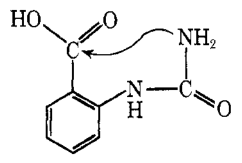

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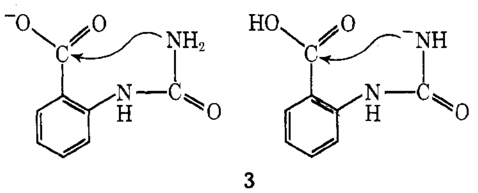

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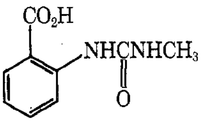


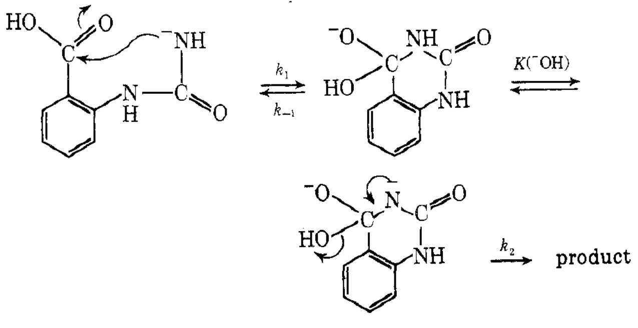
4

voked on the basis of previous data.[4] Because of this ambiguity and because of the uniqueness of mechanism 1,[5] we felt it important to test whether the alternative (or a kinetic equivalent) might be correct.

$$k_{\text{obsd}} = \frac{k_1 k_2 K[\text{OH}^-]}{k_{-1} + k_2 K[\text{OH}^-]} \qquad (1)$$

Unlike the mechanism of Hegarty and Bruice,[2,3] Scheme I requires that the nucleophilic nitrogen of the starting material bear *two* hydrogens. Consequently, we examined 1-*o*-carboxyphenyl-3-methylurea (4), a compound lacking this property. The substrate was found to cyclize at a rate directly proportional to the hydroxide concentration ($k_2 = 9.1 \times 10^{-4}\ M^{-1}\ \text{sec}^{-1}$, 30.0°, 0.6–1.0 *M* hydroxide). Moreover, the rate of cyclization is nearly the same (2.2 times as fast) as that of the corresponding nonmethylated urea. These observations eliminate Scheme I and support the contention that an intramolecular anionic nucleophile can indeed react with a carboxyl anion.[6]

Scheme I



Experimental Section

Materials. *N*-(*o*-Carboxyphenyl)urea was prepared from anthranilic acid and potassium cyanate.[7] 1-*o*-Carboxyphenyl-3-methylurea (4) was prepared from isatoic anhydride and methylamine.[8] The product was crystallized from wet acetone to give white crystals of mp 187–189° (lit.[8] mp 188–189°) and with a satisfactory elemental analysis. Cyclization of the methylurea in 6 *N* HCl to 3-methyl-2,4(1*H*,3*H*)-quinazolinedione was carried out by the procedure of Hayao, *et al.*[8]

Kinetics. A stoppered cuvette containing 3.00 ml of aqueous sodium hydroxide (0.6–1.0 *M*) was equilibrated at 30.0° for 20 min within the thermostated cell compartment of a Cary 14 spectrophotometer. A small amount (25 μl) of a methanolic solution of 1-*o*-carboxyphenyl-3-methylurea was then added to the cuvette (by means of a small stirring rod flattened at one end) such that the initial urea concentration in the cuvette was $2.6 \times 10^{-4}\ M$. The increase in absorbance at 332 nm was traced as a function of time until the reaction was completed. First-order plots were linear to greater than 2 half-lives.

Product Analysis. The spectrum of 3-methyl-2,4(1*H*,3*H*)-quinazolinedione in 1 *N* NaOH was shown to be identical with the "infinity spectrum" of a kinetic run under the same conditions.

Acknowledgment. This work was supported in part by the National Science Foundation.

Registry No.—**2,** 610-68-4; **4,** 4141-12-2.

References and Notes

(1) Recipient of a Camille and Henry Dreyfus Foundation Teacher-Scholar Grant and a National Institutes of Health Research Career Development Award.

(2) A. F. Hegarty and T. C. Bruice, *J. Amer. Chem. Soc.*, **91**, 4924 (1969).

(3) A. F. Hegarty and T. C. Bruice, *J. Amer. Chem. Soc.*, **92**, 6575 (1970).

(4) Indirect evidence, based on estimated rate constants, is presented in ref 3 against Scheme I.

