bis(α-keto oximes) in the nitrosation step; the *trans-trans* (IIIa), the *cis-cis* (IIIb) and the *cis-trans* (IIIc) forms, of which only the first is of use in the formation of fully chelated bisdioximes.



IIIa



IIIb



IIIc

Fortunately however, the *trans* form of an α-keto oxime is usually the highest melting and the least soluble isomer; we therefore believe that the present bis(α-keto oximes) which were purified by multiple precipitation and recrystallisation, are essentially the pure *trans-trans* forms.

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[1] O. Touster, in R. Adams (Ed.), Org. Reactions, Vol. VII, J. Wiley and Sons, Inc., New York, 1953, p. 330.

[2] D.T. Manning and H. A. Stansbury, J. Amer. chem. Soc. **81** (1959) 4885.

In the conversion of the bis(α-keto oximes) to the bis(1,2-dioximes) (IV) again a multiplicity of steric configurations exists of which only one, the *anti-anti* form (as shown in IV) can form polymeric chelates by reaction of both 1,2-dioxime ligands with metal ions. Once again, however, the *anti-anti* isomers were expected to be the least soluble and highest melting forms and hence capable of ready isolation. Furthermore, under the acid conditions employed in the reaction with hydroxylamine hydrochloride, *syn* forms should undergo stereomutation to the more stable *anti* forms[3].

Initial attempts to convert the bis(α-keto oximes) to the bis(1,2-dioximes) by the action of buffered hydroxylamine hydrochloride solution gave only unchanged starting materials even on prolonged boiling. The reaction was readily accomplished in aqueous methanol at pH 2.6. PONZIO and TORRES[4] have similarly found that the conversion of certain α-keto oximes to 1,2-dioximes is best effected in acid solution. The bis(1,2-dioximes) were obtained as high-melting compounds very slightly soluble in organic solvents and were purified by Soxhlet extraction of the impurities with boiling methanol (for propeıties see Table III). From their high melting points and insolubility and the formation from them of polymeric metal chelates (see following paper), the bis(1,2-dioximes) are considered to be essentially pure *anti-anti* forms.

The ultra-violet absorption spectra of the diketones (II) and bis(α-keto oximes) were examined in methanol solution (approximately 10^{-5} M) in the range 200—300 mμ. The positions of the maxima and correponding log ε values are given in Table IV and, as expected, the value of λ_{max} decreases in the order X absent, X = O, CH_2, $(CH_2)_2$, and $(CH_2)_3$.

Experimental

Preparation of bis(acyl) derivatives (Table I)

The majority of these compounds has previously been prepared under a variety of conditions but in our hands the following general procedure was found to be the most convenient.

The hydrocarbon (or diphenyl ether) (1 mole) was dissolved in the acid chloride (2.5 moles) with the addition of sufficient carbon disulfide to effect solution when necessary. This solution was added dropwise to a suspension of powdered anhydrous aluminum chloride (2.5 moles) in carbon disulfide, with ice-cooling. The mixture was stirred and boiled

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[3] G. PONZIO, Gazz. chim. ital. **60** (1930) 49.

[4] G. PONZIO and M. TORRES, Gazz. chim. ital. **59** (1929) 718.

under reflux until the evolution of hydrogen chloride had ceased (about 3 hrs.). After removal of the solvent by distillation, and decomposition of the residue by addition to ice-hydrochloric acid, the product was extracted with chloroform, the organic solution washed (water) and dried. After removal of the solvent, the residue was recrystallized.

Table I. Properties of bisacyl derivatives of general formula $(p\text{—}RCOC_6H_4)_2X$

X	R	M.p. (°C.)	Highest reported m.p. (°C.)	Yield (%)	Solvent for recrystallisation
absent	Me	195—196	192 [a]	35	benzene
	Et	171—172	169 [a]	78	benzene
	Pr^n	178—179	174 [a]	—	benzene
CH_2	Me	94—95	93 [b]	12	ethanol
	Et	62—63	62—63 [c]	50	isopropanol
	Pr^n	87—88 [d]	—	69	isopropanol
$(CH_2)_2$	Me	167—168	169 [e]	36	acetone
	Et	110—111	108 [f]	56	benzene
	Pr^n	99—101	93 [f]	61	benzene
$(CH_2)_3$	Me	86—87	85—86.5 [g]	35	cyclohexane-ethanol
	Et	42—43	42—44 [g]	50	cyclohexane
	Pr^n	37—38 [h]	—	—	aqueous ethanol
O	Me	102—103	100—101 [i]	50	ethanol
	Et	97—98	100 [j]	64	ethanol
	Pr^n	104—105	102—103 [k]	78	ethanol

