[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Hydrogenolysis of Succinates and Glutarates

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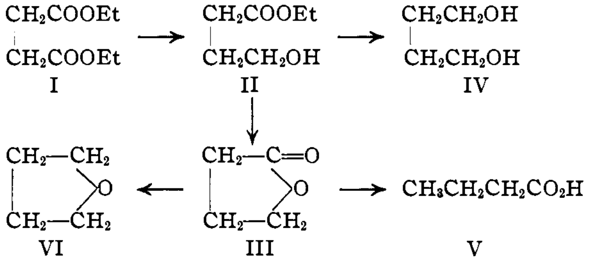
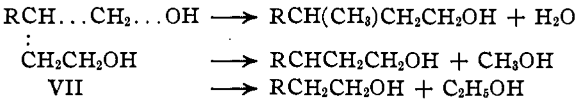
The marked labilizing effect of carbinol and carbethoxy groups in the 3 position upon the cleavage of carbon to oxygen linkages has been observed in the hydrogenolysis of trimethylene glycol, ethyl β-hydroxybutyrate, malonic ester, etc., to the corresponding monohydric alcohols.[1] The effect of an oxygenated substituent in the 4 or 5 position is less marked than in the 3 position, but may be of considerable importance from a preparational standpoint. In order to illuminate this situation, a study has been made of the hydrogenolysis of various substituted succinates and glutarates.

The hydrogenolysis of diethyl succinate I results in the formation of ethyl γ-hydroxybutyrate II, butyrolactone III, tetramethylene glycol IV, butyric acid V and probably of tetrahydrofuran VI.



Cleavage in a substituted succinate may also occur at one of the O to C or at either of two of the C to C linkages as in VIII to X.[2]



$$\begin{array}{lll} \mathrm{RCH\ldots CH_2\ldots OH} & \longrightarrow \mathrm{RCH(CH_3)CH_2CH_2OH + H_2O} & \mathrm{VIII} \\ \quad\vdots & & \\ \mathrm{CH_2CH_2OH} & \longrightarrow \mathrm{RCHCH_2CH_2OH + CH_3OH} & \mathrm{IX} \\ \quad\mathrm{VII} & \longrightarrow \mathrm{RCH_2CH_2OH + C_2H_5OH} & \mathrm{X} \end{array}$$

Fortunately, the major products obtained from a given succinate under the optimum conditions are few in number, as will be evident from the summary of the effect of experimental conditions and structure upon the type and ratio of products.

The successful preparation of tetramethylene glycol from diethyl succinate demands that the reaction be carried out rapidly. Such a rapid hydrogenolysis occurred when 523 g. of pure ester and hydrogen under a pressure of 300 atm. were allowed to react at 250° over 30 g. of copper-chromium oxide. The reaction was almost complete after one hour and

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(1) Connor and Adkins, THIS JOURNAL, **54**, 4678 (1932).

(2) It is not known whether it is the ester or the glycol which suffers C to C cleavage. For convenience the cleavage will be represented as occurring to the glycol. The labile linkages are represented by dotted lines in the formulas.

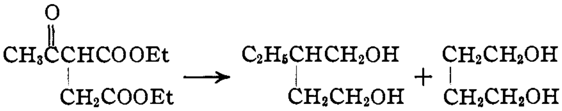
entirely so after two hours. The yield of glycol (200 g.) was 74% of the theoretical accompanied by 44 g. of butyrolactone. Lower pressure of hydrogen or ratio of catalyst to ester resulted in decreasing the yield of glycol because of the deleterious effect of acid and water, formed during the hydrogenolysis, upon the activity of the catalyst. The more rapid the reaction, the lower the concentration of these products and the shorter the period during which the catalyst may deteriorate.

The chief product obtained from succinic anhydride was butyrolactone (31%) while butyric and succinic acids were also formed. It is probable but not certain that tetrahydrofuran was also among the products of reaction. The catalyst does not have a long life in the presence of water, anhydrides and acids, so that it is difficult to obtain complete reaction of the anhydride.

