

EXTENSIONS OF THE TOLLENS CONDENSATION

By

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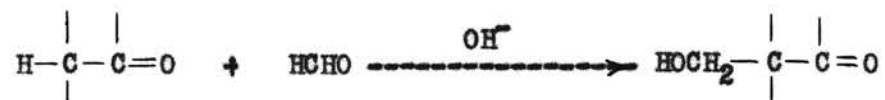
## INTRODUCTION

The purpose of this investigation was to further study the reaction of formaldehyde with carbonyl compounds containing active hydrogen under basic conditions (the Tollens condensation) in the hope of preparing new compounds having high hydroxyl content.

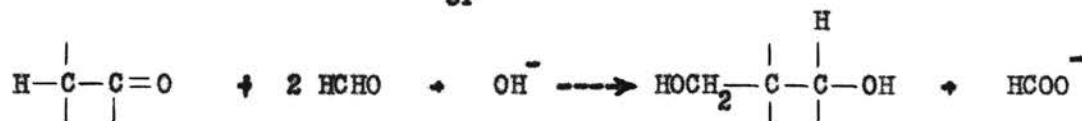
Such compounds have potential value as humectants, in the manufacture of paints and varnishes, and as intermediates for nitrated explosives.

## HISTORICAL

The general reaction known as the Tollens condensation was first studied by Tollens and Wiegand (58) in 1891. The reaction involves the condensation of formaldehyde with a carbonyl compound containing at least one active alpha-hydrogen in the presence of various catalysts ranging from very weak to very strong bases (crossed aldol condensation), followed in some cases by a crossed Cannizzaro reaction between formaldehyde and the carbonyl compound to yield a hydroxyl group in place of the carbonyl group:



or



This thesis is concerned only with reactions of the type involving strongly basic catalysts such as NaOH or Ca(OH)<sub>2</sub> (not including alkali metal carbonates or magnesium oxide), which usually cause substitution of all available alpha-hydrogens with hydroxymethyl groups and subsequent reduction of the remaining carbonyl group to a hydroxyl group via a crossed Cannizzaro reaction with formaldehyde. In a few cases complete substitution of alpha-hydrogens is not obtained or ring formation occurs in the partially or fully hydroxymethylated compounds; however, all of the other above conditions are fulfilled.

These cases will be included.

All reactions of this general type involve essentially the same procedure. The carbonyl compound is dissolved or suspended in water or an alcohol, formaldehyde is added either as formalin or paraformaldehyde and a suitable strong base is added. This base may be added in one portion or in small portions over an extended period of time. The reaction mixture is stirred at 20-100° for periods of time from a few hours to as long as four weeks. At the end of the reaction period, if excess base is present, it is eliminated by neutralization with any one of various acids. The solvent is then evaporated leaving a syrup which either crystallizes or which is treated in a wide variety of ways to obtain the final product free from such side-reaction products as hydroxyaldehydes, sugars, simple aldel products, and formates as well as the inorganic salt produced in the neutralization process. Sometimes catalytic hydrogenation is used to improve yields (61).

A short review of the work done on the Tollens condensation is included in an ACS monograph on reactions of formaldehyde by Walker (59).

The most widely studied and commercially profitable example of this reaction involves the condensation of four moles of formaldehyde with one mole of acetaldehyde in aqueous solution in the presence of a base such as calcium hydroxide to form pentaerythritol:

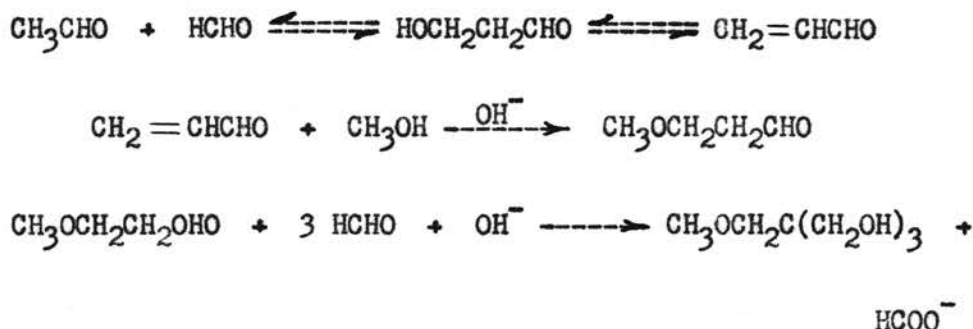




The literature is so voluminous on this important reaction as to be beyond the scope of this work. Hence it will be discussed only very briefly.

Pentaerythritol may be prepared in good yield by the method of Schurink (53).

When pentaerythritol is prepared in methanol solution or if the formaldehyde used is in the form of formalin which contains a large amount of methanol as an impurity, considerable amounts of the mono-methyl and smaller amounts of the dimethyl ether of pentaerythritol are formed (63). A mechanism for the formation of the former is postulated as:



Evidence of the above mechanism is given by Wawzonek and Henry (62), who produced  $\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3$  by subjecting  $\text{CH}_3\text{OCH}_2\text{CH}_2\text{CHO}$  to the Tollens condensation.

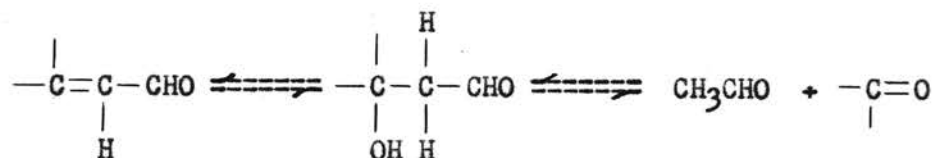
This kind of reaction is evidently involved in the production of dipentaerythritol,  $[(\text{HOCH}_2)_3\text{CCH}_2]_2\text{O}$ , by carrying out the synthesis of pentaerythritol in the presence of preformed pentaerythritol (51).

In the tables that follow, previous work is listed and, if given, specific data are included which will elucidate more clearly procedures used in specific cases. If specific data could not be found, it was assumed that the author cited followed somewhat the general scheme

previously outlined. Methods of Purification (A) and Other Methods of Preparing Products (B) will be found in notes following the tables.

Included in the Appendix are melting points, solvents used in recrystallization, and boiling points of all products mentioned in this table if such data were given in the reference consulted.

Cinnamaldehyde, acetaldo, acrolein, and crotonaldehyde apparently react as acetaldehyde in the Tollens condensation by first undergoing a reverse aldol condensation and consequently will not appear in the table: (9,27,37,41)



However, it has been reported in patent literature (5,12,28) that compounds of the type  $\text{RCH=CHCR}(\text{CH}_2\text{OH})_2$  have been made from unsaturated aldehydes and formaldehyde.

Table 1

## Experimental Procedures for the Preparation of Condensation Products

## A - Aldehydes

Original Carbonyl Compound	Solvent and Catalyst	Molar Ratio Carbonyl: HCHO: Catalyst	Product	Neutralizing Agent	Purification Scheme	Other Methods of Preparing Product	Reference
CH <sub>3</sub> CHO	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	5:27:3	C(CH <sub>2</sub> OH) <sub>4</sub>	HCl	f		53
C <sub>2</sub> H <sub>5</sub> CHO	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	3:10:7	CH <sub>3</sub> C(CH <sub>2</sub> OH) <sub>3</sub>	(CO <sub>2</sub> H) <sub>2</sub>	-	i, iii	31
"	H <sub>2</sub> O/alkali metal hydroxides	-	"	H <sub>2</sub> SO <sub>4</sub>	b		10
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	"	HCO <sub>2</sub> H	a		67
"	H <sub>2</sub> O/NaOH	-	"	H <sub>2</sub> SO <sub>4</sub>	a		18
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	3.3:1:2.7	"	(CO <sub>2</sub> H) <sub>2</sub>	f		56
<u>n</u> -C <sub>3</sub> H <sub>7</sub> CHO	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	C <sub>2</sub> H <sub>5</sub> C(CH <sub>2</sub> OH) <sub>3</sub>	HCO <sub>2</sub> H	a		67
(CH <sub>3</sub> ) <sub>2</sub> CHCHO	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>2</sub> OH) <sub>2</sub>	HCO <sub>2</sub> H	a	ii	67
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	"	-	-		2
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	"	-	-		3

Table 1 (continued)

