

TABLE I

Compound	pK_D	n	Be ⁺⁺	Pb ⁺⁺	Zn ⁺⁺	$-\log K_{fn}$ Ni ⁺⁺	Co ⁺⁺	Mg ⁺⁺	Ca ⁺⁺
α -Methyl-tropolone	9.37	1	10.3	9.4	8.6	8.4	8.0	6.0	5.1
		2	9.0	6.7	7.1	6.7	6.3	4.6	3.4
		3				3.7		2.6	
β -Methyl-tropolone	8.69	1	9.4	9.6	8.4	8.4	7.9	6.0	5.3
		2	7.7	6.6	6.8	6.6	6.2	4.6	3.6
		3			3.6	4.1		3.1	
α -Isopropyl-tropolone	9.75	1	10.7	9.5	8.7	8.6	8.1	6.2	5.2
		2	9.1	7.5	7.5	6.9	6.7	5.2	3.6
		3				3.7			
β -Isopropyl-tropolone	8.70	1	9.1	9.0	8.7	8.5	7.9	6.2	5.4
		2	7.5	6.7	7.0	6.5	6.3	4.8	3.6
		3			3.6	4.0	3.8	3.0	
α -Isopropyl-tropolone	8.7	1				8.4			
		2				6.5			
		3				3.9			
Tropolone	8.12	1	8.4			7.7			
		2	7.0			6.1			
Acetyl-acetone	9.70	1	9.0			6.9			
		2	7.7			5.1			

advanced that \bar{n} was equal to one or greater before the addition of base. To obtain values in the region of $\bar{n}_a = 0.5$, solutions containing two moles of metal ion per mole of chelating agent were titrated. In these cases, constants were not calculated from formation curves, but by the method of Block and McIntyre.⁷

Attempts to titrate an excess of α -isopropyltropolone in the presence of Be ion led to the precipitation of yellow plates, m.p. 177°. *Anal.* Calcd. for $\text{Be}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2$: C, 71.64; H, 6.57. Found: C, 71.36; H, 6.34.

Addition of a solution of $\text{Pb}(\text{NO}_3)_2$ to α -isopropyltropolone in 50% dioxane caused precipitation of light yellow plates, m.p. 164°. *Anal.* Calcd. for $\text{Pb}(\text{C}_{10}\text{H}_{11}\text{O}_2)_2$: C, 45.03; H, 4.13. Found: C, 45.44; H, 4.12.

The Ni and Be complexes of β -isopropyl- γ -(3-methylbut-2-enyl)-tropolone were found to be too insoluble for study by this method.

Discussion

The values determined are shown in Table I. In a previous publication,⁴ it was pointed out that the copper tropolonate was more stable than copper derivatives of β -diketones of comparable acidity. Included in Table I are the values of the Be and Ni derivatives of acetylacetone. If the values of the first or second formation constants of the Ni or Be complexes are plotted *vs.* the pK_D values of the respective chelating agents it is found that the complexes of tropolone and its derivatives group themselves about a single straight line, while the acetylacetone derivative of the metal ion in question is considerably (*ca.* 1.5 log units) removed from the line for the tropolone derivatives. Again it is seen that the tropolone complexes are more stable than those of β -diketones of comparable acidity.

Calvin and Wilson⁸ have postulated that resonance within the chelate ring may considerably enhance the stabilities of compounds such as these. The unusual nature of the plots of $\log K_f$ *vs.* pK_D for the tropolone complexes suggests several possibilities: 1. Resonance energy of the tropolone complexes is unusually high. 2. There is an un-

usually high contribution to stability due to the favorable size of the five-membered chelate ring. 3. Due to the unfavorable oxygen-oxygen distance in tropolone⁹ the weak hydrogen bond causes tropolone to act as an unusually strong acid.

Professor M. Calvin¹⁰ has suggested that the unusual character of these plots is best explained on the basis of the unusually high acidity of the tropolones rather than an unusual stability of these complexes. It is interesting to observe that the behaviors of the two smallest ions studied (H^+ and Be^{++}) are markedly similar; *i.e.*, the α -ions are bound more strongly than the β -substituted ions. For ions larger than Be^{++} , however, only minor differences are noted between the α - and β -compounds.

