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Base-Catalyzed Cleavage of 1,3-Diols[1,2]

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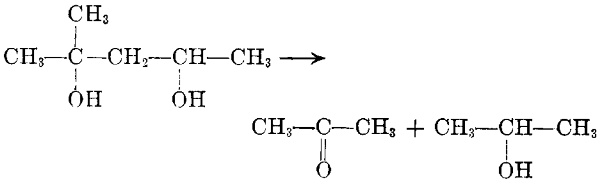
A study of the action of hot alkali with 21 1,3-diols of widely varying structure is reported. The general reaction is carbon-carbon cleavage, forming an alcohol and a carbonyl compound. Generalizations regarding the direction of cleavage of unsymmetrical diols are formulated, and a mechanism is proposed, involving a dehydrogenation to ketol or aldol, retrograde aldol condensation, and hydrogenation of one of the carbonyl products. Investigation of the stereochemistry of the reaction showed preferential cleavage of *cis* isomers of cyclic diols, indicating the importance of an internally hydrogen bonded monoalkoxide ion as an intermediate. The reaction can be used for preparing pure *trans*-1,3-cyclohexanediol from a mixture of the *cis* and *trans* isomers.

In connection with a study of the base-catalyzed cleavage of 1,3-bromoalcohols,[3,4] it was observed that 1,3-diols also are cleaved by treatment with hot alkali. The products from the diols are alcohols and carbonyl compounds, whereas the bromoalcohols break down into olefins and carbonyl compounds. An example of base-catalyzed cleavage of a 1,3-diol is the conversion of 2-methyl-2,4-pentanediol to acetone and isopropyl alcohol in about 90% yields when heated with sodium hydroxide at 150°:



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle OH}{C}}-CH_2-\underset{\displaystyle OH}{CH}-CH_3 \longrightarrow CH_3-\underset{\displaystyle \overset{\|}{O}}{C}-CH_3 + CH_3-\underset{\displaystyle OH}{CH}-CH_3$$

This is clearly a different reaction from the acid-catalyzed cleavage of 1,3-diols, which has recently received detailed study.[5] Besides a difference in products, the structural requirements are quite different, as will be shown.

Alkaline pyrolysis of 1,3-diols appears to have been first observed by Nef,[6] who reported that ethyl alcohol was obtained when a mixture of 1,3-propanediol and sodium hydroxide was heated at 150–160° for 100 min. The yield was only 20%, and propyl alcohol, acetic acid, and hydrogen were also reported to be formed.

In contrast to Nef's account, Cross and Jacobs[7] found that the best method of preparing monosodium salts of diols and triols, including 1,3-propanediol, was by heating with one mole of sodium hydroxide at 135°. They stated that the yield is quantitative, and that the same results are obtained at temperatures up to 175°.

A study of the reaction of 17 acyclic 1,3-diols with caustic alkali at 150–200° showed that cleavage to give an alcohol and a carbonyl compound is quite general. The results are presented in Table I. When the carbonyl product was an aldehyde, however, it was not isolated, although sometimes Cannizzaro[8] or Tishenko products were; *e.g.*, ethanol, in place of acetaldehyde, from X, and butyl butyrate in place of butyraldehyde from VI.

The reaction goes about equally well with sodium or potassium hydroxide, with or without added water. The amount of base used was varied from catalytic to large amounts without much effect on the cleavage process; the minimum practical temperature for the cleavage, however, increases as the amount of base is decreased. In an interesting paper published after our initial report,[2] Brannock and Lappin[9] reported cleaving three 2,2-dialkyl-1,3-propanediols and 2,2,4-trimethyl-1,3-pentanediol by heating with the corresponding sodium alkoxides at 145–175° or with calcium oxide at a slightly higher temperature.[10]

One of the diols studied in this work, 3-methyl-1,1-diphenyl-1,3-propanediol, cleaved to form an olefin, 1,1-diphenylethylene, rather than alcohol. The expected alcohol, 1,1-diphenylethanol, could have been formed first, however, as it is known[11] to

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[1] Abstracted largely from the thesis submitted by E. K. Ives in partial fullfilment of the Ph.D. degree, Kansas State College, 1959.

[2] Most of this material was presented at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, April 1955 (Abstracts, p. 24N).

[3] S. Searles and M. J. Gortatowski, *J. Am. Chem. Soc.*, **75**, 3030 (1953).

[4] S. Searles, R. G. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, submitted.

[5] H. E. Zimmerman and James English, Jr., *J. Am. Chem. Soc.*, **76**, 2294 (1954), and preceding papers.

[6] J. U. Nef, *Ann.*, **335**, 306 (1904).

[7] C. F. Cross and J. M. Jacobs, *J. Soc. Chem. Ind.*, **45**, 320T (1926).