A hydrogenolysis of diethyl α-methylsuccinate under conditions similar to those used for diethyl succinate also gave a good yield (72%) of the corresponding 2-methylbutanediol-1,4. But under milder conditions, fifteen hours and two applications of catalyst were necessary since it was reduced to the red or inactive form. No glycol was obtained in this latter run but the reaction proceeded to give alcohols corresponding to VIII, IX and X in which R is methyl. Similarly, when diethyl α-isopropylsuccinate was submitted to hydrogenolysis at 300 atmospheres a 30% yield of the corresponding glycol (R is isopropyl in VII) was obtained while the chief product (70%) of a slower hydrogenolysis was isohexyl alcohol corresponding to IX, accompanied by 3,4-dimethylpentanol-1 as in VIII.

The strong influence of a phenyl group in the β position to a hydroxyl in labilizing the carbon to oxygen linkage[3] toward hydrogenolysis has so far rendered futile all attempts to prepare 2-phenylbutanediol-1,4 in yields above 13 to 23% from diethyl α-phenylsuccinate. The chief product (70 to 80%) was 3-phenylbutanol-1 as in VIII, while IX and X occurred to a very small extent, if at all.

In addition to the possibilities indicated in I to X, two glycols were produced from acetyl succinate depending upon whether the acetyl group was eliminated as ethanol by hydrogenolysis or was hydrogenated to an ethyl group. Due to the similarity of their boiling points the glycols were not separated.



$$\begin{array}{l} CH_3\overset{O}{\overset{\|}{C}}CHCOOEt \\ \quad | \\ \quad CH_2COOEt \end{array} \longrightarrow \begin{array}{l} C_2H_5CHCH_2OH \\ \quad | \\ CH_2CH_2OH \end{array} + \begin{array}{l} CH_2CH_2OH \\ | \\ CH_2CH_2OH \end{array}$$

XI

Analysis of the mixture for carbon and hydrogen and the acetyl values indicated that the two glycols were present in similar amounts. A considerable yield of a butyrolactone (29%) was also obtained, but it has not been

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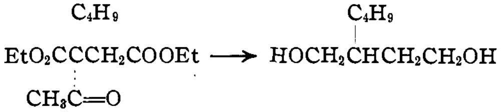
(3) Adkins, Wojcik and Covert, This Journal, 55, 1699 (1933).

established as to whether this compound is an α or β ethyl or an α-β dimethyl butyrolactone.[4]

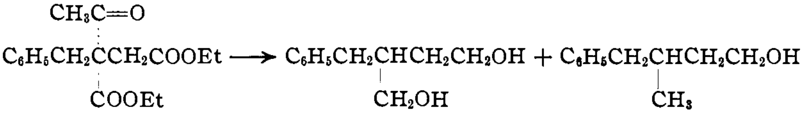
A disubstituted succinate, diethyl α-*n*-butyl α-acetyl succinate, underwent a smooth and rapid hydrogenolysis to give a 79% yield of 2-*n*-butylbutanediol-1,4.



$$\mathrm{EtO_2C\overset{C_4H_9}{\underset{\underset{CH_3C{=}O}{\vdots}}{C}}CH_2COOEt \longrightarrow HOCH_2\overset{\overset{C_4H_9}{|}}{C}HCH_2CH_2OH} \qquad \text{XII}$$

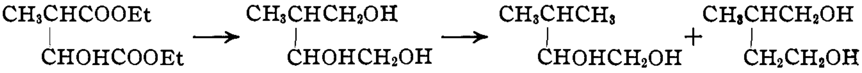
The complete removal of the acetyl group in reaction XII as contrasted with its partial removal in XI is understandable if it is noted that the butylacetylsuccinate is a disubstituted β-keto ester. Such compounds are quantitatively cleaved by hydrogen at the linkage between the carbonyl and the tetrasubstituted carbon atom.[1]