$(\text{CH}_3)_2\text{CHCHO}$	$\text{H}_2\text{O}/\text{NaOH}$	1:2:1	$(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$	-	-	61
"	$\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	-	"	-	-	34,42
"	$\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	2.5:6.7:0.32	"	no acid	d	65
"	$\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	-	"	"	d	54
$\underline{n}\text{-C}_4\text{H}_9\text{CHO}$	-	-	$\underline{n}\text{-C}_3\text{H}_7\text{C}(\text{CH}_2\text{OH})_3$	-	-	iii -
$(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	-	$(\text{CH}_3)_2\text{CHC}(\text{CH}_2\text{OH})_3$	-	-	iv 41
"	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	2:8:1	"	no acid	c	18
$(\underline{\text{iso}}\text{-C}_4\text{H}_9)_2\text{CHCHO}$	-	-	$(\underline{\text{iso}}\text{-C}_4\text{H}_9)_2\text{C}(\text{CH}_2\text{OH})_2$	-	-	v -
$(\text{C}_2\text{H}_5)_2\text{CHCHO}$	$\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	-	$(\text{C}_2\text{H}_5)_2\text{C}(\text{CH}_2\text{OH})_2$	no acid	d	54
$\begin{array}{l} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{CHCHO} \\ \diagup \\ \underline{n}\text{-C}_4\text{H}_9 \end{array}$	$\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	-	$\begin{array}{l} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{C}(\text{CH}_2\text{OH})_2 \\ \diagup \\ \underline{n}\text{-C}_4\text{H}_9 \end{array}$	"	d	54
$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CHCHO} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array}$	-	-	$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{CH}_2\text{OH})_2 \\ \diagup \\ \text{C}_2\text{H}_5 \end{array}$	-	-	vi -
$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{CHCHO} \\ \diagup \\ \underline{n}\text{-C}_3\text{H}_7 \end{array}$	$\text{H}_2\text{O}/\text{KOH}$	-	$\begin{array}{l} \text{CH}_3 \\ \diagdown \\ \text{C}(\text{CH}_2\text{OH})_2 \\ \diagup \\ \underline{n}\text{-C}_3\text{H}_7 \end{array}$	-	-	23

Table 1 (continued)

$n\text{-C}_6\text{H}_{13}\text{CHO}$	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	5:10:5	$n\text{-C}_5\text{H}_{11}\text{C}(\text{CH}_2\text{OH})_3$	$\text{CO}_2$	c	21
$(\text{C}_6\text{H}_5)_2\text{CHCHO}$	$\text{H}_2\text{O}/\text{NaOH}$	6:12:12	$(\text{C}_6\text{H}_5)_2\text{C}(\text{CH}_2\text{OH})_2$	-	d	13
$\begin{array}{l} \text{C}_6\text{H}_5 \diagdown \\ \text{C}_6\text{H}_5 \diagup \end{array} \text{CHCHO}$	$\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}/\text{KOH}$	4:24:4	Gave the corresponding mono-primary alcohol but not by the Cannizzaro reaction			13
$\begin{array}{l} \text{C}_6\text{H}_4 \diagdown \\   \\ \text{C}_6\text{H}_4 \diagup \end{array} \text{CHCHO}$	$\text{C}_2\text{H}_5\text{OH}-\text{H}_2\text{O}/\text{KOH}$	4:20:8	Gave the corresponding mono-primary alcohol but not by the Cannizzaro reaction			13
$\begin{array}{l} \text{C}_6\text{H}_5 \diagdown \\ \text{CH}_3 \diagup \end{array} \text{CHCHO}$	- /KOH	-	$\begin{array}{l} \text{C}_6\text{H}_5 \diagdown \\ \text{CH}_3 \diagup \end{array} \text{C}(\text{CH}_2\text{OH})_2$	-	-	23
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$	$\text{C}_2\text{H}_5\text{OH}/\text{KOH}$	-	$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$	-	-	24
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CHO}$	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/\text{CaO}$	-	$\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3$	-	-	62
2,5-endomethylene-1,2,5,6-tetrahydrobenzaldehyde	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	4:10:10	2,5-endomethylene-3-cyclohexene-1,1-dimethanol	no acid (crystals deposited from alkaline solution)		11
2,5-endomethylene-6-methyl-1,2,5,6-tetrahydrobenzaldehyde	$\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}/\text{NaOH}$	2:6:3	2,5-endomethylene-6-methyl-3-cyclohexene-1,1-dimethanol	HCl	k	11
3-cyclohexenecarboxaldehyde	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/\text{KOH}$	-	3-cyclohexene-1,1-dimethanol	no acid	d	25,54
6-methyl-3-cyclohexenecarboxaldehyde	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/\text{KOH}$	-	6-methyl-3-cyclohexene-1,1-dimethanol	no acid	d	25,54

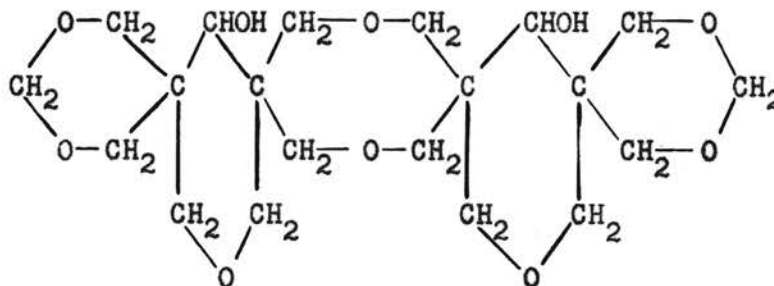
Table 1 (continued)

3,4-dimethyl-6-phenyl-3-cyclohexenecarboxaldehyde	H <sub>2</sub> O-CH <sub>3</sub> OH/ KOH	-	3,4-dimethyl-6-phenyl-3-cyclohexene-1,1-dimethanol	no acid	d	25
3,4,6-trimethyl-3-cyclohexenecarboxaldehyde	H <sub>2</sub> O-CH <sub>3</sub> OH/ KOH	-	3,4,6-trimethyl-3-cyclohexene-1,1-dimethanol	no acid	d	25

B-Ketones

acetone	H <sub>2</sub> O/NaOH	-	tetrahydro-3,3,5,5-tetrakis-(hydroxymethyl)-4-pyranol (I)	-	-	57
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	4:32.3:2	(I)	H <sub>2</sub> SO <sub>4</sub> and (CO <sub>2</sub> H) <sub>2</sub>	j	52
"	H <sub>2</sub> O/Ba(OH) <sub>2</sub>	3:30:2	(I)	H <sub>2</sub> SO <sub>4</sub>	e	57

also



(II)

Table I (continued)

acetone	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	1:8:1	(I)	(CO <sub>2</sub> H) <sub>2</sub>	f	4
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	(I)	H <sub>2</sub> SO <sub>4</sub>	f	39
chloroacetone	H <sub>2</sub> O/NaOH	5.5:16:5.5	3-hydroxymethyl- 3,4-dihydroxy-2- butanone	-	g i	vii 33
"	H <sub>2</sub> O/NaOH	1:2.1:0.27	3-hydroxymethyl- 3-chloro-4-hydroxy- 2-butanone	-	g	33
hydroxyacetone	H <sub>2</sub> O/Ba(OH) <sub>2</sub>	-	3,4-dihydroxy-2- butanone also 3,4-dihydroxy-3- hydroxymethyl-2- butanone	H <sub>2</sub> SO <sub>4</sub>	k	22
methyl ethyl ketone	H <sub>2</sub> O/NaOH	7:30:0.5	3-methyl-3-hydroxy- methyl-4-hydroxy-2- butanone	-	g	44
"	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	4:26:2	tetrahydro-3,3,5- tris-(hydroxy- methyl)-5-methyl- 4-pyranol also 2-methyl-2-hydroxy- methyl-1,3-butane- diol	CH <sub>3</sub> CO <sub>2</sub> H	j	52