The effects of hydrogen bonding and the size of the chelate ring on the nature of plots of $\log K_f$ *vs.* pK_D are being investigated further.

Acknowledgment.—Most of the work reported here was supported by the United States Atomic Energy Commission through contract AT(30-1)-907. We wish also to acknowledge the technical assistance of Mrs. Lillian Berg in a portion of the synthetic work reported here.

(9) J. M. Robertson, *J. Chem. Soc.*, 1222 (1951).

(10) M. Calvin, private communication.

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Extensions of the Tollens Condensation

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The hydroxymethylation and subsequent reduction of carbonyl compounds containing active hydrogen atoms by means of formaldehyde and calcium or sodium hydroxide¹ has been applied to some monosubstituted acetaldehydes, YCH_2CHO , to

(7) B. P. Block and G. H. McIntyre, Jr., *THIS JOURNAL*, **75**, 5667 (1953).

(8) M. Calvin and K. Wilson, *ibid.*, **67**, 2003 (1945).

(1) B. Tollens and P. Wiegand, *Ann.*, **265**, 316 (1891).

TABLE I
 SYNTHESIS AND PROPERTIES OF POLYHYDROXYMETHYLATED COMPOUNDS

Carbonyl compound used	Moles of carbonyl compound	Procedure	Product, 2-Y-2-Hydroxy-methyl-1,3-propanediol, Y =	Yield, crude, %	B.p. at 10-12 mm., °C.	n_D^{27} $t = 27^\circ$	d_4^{27} $t = 27^\circ$	Solvent for recrystn.	M.p. (cor.), °C.
CH ₃ OCH ₂ CHO	1.5	A	Methoxy (II)	15	168-170	1.4820	1.2609	2-C ₂ H ₅ OC ₂ H ₄ OH	69.2-69.5
C ₂ H ₅ OCH ₂ CHO	0.82	A	Ethoxy (III)	24	181			CHCl ₃	80.5-81.0
<i>n</i> -C ₃ H ₇ OCH ₂ CHO	0.3	A	<i>n</i> -Propoxy (IV)	10	173-175	1.4698	1.1448		
C ₆ H ₅ CH ₂ CHO	1.0	A	Phenyl (V)	5	208-212			CHCl ₃	84.5-85.5
<i>n</i> -C ₈ H ₁₁ CHO	1.0	B	<i>n</i> -Butyl (VI)	17	173			CH ₃ CN	63-64
	1.0	C	VI	9	173				
<i>n</i> -C ₇ H ₁₃ CHO	0.25	B	<i>n</i> -Hexyl (VII)	7	175-180			C ₆ H ₆	68.0-68.8
<i>n</i> -C ₈ H ₁₅ CHO	0.5	B	<i>n</i> -Octyl (VIII)	6	190-200			C ₆ H ₆	72.0-73.0
Citronellal	0.5	C ^a	1,5-Dimethyl-5-hexenyl (IX)	5	173-210 ^{b,c}			C ₆ H ₆	55.5-56.0
			2-Y-2-Ethoxymethyl-1,3-propanediol			$t = 23^\circ$	$t = 23^\circ$		
<i>n</i> -C ₈ H ₁₁ CHO	1.0	C	<i>n</i> -Butyl (X)	3	137-142	1.4526	0.9742		
<i>n</i> -C ₈ H ₁₅ CHO	0.3	C	<i>n</i> -Octyl (XI)	7	182-185	1.4562	0.9345		
Citronellal	0.5	C ^a	1,5-Dimethyl-5-hexenyl (XII)	16	161-164 ^b	1.4748	0.9734		
			Other						
CH ₃ COCOCH ₃	0.5	A ^d	I ^e	8 ^f	Not tried				