Another disubstituted succinate, diethyl α-benzyl-α-acetyl-succinate, underwent a similar cleavage to give 2-benzylbutanediol-1,4, but the yield was low (35%) and an equal amount of 3-benzylbutanol-1 was formed. This latter product is the result of the cleavage (under the influence of phenyl) of a C to O linkage as in VIII.



$$\mathrm{C_6H_5CH_2\overset{\overset{CH_3C{=}O}{\vdots}}{\underset{\underset{COOEt}{|}}{C}}CH_2COOEt \longrightarrow C_6H_5CH_2\underset{\underset{CH_2OH}{|}}{C}HCH_2CH_2OH + C_6H_5CH_2\underset{\underset{CH_3}{|}}{C}HCH_2CH_2OH} \qquad \text{XIII}$$

The hydrogenolysis of diethyl α-methyl-β-hydroxysuccinate (XIV) resulted in the formation of two isomeric glycols, 3-methylbutanediol-1,2 (XVI), and 2-methylbutanediol 1-4 (XVII).



$$\underset{\text{XIV}}{\begin{array}{l}\mathrm{CH_3CHCOOEt}\\ \quad|\\ \mathrm{\ CHOHCOOEt}\end{array}} \longrightarrow \underset{\text{XV}}{\begin{array}{l}\mathrm{CH_3CHCH_2OH}\\ \quad|\\ \mathrm{\ CHOHCH_2OH}\end{array}} \longrightarrow \underset{\text{XVI}}{\begin{array}{l}\mathrm{CH_3CHCH_3}\\ \quad|\\ \mathrm{\ CHOHCH_2OH}\end{array}} + \underset{\text{XVII}}{\begin{array}{l}\mathrm{CH_3CHCH_2OH}\\ \quad|\\ \mathrm{\ CH_2CH_2OH}\end{array}}$$

The ratio of products was determined by the relative rates of cleavage of the two β-hydroxyl groups in the triol XV, each of which was labilizing the other. The difference between the sum of the yields of glycols (74%) and the theoretical is no doubt accounted for by the cleavage of carbon to carbon linkages as in VIII, IX and X.

The hydrogenation to the glycols of the ethyl esters of unsubstituted acids above succinic presents no difficulties. Pentamethylene, hexamethylene, decamethylene and tetradecamethylene glycols have been prepared in yields above 95% from the esters of the corresponding acids. Even the substitution of a phenyl group on the middle carbon of diethyl glutarate did not have much effect as an 89% yield of $C_6H_5CH(CH_2CH_2OH)_2$ was obtained.

An acetyl group on an α carbon of glutaric ester has the same effect

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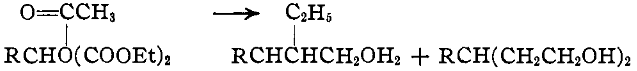
(4) Glycols and alcohols containing the group CH_3CHOH— are possible products from the hydrogenolysis of α-acetyl succinates, glutarates, etc. However, tests by the haloform reaction showed that such alcohols and glycols were not present in the reaction products referred to in this paper.

as in a succinate, that is, two glycols are produced in about equal amounts, each of which contains one more methylene group than the glycols from the succinate in XI. In contrast with this is the behavior of a disubstituted acetoacetic ester, α-acetyl-α-ethyladipic ester, which upon hydrogenation gave a single glycol 2-ethyl-hexanediol-1,6, the acetyl group in the ester having been completely removed by hydrogenolysis.