Table 1 (continued)

diethyl ketone	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/$ $\text{NaOH}$	6:10:0.3	1-hydroxy-2-hydroxy- methyl-2-methyl-3- pentanone also 1,5-dihydroxy-2- hydroxymethyl-2,4- dimethyl-3-pentan- one	-	g	44
"	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	1:5.5:0.5	tetrahydro-3,5-bis- (hydroxymethyl)-3,5- dimethyl-4-pyranol	$\text{H}_2\text{SO}_4$ and $(\text{CO}_2\text{H})_2$	j	52
cyclopentanone	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	1:4:0.05	2,2,5,5-tetrakis- (hydroxymethyl)- cyclopentanone	no acid (crystals deposited from crude solution)		40
"	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	2.4:10:0.06	"	HCl	-	49
cyclohexanone	$\text{H}_2\text{O}/\text{Ca}(\text{OH})_2$	2:11:0.2	2,2,6,6-tetrakis- (hydroxymethyl)- cyclohexanol	$\text{H}_2\text{SO}_4$	f	40
"	$\text{H}_2\text{O}/\text{CaO}$	2:11:1	"	$\text{HCO}_2\text{H}$	i	66
4-methylcyclohexanone	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/$ $\text{Ca}(\text{OH})_2$	1:5.5:0.1	2,2,6,6-tetrakis- (hydroxymethyl)-4- methylcyclohexanol	$\text{HCO}_2\text{H}$	f	40
2-methylcyclohexanone	$\text{H}_2\text{O}-\text{CH}_3\text{OH}/$ $\text{Ca}(\text{OH})_2$	-	2,6,6-tris-(hydroxy- methyl)-2-methyl- cyclohexanol	$\text{HCO}_2\text{H}$	h	40



Table 1 (continued)

menthene, campher, and carvone	H <sub>2</sub> O/Ca(OH) <sub>2</sub>	-	no reaction	40
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## Notes to Table:

## A - Methods of Purification

- (a) The crude mixture was evaporated in vacuo to remove the solvent. An equal volume of acetone was boiled with the pasty residue. A precipitate formed and was filtered out. The filtrate was evaporated to remove the acetone and yield a product of 95% purity.
- (b) The crude mixture was evaporated in vacuo to remove the solvent. Volatile impurities were distilled out in vacuo. Vacuum steam distillation gave a product with a high degree of purity.
- (c) The crude mixture was filtered hot by suction and evaporated somewhat, three times its volume of ethanol was added, the precipitated calcium formate was removed by filtration, and the filtrate was stripped of alcohol and distilled in vacuo.
- (d) The crude mixture was ether-extracted and the ether extract distilled in vacuo.
- (e) The crude mixture was filtered, evaporated in vacuo, extracted with hot isopentyl alcohol, the alcohol solution evaporated, the residue dissolved in benzene and the benzene solution extracted with water. The water layer yielded I while the benzene layer gave II.
- (f) The crude mixture was filtered and evaporated in vacuo. The product separated as a crystalline solid on standing.
- (g) The crude mixture without any neutralization (only a small amount of alkali was used and all was used up in the condensation reaction) was fractionally distilled.
- (h) The crude mixture was filtered and evaporated in vacuo. The resulting syrup was treated with benzaldehyde and HCl to yield a benzylidene derivative. This was hydrolyzed to the original compound which was obtained by alcoholic extraction of the evaporated hydrolyzate.
- (i) The crude mixture was evaporated in vacuo, treated with methanol and freed from calcium formate by filtration. Evaporation of the methanol gave the desired product.
- (j) The presence of the stated products was proved by allylation of the crude syrup and analysis of the various fractions obtained upon fractionation of the crude allylated mixture. No pure polyhydroxy compounds were isolated.
- (k) The crude mixture was evaporated in vacuo and vacuum-distilled.

## B - Other Methods of Preparation

- (i) Koch and Zerner (36) prepared  $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$  by reducing  $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_2\text{CHO}$  with aluminum amalgam.
- (ii) Wessely (64) prepared  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$  by reducing  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})\text{CHO}$  in water solution with aluminum amalgam and also by treating  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})\text{CHO}$  in either aqueous or alcoholic solution with KOH and either excess formaldehyde or excess isobutyraldehyde.
- Böhm (8) prepared  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$  by reducing  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})\text{CHO}$  in alcoholic solution with sodium amalgam.
- Bincer and Hess (7) treated  $\text{C}(\text{CH}_2\text{OH})_2(\text{CH}_2\text{I})_2$  with an excess of hydrogen at 50-55° in alcohol and pyridine to which palladized barium sulfate and magnesium oxide had been added to obtain  $(\text{CH}_3)_2\text{C}(\text{CH}_2\text{OH})_2$ .
- (iii) By irradiating a solution of formaldehyde in dibutyl ether,  $\text{C}_3\text{H}_7\text{C}(\text{CH}_2\text{OH})_3$  was prepared; by irradiating a solution of formaldehyde in diethyl ether,  $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$  was prepared (48).
- (iv) Lichtenstern (38) reduced  $(\text{CH}_3)_2\text{CHC}(\text{CH}_2\text{OH})_2\text{CHO}$  with aluminum amalgam in a water-alcohol solution to obtain  $(\text{CH}_3)_2\text{CHC}(\text{CH}_2\text{OH})_3$ .
- (v) Freylen (26) treated diethyl di-isobutylmalonate with sodium in alcohol to obtain  $(\text{iso-C}_4\text{H}_9)_2\text{C}(\text{CH}_2\text{OH})_2$ .
- (vi) Neustädter (45) treated  $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})\text{CHO}$  with alcoholic KOH to obtain  $\text{C}_2\text{H}_5\text{C}(\text{CH}_3)(\text{CH}_2\text{OH})_2$ .
- (vii) 3-Hydroxymethyl-3-chloro-4-hydroxy-2-butanone was treated with alcoholic KOH to yield 3-hydroxymethyl-3,4-dihydroxy-2-butanone (33).

## EXPERIMENTAL

### I. PREPARATION OF ALDEHYDES

#### A. Apparatus Used in Preparing Alkoxyacetaldehydes by Catalytic Dehydrogenation of the Corresponding Alkoxyethanols

The proper alcohol was allowed to run from a burette at a fixed rate into a heated distilling flask where it was vaporized. It was thence passed over a preheater into the catalyst chamber.

The catalyst chamber was a glass tube 120 cm. long with an inside diameter of 28 mm., wrapped once with asbestos paper which was sealed on with a dilute solution of sodium silicate. Forty feet of B&S #24 gauge nichrome wire was wrapped around the asbestos-covered tube, the wrappings being about 1/4 inch apart. Approximately 3 cm. of tube was left unwrapped at each end. Four more layers of asbestos paper were then wrapped around the tube in a similar manner and the entire tube was allowed to dry in a warm place overnight.

A rheostat and a switch were placed in series with the chamber. At 110 volts, a maximum temperature of 300-30° could be maintained in the tube. At 220 volts, a temperature of 450° was easily obtainable, with temperatures much higher possible.

A glass tube 120 cm. long with an inside diameter of 17 mm. was placed in the larger tube; it served as the actual chamber in which the catalyst was placed. About 90 cm. of this tube was packed with catalyst. Before use, the entire asbestos-covered outside tube was

given a heavy wrapping of glass wool. Corks were used for all connections. (Ground glass connections at either end of the inner catalyst tube would serve well.)

The vapors coming from the catalyst tube were condensed with an ordinary water condenser and were collected in a large suction flask immersed in an ice bath. The hydrogen evolved passed out of the suction flask through the sidearm and was led to a vent.

#### B. Preparation of Methoxyacetaldehyde

Vapors of methoxyethanol, either as the pure material or mixed with 10% water by volume, were passed over copper chromite catalyst supported on copper screen wire at 290-330° at atmospheric pressure and at rates of 50-200 ml./hour according to the method of Redemann and Ickes (50). Overall yields of less than 2% were obtained consistently. This method was discarded as unsatisfactory and a new catalyst tried.

The tube was repacked with short pieces of copper oxide wire and a stream of hydrogen was passed through the tube at 200° to reduce the copper oxide to copper (20). Vapors of methoxyethanol mixed with 10% by volume of water were passed through the chamber at 300-30° at atmospheric pressure and rates of 75-150 ml./hour/400 grams of catalyst. Fractional distillation of the condensate yielded an aldehyde fraction boiling at 88-95°. This was analyzed for methoxyacetaldehyde by the method of Dornally (19). Maximum yield was obtained at a rate of 120 ml./hour/400 grams of catalyst, when an overall yield of 16% and a yield based on unrecovered alcohol of 32% was obtained.