[8] Even aldehydes with α-hydrogen are known to undergo the Cannizzaro reaction at 150–200° (A. Lederer, *Monatsh.*, **22**, 536 (1901); M. Hauserrmann, *Helv. Chim. Acta*, **34**, 1211 (1951).

[9] K. C. Brannock and G. R. Lappin, *J. Am. Chem. Soc.*, **77**, 6052 (1955).

[10] It has been reported that 2,2-dimethyl-1,3-propanediol is cleaved by heating with activated alumina [R. W. Brown and G. Dougherty, *J. Org. Chem.*, **13**, 173 (1948)]. The products, however, are different (isobutryraldehyde and methanol), rather than isobutyl alcohol and (initially) formaldehyde.[9] We have confirmed this observation, but find that alumina will not cleave some of the diols most easily cleaved by hot caustic, for example, 2-methyl-2,4-pentanediol. This apparently is a different reaction, which requires a quaternary carbon between the carbinol groups, suggesting cleavage to a carbonium ion intermediate.

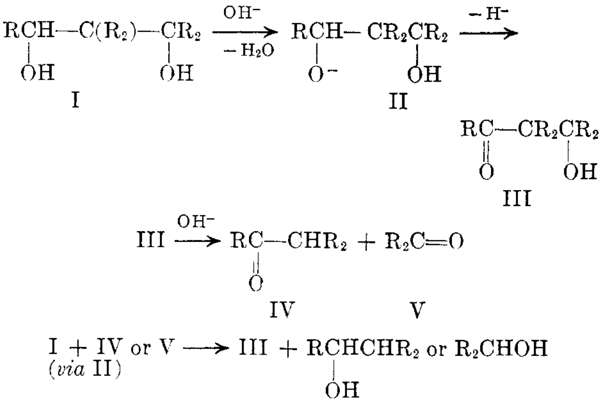
[11] M. Tiffeneau, *Ann. Chim.* (**8**), **10**, 359 (1907).

dehydrate at 200°, which was the reaction temperature.

Four compounds were not cleaved by caustic at 200°. One of them, 1,3-propanediol, was cleaved at somewhat higher temperature, and it is possible that the others would be too.

With unsymmetrically substituted 1,3-diols generally only one of the two possible modes of cleavage was observed.[12] The direction of cleavage observed can be generalized as follows: (1) The ease of cleavage of carbinol groups in 1,3-diols from an unsubstituted central methylene group, is in the order: $Me_2COH > CH_2OH > MeCHOH$ (or RCH-OH) $> \phi CHOH$ or ϕ_2COH. (2) When the central methylene is substituted, as well as one of the carbinols, cleavage of the most substituted carbinol occurs. This may result in reversing the point of cleavage predicted from the first generalization, as in compounds VI and VIII.[13]

For a mechanism one might logically postulate the following chain process: (1) base-catalyzed dehydrogenation of the diol (I) to a β-hydroxyketone or β-hydroxyaldehyde (III), by way of an intermediate monoalkoxide ion (II); (2) cleavage of III by the retrograde aldol condensation; and (3) Meerwein-Ponndorf reduction of one of the carbonyl products formed in step 2, by the diol I.



$$\underset{\displaystyle \text{OH}}{\text{RCH}}\text{—C(R}_2\text{)—}\underset{\displaystyle \text{OH}}{\text{CR}_2} \xrightarrow[-\text{H}_2\text{O}]{\text{OH}^-} \underset{\displaystyle \text{O}^-}{\text{RCH}}\text{—CR}_2\underset{\displaystyle \text{OH}}{\text{CR}_2} \xrightarrow{-\text{H}^-} \underset{\displaystyle \text{O}}{\overset{}{\text{RC}}}\text{—CR}_2\underset{\displaystyle \text{OH}}{\text{CR}_2}$$

I II III

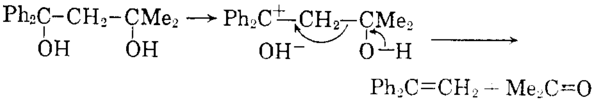
$$\text{III} \xrightarrow{\text{OH}^-} \underset{\displaystyle \text{O}}{\text{RC}}\text{—CHR}_2 + \text{R}_2\text{C=O}$$

IV V

$$\underset{(via\ \text{II})}{\text{I} + \text{IV or V}} \longrightarrow \text{III} + \text{RC}\underset{\displaystyle \text{OH}}{\text{H}}\text{CHR}_2 \text{ or } \text{R}_2\text{CHOH}$$

The first and last steps are analogous to those that are considered to occur in the Guerbet reaction[14] and in the base-catalyzed alkylation of fluorene with alcohols,[15] both of which occur in alkaline medium at 200–230°.