^a An excess of alkali (20% over the calculated amount) was added after 27 hours at room temperature and 4 hours refluxing; after 30 minutes more boiling, the aldehydes had all reacted. ^b At 8 mm. ^c Only 100 mg. of IX crystallized out of the crude sirup in a month. ^d The ratio 8HCHO:1CH₃COCOCH₃:30H₂O:1CaO was used. ^e This compound was isolated only as its tribenzylidene derivative, prepared by the method of Hann, Ness and Hudson [R. M. Hann, A. T. Ness and C. S. Hudson, *THIS JOURNAL*, **68**, 1769 (1946)], m.p. 172.5-173.5° (cor.) (from 2-ethoxyethanol). *Anal.* Calcd. for C₃₁H₃₆O₈: C, 69.36; H, 6.76; benzylidene [S. J. Angyal and J. V. Lawler, *ibid.*, **66**, 837 (1944)], 50.4. Found: C, 69.47; H, 6.96; benzylidene, 50.4. An attempt to obtain I by hydrolysis of the tribenzylidene derivative failed. ^f Calculated from the yield of tribenzylidene derivative from an aliquot of the sirup.

 TABLE II
 ANALYTICAL DATA FOR NEW POLYHYDROXY COMPOUNDS

Compound	Molecular weight Calcd.	Found	Molecular refraction Calcd.	Found	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Hydroxyl, % Calcd.	Found ^a
II	136	134 ^b	31.5	30.8	44.11	43.98	8.89	9.10	37.5	37.7
III	150	148 ^b			47.97	47.52	9.39	9.51	34.0	33.7
IV			40.7	40.0	51.22	50.93	9.83	9.80	31.1	31.1
V	182	182 ^b			65.91	65.77	7.74	7.88	28.0	28.0
VI	162	158 ^b			59.26	59.47	11.19	11.41	30.7	30.7
VII	190	180 ^c			63.10	63.19	11.65	11.70	26.8	26.8
VIII	218	198 ^c			66.01	66.06	12.00	12.22	23.4	23.2
IX					66.62	66.76	11.18	11.84		
X			53.1	52.8	63.10	61.58 ^d	11.65	12.14 ^d	17.9	18.5 ^d
XI			71.6	71.7	68.23	67.54	12.27	12.46	13.8	14.1
XII			69.4	70.7	68.82	68.58	11.54	11.19	13.9	14.0

^a S. Siggia, "Quantitative Organic Analysis Via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 4. ^b Cryoscopically in water. ^c Cryoscopically in *t*-butyl alcohol. ^d Compound evidently impure.

produce small yields of the expected triols of the form YC(CH₂OH)₃. Y may be an alkyl radical (*n*-butyl, *n*-hexyl, *n*-octyl), phenyl, or a simple alkoxy radical. The reaction in aqueous medium was considerably facilitated for slightly soluble aldehydes by addition of an emulsifying agent. Chloroacetaldehyde gave only an uncharacterized sirup, and citronellal failed to react with aqueous formaldehyde. However, reaction in ethanol converted citronellal, as well as hexanal and decanal, to ether-alcohols of the type YC(CH₂OH)₂CH₂OC₂H₅; this further demonstrates the ease with which alcohols participate in the Tollens reactions.² Of the two ketones tried, camphor did not react at all, even in hot alcoholic solution, but aqueous butanedione gave a sirup which with benzaldehyde yielded

the tribenzylidene derivative of the expected polyalcohol, 2,2,5,5-tetrakis-(hydroxymethyl)-1,3,4,6-hexanetetrol, (HOCH₂)₃CCHOHCHOHC(CH₂OH)₃ (I). The polyalcohol itself was not isolated.

The action of thionyl chloride and pyridine³ on the lower 2-alkoxy-2-hydroxymethyl-1,3-propanediols converted them to mixed liquid chlorinated compounds, of which only 1,3-dichloro-2-chloromethyl-2-methoxypropane was obtained pure.

Experimental

Preparation of Aldehydes.—Methoxyacetaldehyde was prepared by passing vaporized 2-methoxyethanol containing 10% water over copper wire (freshly reduced from the oxide at 200°) at 300-330° at the rate of 120 ml. liquid/hour/400 g. of catalyst.⁴ Fractional distillation of the condensate

(3) A. Mooradian and J. B. Cloke, *ibid.*, **67**, 942 (1945).