#### C. Preparation of Ethoxyacetaldehyde

The catalyst tube was packed with short pieces of copper oxide

wire and a stream of hydrogen was passed through the tube at 200° to reduce the copper oxide to copper (20). Vapors of ethoxyethanol were passed through the chamber at 300-425° at atmospheric pressure and rates of 40-120 ml./hour/400 grams of catalyst. Fractional distillation of the condensate yielded an aldehyde fraction boiling at 90-110°. This was analyzed for ethoxyacetaldehyde content by the method of Donnally (19). A consistent overall yield of 3% and a yield based on unrecovered alcohol of 8-13% were obtained.

#### D. Preparation of n-Propoxyacetaldehyde

Glycerol alpha-monochlorohydrin was prepared according to the method of Conant and Quayle (14) with a yield of 65% of redistilled product boiling at 115-18°/15 mm.

Three hundred and fifty-three grams of glycerol alpha-monochlorohydrin was slowly added to 75 grams of sodium dissolved in 700 ml. of hot n-propyl alcohol. A vigorous reaction ensued and a precipitate of sodium chloride formed. After reflux for an hour, the mixture was filtered by suction, the precipitate washed with methanol, and the combined filtrates distilled in vacuo to yield 177 grams of glycerol alpha-mono-n-propyl ether boiling at 109-14°/9 mm. This represented a yield of 41%.

Lead tetraacetate was prepared by the method of Bailar (6) and was used to prepare n-propoxyacetaldehyde according to the method of Hatch and Nesbitt (30).

Four hundred and forty-three grams (1 mole) of lead tetraacetate was made into a slurry with 800 ml. of benzene and gradually treated at 20-30° with 134 grams (1 mole) of glycerol alpha-mono-n-propyl ether. The reaction mixture was stirred continuously during the

addition of alcohol and for an hour afterward. The mixture was filtered by suction and the filtrate washed with saturated aqueous sodium chloride solution. Vacuum fractionation of the filtrate yielded 74 grams of crude product boiling at 60-80°/105 mm.

E. Attempted Preparation of n-Butoxyacetaldehyde

1. By catalytic dehydrogenation. Vapors of n-butoxyethanol were passed over copper at 300° (43) and atmospheric pressure but gave only traces of the desired aldehyde plus a large amount of high-boiling residue.

2. By hydrolysis of n-butoxyacetaldehyde diethyl acetal. Bromoacetal was refluxed with sodium n-butoxide to yield n-butoxyacetaldehyde diethyl acetal. This product was refluxed with dilute aqueous acid and the resulting solution distilled, but no aldehyde fraction was obtained.

3. By oxidation of n-butoxyethanol. n-Butoxyethanol was oxidized with potassium dichromate and sulfuric acid according to the method of Hurd and Abernathy (32) but fractional distillation of the crude distillate produced no n-butoxyacetaldehyde.

F. Preparation of Succinaldehyde

The method of Keagle and Hartung (35) was followed. One liter of denatured ethanol (should have been anhydrous), 107 grams of freshly distilled pyrrole, and 225 grams of hydroxylamine hydrochloride were stirred together and heated to reflux temperature. As soon as solution was complete, 170 grams of anhydrous sodium carbonate was added. The resulting suspension was refluxed for 24 hours. At the end of this time, the mixture was filtered and the filtrate evaporated in vacuo on the steam bath to a brown semi-solid residue. This

residue was dissolved in hot water, treated with charcoal, and placed in the icebox for crystallization. Fifteen grams of yellow crystals of succinaldehyde dioxime were obtained. This represented a yield of 8%.

Eleven and six-tenths grams of the dioxime was dissolved in 108 ml. of 10% sulfuric acid and the solution cooled to 0°. Fourteen grams of solid sodium nitrite was added in small portions to the solution. When all the sodium nitrite had been added, the mixture was allowed to come to room temperature and distilled to give a water solution of the desired aldehyde. According to Keagle and Hartung, the yield should have been approximately 90% or 7.7 grams.

#### G. Preparation of Glutaraldehyde

The method of Cope, Dryden, Overberger and Addieco (15) was followed. To 174 grams of pyridine and one liter of absolute methanol was added 51 grams of sodium in about 5-gram pieces. The resulting solution was cooled to 0° and a slurry of 154 grams of hydroxylamine hydrochloride in 140 ml. of water and 140 ml. of ethanol was added, immediately followed by 140 ml. of concentrated hydrochloric acid in 275 ml. of 95% ethanol. After refluxing for 2 hours, the mixture was filtered and the filtrate evaporated to 300 ml. Upon cooling, a white solid separated; this was dissolved by adding 154 grams of sodium hydroxide in 440 ml. of water. After ether extraction of the solution, 600 ml. of dilute hydrochloric acid (1:1) was added with formation of a flocculent white precipitate. After cooling the mixture to 10°, the precipitate was isolated by filtration, washed, and dried. Sixty-five grams (a yield of 50% based on the sodium used) of glutaraldehyde dioxime was obtained.



Sixty-five grams of the dioxime was dissolved in 350 ml. of 10% hydrochloric acid and the solution cooled to  $-10^{\circ}$ . A solution of 69.4 grams of sodium nitrite in 100 ml. of water was slowly added to the acid solution, the temperature being kept below  $-5^{\circ}$ . The reaction mixture was treated with sodium carbonate until neutral. The resulting solution was filtered and according to Cope and coauthors, the yield of glutaraldehyde should have been approximately 90% or 48 grams.

## II. PREPARATION OF POLYHYDROXYMETHYLATED COMPOUNDS

### A. Preparation of 2-Methoxy-2-hydroxymethyl-1,3-propanediol

One hundred and thirty-five grams (4.5 moles) of formaldehyde (as 37% formalin), 108 grams (1.5 moles) of methoxyacetaldehyde (the 88-95 $^{\circ}$  fraction obtained from catalytically dehydrogenating methoxyethanol — see Section I-B), 42 grams (0.75 moles) of calcium oxide, and 1400 ml. of water were stirred together for 30 hours, the temperature being kept below  $40^{\circ}$  at all times. At the end of this time the aldehyde content of the mixture was negligible as determined by the titration method of Donnally (19). The solution was neutralized with dilute sulfuric acid and filtered by suction, using Super-Cel as a filter aid. Vacuum evaporation of the filtrate on the steam bath yielded a viscous, dark brown syrup. This syrup was dissolved in an equal volume of hot methanol and diluted with acetone until no further precipitation was noted. The mixture was filtered, using Super-Cel as a filter aid, and the filtrate evaporated in vacuo on the steam bath.

The precipitate obtained by acetone dilution of the methanol solution was a light brown mass turning to a black tar on contact with the air and was found to contain a large amount of calcium salts. It was assumed to be calcium formate, calcium sulfate, and some

polymeric, sugar-like impurities which were insoluble in acetone. It was discarded.

The viscous syrup resulting from evaporation of the filtrate was dissolved in a small amount of water, and extracted twice with ether to remove the yellow color present. Vacuum evaporation of the water on the steam bath gave a water-white syrup which, when distilled, yielded 30 grams of colorless syrup boiling at  $168-70^{\circ}/11$  mm. This represented a yield of 15% of  $\text{CH}_3\text{OC}(\text{CH}_2\text{OH})_3$ .

The following physical constants were determined:  $n_D^{27}$  1.4820;  $n_D^{20}$  1.4836;  $d_4^{27}$  1.261.

The syrup crystallized after standing for 3 months to a white solid which melted at  $69.2-69.5^{\circ}$  (corr.) after recrystallization from 2-ethoxyethanol.

The solid was soluble in cold water, pyridine, methanol, ethanol, and acetone, insoluble in cold chloroform, and slightly soluble in hot chloroform.

#### B. Preparation of 2-Ethoxy-2-hydroxymethyl-1,3-propanediol

Seventy-five grams (2.5 moles) of formaldehyde (as 37% formalin), 74 grams (0.82 moles) of ethoxyacetaldehyde (the  $90-110^{\circ}$  fraction obtained from catalytically dehydrogenating ethoxyethanol — see Section I-C), 23 grams (0.41 moles) of calcium oxide, and one liter of water were stirred together for 16 hours at temperatures below  $45^{\circ}$ . At the end of this time, the solution was yellow and showed little aldehyde remaining, as determined by the method of Donnally (19). The solution was converted to purified syrup and vacuum-distilled just as in the case of the methoxy compound (see Section II-A). It yielded 36 grams of colorless syrup boiling at  $181^{\circ}/11$  mm. This represented a yield of 24% of  $\text{C}_2\text{H}_5\text{OC}(\text{CH}_2\text{OH})_3$ . The syrup immediately

set to a white crystalline solid which was recrystallized from chloroform; it then melted at 80.5-81.0°(corr.).

