Copper-carnosine and copper-anserine were prepared by the procedure of Deutsch, *et al.*[13]

N-acetylcarnosine was prepared by the previously described procedure for the preparation of *N*-acetylamino acids.[14] L-Carnosine was refluxed at 100° for 2 hr. with 2 equivalents of acetic anhydride and 10 equivalents of glacial acetic acid. After repeatedly adding water and evaporating to dryness *in vacuo,* the product was crystallized from absolute methanol. It was recrystallized to a constant melting point of 209–210° (uncor.) and gave a negative ninhydrin reaction.

Anal. Calcd. for $C_{11}H_{16}N_4O_4$: C, 49.20; H, 5.97. Found: C, 48.70; H, 5.86.

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[13] A. Deutsch, M. G. Eggleton, and P. Eggleton, *Biochem. J.*, 32, 203 (1938).

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Thermal Properties of a Series of Copper Bis(β-diketone) Polymers as a Function of the Number of Connecting Methylene Groups

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Preparation of coordination polymers of bis-(β-diketones) have been reported by several investigators.[1,2] In all cases the copper chelate is obtained as a powder. By increasing the length of the methylene chain joining coordination sites, the properties of the polymers might be expected to approach the properties of long chain hydrocarbons. Such changes in properties would result from a decrease in the average bulk of the polymer per unit length and a decrease in the interaction between coordination sites per unit length of polymer. The effect on the thermal properties of this increase in the number of methylene groups in the bridge between complex sites is reported here. The possibility of obtaining a melt before decomposition occurs was investigated by differential thermal analysis, and visual observation of the copper(II) chelates of bis(β-diketones) of the type $C_6H_5COCH_2CO(CH_2)_nCOCH_2COC_6H_5$.

The change in thermal stability with increasing number of methylene groups between coordination sites for the copper chelates of a series of bis-(β-diketones) is shown in Table I.

TABLE I

THERMAL DECOMPOSITION TEMPERATURES OF COPPER CHELATES OF BIS(β-DIKETONES) OF THE TYPE $C_6H_5COCH_2CO(CH_2)_nCOCH_2COC_6H_5$

n	Decomposition by D.T.A.	Visual Decomposition
2	—	300 (darkens)
3	273	273 (darkens) 287 (melts)
4	272	279 (darkens) (does not melt)
5	258	272 (darkens) 278 (melts)
7	240	262 (melts and darkens)
8	230	231 (melts and darkens)

The temperature of the initial break in the base line of the differential plot was taken as the temperature at which the decomposition rate of the sample becomes appreciable. Although the peak maximum is a function of the heating rate, initial breaks are constant within the range investigated. Maxima would be expected to result from a complex relationship between the diffusion of heat into the sample and the heat of decomposition. A large dependence on heating rate would then be expected. Initial breaks in the differential plot are directly related to reactions within the sample. If heating rates are extremely slow, broad peaks are obtained and selection of the initial break is difficult. As differential thermal analysis equipment is more sensitive than is visual observation, it is not surprising that visual decomposition temperatures tend to be higher.

All decompositions are endothermic.

The linear decrease in thermal stability with increase in the methylene chain length is in line with the behavior of organic compounds containing extended chains. It indicates that simple cleavage of the metal ligand bond is not the mode of decomposition. If the complex site alone were cleaved, the decomposition temperature might be expected to be approximately constant.

The data indicate that no unusual thermal properties are conferred by the bis(β-diketone) coordination sites. The presence of the metal complex appears to present a mechanism which allows the hydrocarbon portion of the molecule to approach its true thermodynamic stability[3] more easily than in the case of the simple linear hydrocarbons.

EXPERIMENTAL

1,8-Diphenyloctane-1,3,6,8-tetraone (succinyldiacetophenone) was prepared by the method of Daub and Johnson,[4] m.p. 94–96°; reported 92–94°.

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[1] J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711, November 17, 1953.

[2] E. H. Holst, Ph.D. dissertation, The Pennsylvania State University, 1958.

[3] G. S. Parks and H. M. Huffman, *The Free Energies of Some Organic Compounds,* Chemical Catalog Company, New York, N. Y., 1932, p. 99.

[4] G. H. Daub and W. S. Johnson, *J. Am. Chem. Soc.*, 72, 501 (1950).

1,9-Diphenylnonane-1,3,7,9-tetraone was prepared by the method of Martin, Shamma, and Fernelius[5] for azelyldiacetophenone, m.p. 56–59°; reported, not over 72°.

Anal. Calcd. for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99. Found: C, 75.03; H, 5.98.

1,10-Diphenyldecane-1,3,8,10-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 117–118°; reported, 117–118°.

1,11-Diphenylundecane-1,3,9,11-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 55–57°, reported 64.5–65.5°.

Anal. Calcd. for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 75.69; H, 6.52.

1,13-Diphenyltridecane-1,3,11,13-tetraone was prepared by the method of Martin, Shamma, and Fernelius,[5] m.p. 69–69.5°; reported 62.5–63.5°.