The α,γ-diacetyl-β-methyl-(or phenyl)-glutarates (XVIII) may be regarded as monosubstituted acetoacetic esters and so might give the two types of cleavage. The C to C cleavage appears to occur only to a slight extent, the main product being 3-methyl-(or phenyl)-2,4-diethyl pentanediol-1,5 resulting from the hydrogenation of the acetyl groups. Connor[1] first observed this reaction and upon the basis of the high yields obtained, and the analysis of the glycols for carbon and hydrogen, it was concluded that the acetyl group had not been split off. The high yields (96 or 97%) of glycols are significant in this connection because if the ethyl groups were not present in the glycols, the yields obtained would be considerably over 100%. However, the analysis for carbon and hydrogen was always somewhat low for the indicated compounds. His experiments were repeated several times, and an intermediate dihydroxy ester prepared and submitted to hydrogenolysis. The results were always the same, *i. e.*, excellent yields of a glycol which analyzed low in carbon and hydrogen. These low analyses are probably due to the presence of a small amount of glycol XX which could not be removed from the two racemic mixtures of glycol XIX by fractionation.



$$\underset{\text{XVIII}}{\begin{array}{l}O{=}CCH_3\\ \quad\;\;|\\ RCHC(COOEt)_2\end{array}} \longrightarrow \underset{\text{XIX}}{\begin{array}{l}\qquad\;\; C_2H_5\\ \qquad\quad |\\ RCHCHCH_2OH_2\end{array}} + \underset{\text{XX}}{RCH(CH_2CH_2OH)_2}$$

Finally four dicarbethoxyglutarates XXI, where R is H, CH_3, C_3H_7 or C_6H_5 (prepared by the condensation of formaldehyde, acetaldehyde, butyraldehyde or benzaldehyde with malonic ester) were submitted to hydrogenolysis. These compounds, which may be regarded as monosubstituted malonic esters, behave as do the simpler monosubstituted malonic esters. That is, the main reaction is the elimination of one of each of the carbethoxy groups of the malonic ester residues with the formation of a glycol XXII. The yield of glycol from three of the esters was 70 to 91%. A small yield (1%) of a solid glycol of type XXIII was obtained when R is phenyl. The β-phenyl and β-propyl dicarbethoxyglutarates in addition to the glycols gave 27 to 30% yields of 3-phenylpropanol-1 and hexanol-1, respectively, by cleavage between the α and β carbons as in XXIV.

$$\underset{\text{XXI}}{RCH(CH(COOEt)_2)_2} \longrightarrow \underset{\text{XXII}}{RCH(CH_2CH_2OH)_2} + \underset{\text{XXIII}}{RCH(CH(CH_3)CH_2OH)_2} + \underset{\text{XXIV}}{R(CH_2)_3OH}$$

The experimental results are summarized in the tables.

TABLE I

EXPERIMENTAL RESULTS[a]