The solid was soluble in cold water, pyridine, methanol, ethanol and acetone.

C. Preparation of 2-n-Propoxy-2-hydroxymethyl-1,3-propanediol

Twenty-four grams (0.2 moles) of formaldehyde (as 37% formalin), 30 grams (0.3 moles) of n-propoxyacetaldehyde (as the crude distillate obtained from the lead tetraacetate oxidation of glycerol alpha-mone-n-propyl ether, boiling at 60-80°/105 mm. — see Section I-D), 8 grams (0.15 moles) of calcium oxide, and 300 ml. of water were stirred together for 7 hours at temperatures below 35°. At the end of this time, titration showed negligible amounts of aldehyde present. The solution was converted to syrup as before (see Section II-A); two distillations yielded 5 grams of light yellow syrup boiling at 173-5°/11 mm. This represented a yield of 10% of n-C<sub>3</sub>H<sub>7</sub>OC(CH<sub>2</sub>OH)<sub>3</sub>.

The following physical constants were determined:  $n_D^{27}$  1.4698;  
 $d_4^{27}$  1.145.

D. Reaction of Succinaldehyde with Aqueous Formaldehyde in the Presence of Calcium Hydroxide

Sixteen grams (0.53 moles) of formaldehyde (as 37% formalin), 7.7 grams (0.09 moles) of succinaldehyde (as the crude aqueous distillate obtained from hydrolyzing the dioxime — see Section I-F), and 5 grams (0.09 moles) of calcium oxide were stirred together for 36 hours at temperatures below 35°. The mixture was neutralized with sulfuric acid, filtered, and the filtrate evaporated in vacuo on the steam bath to yield a small amount of dark brown, very viscous syrup. The syrup was dissolved in hot methanol, filtered, and treated with

acetone until no further precipitation was noted. Filtration and evaporation of the filtrate gave no product. The precipitate turned to a black tar on exposure to the air and contained a large percentage of calcium salts. No product could be isolated from it.

E. Reaction of Glutaraldehyde with Aqueous Formaldehyde in the Presence of Calcium Hydroxide

Eighty-six grams (2.9 moles) of formaldehyde (as 37% formalin), 48 grams (0.48 moles) of glutaraldehyde (as the crude, undistilled solution obtained from hydrolyzing the dioxime -- see Section I-C), 28 grams (0.5 moles) of calcium oxide, and 700 ml. of water were stirred together for 5 hours at temperatures below 35°, neutralized with sulfuric acid, filtered, and evaporated in vacuo on the steam bath. A dark brown syrup was obtained which was extracted repeatedly with hot ethanol until only a white precipitate of inorganic salts remained. The ethanol solution was filtered and evaporated in vacuo to a small volume. A large excess of acetone was added to the remaining alcoholic solution. A brown syrup oiled out leaving a light yellow acetone-ethanol solution. The brown syrup contained a large amount of inorganic salts and did not crystallize within a month. The acetone-ethanol solution was evaporated in vacuo to yield a light yellow, viscous syrup which did not crystallize after standing for a month.

F. Attempted Reaction of Campher with Formaldehyde in the Presence of Alcoholic Potassium Hydroxide

Forty-five grams (1.5 moles) of formaldehyde (as 37% formalin), 75 grams (0.5 moles) of campher, and 28 grams (0.5 moles) of potassium hydroxide dissolved in 200 ml. of 95% ethanol were stirred together

for 8 hours at room temperature, refluxed for an additional 12 hours, treated with another 28 grams of potassium hydroxide and refluxed for another 4 hours. The mixture was neutralized with sulfuric acid, filtered, and evaporated in vacuo on the steam bath. The brown residue was extracted with ether, leaving a residue of potassium sulfate and potassium formate. Upon evaporation of the ether, all that remained was camphor.

G. Reaction of Citronellal with Formaldehyde in the Presence of Aqueous Calcium Hydroxide

Seventy-two grams (2.4 moles) of formaldehyde (as 37% formalin), 123 grams (0.8 moles) of citronellal, 25 grams (0.4 moles) of calcium oxide, and 500 ml. of water were vigorously stirred together for 5 hours at room temperature and then heated on the steam bath for 15 minutes. The two-phase mixture was neutralized with sulfuric acid, filtered, and separated into the two layers. The aqueous layer when evaporated in vacuo on the steam bath yielded a brown tar. The organic layer was washed with water and distilled in vacuo. Five milliliters of material distilling at 180-250°/10 mm. and a large amount of citronellal and citronellol were obtained. The high-boiling distillate did not deposit crystals on standing for a month.

H. Reaction of Chloroacetaldehyde with Aqueous Formaldehyde in the Presence of Calcium Hydroxide

Ninety grams (3 moles) of formaldehyde (as 37% formalin), and 79 grams (1 mole) of chloroacetaldehyde (as 40% aqueous solution) were stirred together with 400 ml. of water. Twenty-eight grams (0.5 moles) of calcium oxide was added to the solution in small portions over an hour. At the end of 6 hours, the solution was neutralized with sulfuric

acid, filtered, and evaporated in vacuo on the steam bath. The viscous yellow syrup obtained was dissolved in hot methanol and filtered. Upon evaporation of the methanol, a viscous light yellow syrup was again obtained. When vacuum distillation was attempted, charring and frothing occurred. Therefore, the syrup was placed in the icebox for crystallization. It did not crystallize upon standing within one month although a definite cloudiness was noted.

I. Preparation of 2,2,5,5-Tetrakis-(hydroxymethyl)-1,3,4,6-hexanetetrol

One hundred and twenty grams (4 moles) of formaldehyde (as 37% formalin), 43 grams (0.5 moles) of biacetyl, 28 grams (0.5 moles) of calcium oxide, and 500 ml. of water were stirred together, the calcium oxide being added in small amounts over a period of about 30 minutes. The yellow color of the biacetyl left immediately and the mixture heated up so much that external cooling was necessary. After 12 hours of stirring at temperatures below 50°, the aldehyde content was negligible and the mixture was neutralized with sulfuric acid and filtered. The filtrate was evaporated in vacuo on the steam bath to a viscous syrup which was dissolved in hot ethanol and filtered.

Upon vacuum evaporation of the alcohol from the filtrate, 134 grams of a clear yellow syrup was obtained. The syrup did not crystallize on standing for a month. However, by preparing a benzylidene derivative from the crude syrup (see Section V), it was shown that a yield of approximately 8% of  $\left[ \text{CHOHC}(\text{CH}_2\text{OH})_3 \right]_2$  was obtained.

J. Preparation of 2-Phenyl-2-hydroxymethyl-1,3-propanediol

Ninety grams (3 moles) of formaldehyde (as 37% formalin), 120 grams (1 mole) of phenylacetaldehyde, 28 grams (0.5 moles) of calcium

oxide, and 800 ml. of water were vigorously stirred at temperatures below  $40^{\circ}$  for 2 hours. The phenylacetaldehyde did not dissolve to any great extent in the solution during the reaction. At the end of 2 hours only traces of aldehyde were found in the reaction mixture. The mixture was neutralized with sulfuric acid, filtered, and the precipitate washed with ether. The ether solution was combined with the original filtrate and the two were evaporated in vacuo on the steam bath. The brown syrup obtained was distilled twice in vacuo to yield 8 grams of light yellow liquid boiling at  $208-12^{\circ}/10$  mm. This represented a yield of 5% of  $C_6H_5C(CH_2OH)_3$ .

Over a period of two days, the liquid crystallized to a yellow waxy solid. Recrystallization from chloroform gave large white plates melting at  $84.5-85.5^{\circ}$ (corr.).

K. Preparation of 2-n-hydroxymethyl-1,3-propanediol

Ninety grams (3 moles) of formaldehyde (as 37% formalin), 100 grams (1 mole) of hexanal, and 500 ml. of water were stirred vigorously together. Twenty-eight grams (0.5 moles) of calcium oxide was added over a period of 15 minutes and the reaction mixture externally cooled to prevent the reaction temperature from exceeding  $50^{\circ}$ . The hexanal did not entirely dissolve in the water but emulsified sufficiently to react. At the end of two hours, all but traces of aldehyde were gone. The mixture was neutralized with sulfuric acid, filtered, and the two layers of the filtrate were separated. The water layer on vacuum evaporation yielded only a brown tar with calcium salts mixed with it. The organic layer was washed three times with water and distilled twice in vacuo to yield 28 grams of a light yellow, viscous liquid boiling at  $173^{\circ}/12$  mm. This represented a yield of 17% of  $C_4H_9C(CH_2OH)_3$ . It immediately crystallized to a



yellow solid. Upon recrystallization from acetonitrile, rectangular white needles were obtained which melted at  $63-4^{\circ}$ (corr.).