Anal. Calcd. for $C_{25}H_{28}O_4$: C, 76.50; H, 7.19. Found: C, 75.99; H, 7.18.

1,14-Diphenyltetradecane-1,3,12,14-tetraone was prepared by the method of Martin, Shamma, and Fernelius[5] for azelyldiacetophenone. The observed melting point is 113.4–114°.

Anal. Calcd. for $C_{26}H_{30}O_4$: C, 76.84; H, 7.44. Found: C, 76.61; H, 7.48.

Copper chelates. A mixture consisting of a 1:1 mole ratio of bisacetylacetonatocopper(II) and the bis(β-diketone) was ground together in a mortar and heated under vacuum at 60° for 1 day. The temperature was raised to 105–110° and the sample was allowed to come to constant weight. Completion of the reaction was also checked by a comparison of theoretical versus observed weight loss. Attempts to speed the reaction by initial heating at 110° resulted in charring. All of the mixtures were pale blue before heating; after heating the color changed to pale green.

Thermal stability by differential thermal analysis. Thermal stability of the copper chelates of the bis(β-diketones) was measured on a 0.1-g. sample of chelate diluted with 1.9 g. of aluminum oxide. A 2.0-g. sample of aluminum oxide was used as the reference standard. Samples were heated at the rate of 2° to 8° per min. in an aluminum block. The differential temperature was measured by two thermopiles of four, iron-constantan thermocouples inside a thin wall capillary. Temperature was measured by a single iron-constantan thermocouple placed in the sample. Both absolute and differential temperatures were recorded by a Brown 2 point automatic recording potentiometer. The scale for measurement of the temperature was extended by use of a "buck out" potential from a Rubicon Co. potentiometer. Differential temperatures of 0.02° could be observed. Temperatures could be determined to ±0.5°. Samples were heated in air.

Visual observation of decomposition. Visible signs of decomposition were observed with a Kofler hot stage. Samples were observed in air and in an atmosphere of carbon dioxide. No change in decomposition temperature was noted.

Melting was accompanied by evolution of a small amount of gas in both air and carbon dioxide.

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[5] D. F. Martin, M. Shamma, and W. C. Fernelius, *J. Am. Chem. Soc.*, **80**, 4891 (1958).

Salt Effects in the Solvolysis of Benzhydryl Chloride[1]

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In an extension of our studies on medium effects and relative rates,[2,3] we desired to examine the effects of salts upon the Henry's law constant for the substrate and upon the specific rate constant for a simple organic reaction in a typical organic medium. In view of the importance to theoretical organic chemistry of the solvolysis reactions of benzhydryl derivatives,[4] we undertook a study of the system, benzhydryl chloride in 90% (w./w.) aqueous bis(2-ethoxyethyl) ether at 25°. Unfortunately, our experimental technique[3] was not sufficiently sensitive to provide meaningful values of Henry's law constants for benzhydryl chloride in these solutions, so a complete study was not possible. However, we did collect some data on the kinetic salt effects observed in this system and have recorded them in Table I.

TABLE I

INITIAL FIRST-ORDER SPECIFIC RATE CONSTANTS FOR THE DEVELOPMENT OF ACID IN THE SOLVOLYSIS OF BENZHYDRYL CHLORIDE IN 90% (W./W.) AQUEOUS BIS(2-ETHOXYETHYL) ETHER AT 25.06° IN THE PRESENCE OF SALTS

Salt	Salt Concn. (moles/l.)	$10^6 \times k_0$ (sec.$^{-1}$)
None	—	1.01
$(n\text{-Bu})_4NCl$	0.100	1.12
$(n\text{-Bu})_4NBr$	.100	1.08
$(n\text{-Bu})_4NClO_4$	.100	1.31
$LiClO_4$	.100	2.51
$NaClO_4$	.100	2.48
NH_4ClO_4	.100	2.48
$HClO_4$	.097	1.7
$Mg(ClO_4)_2$	.0333	3.25
$Mg(ClO_4)_2$	.0500	4.05
$Mg(ClO_4)_2$	.100	6.03

EXPERIMENTAL[5]

Materials. Bis(2-ethoxyethyl) ether, b.p. 72–74° (10 mm.), was obtained by distillation of commercial material from lithium aluminum hydride and was stored under nitrogen at 8° in glass-stoppered paraffin-sealed flasks. *Benzhydryl*

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[1] Abstracted from a portion of the Ph.D. dissertation of Kirk D. McMichael, Department of Chemistry, University of Chicago, 1960.

[2] R. A. Clement and M. R. Rice, *J. Am. Chem. Soc.*, **81**, 326 (1959).

[3] R. A. Clement, J. N. Naghizadeh, and M. R. Rice, *J. Am. Chem. Soc.*, **82**, 2449 (1960).

[4] *e.g.*, (a) G. Kohnstam and B. Schillaker, *J. Chem. Soc.*, 1915 (1959). (b) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 365.

[5] The temperature of the constant temperature bath was 25.06 ± 0.02° as determined by an N.B.S. calibrated thermometer.