Because of upward drifts in k_S/k_E during some of the early runs which were apparently caused by oxidation, reaction vessels were purged with a slow stream of nitrogen during the removal of aliquots for titration. Even so, some drift in k_S/k_E persisted in the slow runs. In these cases, the value of the ratio obtained early in the titration was considered more significant and is reported in Table III.

Table III summarizes all the measurements carried out in this work. Table I contains average values calculated from Table III.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Heat Stability Studies on Chelates from Schiff Bases of Salicylaldehyde Derivatives[1]

BY C. S. MARVEL AND N. TARKÖY

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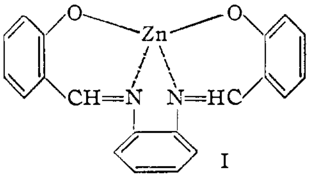
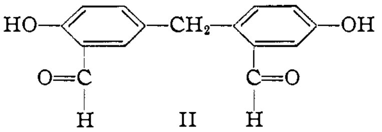
5,5'-Methylene-bis-salicylaldehyde has been prepared and converted to a polymeric Schiff base with a molecular weight of about 10,000 by heating with *o*-phenylenediamine. The metal chelates of this polymeric material are less heat stable than are the corresponding compounds prepared from salicylaldehyde itself. Some other effects of substitution on heat stability in this series have been noted.

The zinc chelate (I) of the condensation product of salicylaldehyde and *o*-phenylenediamine showed promising stability at 250°.[2] We have now prepared a related polymeric chelate. The monomeric dialdehyde II was obtained in 48% yield by treating salicylaldehyde with trioxane and sulfuric acid in acetic acid solution, a procedure that is analogous to that used by Smith[3] for the preparation of the corresponding diacid from salicylic acid.



I



II

The yield of the dialdehyde is related to the amount of sulfuric acid catalyst used (see Table I) and this relationship can be rationalized on the assumption that the salicylaldehyde to formaldehyde ratio must be very high in order that the dialdehyde be formed rather than a polymeric product. It has been shown[4] that the rate of acid-catalyzed depolymerization of trioxane to formaldehyde bears a close correlation to the acid concentration of the reaction medium. Thus a low acid concentration helps keep the ratio of salicylaldehyde to formaldehyde favorable for the preparation of the dialdehyde.

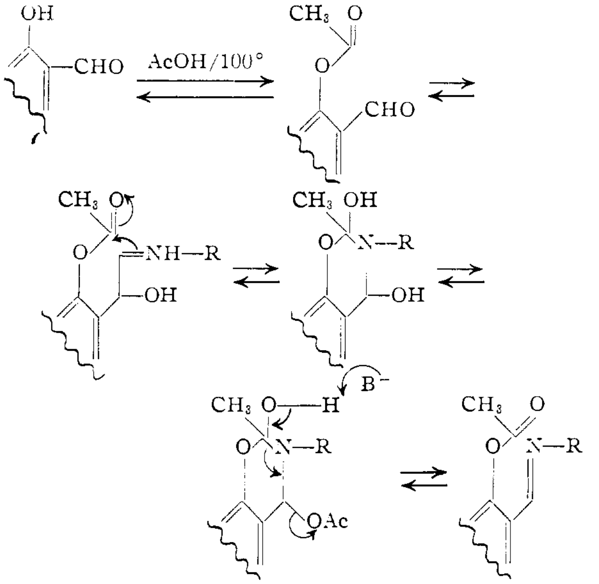
TABLE I

EFFECT OF ACID CONCENTRATION ON THE FORMATION OF DIALDEHYDE II

Temp. of reacn., °C.	Mole H_2SO_4 per l. CH_3CO_2H	Yield of dialdehyde, %
20	0.15	0
115	.3	18
105–110	.15	41.5
90–95	.07	42.8

The dialdehyde II was converted to a polymeric Schiff base by heating it with *o*-phenylenediamine in tetrahydrofuran solution. This gave a 65% yield of a yellow product (III) which had an inherent viscosity of 0.05 (concn. 1 g./100 ml.) in tetrahydrofuran. Attempts to determine the molecular weight of this polymer by the boiling point elevation method of Menzies and Wright[5] and by the Rast method[6] showed that the molecular weight was too great to be within the scope of either. The polymer shows weak absorption at 1652 cm.$^{-1}$ (in Nujol) in the infrared which indicates that there are aldehyde end groups.

The same polymer was obtained in 88% yield in less than a minute at water-bath temperature when acetic acid was used as the solvent. This marked catalysis by acetic acid may be due to some such sequence of reaction as



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(1) This work was performed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman, project engineer.