The solid was soluble in cold methanol, ethanol, chloroform, acetone, pyridine, and ether, slightly soluble in cold water, insoluble in cold benzene, and soluble in hot benzene.

L. Preparation of 2-n-Hexyl-2-hydroxymethyl-1,3-propanediol

Twenty-three grams (0.75 moles) of formaldehyde (as 37% formalin), 32 grams (0.25 moles) of octanal, 7 grams (0.13 moles) of calcium oxide, and 200 ml. of water were stirred together vigorously. Five milliliters of 2% Aerosol OT solution were added as an emulsifying agent. The mixture was warmed to  $50^{\circ}$  on the steam bath and held at that temperature for 2 hours, when titration showed only traces of aldehyde present. The mixture was treated just as for the *n*-butyl homolog (see Section II-K). It thus yielded 3 grams of a light yellow, viscous liquid boiling at  $175-80^{\circ}/10$  mm. This represented a yield of 7% of  $C_6H_{13}C(CH_2OH)_3$ . The liquid gradually crystallized to a yellow solid which, when recrystallized from benzene, yielded tiny white needles melting at  $68.0-68.8^{\circ}$ (corr.).

M. Preparation of 2-n-Octyl-2-hydroxymethyl-1,3-propanediol

Forty-five grams (1.5 moles) of formaldehyde (as 37% formalin), 75 grams (0.5 moles) of decanal, 14 grams (0.25 moles) of calcium oxide, and 200 ml. of water were stirred together vigorously below  $50^{\circ}$ . Five milliliters of 2% Aerosol OT solution were added as an emulsifying agent. At the end of 4 hours only traces of aldehyde were found present. The mixture was converted as usual (see Section II-K) to 6 grams of light yellow, viscous liquid boiling at  $190-200^{\circ}/10$  mm. This represented a yield of 6% of  $C_8H_{17}C(CH_2OH)_3$ . The liquid



gradually crystallized to a yellow solid which was recrystallized from benzene to yield tiny white needles melting at 72.0-73.0°(corr.).

### III. PREPARATION OF MONOETHYL ETHERS OF TRIMETHYLOL COMPOUNDS

#### A. Preparation of 2-n-Butyl-2-ethoxymethyl-1,3-propanediol

Ninety grams (3 moles) of formaldehyde (as 37% formalin), 100 grams (1 mole) of hexanal, and 400 ml. of ethanol were stirred together and a solution of 56 grams (1 mole) of potassium hydroxide in 200 ml. of ethanol and 20 ml. of water was gradually added to the solution. The mixture was externally cooled initially to keep the temperature below 50°. The solution was stirred for 26 hours and by that time almost all aldehyde had reacted. The solution was neutralized with sulfuric acid, filtered, and the filtrate evaporated in vacuo on the steam bath. The resulting viscous liquid was washed twice with water and distilled three times in vacuo to obtain two fractions: (a) 10 grams boiling at 137-42°/10 mm. and (b) 26 grams boiling at 161-4°/10 mm. Fraction (b) proved to be 2-n-butyl-2-hydroxymethyl-1,3-propanediol and was added to another portion of the same material (made in Section II-K). Fraction (a) proved to be  $C_4H_9C(CH_2OH)_2CH_2OC_2H_5$ , the monoethyl ether of the higher-boiling fraction (b), in 3% yield.

The following physical constants were determined for fraction (a):  
 $n_D^{23}$  1.4526;  $d_4^{23}$  0.974.

#### B. Preparation of 2-(1,5-Dimethyl-5-hexenyl)-2-ethoxymethyl-1,3-propanediol

Forty-five grams (1.5 moles) of formaldehyde (as 37% formalin), 77 grams (0.5 moles) of citronellal, and 200 ml. of ethanol were stirred together vigorously. Twenty-eight grams (0.5 moles) of

potassium hydroxide dissolved in 100 ml. of ethanol and 10 ml. of water was gradually added to the mixture. The solution was stirred for 27 hours at room temperature, refluxed for 4 hours, treated with 5 grams of potassium hydroxide to make the solution basic again and refluxed for an additional 30 minutes. At this time, the aldehyde content was found to be negligible. The solution was neutralized with sulfuric acid, filtered, and the filtrate evaporated in vacuo on the steam bath. The resultant two-layer liquid residue was separated into a water layer which was discarded and an organic layer which was washed three times with water and distilled twice in vacuo to obtain two fractions:

(a) 15 grams of light yellow, viscous liquid boiling at  $161-4^{\circ}/8$  mm. and (b) 5 grams of yellow syrup boiling at  $173-210^{\circ}/8$  mm.

Fraction (b) deposited 100 milligrams of crystals after standing for a month. These crystals were soluble in cold acetone, methanol, ethanol, ether, pyridine and chloroform and insoluble in hot water. Recrystallization from benzene gave tiny needles which melted at  $55.5-56.0^{\circ}$ (corr.). This compound was almost certainly 2-(1,5-dimethyl-5-hexenyl)-2-hydroxymethyl-1,3-propanediol, but only enough material was available for determination of carbon and hydrogen.

Fraction (a) represented a yield of 16% of  $C_8H_{15}C(CH_2OH)_2CH_2OC_2H_5$ . The following physical constants were determined for this fraction:  
 $n_D^{23}$  1.4748;  $d_4^{23}$  0.973.

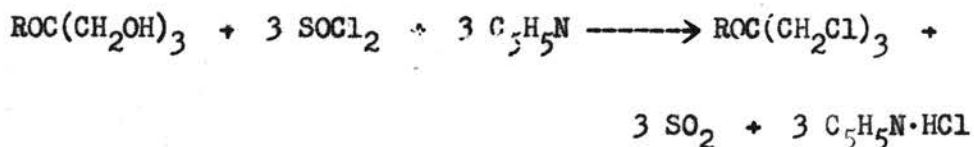
C. Preparation of 2-n-Octyl-2-ethoxymethyl-1,3-propanediol

Twenty-six grams (0.9 moles) of formaldehyde (as 37% formalin), 45 grams (0.3 moles) of decanal, 800 ml. of ethanol, and 500 ml. of water were stirred together. Seventeen grams (0.3 moles) of potassium hydroxide dissolved in 100 ml. of ethanol and 10 ml. of water

was added gradually over a period of 30 minutes. The mixture was stirred for 40 hours at room temperature at the end of which time the aldehyde content was negligible. The mixture was neutralized with sulfuric acid, filtered, and the filtrate evaporated in vacuo on the steam bath until the volume was about 500 ml. The two layers present were separated and further evaporated in vacuo on the steam bath. The water layer yielded only black tar and inorganic salts. The organic layer was evaporated in vacuo until all water had been removed. When distilled twice in vacuo, it gave 5 grams of light yellow liquid boiling at 182-5°/10 mm. This represented a yield of 7% of  $C_8H_{17}C(CH_2OH)_2CH_2OC_2H_5$ .

The following physical constants were determined:  $n_D^{23}$  1.4562;  
 $d_{40}^{23}$  0.935.

IV. PREPARATION OF TRICHLORO DERIVATIVES OF 2-METHOXY-, 2-ETHOXY-, AND 2-n-PROPOXY-2-HYDROXYMETHYL-1,3-PROPANEDIOL



The method used was that of Mooradian and Cloke (43). According to these authors, one mole of trimethylol compound was dissolved in 3 moles of pyridine, the solution cooled in an ice bath, and 3 moles of thionyl chloride slowly added to the solution with vigorous mechanical stirring. The mixture was heated under reflux until vapors of sulfur dioxide ceased to come off, cooled, and treated with a volume of water equal to the volume of solution. The mixture was extracted with ether; upon evaporation of the ether, the desired compound was obtained.

By the above method, a solid trichloro derivative of the 2-methoxy compound was prepared which, after recrystallization from alcohol, comprised white needles melting at  $59.0-59.2^{\circ}$  (corr.). A relatively large portion of high-boiling chlorine-containing liquid was also obtained which was probably a mixture of the mono- and di-chlorinated 2-methoxy compounds.