(2) S. Wawzonek and D. A. Rees, *THIS JOURNAL*, **70**, 2433 (1948); S. Wawzonek and J. P. Henry, *ibid.*, **75**, 1258 (1953); S. Wawzonek and C. Issidorides, *ibid.*, **75**, 2373 (1953).

(4) Essentially the method of N. L. Drake, H. M. Duvall, T. L. Jacobs, H. T. Thompson and H. M. Sonnichsen, *ibid.*, **60**, 73 (1938). The copper chromite catalyst used by C. E. Redemann and R. N. Ickes, *J. Org. Chem.*, **8**, 159 (1943), was much less satisfactory.

gave the crude aqueous azeotrope, b.p. 88–95°, which upon analysis⁵ proved to represent a yield of 16% based on starting material or 32% on 2-methoxyethanol consumed. The ethoxyacetaldehyde azeotrope, b.p. 90–110°, was similarly made at 300–425° in yields of 8–13% based on 2-ethoxyethanol consumed, but the dehydrogenation failed for *n*-butoxyacetaldehyde. Conversion of glycerol α -monochlorohydrin to glycerol α -*n*-propyl ether, b.p. 109–114° (9 mm.) (41% yield) and oxidation with lead tetraacetate, all according to the method of Hatch and Nesbitt,⁶ gave crude *n*-propoxyacetaldehyde, b.p. 60–80° (105 mm.), in 72% yield based on the ether.

Preparation of Polyhydroxymethylated Compounds. **Procedure A.**—A mixture of formaldehyde (as 37% formalin), carbonyl compound, water, and calcium oxide in the molar ratio 3:1:50:0.5 was stirred and kept below 40° until the aldehyde titer⁶ was negligible; this required 7–30 hours. The mixture was neutralized with dilute sulfuric acid, treated with Super-Cel filter aid, filtered by suction, and evaporated under reduced pressure on the steam-bath to a viscous brown sirup. This sirup was dissolved in an equal volume of hot methanol, diluted with acetone until precipitation ceased, and filtered as before. Renewed vacuum evaporation, solution in a little water, extraction with ether to remove colored impurities, and vacuum distillation gave a light yellow or colorless sirup, which sometimes crystallized upon standing.

Procedure B.—The reaction mixture was like that in procedure A but additionally contained 5 ml. of 2% Aerosol OT solution per 200 ml. of water. This was caused to react at 50°, neutralized, filtered, and separated into its two layers. The organic layer was washed repeatedly with water and distilled under reduced pressure to yield a sirup which soon crystallized.

Procedure C.—A solution of formaldehyde (as 37% formalin) and the other aldehyde in ethanol was stirred and gradually treated with potassium hydroxide in 90% ethanol: the molar ratio was 3HCHO:1RCHO:1KOH:10C₂H₅OH total. Initial cooling was necessary to keep the temperature below 50°. When all the aldehyde had disappeared (20–40 hours, mostly at room temperature), the solution was neutralized with sulfuric acid, filtered, and evaporated *in vacuo* on a steam-bath. If two layers appeared, the water layer was discarded and the organic layer was washed with water before fractional vacuum distillation. This usually yielded two yellow sirup fractions, the triol and its monoethyl ether (appearing in reverse order).

The applications of these syntheses and physical properties of products are shown in Table I, and analytical data in Table II.

1,3-Dichloro-2-chloromethyl-2-methoxypropane.—This was prepared⁸ from 2-hydroxymethyl-2-methoxy-1,3-propanediol, pyridine and thionyl chloride in the molar ratio 1:3:3. Besides a relatively large amount of high-boiling chlorine-containing liquid, presumably a mixture of the mono- and dichlorinated compounds, the desired trichloro compound was obtained as a white solid melting at 59.0–59.2° (cor.) after recrystallization from ethanol.

Anal. Calcd. for C₅H₉OCl₃: Cl, 55.6. Found: Cl, 56.1.