Esters diethyl	Boiling pt. °C.	Mm.	G.	Time, hrs.	Products G.	Products
α-Methylsuccinate[5]	98–99	10	228	1	9	Isoamyl alcohol, 127–129°
					90	2-Methylbutanediol-1,4 126–127° (14 mm.)[13]
α-Methylsuccinate	98-99	10	115	0.7[h]	11	α-Methylbutyrolactone (84–86° (12 mm.)
					40	Diol
α-Isopropylsuccinate[6]	112–114	9	22	3[b]	2.4	Alcohols, 103–138°
					7.9	Isohexyl alcohol 146–151°[14]
α-Isopropylsuccinate	112–114	9	100	6.5	7.3	Alcohols, 123–137°
					8.1	Isohexyl alcohol
					3.2	3,4-Dimethylpentanol-1, 159–162°
					11.8	Unchanged ester
					16.4	2-Isopropylbutanediol-1,4 (119–122°) (3 mm.)
α-Butyl-α-acetylsuccinate[7]	136–138	4	75	1	37.4	2-*n*-Butylbutanediol-1,4, 135–137° (3 mm.)
α-Benzyl-α-acetylsuccinate[7, 15]	165–167	4	40	1	8.4	3-Benzylbutanol-1, 103–107° (3 mm.)
					8.1	2-Benzylbutanediol-1,4, 162–165° (3 mm.)
α,γ-Dicarbethoxyglutarate[8]	193–195	14	166	5	47.2	Pentanediol-1,5, 229–231°[c]
β-Methyl-α,γ-dicarbethoxyglutarate[9]	185–190	6	65	10	18.2	3-Methylpentanediol-1,5, 134–137° (6 mm.)[d]
β-Phenyl-α,γ-dicarbethoxyglutarate[20]	184–186	3	153	7.5	13.8	3-Phenylpropanol-1, 105–107° (5 mm.)
					47.6	3-Phenylpentanediol-1,5, 174–176° (5 mm.)
					1.1	2,4 - Dimethylphenylpentanediol - 1,5, m. p., 115–116°
β-Propyl-α,γ-dicarbethoxyglutarate[9]			40	2	14.2	Alcohols and water, 76–79°
					3.7	*n*-Hexyl alcohol, 146–150°
					8.7	3-Propylpentanediol-1,5, 134–136° (10 mm.)
α,γ-Diacetyl-β-phenylglutarate[10,11]	M151–152		79	8	49	2,4 - Diethyl - 3 - phenylpentanediol - 1,5, 174–179° (2–3 mm.)
Dodecamethylenedicarboxylate[12,e]			202	4	141	Tetradecanediol-1,14, m. p. 85°[e]
α-Keto-β-methylsuccinate[f]	144–146	21	202	14	184	Diethyl α-hydroxy-β-methylsuccinate, 109–113° (5 mm.)
α-Hydroxy-β-methylsuccinate[18]	109–113	5	102	10	53.5	Alcohols and water, 75–88°
					19.3	3-Methylbutanediol-1,2, 81–83° (5 mm.)[16,17]
					13.2	2-Methylbutanediol-1,4, 105–107° (7 mm.)[j]
α-Acetyl-α-ethyladipate[7]			46	3	2.6	Alcohols, 45–90° (4 mm.)
					18.1	2-Ethylpentanediol-1,5
α,γ-Diacetyl-β-phenylglutarate[10,11]	M151–152		35	[g]	34.1	3,5 - Dicarbethoxy - 4 - phenylheptanediol-2,6, m. p. 162–163°
α-Phenylsuccinate[h]	153–155	6	38	3	16.2	3-Phenylbutanol-1, 110–111° (6 mm.)
					3.2	2-Phenylbutanediol-1,4, 162–165° (7 mm.)
α-Acetylsuccinate[7]	142–144	16	144	2	40.2	Alcohols and water, 70–86°
					21.2	A lactone[i] $C_6H_{10}O_2$, 85–87° (5 mm.)[18]
					38.9	Glycols, 113–114° (5 mm.)
β-Phenylglutarate			35	1.5	21.2	3-Phenylpentanediol-1,5, 190–192° (14 mm.)[l]
α-Acetylglutarate	150–153	16	139	11.5	48.3	2-Ethylpentanediol-1,5 and pentanediol-1,5, both 129–130° (7 mm.)[k,19]
Succinic anhydride	M118–119		100	24	28.9	Butyrolactone, 196–200°[m]

Unless specified otherwise, the reactions were at 250° under 200 to 300 atmospheres pressure of hydrogen with approximately 1 part of copper–chromium oxide for 10 parts of ester. [b] 100 atmospheres. [c] The saponification value of the diacetate was 7 to 8 units high indicating the presence of a little of the 2,4-dimethylpentanediol-1,5. [d] The glycol contained enough of the 2,4-dimethyl compound to make the saponification equivalent 12 to 14 units high (see table). [e] The ester was prepared and the glycol isolated by Dr. E. Prill. [f] In 300 ml. of EtOH at 200°. [g] Reaction was complete by the time the temperature reached 150°. [h] At 150 atm. (Covert obtained yields of the glycol as high as 23% by interrupting the hydrogenation when 75% of the ester had reacted with hydrogen). [i] Saponification value for the lactone $C_6H_{10}O_2$: found 113. calcd.114. [j] Both glycols were identified by saponification values of their acetates and by comparison with physical constants previously described.[11] [k] Two applications of catalyst. [l] 150 atm., 50 ml. of EtOH as solvent. [m] There was a considerable amount of very volatile material, tetrahydrofuran (?), butyric acid, succinic acid and water.