(2) C. S. Marvel, S. A. Aspey and E. A. Dudley, THIS JOURNAL, **78**, 4905 (1956).

(3) W. H. Smith, E. E. Sager and I. J. Siewers, *Anal. Chem.*, **21**, 133 (1949).

(4) R. P. Bell, K. N. Bascombe and J. C. M. Coutrey, *J. Chem. Soc.*, 1286 (1956).

(5) A. W. C. Menzies and S. L. Wright, Jr., THIS JOURNAL, **43**, 2315 (1921).

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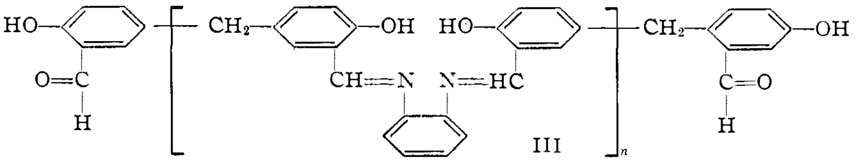
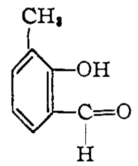


III

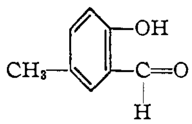
This would be a neighboring group effect similar to that reported by Boschan and Winstein[7] for the glycol → chlorohydrin reaction.

The polymeric Schiff base III was converted to the chelates of the divalent metals, copper, cobalt, zinc, nickel, iron and cadmium. The heat stability of the chelates increased in the order of the metals listed, but none was as stable as the monomeric zinc derivative I previously reported.[2] All of the polymeric materials lost 11–26% of their weight in 3 hr. at 250°.

In the earlier work[2] it had been noted that the *o*-cresolaldehyde (IV) gave a less stable chelated Schiff base than that from salicylaldehyde. We had assumed this might be due to a steric effect of



IV



V

the *o*-methyl group. In view of the instability of the *para* substituted polymer, we have now examined the heat stability of the product derived from *p*-cresolaldehyde (V). The ethylenediamine Schiff base was available[8] and the chelates were prepared. The exact order of the heat stability of its various metal derivatives was not quite the same as for the polymeric material or for the *o*-methyl derivative, but all were less stable than the unsubstituted chelates.

The decrease in heat stability noted in the methyl substituted salicylaldehyde chelates parallels changes in coördination power of salicylaldehyde and its oximes when methyl groups are introduced into the 3- or 5-position. Endo and Mashima[9] have reported that these methyl substituted derivatives do not possess the property of the unsubstituted compound to precipitate V^{III}, Zn^{II} and Cd^{II}. A somewhat similar destabilizing effect of *o*-methyl groups on chelates has been recorded in the 8-hydroxyquinoline series.[10] It may also be thought that the presence of the *o*-methyl group in pyridoxal contributes to the ease of splitting the intermediate Schiff base chelate system of vitamin B_6 catalyzed reactions.[11]

Experimental[12]

Preparation of Schiff bases, chelating of Schiff bases with metals and the tests on heat stabilities of the chelates were performed as described in an earlier communication.[2]

Preparation of 5,5'-Methylene-bis-salicylaldehyde.—To a solution of 69 ml. (80 g., 0.655 mole) of redistilled salicylaldehyde (b.p. 80° (11 mm.)) in 50 ml. of glacial acetic acid, in which 7.0 g. (0.206 mole) of trioxane (du Pont) was dissolved (salicylaldehyde:formaldehyde ratio = 1.6:1 mole), a mixture of 0.5 ml. of concentrated sulfuric acid and 2.5 ml. of glacial acetic acid was added slowly with magnetic stirring in a nitrogen atmosphere at a temperature of 90–95°. This temperature was maintained for 22 hr., and stirring continued over the whole reaction period.

The reaction mixture was then poured into 3-l. of ice-water and allowed to stand overnight. The deposited solid was filtered and extracted twice with 100 ml. of petroleum ether. From these petroleum ether solutions, after extraction of the water phase, part of the used excess of salicylaldehyde could be recovered.

The isolated solid then was three times triturated with 80 ml. of ether and the ether solutions were decanted (the ether solution contained only tarry material). The remaining solid weighed 25.5 g. (48.2%), m.p. 130–135°. Recrystallization from 150 ml. of acetone (cooling overnight) furnished 17.0 g. of pure dialdehyde, m.p. 141–142° (concentrating the mother liquors to 50 ml. and cooling gave 3.5 g. of less pure material, m.p. 129–130°).

The analytical sample was four times recrystallized from acetone, m.p. 142–143°.

Anal. Calcd. for $C_{15}H_{12}O_4$: C, 70.31; H, 4.69. Found: C, 70.74; H, 5.04.