This mechanism fits all the cases studied except one, the observed cleavage of 3-methyl-1,1-diphenyl-1,3-butanediol. This di-*tert*-glycol, of course, cannot undrgo dehydrogenation to a ketol, but the benzhydrol-type structure may permit operation of ionization process in the polar medium at these high temperatures, as shown:

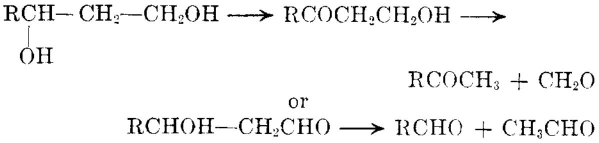


$$\text{Ph}_2\underset{\displaystyle \text{OH}}{\text{C}}\text{–CH}_2\text{–}\underset{\displaystyle \text{OH}}{\text{CMe}_2} \longrightarrow \underset{\displaystyle \text{OH}^-}{\text{Ph}_2\text{C}^+}\text{—CH}_2\text{—}\underset{\displaystyle \text{O—H}}{\text{CMe}_2} \longrightarrow \text{Ph}_2\text{C=CH}_2 + \text{Me}_2\text{C=O}$$

An analogy that may be cited is the cleavage of 3-dialkylamino-1,1-diphenylpropanols to 1,1-diphenylethylene and other products when heated in refluxing acetic anhydride.[16] The other di-*tert*-glycol, 2,4-dimethyl-2,4-pentanediol, does not have the benzhydrol structure and is not cleaved by hot alkali.

The direction of cleavage of unsymmetrical diols is in agreement with this mechanism. This is a particularly good test in the cases of 3-methyl-1,3-butanediol and 2-methyl-2,4-pentanediol, each of which has one tertiary carbinol and thus can cleave by this mechanism in only one direction. Furthermore, examination of the products by gas chromatography gave no evidence for cleavage in the other direction. Had cleavage proceeded merely by thermal dissociation of the diol monoalkoxide (II),[17] which would be a mixture, cleavage in each direction should occur to some extent.

In the case of di-*secondary* or *primary-secondary* diols, cleavage might occur in either direction, depending on the relative ease of dehydrogenation of the carbinol group, *e.g.*:



$$\underset{\displaystyle \text{OH}}{\text{RCH}}\text{—CH}_2\text{—CH}_2\text{OH} \longrightarrow \text{RCOCH}_2\text{CH}_2\text{OH} \longrightarrow \text{RCOCH}_3 + \text{CH}_2\text{O}$$

or

$$\text{RCHOH—CH}_2\text{CHO} \longrightarrow \text{RCHO} + \text{CH}_3\text{CHO}$$

As the carbinol group cleaved off is the one *not* dehydrogenated, one may surmise that the ease of dehydrogenation of carbinol groups in 1,3-diols (with a CH_2 group between the carbinol groups) under the conditions used is:

$RCORAr_2$ or
$RCH(OH)Ar > RCH(OH)R' > RCH_2OH > RC(OH)Me_2$

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(12) Where low yields of cleavage products were observed, fairly good recovery of starting diol was made so that it seems unlikely that any considerable amounts of products from the opposite modes of cleavage were formed. Furthermore, gas phase chromatography of the unfractionated reaction products gave no indication of any additional cleavage products in the several cases where this technique was used (Nos. II, VI, IX, X, and XIV in Table I). Due to the difficulty of recovering the starting diols efficiently, it was not possible to calculate conversion yields with any accuracy.

(13) There are two other examples of alkali cleavage of such diols in the literature and both agree with this generalization. Brannock and Lappin (Ref. 11) found that 2,2,4-trimethyl-1,3-pentanediol was cleaved almost entirely into isobutyl alcohol and isobutyraldehyde when heated with dissolved sodium. E. G. E. Hawkins, D. J. G. Long, and F. W. Major, *J. Chem. Soc.*, 1462 (1955), reported that a diol assigned the structure, 1-methylol-1-(3^1-cyclohexenylmethylol)-3-cyclohexene, was converted by heating with alkali at 200° into 1,2,3,6-tetrahydrobenzyl alcohol and 1,2,3,6-tetrahydrobenzoic acid, along with some material of higher molecular weight.

(14) H. Machemer, *Angew. chem.*, **64,** 213 (1952).

(15) K. L. Schoen and E. I. Becker, *J. Am. Chem. Soc.*, **77,** 6030 (1955).

(16) D. W. Adamson, *Nature*, **164,** 500 (1949).

(17) This direct cleavage of the monoalkoxide ion (II) was favored previously (Ref. 2), because the isopropyl alcohol formed from 3-methyl-1,3-propanediol was incorrectly identified as *tert*-butyl alcohol.