TABLE II

ANALYTICAL DATA

Name of compound	Mol. formula	n^{25}_D	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Mol. weight of acetate Calcd.	Mol. weight of acetate Found
3,4-Dimethylpentanol-1	$C_7H_{16}O$	1.4261	72.41	72.27	13.79	13.34	158	161
2-Isopropylbutanediol-1,4	$C_7H_{16}O_2$	1.4535	63.63	63.53	12.12	12.04	...	...
2-*n*-Butylbutanediol-1,4	$C_8H_{16}O_2$	1.4530	65.75	65.66	12.32	12.11	230	234
2-Ethylbutanediol-1,4	$C_8H_{18}O_2$	1.4568	65.75	65.65	12.32	12.29	...	...
Diethyl α-ethyl α-acetyl adipate	$C_{14}H_{24}O_5$	1.4445	61.76	61.63	8.82	8.81	...	...
2-Benzylbutanediol-1,4	$C_{11}H_{16}O_2$	1.5210	73.33	73.24	8.88	9.20	...	...
4-Phenyl-3-methylbutanol-1	$C_{11}H_{16}O$	1.5078	80.48	80.13	9.75	9.70	206	211
3-*n*-Propylpentanediol-1,5	$C_8H_{18}O_2$	1.4569	65.75	66.14	12.32	12.19	...	...
3-Phenyl-2,4-dimethylpentanediol-1,5	$C_{13}H_{20}O_2$	[a]	75.00	74.63	9.61	9.39	...	...
3-Methylpentanediol-1,5	$C_6H_{14}O_2$	1.4512	61.01	61.94	11.86	11.74	202	214
3-Phenyl-2,4-diethylpentanediol-1,5	$C_{15}H_{24}O_2$	[a]	76.27	75.59	10.17	9.45	...	...
3-Methyl-2,4-diethylpentanediol-1,5	$C_{10}H_{22}O_2$	[a]	69.00	67.5	12.64	10.7	...	...
4-Phenyl-3,5-dicarbethoxyheptanediol-2,6	$C_{19}H_{28}O_6$	....	64.77	64.73	7.95	7.67	...	..
Diacetate of 2,4-diethyl-3-phenylpentanediol-1,5	$C_{19}H_{28}O_4$	....	71.25	71.85	8.75	8.40	...	...
Diethyl α-acetyl α-*n*-butylsuccinate	$C_{14}H_{24}O_5$	1.4335	61.76	61.67	8.82	8.99	...	...

[a] This product as indicated in the discussion was probably not homogeneous.

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(5) Bruhl, *Ber.*, **26**, 338 (1893).

(6) Kachler, *Ann.*, **169**, 172 (1873).

(7) Isbell, Wojcik and Adkins, THIS JOURNAL, **54**, 3684 (1932).

(8) Welch, *J. Chem. Soc.*, 673 (1931).

(9) Kotz and Stalmann, *J. prakt. Chem.*, [2] **68**, 157 (1903).

(10) Hantzsch, *Ber.*, **18**, 2583 (1885).

(11) Knoevenagel, *Ann.*, **281**, 75 (1894).

(12) Chuit, *Helv. Chim. Acta*, **9**, 272 (1926).

(13) Faworsky, *Ann.*, **354**, 383 (1907).

(14) Rossi, *ibid.*, **133**, 180 (1865).

(15) Conrad, *Ber.*, **11**, 1058 (1878).