Attempted preparation of trichloro derivatives of the 2-ethoxy and 2-n-propoxy compounds by the above method yielded only liquid products containing chlorine. These were probably mixtures of the mono- and di-chlorinated 2-ethoxy and 2-n-propoxy compounds.

#### V. PREPARATION OF BENZYLIDENE DERIVATIVES FROM THE NON-CRYSTALLIZING SYRUPS OBTAINED FROM CHLOROACETALDEHYDE, GLUTARALDEHYDE AND BIACETYL

The method used was that of Hann, Ness, Hudson (29). Ten grams of syrup was dissolved in 20 grams of concentrated hydrochloric acid, the solution cooled to  $0^{\circ}$ , and 10 ml. of benzaldehyde added. The mixture was placed in the ice box for 24 hours and was shaken occasionally. At the end of this time, the mixture was filtered and the precipitate washed successively with water, alcohol and ether and then recrystallized.

The chloroacetaldehyde and glutaraldehyde syrups gave no precipitate by the above method.

The biacetyl syrup yielded a white powder which was recrystallized from 2-ethoxyethanol and, after the last recrystallization, was washed with ether to yield white needles which melted at  $172.5-173.5^{\circ}$  (corr.). This ultimately proved to be tribenzylidene 2,2,5,5-tetrakis-(hydroxymethyl)-1,3,4,6-hexanetetrol.

## VI. MISCELLANEOUS REACTIONS

### A. Hydrolysis of the Benzylidene Derivative

Acid hydrolysis of this derivative was attempted in the hopes of obtaining the pure parent compound but no crystalline product was obtained upon working up the hydrolysis mixture.

## VII. ANALYTICAL METHODS AND RESULTS

Carbon and hydrogen determinations were made by the dry combustion method of Niederl and Niederl (46).

Molecular weights were determined cryoscopically by the method of Daniels, Mathews, and associates (16).

Hydroxyl determinations were made by the method of Siggia (55).

Chlorine determinations were made by the Parr bomb method followed by gravimetric determination as AgCl.

Benzylidene determinations were made by the method of Angyal and Lawler (1).

Table 2

## Analytical Data for New Compounds

Compound	Molecular Wt.		Mol. Refraction		% Carbon		% Hydrogen		% Hydroxyl	
	Theory	Found	Theory	Found	Theory	Found	Theory	Found	Theory	Found
$\text{CH}_3\text{OC}(\text{CH}_2\text{OH})_3$	136.2	134 <sup>a</sup>	31.51	30.80	44.11	43.98	8.89	9.10	37.5	37.7
$\text{C}_2\text{H}_5\text{OC}(\text{CH}_2\text{OH})_3$	150.2	148 <sup>a</sup>	-	-	47.97	47.52	9.39	9.51	34.0	33.7
$\text{C}_3\text{H}_7\text{OC}(\text{CH}_2\text{OH})_3$	164.2	-	40.74	40.02	51.22	50.93	9.83	9.80	31.1	31.1
$\text{C}_4\text{H}_9\text{C}(\text{CH}_2\text{OH})_3$	162.2	158 <sup>a</sup>	-	-	59.26	59.47	11.19	11.41	30.7	30.7
$\text{C}_6\text{H}_{13}\text{C}(\text{CH}_2\text{OH})_3$	190.3	180 <sup>c</sup>	-	-	63.10	63.19	11.65	11.70	26.8	26.8
$\text{C}_8\text{H}_{15}\text{C}(\text{CH}_2\text{OH})_3$	216.3	-	-	-	66.62	66.76	11.18	11.84	-	-
$\text{C}_8\text{H}_{17}\text{C}(\text{CH}_2\text{OH})_3$	218.3	198 <sup>c</sup>	-	-	66.01	66.06	12.00	12.22	23.4	23.2
$\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{OH})_3$	182.2	182 <sup>a</sup>	-	-	65.91	65.77	7.74	7.88	28.0	28.0
$\text{C}_4\text{H}_9\text{C}(\text{CH}_2\text{OH})_2$   $\text{CH}_2\text{OC}_2\text{H}_5$	190.3	265 <sup>b</sup>	53.07	52.83	63.10	61.58	11.65	12.14	17.9	18.5
$\text{C}_8\text{H}_{17}\text{C}(\text{CH}_2\text{OH})_2$   $\text{CH}_2\text{OC}_2\text{H}_5$	246.4	364 <sup>b</sup>	71.55	71.68	68.23	67.54	12.27	12.46	13.8	14.1
$\text{C}_8\text{H}_{15}\text{C}(\text{CH}_2\text{OH})_2$   $\text{CH}_2\text{OC}_2\text{H}_5$	244.3	294 <sup>b</sup>	69.36	70.65	68.82	68.58	11.54	11.19	13.9	14.0

Table 2 (continued)

Tribenzylidene derivative of 2,2,5,5-tetrakis- (hydroxymethyl)- 1,3,4,6-hexane- tetrol, C <sub>31</sub> H <sub>36</sub> O <sub>8</sub>	536.6	-	-	-	69.36	69.47	6.76	6.96	% Benzylidene	
									Theory	Found
									50.4	50.4
									% Chlorine	
									Theory	Found
CH <sub>3</sub> OC(CH <sub>2</sub> Cl) <sub>3</sub>	191.5	-	-	-	-	-	-	-	55.6	56.1

<sup>a</sup>Cryoscopically in water

<sup>b</sup>Cryoscopically in benzene

<sup>c</sup>Cryoscopically in tert.-butyl alcohol

## DISCUSSION

Attempted preparation of n-butoxyacetaldehyde by catalytic dehydrogenation failed apparently, largely because of the high boiling point of the original alcohol. Working at pressures below atmospheric should bring the yields by this method into the useful range.

Apparently acid hydrolysis of n-butoxyacetaldehyde diethyl acetal should have been carried out in an inert atmosphere. All that was obtained when the hydrolysis was attempted in air was the starting material and high-boiling substances.

It is doubtful whether any succinaldehyde or glutaraldehyde was obtained as such by cold nitrous acid hydrolysis of the respective dioximes. The authors of the two articles which were followed in preparing these aldehydes expressed this same doubt, but fortunately the reactions in which they were using the aldehydes were such that the dioximes would serve almost as well as the aldehydes themselves. A good method for the preparation of these two aldehydes is definitely lacking.

Several syrups made in this work, namely, those made from glutaraldehyde, chloroacetaldehyde, and biacetyl, had not crystallized at the time of writing of this thesis. Further work could be done on isolating the various products which are undoubtedly present in the syrups but time was not available for this work. Many of the methods of purifying syrups mentioned earlier (Historical



Section) could be tried and possibly one would be found which would prove successful in the isolation of desired products.

Campher in previous work (40) was shown to be unreactive in the Tollens condensation when the synthesis was performed in aqueous calcium hydroxide. Apparently the internal bridge deactivates the hydrogens in the alpha position to the keto group almost completely since it has now been shown that the reaction does not proceed even in hot alcoholic potassium hydroxide. Both 2- and 4-methylcyclohexanone yielded the fully hydroxymethylated and reduced product (32). It would be interesting to see if 2-methyl-4-isopropylcyclohexanone would give 2,6,6-tris-(hydroxymethyl)-2-methyl-4-isopropylcyclohexanol.

Citronellal was found to be unreactive with formaldehyde in aqueous calcium hydroxide but did react to give the monoethyl ether of the fully hydroxymethylated compound and a tiny yield of the trimethylol compound itself in alcoholic potassium hydroxide. Its unreactivity in aqueous solution is apparently due to its water-insolubility. By the use of Aerosol OT, octanal and decanal, both water-insoluble, did react. Emulsification may be advantageous in many Tollens syntheses in which the aldehyde or ketone used is insoluble in water, including the synthesis based on citronellal.

The yields on the polyhydroxy compounds obtained in this work do not by any means represent the maximum obtainable. Yield data were included only as a matter of course. In any new synthesis, much product is lost along the experimental path owing to unfamiliarity with the process. No doubt yields in most cases could be made to correspond to those obtained in the synthesis of pentaerythritol

(60-80%) if work were directed specifically along that line.