TABLE I

CLEAVAGE OF ACYCLIC 1,3-DIOLS

No.	Diol Structure	Max. Temp.	Conditions, Time	M. Base/ M. Diol	Products Identified	Yield, %^{m}
I	$CH_2OHCH_2CH_2OH^a$	225°	5	2	C_2H_5OH	7
II	$CH_2OHCMe_2CH_2OH^a$	170	1	1	Me_2CHCH_2OH	50
III	$CH_2OHCEt_2CH_2OH^b$	200	1.5	3	Et_2CHCH_2OH	60
IV	$CH_2OHCHPhCH_2OH^b$	200	2	6	$PhCH_2CH_2OH$	68
V	$CH_2OHCMePhCH_2OH^c$	210	1.5	5	no reaction	
VI	$PrCHOHCHEtCH_2OH^a$	180	2	1	BuOH	60
					PrCOOBu	15
VII	$PhCHOHCH_2CH_2OH^d$	210	2	6	$PhCH_2CH_2OH$	18
VIII	$PhCHOHCMe_2CH_2OH^e$	175	2	1.2	Me_2CHCH_2OH	48
					$PhCH_2OH$	100
					PhCOOH	54
IX	$MeCHOHCH_2CH_2OH^a$	200	2	2	Me_2CHOH	67
					Me_2CO	15^n
X ·	$Me_2COHCH_2CH_2OH^c$	200	2	2.7	Me_2CHOH	43
					Me_2CO	10^n
XI	$MeCHOHCH_2CHOHMe^f$	150	1	2	Me_2CHOH	74
					EtOH	8
XII	$MeCHOHCH_2CHOHPh^g$	200	2	10	PhCHOHMe	40
XIII	$PhCHOHCH_2CHOH\phi$	200	1.5	10	no reaction^k	
XIV	$Me_2COHOH_2CHOHMe^a$	150	1	1	Me_2CHOH	93
					Me_2CO	93
XV	$Me_2COHCH_2COHMe_2{}^h$	200	2	9	no reaction^k	
XVI	$Me_2COHCH_2CHOHPh^i$	200	1.5	5	$MeCHOHPh^l$	28
XVII	$Me_2COHCH_2COHPh_2{}^j$	200	1.5	9	$Ph_2C{=}CH_2{}^l$	60

[a] Commercial source. [b] Ref. 4. [c] Procedure of W. H. Mills and L. Bain, *J. Chem. Soc.*, 2502 (1925). [d] Preparation described in experimental section. [e] Method of Reik, *Monatsh.*, **18,** 599 (1877) as cited in Beilstein's "Handbuch der Organischen Chemie," Vol. VI, Springer, Berlin, 1923, p. 949. [f] Ref. 25. [g] A. Franke and M. Kohn, *Monatsh.*, **27,** 1115 (1906). [h] A. Franke and M. Kohn, *Ber.*, **37,** 4731 (1904). [i] A. McKenzie and G. Martin, *J. Chem. Soc.*, **103,** 112 (1913). [j] M. I. Berberian, *Chem. Zentr.*, **1913 II,** 766. [k] No cleavage products isolated and starting material recovered the extent of 75% or more. [l] The other product, acetone, eluded isolation probably because of the small scale and conversion for these experiments; only about 1 g. of acetone would have been expected. [m] Based on amount of starting diol, and based on the assumption that cleavage of unsymmetrical diols occurs in only one direction. [n] Estimated from gas chromatographic analysis.

This order is in agreement with that for ease of dehydrogenation of simple alcohols in aqueous solution, as determined polarographically.[18]

The cleavage of the various diols thus can be explained quite reasonably on the basis of this mechanism. For example, 1,3-butanediol is dehydrogenated to 4-hydroxy-2-butanone, which cleaves to acetone and formaldehyde, and the acetone is reduced mainly to isopropyl alcohol, the diol being oxidized to more ketol. The fate of the formaldehyde is not known; one might expect it to undergo the Cannizzaro reaction, forming methanol and formate ion, but since no methanol was detected, even by gas chromatography, perhaps it just goes to formate ion with evolution of hydrogen gas. The considerable tar formed may be polymer of the unsaturated ketone derived from the ketol.

As would be predicted from this mechanism, methylation of either hydroxyl group in a 1,3-diol prevents the cleavage reaction from occurring. The two monomethyl ethers of the easily cleavable 2-methyl-2,4-pentanediol were prepared by unambiguous methods.[19] 2-Methyl-4-methoxy-2-pentanol was prepared by the reaction of methyl 3-methoxybutyrate with methylmagnesium bromide. 4-Methyl-4-methoxy-2-pentanol was prepared by lithium aluminum hydride reduction of 4-methyl-4-methoxy-2-pentanone. Neither of these compounds could be cleaved by alkali at temperatures up to 280°, about 90% of the starting compounding being recovered in each case.

Also in accord with this mechanism was the failure of diols other than 1,3-diols to cleave in alkali. Attempts to cleave the following in hot caustic were unsuccessful: 1,2-propanediol, glycerol, 1,4-butanediol and 1,5-pentanediol.