[a] L. M. Long and H. R. Henze, J. Amer. chem. Soc. **63** (1941) 1939. — [b] M. H. Duval, C. R. hebd. Séances Acad. Sci. **146** (1908) 342. — [c] J. Abell and D. J. Cram, J. Amer. chem. Soc. **76** (1954) 4411. — [d] Anal., Calcd. for $C_{21}H_{24}O_2$: C 81.75, H 7.84, O 10.37. Found: C 81.81, H 7.97, O 10.34. — [e] S. Yura and R. Oda, J. Soc. chem. Ind. Japan **44** (1941) Suppl. binding 468. — [f] Ng. Ph. Buu-Höi and R. Royer, Bull. Soc. chim. France **1947**, 820. — [g] D. J. Cram and H. Steinberg, J. Amer. chem. Soc. **73** (1951) 5701. — [h] Anal., Calcd. for $C_{23}H_{28}O_2$: C 82.10, H 8.39, O 9.51 Found: C 82.33, H 8.39, O 9.38. — [i] W. Dilthey, E. Bach, H. Grütering, and E. Hausdörfer, J. prakt. Chem. **117** (1927) 350. — [j] Ng. Ph. Buu-Höi, Ng. D. Xuong, and D. Lavit, J. chem. Soc. [London] **1954**, 1038. — [k] A. R. Brown and F. C. Copp, J. chem. Soc. [London] **1954**, 876.

Preparation of bis(α-keto oximes) (Table II)

The following description of the preparation of α,β-bis[*p*-(2-oximinopropionyl)phenyl]-ethane (IIIc, X = $(CH_2)_2$) is a representative example of the general nitrosation procedure followed. Freshly distilled *n*-butyl nitrite (7.0 g., 1 mole) was added dropwise to a stirred solution of 4,4′-dipropionyldibenzyl (10 g., 0.5 mole) in chloroform (125 ml.), a stream of hydrogen chloride (4 bubbles per second) being passed through the solution. Precipitation of the product as a cream-coloured solid occurred; when complete, the product was collected, washed (chloroform) and dried; yield, 13.0 g., quantitative; m.p. 181—183 °C. Four recrystallisations from ethanol raised the m.p. to 187—189 °C.

Attempted nitrosation of the diacetyl and dibutyryl derivatives under similar conditions and with other catalysts[2)] yielded either the unchanged diacyl compounds after chromatographic purification of the gummy products, or gums which failed to yield any crystalline material.

Table II. Properties of bis (α-keto oximes) of general formula $[p\text{—}MeC(=NOH)COC_6H_4]_2X$

X	M.p. (with decomp.) (°C.)	Yield (%)	Solvent for crystallisation	Formula	Analyses a) Calcd. b) Found				
						% C	% H	% N	% O
absent	238	92	ethanol	$C_{18}H_{16}N_2O_4$	a)	66.68	4.97	8.64	19.73
					b)	66.63	5.06	8.51	19.78
CH_2	180—181	41	aq. ethanol	$C_{19}H_{18}N_2O_4$	a)	67.45	5.36	8.28	18.92
					b)	67.50	5.63	8.62	19.15
$(CH_2)_2$	205—206	100	aq. ethanol	$C_{20}H_{20}N_2O_4$	a)	68.17	5.72	7.95	18.17
					b)	68.52	5.81	7.47	18.36
$(CH_2)_3$	178—179	23	aq. methanol	$C_{21}H_{22}N_2O_4$	a)	68.82	6.05	7.65	17.47
					b)	68.54	6.05	7.58	17.63
O	217—218	56	aq. methanol	$C_{18}H_{16}N_2O_5$	a)	63.53	4.74	8.23	23.51
					b)	64.19	4.85	7.60	24.03

Table III. Properties of bis (1,2-dioximes) of general formula
$[p\text{—}MeC(=NOH)C(=NOH)\ C_6H_4]_2X$