(16) Chauloroff, *Ann.*, **226**, 338 (1884); Fichter and Busswenger, *Ber.*, **36**, 1204 (1903)

(17) Wagner, *ibid.*, **21**, 1232 (1888).

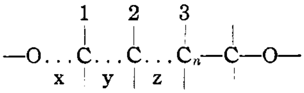
(18) Wislicenus, *ibid.*, **25**, 202 (1892).

(19) Manske, THIS JOURNAL, **53**, 1109 (1931).

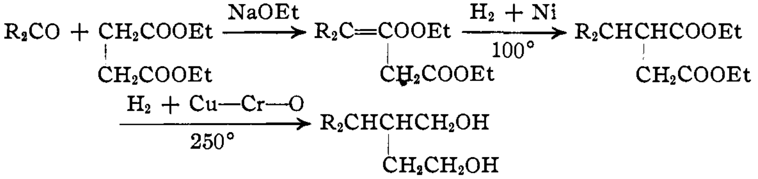
(20) Kotz, *J. prakt. Chem.*, [2] **75**, 488 (1907).

Conclusions

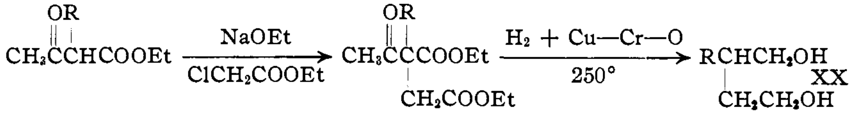
The system under study may be represented as shown, where the dotted lines indicate the labile linkages, x, y, z. The effect of substitution upon readiness of hydrogenolysis may be stated as follows: a phenyl or benzyl group at 1 or 2 weakens the x linkage. A methyl group at 2 has little labilizing effect while a branched chain (isopropyl) at 2 weakens y, and to a less extent x. An oxygenated substituent $\left(\text{—COOEt or } CH_2OH,\ CH_3\overset{O}{\overset{\|}{C}}\text{— or } CH_3CHOH\text{—}\right)$ at 2 weakens x and y equally. Methyl at 1 with —COOEt (or CH_2OH) at 2 facilitates cleavage at x. An alkyl or aryl group at 3 with an oxygenated substituent at 2 weakens z. With both an alkyl and an oxygenated substituent at 2, y is cleaved almost quantitatively. An increase in *n* stabilizes y and z.



The reactions described above make it feasible to prepare 2-alkylbutanediols-1,4 by means of two series of reactions



$$R_2CO + \underset{CH_2COOEt}{\underset{|}{CH_2COOEt}} \xrightarrow{NaOEt} R_2C{=}\underset{CH_2COOEt}{\underset{|}{C}}OOEt \xrightarrow[100^\circ]{H_2 + Ni} R_2CH\underset{CH_2COOEt}{\underset{|}{C}}HCOOEt \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} R_2CH\underset{CH_2CH_2OH}{\underset{|}{C}}HCH_2OH$$



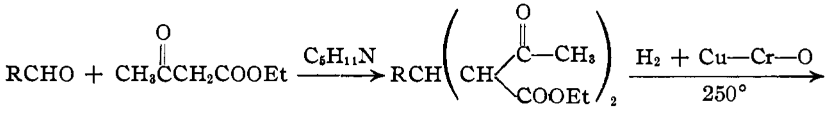
$$CH_3\overset{OR}{\overset{\|\ |}{C}}CHCOOEt \xrightarrow[ClCH_2COOEt]{NaOEt} CH_3\overset{OR}{\overset{\|\ |}{C}}\underset{CH_2COOEt}{\underset{|}{C}}COOEt \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} \underset{CH_2CH_2OH}{\underset{|}{RCHCH_2OH}}$$

XXV

A 2-alkylpentanediol-1,5 may be prepared by the method (XXV) above by substituting β-chloropropionic ester for α-chloroacetic ester. A fairly pure 3-alkyl-(or aryl)-pentanediol-1,5 may be made by the series of reactions