The stereochemistry of the reaction was investigated by a study of *cis* and *trans* cyclic 1,3-diols. Although the same ketol would be formed from each isomer, one might expect some differences in ease of dehydrogenation of the isomers.

The pure *cis* and *trans* isomers of both 1,3-cyclohexanediol and 1,3-cyclopentanediol were treated with alkali at 200°. As shown in Table II, the *cis* isomer in each series was more easily cleaved than the *trans* isomer. The difference in rate can be made use of in preparing *trans*-1,3-cyclohexanediol from the mixture of *cis* and *trans* isomers obtained by hydrogenation of resorcinol. The hot alkali treatment of this mixture

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(18) H. Adkins and F. W. Cox, *J. Am. Chem. Soc.*, **60,** 1151 (1938).

(19) Methylation of the diol with methyl sulfate and alkali was not a suitable method to prepare either monomethyl ether in pure form.

TABLE II

Alkaline Cleavage of Cyclic 1,3-Diols

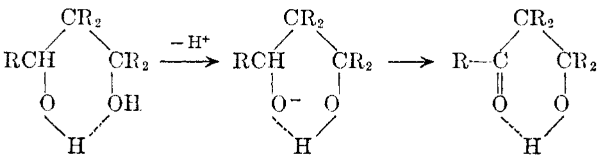
Compound	Temp.	Time, Hr.	Recovered Diol	
			%	Isomer
cis-1,3-Cyclopentanediol	200	0.5	0	
trans-1,3-Cyclopentanediol	200	0.5	50	*trans*
cis-1,3-Cyclohexanediol	150	0.1	33	*cis*
trans-1,3-Cyclohexanediol	150	0.1	67	*trans*
cis- and *trans*-1,3-Cyclohexanediol[a]	170	0.25	33[b]	*trans* only

[a] From catalytic hydrogenation of resorcinol. [b] Corresponds to 0% recovery of *cis* isomer and 66% recovery of *trans* isomer, if the starting product were a mixture of 50% of each isomer.

preferentially cleaved the *cis* isomer, so that the pure *trans* isomer could be recovered.

At temperatures above 150°, the *trans* isomer reacted also, although apparently more slowly than the *cis* isomer. It is possible that these conditions were sufficiently rigorous to allow interconversions of the *cis* and *trans* isomers, so that the *trans*-diol was actually reacting by way of the *cis* isomer.

The faster rate of cleavage of the *cis* isomer in each series may be attributed to the stabilization of the monoalkoxide by internal hydrogen bond formation. It seems reasonable that the base-catalyzed dehydrogenation of a carbinol group would involve the alkoxide as an intermediate, and thus factors favoring formation of alkoxide would also favor dehydrogenation. Similar chelation of monoalkoxides of 1,2-diols has been proposed by Hine and Hine[20] to account for their acidities being considerably greater than for their monoalkyl ethers. Strong intramolecular hydrogen bonding has been demonstrated spectrally for open-chain 1,3-diols and for *cis*-1,3-cyclohexanediol, whereas practically no chelation was found for *trans*-1,3-cyclohexanediol.[21] One might expect similar and probably greater differences between the *cis* and the *trans* isomers of 1,3-cyclopentanediol, where the ring is more rigid.



EXPERIMENTAL

All of the 1,3-diols used were known compounds. They were either commercial samples or samples prepared by previously described methods, except the three described below. In each case, purification was carried out by fractional distillation until the physical constants (b.p. and n_D, or m.p.) agreed with the literature values.

Methyl 3-methyl-3-hydroxybutyrate. A solution of 226 g. of methyl bromoacetate, 103 g. of acetone, and 50 g. of dry ether was added with good stirring to 118 g. of activated zinc in 100 ml. of ether at a rate that gave gentle refluxing. The reaction mixture was stirred several hours more at room temperature; if the temperature were allowed to rise and the ether distilled out, only methyl 3-methylacrylate was obtained as product. Following the customary method of processing a Reformatsky reaction mixture,[22] vacuum distillation (spinning band column) gave 28.5 g. (15%) of a clear, colorless liquid, b.p. 70° (12 mm.), n_D^{20} 1.4220.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.54, H, 8.96.