The infrared spectrum (in Nujol) shows bands at 2730, 1660, 848 and 814 cm.$^{-1}$ and a broad band in the 2900 cm.$^{-1}$ region. The bis-oxime of this aldehyde was prepared as follows: 1.0 g. of dialdehyde and 1.0 g. of hydroxylamine hydrochloride were dissolved in 10 ml. of ethanol; 1 ml. of pyridine was then added and the solution heated under reflux on the water-bath for 40 minutes. The mixture then was evaporated to dryness under reduced pressure and allowed to cool. The residue then was triturated with 10 ml. of water and the insoluble material filtered; the analytical sample was recrystallized five times from ethanol–water, m.p. 221.5–222.0°.

TABLE II

METAL CHELATES OF POLYMERIC SCHIFF BASE III

Formula[a]	Color	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Weight loss on heating in air, % 250° 1st hr.	210° 2nd hr.	250° 3rd hr.
$C_7H_5O_2(C_{21}H_{19}O_2N_2Zn \cdot H_2O)_{45}C_8H_7O_2$	Dark yel.	61.8	61.2	3.9	4.4	9	10	12
$C_7H_5O_2(C_{21}H_{19}O_2N_2Cu \cdot H_2O)_{45}C_8H_7O_2$	Brown	62.1	62.0	4.0	4.4	10	12	26
$C_7H_5O_2(C_{21}H_{19}O_2N_2Fe \cdot H_2O)_{45}C_8H_7O_2$	Brown	60.6	61.2	4.3	4.5	1	1	11
$C_7H_5O_2(C_{21}H_{19}O_2N_2Ni \cdot 2H_2O)_{45}C_8H_7O_2$	Red	60.1	60.3	4.3	4.3	6	7	11
$C_7H_5O_2(C_{21}H_{19}O_2N_2Co \cdot 2H_2O)_{45}C_8H_7O_2$	Brown	60.1	57.4	4.3	4.6	9	11	18

[a] These formulas are based on formula III, $n = 45$, with the noted water of hydration. In calculating the weight loss, the weight of water due to hydration was subtracted before the percentage weight loss on dry material was calculated.

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[7] R. Boschan and S. Winstein, THIS JOURNAL, **78**, 4921 (1956).

[8] J. C. Duff, *J. Chem. Soc.*, 547 (1941).

[9] J. Endo and M. Mashima, *J. Chem. Soc. Japan (Pure Chem. Section)*, **73**, 386 (1952); *C.A.*, **47**, 2627 (1953).

[10] J. P. Phillips and L. L. Merritt, Jr., THIS JOURNAL, **71**, 3984 (1949).

[11] J. B. Longenecker and E. E. Snell, *ibid.*, **79**, 142 (1957), and previous papers.

[12] The melting points are not corrected.

MODEL COMPOUNDS

DERIVATIVES OF SALICYLALDEHYDE

BIS-SCHIFF BASE FROM SALICYLALDEHYDE AND ETHYLENEDIAMINE (A)

Compound	Formula	Color	M.p., °C.		Analyses, %		
					C	H	N
A	$C_{16}H_{16}N_2O_2$	Yellow	126–127 (EtOH)	Calcd.	71.64	5.97	10.45
				Found	71.48	6.23	10.51
Ni chelate of A	$C_{16}H_{14}N_2O_2Ni$	Rust-brown needles	330–333 (MeOH)	Calcd.	59.13	4.31	
				Found	58.95	4.17	
Cu chelate of A	$C_{16}H_{14}N_2O_2Cu$	Green	Decomp. over 300 ($CHCl_3$/petr. ether)	Calcd.	58.26	4.25	8.51
				Found	58.12	4.23	8.35
Zn chelate of A	$C_{16}H_{14}N_2O_2Zn$	Light yellow	>340 (Py)	Calcd.	57.94	4.22	8.45
				Found	57.65	4.32	8.00

DERIVATIVES OF 3-METHYLSALICYLALDEHYDE

BIS-SCHIFF BASE FROM 3-METHYLSALICYLALDEHYDE AND ETHYLENEDIAMINE (B)

Compound	Formula	Color	M.p., °C		Analyses, %		
					C	H	N
B	$C_{18}H_{20}N_2O_2$	Yellow	115 (EtOH)	Calcd.	72.97	6.76	9.46
				Found	73.13	6.92	9.65
Ni chelate of B	$C_{18}H_{18}N_2O_2Ni$	Brown	Dec. over 300 (acetone)	Calcd.	61.24	5.10	
				Found	61.54	5.30	
Cu chelate of B	$C_{18}H_{18}N_2O_2Cu$	Green	Dec. over 310 (MeOH)	Calcd.	60.40	5.03	7.83
				Found	60.40	5.11	8.10
Zn chelate of B	$C_{18}H_{18}N_2O_2Zn$	Light yellow	>340 (benzene/petr. ether)	Calcd.	60.10	5.01	
				Found	59.84	4.96	