Attempted preparation of the corresponding ethoxy and *n*-propoxy compounds by the same method gave only unpurifiable oils.

(5) L. H. Donnelly, *Ind. Eng. Chem., Anal. Ed.*, **5**, 91 (1933).

(6) L. F. Hatch and S. S. Nesbitt, *THIS JOURNAL*, **67**, 39 (1945).

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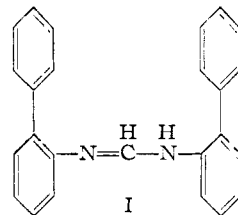
Improved Phenanthridine Syntheses with Polyphosphoric Acid

By E. C. TAYLOR, JR., AND NORMAN W. KALENDA

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The cyclization of 2-formamidobiphenyl to phenanthridine represents the simplest and most straightforward route to this compound, but the methods which have been described for effecting

this cyclization are somewhat unsatisfactory. The use of zinc chloride gives only a 42% yield of phenanthridine,¹ while an improved cyclization procedure, although raising the yield of 90%, employs a mixture of phosphorus oxychloride, nitrobenzene and anhydrous stannic chloride.² In view of the versatility of polyphosphoric acid in effecting numerous cyclization reactions,³ we have investigated its application in the present case. Phenanthridine is formed in yields consistently over 90% by heating a stirred mixture of 2-formamidobiphenyl and polyphosphoric acid for one hour at 140–160° and then pouring the reaction mixture into water. Constant stirring during the heating period is essential; without stirring, the only product isolated was a compound C₂₅H₂₀N₂, which is probably *N,N'*-bis-(*o*-biphenyl)-formamidine (I).



The most convenient route to phenanthridone reported involves aluminum chloride cyclization of *o*-biphenyl isocyanate.⁴ It has now been found that this cyclization may be carried out conveniently and in improved yields (87%) by heating a stirred mixture of polyphosphoric acid and *o*-biphenyl isocyanate for two hours at 140–160° and pouring the reaction mixture into water. Some di-(*o*-biphenyl)-urea is also formed, probably as a result of hydrolysis of a small amount of unreacted *o*-biphenyl isocyanate during the isolation procedure.

Experimental⁵

Phenanthridine.—A mixture of 20 ml. of polyphosphoric acid and 2.0 g. of 2-formamidobiphenyl in a 100-ml. round-bottom flask was heated at 140–160° for one hour with constant stirring. The viscous reaction mixture was then poured into 200 ml. of cold water, the resulting milky solution adjusted to pH 10 with strong sodium hydroxide solution and allowed to stand several hours at room temperature. The light pink solid which separated was collected by filtration and washed well with water; yield 1.70 g. (93.4%), m.p. 104.5–106°. One recrystallization from ligroin using Norit gave colorless needles, m.p. 106–107°.

***N,N'*-Bis-(*o*-biphenyl)-formamidine (I).**—A mixture of 2.00 g. of 2-formamidobiphenyl and 20 ml. of polyphosphoric acid was heated at 175–180° without stirring for a period of one hour. The reaction mixture was then cooled, diluted with 200 ml. of water and the resulting solution adjusted to pH 10 with strong sodium hydroxide solution. This basic solution was extracted several times with 100-ml. portions of ether and the combined ether extracts extracted with three 80-ml. portions of 6 *N* hydrochloric acid. The combined acid extracts were adjusted to pH 10 with strong sodium hydroxide solution and allowed to stand for several

(1) G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 2225 (1932).

(2) D. W. Ockenden and K. Schofield, *ibid.*, 717 (1953).

(3) See for example: H. R. Snyder and F. X. Werber, *THIS JOURNAL*, **72**, 2962, 2965 (1950); E. C. Horning, J. Koo and G. N. Walker, *ibid.*, **73**, 5826 (1951).

(4) J. M. Butler, *ibid.*, **71**, 2578 (1949).

(5) The polyphosphoric acid was generously supplied by the Victor Chemical Works, Chicago, Illinois, and the *o*-biphenyl isocyanate by Dr. J. H. Saunders, Monsanto Chemical Company, Anniston, Alabama.