The same compounds, synthesized by another method, has been reported to have b.p. 70–71° (10 mm.), n_D^{20} 1.4126.[23]

3-Methyl-1,3-butanediol. A solution of 28 g. of methyl 3-methyl-3-hydroxybutyrate in 50 ml. of ether was added to a solution of 8.2 g. of lithium aluminum hydride in 150 ml. of ether. After refluxing 3 hr., the mixture was cooled and hydrolyzed with 20% sodium carbonate solution. The product was extracted with ether and dried over magnesium sulfate; distillation gave 15 g. (67%) of a colorless, viscous sirup, b.p. 104° (14 mm.), 118–119° (30 mm.), 198–200° (740 mm.), n_D^{20} 1.4415. The phenylurethan derivative melted at 88–89°. Previously reported for this compound, synthesized by other methods, are b.p. 202–204°,[24] 80° (5 mm.),[25] phenylurethan derivative m.p. 87–88°.[24,25]

1-Phenyl-1,3-propanediol. Methyl 3-hydroxy-3-phenylpropionate[26] (113 g.) was reduced with 60 g. of lithium aluminum hydride in the manner described above, to give 54.5 g. (56%) of the diol, b.p. 180–185° (17 mm.), n_D^{22} 1.5425. The literature gives b.p. 175° (11 mm.).[27]

1,3-Diphenyl-1,3-propanediol. Dibenzoylmethane,[28] was reduced with lithium aluminum hydride by the above general procedure to give a 12% yield of 1,3-diphenyl-1,3-propanediol, b.p. 190–195° (5 mm.), m.p. 24–25°. The literature values[29] are somewhat higher: b.p. 214–218° (4 mm.), m.p. 94–98°. The infrared spectrum of our compound, however, was entirely in accord with expectations, showing strong absorption characteristic of chelated hydroxyl and no carbonyl absorption bands; and it analyzed satisfactorily.

Anal.[30] Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.04; H, 7.32.

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(20) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(21) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

(22) R. L. Shriner, Organic Reactions, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 17.

(23) A. M. Gakhokidze, *Soobshcheniya Akad. Nauk. Gruzin. S.S.R.*, **10**, No. 4, 193 (1949); *Chem. Abstr.*, **47**, 3236 (1953).

(24) F. V. Favorsky and A. I. Lebedeva, *Bull. soc. chim. France*, **6**, 1347 (1939).

(25) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 78 (1955).

(26) W. H. Mills and L. Bains, *J. Chem. Soc.*, 2503 (1924).

(27) H. Rupe and H. Muller, *Helv.* **4**, 841 (1921).

(28) *Org. Syntheses*, **Coll. Vol. I**, 205 (1941).

(29) J. M. Sprague and H. Adkins, *J. Am. Chem. Soc.*, **56**, 2669 (1934).

(30) Microanalyses performed by Geller Laboratories, Hackensack, N. J.

TABLE III

IDENTIFICATION OF CLEAVAGE PRODUCTS

Compound	Parent Diol	B.P. (Mm.)		n_D^{20}		Derivative	M.P.	
		Obs.[a]	Lit.[b]	Obs.	Lit.[b]		Obs.	Lit.[b]
Acetone	XIV	55–57	56	1.3595	1.3590	2,4-DNP	127–128	127–128
2-Propanol	IX, XI, XIV	78–81	82.5	1.3768	1.3793	α-Naphthylurethane	105–106	106
2-Propanol	X	80–81	82.5	1.3776	1.3793	Phenylurethane 3,5-Dinitrobenzoate	83–85 119–120	88 122
2-Methyl-1-propanol	II, XI, VIII	104–105	107–108	1.3972	1.3968	Phenylurethane *p*-Nitrobenzoate	87–88 67–68	88 68.5–69
1-Butanol	VI	115–117	116	1.3995	1.3991	α-Naphthylurethane	70–71	71
2-Ethyl-1-butanol	III	145–147	148	1.4212	1.4208	3,5-Dinitrobenzoate	49–51	51
n-Butyl *n*-butyrate	VI	165–168	165	1.4298	1.4305	[c]		
1-Phenylethanol	XVI	203–205	203–204	1.5220	1.5212	*p*-Nitrobenzoate 3,5-Dinitrobenzoate	42–43 92–93	43 93
2-Phenylethanol	IV	110–112 (17)	104 (14)	1.5322	1.533	Phenylurethane	78–79	79
1,1-Diphenylethylene	XVII	145–150 (14)	156 (20)	1.6075	1.6085	[d]		
Benzyl alcohol	VIII	103–105 (25)	107 (25)	1.5157	1.5275	*p*-Nitrobenzoate	83–84	85
Benzoic acid	VIII	...	...	...	...	...	121	121

[a] Observed boiling points are for 730–740 mm., unless otherwise stated. [b] As cited by E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds, *Order I*," John Wiley & Sons, Inc., New York, N. Y., 1941, or in Beilstein's "Handbuch der Organischen Chemie." [c] Saponification equivalents are: observed, 144; calcd., 142.5. [d] As in the other cases, the structure was confirmed also by infrared analysis; the infrared spectrum of this compound showed the presence of a phenyl group and of a terminal double bond, as well as the absence of hydroxyl and carbonyl functions.

A 3,5-dinitrobenzoate, m.p. 137–138° and (later) 149–150° was prepared.