DERIVATIVES OF 5-METHYLSALICYLALDEHYDE

BIS-SCHIFF BASE FROM 5-METHYLSALICYLALDEHYDE AND ETHYLENEDIAMINE (C)

Compound	Formula	Color	M.p., °C.		Analyses, %		
					C	H	N
C	$C_{18}H_{20}N_2O_2$	Yellow	169 (acetone)	Calcd.	72.97	6.76	9.46
				Found	73.22	6.95	9.49
Ni chelate of C	$C_{18}H_{18}N_2O_2Ni$	Brown	Dec. over 300 ($CHCl_3$/petr. ether)	Calcd.	61.24	5.10	7.95
				Found	60.95	4.90	8.14
Cu chelate of C	$C_{18}H_{18}N_2O_2Cu$	Greenish-blue	Dec. over 310 (tetrahydrofuran/petr. ether)	Calcd.	60.40	5.03	7.83
				Found	60.91	5.18	7.72
Zn chelate of C	$C_{18}H_{18}N_2O_2Zn$	Light yellow	>340 (Py./petr. ether)	Calcd.	60.10	5.01	
				Found	60.06	5.13	

Anal. Calcd. for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.89; N, 9.73. Found: C, 62.90; H, 4.97; N, 10.03.

Preparation of the Polymer Schiff Base from 5,5'-Methylene-bis-salicylaldehyde and *o*-Phenylenediamine.—To a solution of 1.507 g. of the dialdehyde (m.p. 141–142°) (6.08 millimoles) in 5 ml. of tetrahydrofuran and 20 ml. of glacial acetic acid was added a warm solution of 666 mg. (6.08 millimoles) of *o*-phenylenediamine (three times recrystallized, m.p. 102–103°) in 10 ml. of glacial acetic acid. On warming on the water-bath, in about 10 seconds a bright orange precipitate formed. After dilution with 200 ml. of methanol, the precipitate was filtered, washed with water, methanol and ether and dried: 1.750 g. (87.5%).

The analytical sample was reprecipitated five times from tetrahydrofuran–methanol. The composition of this polymer was calculated on the assumption that *ca.* 45 monomer units were linked together (in accordance with the viscosity value), the end-groups being aldehydes (infrared and other evidence).

Anal. Calcd. for $(C_{21}H_{16}N_2O_2)_{45}$ with -CHO- end groups: C, 76.85; H, 4.88; N, 8.55. Found: C, 76.80; H, 4.88; N, 8.41.

The infrared spectrum (in Nujol) shows bands at 1652, 1620, 1277, 832, 794 and 754 cm.$^{-1}$ and a broad band in the 2900 cm.$^{-1}$ region.

Chelation of the Polymer Schiff Base with Metals.—Three and three-tenths grams of the polymer Schiff base was dissolved in 100 ml. of tetrahydrofuran. To 10-ml. portions of this solution a twofold excess of 0.1 molar metal solutions (metal acetates dissolved in tetrahydrofuran + water or tetrahydrofuran + acetic acid) was added. The precipitate was stirred at room temperature for six days, filtered with suction, washed successively with water, tetrahydrofuran, alcohol and ether and dried overnight at room temperature and 0.01 mm. pressure. The insolubility of these chelates made their purification difficult.

The new chelates and their percentage weight loss at 250° are listed in Table II.

Heat Stability Tests on Model Compounds.—Samples of the chelates were heated in air at 250° and the weight loss determined hourly for 3 hr. The results are collected in Table III.

TABLE III

HEAT STABILITY TESTS ON MODEL COMPOUNDS

Schiff base	Metal	Weight loss in %		
		1 hr.	2 hr.	3 hr.
A	Zn(II)	0.5	1.0	1.0
B	Zn(II)	5.5	9.0	9.0
C	Zn(II)	0.	0.5	0.5
A	Ni(II)	0.5	0.5	0.5
B	Ni(II)	0.	0.5	0.5
C	Ni(II)	7.5	7.5	7.5
A	Cu(II)	0.	0.	0.
B	Cu(II)	0.	1.5	4.0
C	Cu(II)	3.5	4.5	5.0

All of these samples were essentially completely destroyed by heating at 250° for 28 hr. in the air.

Acknowledgment.—We are indebted to Mr. J. J. Brader, Jr., for the infrared data, and to Mr. J. Nemeth for the microanalyses.

URBANA, ILLINOIS