All molecular weights determined cryoscopically in benzene were consistently too high. Since the compounds for which the molecular weights were being determined would hardly be expected to dissolve in such a solvent as benzene without a great deal of hydrogen bonding among the hydroxyl groups of the alcohols, these high values can probably be attributed to this phenomenon.

From this and previous work it appears the Tollens condensation gives the predicted products for aldehydes of the type  $\gamma\text{CH}_2\text{CHO}$  and  $\gamma_2\text{CHCHO}$  almost without exception. Ketones, in general, give Tollens products with greater difficulty than aldehydes, especially when the ketone is partially aromatic in nature. This is probably due to steric hindrance and to the lesser reactivity of ketones, in general, as compared to aldehydes.

A whole new line of syntheses has apparently been opened by the discovery that Tollens condensations carried out in ethanol proceed like the synthesis of pentaerythritol in methanol (63). It should be possible to make a whole series of monoalkyl and monoaryl ethers of polyhydroxymethyl compounds simply by varying the alcohol in which the synthesis is carried out.

If yields of the octahydroxy compound made from biacetyl and formaldehyde could be raised to a practical level, it would appear this compound would offer pentaerythritol competition in such fields as explosives, resins, drying oils, and insecticides.

If trichloro compounds could be made from the 2-alkoxy-2-hydroxymethyl-1,3-propanediols, they might easily become effective insecticides since they contain an ether linkage which might make

the compounds easily absorbed into the bodies of insects and consequently allow the halogen portion of the molecule to enter the insect's body. In fact, polyhalo compounds of any of the other newly-synthesized compounds might also prove useful in this field.

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## APPENDIX

## Physical Constants of Known Products of Tollens Condensations

Compound	Melting Point and Recrystallizing Solvent	Refer- ence	Boiling Point	Refer- ence
$C(CH_2OH)_4$	260.5°/water	59		
$CH_3C(CH_2OH)_3$	198.0-198.2°/ ethanol	18		
	199°/ethanol	36		
	200.5°	56		
$C_2H_5C(CH_2OH)_3$	58.8-59.0°/ acetone-ether	17		
$(CH_3)_2CHC(CH_2OH)_3$	83.0-83.5°/ether	41	156-8°/15 mm.	38
	82.0-82.1°/ether	18	170-5°/6 mm.	18
$(CH_3)_2C(CH_2OH)_2$	127°/benzene	34	206°/747 mm.	34
	127-8°/trichloro- ethylene	61	125-30°/15 mm.	34
	129°/benzene	2	203-4°/738 mm.	64
	130°	54		
	126-8°/benzene- petroleum ether	65		
$(C_2H_5)_2C(CH_2OH)_2$	61.0-61.6°	54	131°/13 mm.	54
$(iso-C_4H_9)_2C(CH_2OH)_2$	75-6°	26	150-5°/15 mm.	26
$\begin{array}{l} CH_3 \\ \diagdown \\ C(CH_2OH)_2 \\ \diagup \\ C_2H_5 \end{array}$	42°	45	113°/12 mm.	45
$\begin{array}{l} CH_3 \\ \diagdown \\ C(CH_2OH)_2 \\ \diagup \\ n-C_3H_7 \end{array}$	44°	23	230°/753 mm. 121°/10 mm.	23 23
$\begin{array}{l} C_2H_5 \\ \diagdown \\ C(CH_2OH)_2 \\ \diagup \\ n-C_4H_9 \end{array}$	41.4-41.9°	54	152°/10 mm.	54
$n-C_5H_{11}C(CH_2OH)_3$	59°	21	190°/12 mm.	21
$(C_6H_5)_2C(CH_2OH)_2$	102-3°/benzene- pentene	13		



$\text{C}_6\text{H}_5\text{C}(\text{CH}_2\text{OH})_2$ $\text{CH}_3$	75°/ethanol	23	295-6°/753 mm.	23
			165°/12 mm.	23
$\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{CH}_2\text{OH})_3$	76°/benzene	24		
$\text{CH}_3\text{OCH}_2\text{C}(\text{CH}_2\text{OH})_3$	70°/chloroform	62		
	72°	47		
2,5-endomethylene- 3-cyclohexene-1,1- dimethanol			142-55°/2-3 mm.	11
2,5-endomethylene 3-cyclohexene-6- methyl-1,1-dimeth- anol	121°/nitromethane 69-71°/petroleum. ether	11 11	135-55°/1-3 mm.	11
3-cyclohexene-1,1- dimethanol	92.0°	54	128°/3 mm.	54
6-methyl-3-cyclo- hexene-1,1-dimeth- anol	45° 45°	25 54		
3,4,6-trimethyl-3- cyclohexene-1,1- dimethanol	86.5°	25		
3,4-dimethyl-6- phenyl-3-cyclohex- ene-1,1-dimethanol	131.5°	25		
tetrahydro-3,3,5,5- tetrakis-(hydroxy- methyl)-4-pyranol	155.6°	2		
3-chloro-3-hydroxy- methyl-4-hydroxy- 2-butanone	61-2°/heptane	33		
3-methyl-3-hydroxy- methyl-4-hydroxy- 2-butanone	60°/chloroform- ligroin	44	138°/16 mm.	44
2,2,4-tris-(hydrox- ymethyl)-3-penta- none	91°/chloroform	44		
2,2,5,5-tetrakis- (hydroxymethyl)- cyclopentanone	143°/ethanol	40		

2,2,6,6-tetrakis- (hydroxymethyl)- cyclohexanol	131°/ethanol	40
2,2,6,6-tetrakis- (hydroxymethyl)- 4-methylcyclo- hexanol	150°/ethanol	40
2,6,6-tris-(hydrox- ymethyl)-2-methyl- cyclohexanol	100°/ethanol	40

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Scope and Method of Study: The original purpose of this investigation was to determine whether aldehydes of the type  $\text{ROCH}_2\text{CHO}$  would undergo the Tollens condensation. This condensation should lead to products of the type  $\text{ROC}(\text{CH}_2\text{OH})_3$ . The investigation was later enlarged to include several aldehydes of the type  $\text{RCH}_2\text{CHO}$ . Attempts were made to perform the Tollens condensation with succinaldehyde, glutaraldehyde, chloroacetaldehyde, camphor and biacetyl. Derivatives of some of the final products were prepared.

Findings and Conclusions: Aldehydes of the type  $\text{ROCH}_2\text{CHO}$  gave the expected new products  $\text{ROC}(\text{CH}_2\text{OH})_3$ , where R represents methyl, ethyl, and n-propyl. Aldehydes of the type  $\text{RCH}_2\text{CHO}$  gave  $\text{RC}(\text{CH}_2\text{OH})_3$  when the reaction was carried out in aqueous media; this was newly accomplished for R = phenyl, n-butyl, n-hexyl, and n-octyl. The addition of an emulsifying agent to the solution when large, water-insoluble aldehydes were used proved beneficial in reaction. Citronellal failed to react in an aqueous medium. When the reaction was carried out in ethanol, compounds of the type  $(\text{RC}(\text{CH}_2\text{OH})_2\text{CH}_2\text{OC}_2\text{H}_5)$  were obtained for cases in which R = n-butyl, n-octyl, and 1,5-dimethyl-5-hexenyl (from citronellal). Tris-(hydroxymethyl) compounds were isolated in good yield for the case where R was n-butyl and in tiny amount for the case where R was 1,5-dimethyl-5-hexenyl. These results confirm the finding of a previous investigator that pentaerythritol monomethyl ether is formed from acetaldehyde and formaldehyde in methanol. A new route to monoalkyl and monoaryl ethers of polyhydroxymethylated compounds is apparently available. Camphor failed to react to form a hydroxymethylated compound in hot ethanolic potassium hydroxide solution. Uncharacterized syrups were obtained when succinaldehyde, glutaraldehyde, and chloroacetaldehyde were condensed with formaldehyde in aqueous media. Biacetyl reacted with formaldehyde in aqueous medium to give a syrup which had just begun to yield a solid product as this thesis was completed. By preparing a benzylidene derivative from the crude syrup, it was possible to demonstrate that the fully hydroxymethylated product, 2,2,5,5-tetrakis-(hydroxymethyl)-1,3,4,6-hexanetetrol, was present. A trichloro derivative,  $\text{CH}_3\text{OC}(\text{CH}_2\text{Cl})_3$ , was prepared from  $\text{CH}_3\text{OC}(\text{CH}_2\text{OH})_3$ . Chloro derivatives of this type may have insecticidal properties.