2-Methyl-4-methoxy-2-pentanol. Methyl 3-methoxybutyrate[31] (150 g.) was added dropwise to a cold, stirred Grignard reagent prepared from 535 g. of methyl bromide and 123 g. of magnesium turnings in 1 l. of ether. The conditions and method of work-up were the same as for the last described compound. The yield was 104 g. (79%) of 2-methyl-4-methoxy-2-pentanol, b.p. 154–155° (735 mm.), n_D^{22} 1.4143. The infrared spectrum was in agreement with the structure assigned.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.63; H, 12.12. Found: C, 63.62; H, 12.02. The 3,5-dinitrobenzoate was prepared, m.p. 68–69°.

4-Methyl-4-methoxy-2-pentanol. 4-Methoxy-4-methyl-2-pentanone[32] (43 g.) was reduced with 16 g. of lithium aluminum hydride in ether. The excess hydride was decomposed with 50 ml. ethyl acetate, and dilute hydrochloric acid was used for hydrolysis of the reaction mixture. After the usual washing and drying, distillation gave 25 g. (58%) of 4-methoxy-4-methyl-2-pentanol, b.p. 165–170° (730 mm.), n_D^{20} 1.4388.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.63; H, 12.12. Found: C, 63.43; H, 11.84.

The 3,5-dinitrobenzoate melted at 69–70°.

2-Methyl-2,4-dimethoxypentane. In an attempt to prepare one of the above monomethyl ethers, 360 g. of dimethyl sulfate was added slowly with stirring to a solution of 160 g. of 2-methyl-2,4-pentanediol, 150 g. of sodium hydroxide in 1.5 l. of water maintained at 60–70°. The temperature was then increased to 95° for 1 hr. The mixture was cooled, while 200 ml. of 3*N* potassium hydroxide was added and extracted with ether. Distillation of the dried extracts gave 25 g. (16%) of the pure dimethoxy compound, b.p. 148–152° (735 mm.), n_D^{20} 1.4150. The infrared spectrum showed absence of hydroxyl groups and of double bonds, and presence of the ether linkage. The method was not suitable for either of the monomethyl ethers.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.98; H, 12.30. Found: C, 66.39; H, 11.84.

Alkaline pyrolysis. The general procedure used is illustrated by the following: 2-methyl-2,4-pentanediol (118 g.) was added dropwise to a stirred solution of 150 g. of potassium hydroxide in 20 ml. of water, maintained at 145–150°. The products distilling were passed through a 6-in. Vigreux column and a water-cooled condenser to a receiver, which in turn was connected to a Dry Ice–acetone trap and a bubbler containing bromine in carbon tetrachloride. (The latter was for detection of any low boiling olefins, but in no case was anything collected in the Dry Ice trap, or the bromine decolorized.)

The contents of the receiver were saturated with sodium chloride, and the organic layer dried and distilled through a 1-ft. Fenske column: 32 g. of acetone (60%) and 53 g. of isopropyl alcohol (88%) was obtained. In addition 10–20 g. of a sticky, dark brown, aromatic-smelling tar was formed; operation at higher temperatures gave more tar and less acetone and isopropyl alcohol.

A number of variations of this procedure were tested, but without any striking differences in the results. The water used was not necessary. Sodium hydroxide could be substituted for potassium hydroxide. The amount of base used could be decreased to 0.5 molar quantities without noticeable effect, but below that, higher reaction temperatures were required. A temperature of 180° was required for a reasonable rate of cleavage when 4 g. of sodium hydroxide (no water) was used with 118 g. of the above diol. There was practically no tar formation, however, with this small amount of base, and the yields of isopropyl alcohol and acetone was 92% and 56%, respectively. The best results were obtained when 40 g. of sodium hydroxide and 118 g. of the diol were heated with stirring at 150°, yielding 56 g. of isopropyl alcohol and 54 g. of acetone (93% of each).

The composition of the ethanol-isopropanol mixture, formed by the cleavage of 2,4-pentanediol, was determined by infrared spectral analysis because of the difficulty of fractional distillation. The presence of isopropyl alcohol was demonstrated by oxidation with potassium dichromate and sulfuric acid. The oxidation products were distilled from the reaction, dried and fractionally distilled to give a 25% yield (based on starting diol) of acetone, b.p. 54–55° (735 mm.), n_D^{22} 1.3595, 2,4-DNP m.p. 125–126° (lit. 127–128°[33]). The acetaldehyde formed was collected in a water solution and characterized as the DNP, m.p. 147–148° (lit., 148°[33]).

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(31) T. Purdie and W. Marshall, *J. Chem. Soc.*, 476 (1891).

(32) A. Hoffman, *J. Am. Chem. Soc.*, 49, 530 (1927).

(33) Ref. b, Table III.

In cases where the products were high boiling and did not distill, the reaction mixture was neutralized with dilute hydrochloric acid and extracted with ether, benzene, or chloroform. After removal of the solvent, the product was either crystallized or distilled. With the cyclic diols, however, no cleavage products were isolated (probably on account of high water solubility, since these products would be expected to be diols and hydroxy acids).