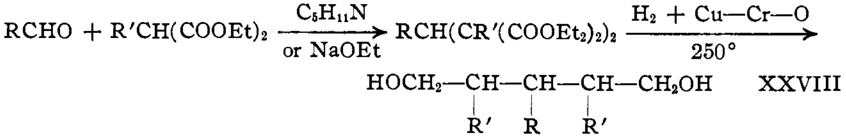
$$RCHO + CH_2(COOEt)_2 \xrightarrow[\text{or } NaOEt]{C_5H_{11}N} RCH(CH(COOEt)_2)_2 \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} RCH(CH_2CH_2OH)_2 \quad \text{XXVI}$$

or a 3-alkyl-(or aryl)-2,4-diethylpentanediol-1,5 by the reactions



$$RCHO + CH_3\overset{O}{\overset{\|}{C}}CH_2COOEt \xrightarrow{C_5H_{11}N} RCH\left(CH\begin{matrix}\diagup \overset{O}{\overset{\|}{C}}—CH_3\\ \diagdown COOEt\end{matrix}\right)_2 \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} RCH(CH(C_2H_5)CH_2OH)_2 \quad \text{XXVII}$$

However, the best way to prepare a pure 2,4-dialkylpentanediol-1,5 would be through the use of a monosubstituted acetoacetic or malonic ester having the proper substituent, for example



$$RCHO + R'CH(COOEt)_2 \xrightarrow[\text{or NaOEt}]{C_5H_{11}N} RCH(CR'(COOEt_2)_2)_2 \xrightarrow[250^\circ]{H_2 + Cu—Cr—O} HOCH_2—\underset{R'}{CH}—\underset{R}{CH}—\underset{R'}{CH}—CH_2OH \qquad XXVIII$$

Summary[21]

A number of ethyl esters of dibasic acids containing four or more carbons, variously substituted, have been subjected to the action of hydrogen at 100 to 300 atmospheres at 250° over copper–chromium oxide. The isolation of the major products from these reactions has led to certain conclusions with regard to the relation of structure to susceptibility to cleavage of C to C and C to O linkages, and with regard to feasible methods for preparing various glycols and alcohols.

[21] I wish to record here my indebtedness to Charles Sumner Slichter who, as Dean of the Graduate School and Chairman of the University Research Committee, has for thirteen years unwaveringly supported me through the allotment of funds for the purchase of important apparatus and for the employment at various times of B. H. Nissen, W. A. Lazier, A. E. Broderick, Howard Cramer, Karl Folkers, Ralph Connor and Bruno Wojcik as research assistants.

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The Rates of the Thermal Decomposition of Certain Triphenylmethyl Alkyl Ethers[1]

BY JAMES F. NORRIS AND ARTHUR CRESSWELL

It has been shown[2] that ethers of the type $(C_6H_5)_3C—O—R$, in which R represents an alkyl radical, decompose under the influence of heat into triphenylmethane and a product formed from the alkoxyl group as the result of the loss of one hydrogen atom; in the case of the ethyl ether acetaldehyde is formed. The temperature at which pyrolysis begins to be evident is definite when an ether of this type is heated in such a way that the temperature is raised at a fixed rate. Under the same conditions the several ethers decompose at different temperatures.

Since pyrolysis takes place in a relatively simple way and the primary products are stable under the conditions used, it seemed probable that the study of the rates at which typical ethers of this structure undergo pyrolysis would yield information of value. The methyl, ethyl and isopropyl ethers derived from triphenylcarbinol were studied with the expectation that something would be learned in regard to the order of the decompositions, their temperature coefficients and the effect on the rate of the tem-

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[1] From a part of the thesis presented by Arthur Cresswell in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1932.

[2] Norris and Young, THIS JOURNAL, **52**, 753 (1930).