X	M.p. (with decomp.) (°C.)	Yield (%)	Formula	Analyses a) Calcd. b) Found				
					% C	% H	% N	% O
absent	360	38	$C_{18}H_{18}N_4O_4$	a)	61.01	5.12	15.81	18.06
				b)	61.89	5.23	14.67	17.83
CH_2	278	55	$C_{19}H_{20}N_4O_4$	a)	61.94	5.47	15.22	17.38
				b)	62.38	5.48	14.74	17.52
$(CH_2)_2$	300	65	$C_{20}H_{22}N_4O_4$	a)	62.81	5.80	14.65	16.73
				b)	63.34	5.83	14.12	16.59
$(CH_2)_3$	274—276	48	$C_{21}H_{24}N_4O_4$	a)	63.62	6.10	14.14	16.14
				b)	64.18	6.09	13.42	16.41
O	279—280	38	$C_{18}H_{18}N_4O_5$	a)	58.37	4.90	15.13	21.60
				b)	58.50	5.08	14.93	21.84

Preparation of bis(1,2-dioximes) (Table III)

The following description of the preparation of α,β-bis[*p*-(1,2-dioximinopropyl)phenyl]-ethane (IV; R = Me, X = $(CH_2)_2$) is typical of the oximation procedure employed.

Table IV. Ultra-violet absorption characteristics for compounds of general formula $(p-RCOC_6H_4)_2X$

R	X											
	Absent		O				CH_2		$(CH_2)_2$		$(CH_2)_3$	
	λmax (mμ)	log ε	$λ^1$max (mμ)	log ε	$λ^2$max (mμ)	log ε	λmax (mμ)	log ε	λmax (mμ)	log ε	λmax (mμ)	log ε
Me	294.5	4.61	225.5	3.78	277.5	4.24	259	4.56	257	4.51	255	4.53
Et	294	4.86	225	4.27	275	4.64	258	4.53	257.5	4.60	255	4.53
Pr^n	292	5.58	228.5	4.36	275.5	4.66	259	4.73	256	4.63	254	4.38
MeC(=NOH)	305.5	4.63	230.5	4.23	291	4.37	271	4.40	267.5	3.71	267	4.41

A mixture of hydroxylamine hydrochloride (0.83 g., 1 mole) dissolved in the minimum volume of water, and α,β-bis[(2-oximinopropionyl)-phenyl]ethane (IIIc; X = $(CH_2)_2$) (2 g., 0.5 mole) in *methanol (pH of mixture, 2.6)*, was boiled under reflux until no further product separated (about 12 hrs.). The colourless solid was collected, washed (methanol) and dried; yield, 1.3 g., 58%; m.p. 300 °C. with decomposition. Extraction of impurities with boiling methanol yielded the analytically pure product, m.p. 300 °C. with decomposition.

During the preparation of certain of the bis(1,2-dioximes), no precipitation of the product occurred during the period of boiling. On these occasions, the solvent was evaporated under reduced pressure until the solution became turbid. Continued boiling under reflux then caused the product to separate.

p,p′-Bis(2-O-methyloximinopropionyl)-diphenyl (The di-O-methyl ether of III; R = Me, X absent)

Dimethyl sulphate (1.64 g., 2.1 moles) was slowly added with stirring to *p,p′*-bis(2-oximinopropionyl)diphenyl (2.0 g., 1 mole) in a solution of sodium hydroxide (0.52 g., 2.1 moles) in water (20 ml.). After stirring for 15 min. the product was collected, washed (water), dried and recrystallized from aqueous ethanol m.p. 168–170 °C.

Anal. Calcd. for $C_{20}H_{20}N_2O_4$:
C 68.17 H 5.72 N 7.95 O 18.17

Found:
C 68.69 H 5.70 N 7.46 O 18.08

α,β-Bis[p-(2-O-methyloximinopropionyl)phenyl]ethane (The di-O-methyl ether of III; R = Me, X = (CH$_2$)$_2$)

This product was prepared in the manner described above, m.p. 111—112 °C. after recrystallisation from methanol.

Anal.					
	Calcd. for $C_{22}H_{24}N_2O_4$:	C 69.51	H 6.31	N 6.36	O 16.82
	Found:	C 70.23	H 6.46	N 6.59	O 16.80

Microanalyses were carried out by Drs. E. and F. PASCHER, Bonn. We thank Mr. G. CREEDY for assistance with the experimental work, and the Directors of CIBA (A.R.L.) Ltd. for permission to publish this paper.