The products obtained from the diols numbered II, VI, IX, X, and IV (Table I) were passed through a gas-phase chromatographic column employing tricresyl phosphate on celite. All the peaks observed were consistent with the materials already known to be present, as given in Table I.

The methods of identifying the cleavage products are listed in Table III.

Alkaline pyrolysis by the above general procedure appeared to give practically no cleavage in the following cases: (1) 2-methyl-4-methoxy-2-pentanol, 44 g. of an initial 50 g. being recovered after treatment with 100 g. of potassium hydroxide at temperatures up to 280°. (2) 4-Methyl-4-methoxy-2-pentanol, with similar recovery after similar treatment. (3) 1,2-Propanediol. (4) Glycerol. (5) 2-Ethyl-1-hexanol. (6) 2,2-Dimethyl-1-propanol. (7) 2-Methyl-2-butanol, although 1% of 2-butanone, b.p. about 90°, m.p. of DNP 116–117°, was obtained, reminiscent of the cleavage of 2-butyl-2-hexanol to 2-hexanone at 600°.[34]

trans-1,3-Dihydroxycyclohexane. Resorcinol was catalytically reduced over Raney nickel catalyst, forming a mixture of *cis-* and *trans*-1,3-dihydroxycyclohexane, b.p. 145–147° (15 mm. in 90% yield).[35] This product contains approximately equal amounts of both isomers.[35,36]

An intimate mixture of 20 g. of this material and 50 g. of powdered, 85% potassium hydroxide was heated at 170° for 15 min., followed by cooling, addition of water, and extraction with hot benzene. After drying and removal of solvent, 6.5 g. of *trans*-1,3-dihydroxycyclohexane, b.p. 137–144° (15 mm.) m.p. 110–115° (from acetone), m.p. trityl ether, 197–198° (lit.[35,36] values, b.p. 135° (13 mm.), m.p. 118°, trityl ether m.p. 199°).

The same procedure was used for pyrolysis of the other cyclic diols.

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(35) H. Lindemann and H. Baumann, *Ann.*, **477**, 78 (1930).

(36) W. Rigby, *J. Chem. Soc.*, 1586 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DEPAUL UNIVERSITY]

Synthesis of Dinaphthylamines and Tetranaphthyl Hydrazines[1]

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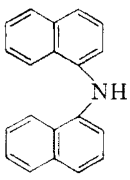
An improved procedure for the synthesis of the three isomeric 1,1′-, 2,2′- and 1,2′-dinaphthylamines has been devised and their oxidation, by neutral permanganate in acetone, to the corresponding symmetrical tetranaphthyl hydrazines achieved. The treatment of *N*-acetyldinaphthylamines under the same conditions results in recovery of starting material. New properties for the *N*-acetyldinaphthylamines are described. The syntheses of 1,2-dimethyl-1,2-di(1-naphthyl)- and 1,2-diphenyl-1,2-di(1-naphthyl)-hydrazines are also described.



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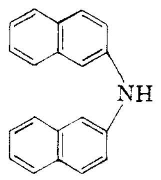

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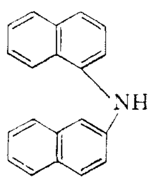

III

The synthesis of heavily tetra-substituted hydrazines was undertaken with the objective of studying their dissociation in solution to disubstituted nitrogen radicals. The procedure adopted for obtaining the desired hydrazines from the corresponding secondary amines was the method described by Wieland[3] for converting diphenylamine to tetraphenyl hydrazine by oxidation with neutral potassium permanganate. As a prelude to the synthesis of tetranaphthyl hydrazines, the synthesis of three isomeric dinaphthylamines, namely, the 1,1′ (I); the 2,2′ (II); and, the 1,2′ (III), was investigated. A survey of the literature[4–8] revealed that I, II, and III have been synthesized by a variety of procedures. These, in general, comprised heating naphthols or naphthylamine, either singly on in admixture, at temperatures ranging from 150–300° for extended periods of time, in the presence of substances such as ammonia chloride, zinc chloride, calcium chloride, and sodium acetate. In our hands these methods led only to tarry solids from which only the starting materials could be recovered on a very depleted scale. The method finally adopted was a variation of the procedure described by Merz and Weith[4,5] and represents a distinct improvement over that previously described. The procedure consists in gently heating a mixture of equal parts of a naphthylamine, a naphthol, freshly fused zinc chloride and ammonium chloride to the molten state. A spontaneous, exothermic reaction sets in

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(3) C. Weygand, *Organic Preparations*, Interscience Publishers, Inc., New York, N. Y., 1945, p. 244.

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(5) V. Merz and W. Weith, *Ber.*, **14**, 2344 (1881).

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(8) L. Landshoff, *Ber.*, **11**, 639 (1978).