(5) This reaction seems to be the only known example of an anionic nucleophilic displacement upon a carboxylate not involving a metal ion.

(6) A variation of Scheme I entails loss of the proton on the nitrogen bonded to the phenyl ring followed by formation of an *o*-quinoid-type intermediate. Attempts to test this mechanism were hampered by repeated failure to prepare 1-*o*-carboxyphenyl-1-methylurea and 1-*o*-carboxylphenyl-1,3-dimethylurea. Apparently, the compounds cyclize spontaneously during their preparation. This may be due to the 1-methyl group conformationally directing the 3 nitrogen into the proximity of the carboxyl group.

(7) N. A. Lange and F. E. Sheibley, "Organic Syntheses," Collect. Vol. II, Wiley, New York, N. Y., 1943, p 79.

(8) S. Hayo, H. J. Havera, W. G. Strycker, T. J. Leipzig, R. A. Kulp, and H. E. Hartzler, *J. Med. Chem.*, **8**, 807 (1965).

Glyoxal Derivatives. VI. The Formation of Glycolates and the Acid-Catalyzed Decomposition of Glyoxal Acetals[1a]

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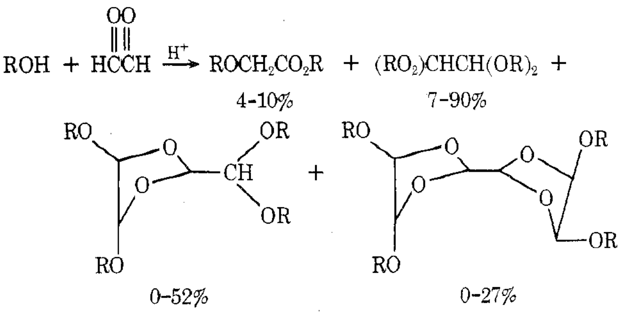
In our previous report[1a] we showed that aqueous glyoxal reacts with alkanols in the presence of acid catalysts to give glycolates, bisacetals, dioxolane, and bisdioxolane derivatives in varying yields depending upon the initial alcohol/glyoxal ratio. Although the yields of acetal-type products could be controlled by the variation in the alcohol/glyoxal ratio, the yields of glycolates were relatively constant. In this report we describe the reaction of cyclohexanol to give glycolates in major amounts, and of other alcohols with glyoxal in which great differences in product type are observed depending upon reaction conditions. These observations plus a study of the hydrolysis and acid-catalyzed decomposition of glyoxal acetals allows us to suggest a mechanistic explanation for the differences observed.



$$\text{ROH} + \text{HC(=O)C(=O)H} \xrightarrow{\text{H}^+} \text{ROCH}_2\text{CO}_2\text{R} + (\text{RO}_2)\text{CHCH(OR)}_2 +$$

Results

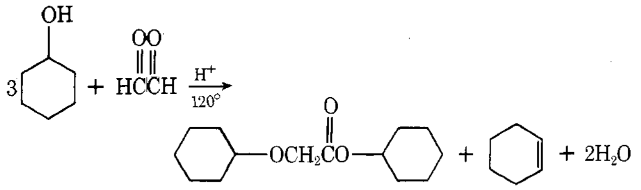
Unlike *all* of the other alkanols brought into reaction with glyoxal at 100–120°, cyclohexanol reacts to give gly-

Table I
Conditions, Reactants, and Products for Glycolate-Forming Reactions

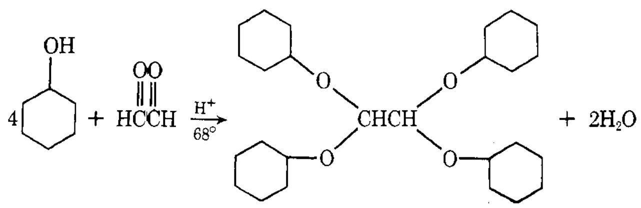
Expt	Glyoxal, mol	Alcohol (mol)	Acid (wt %)	Moles of alcohol recovered	Acetal		Olefin		Ether		Glycolate	
					% yield	Eff	% yield	Eff	% yield	Eff	% yield	Eff
1	1.0	1-Butanol (5.0)	H_2SO_4 (3.8)	1.48	13.0	13.0 (G)[a] 14.8 (B)			23.6	33.5	60.0	60.0 (G) 34.1 (B)
Glyoxal efficiency = 73.0% (total) 1-Butanol efficiency = 82.4% (total)												
2	1.0	1-Butanol (5.0)	*p*-TsOH (3.4)	1.79	4.0	4.0 (G) 5.0 (B)			10.4	16.2	86.6	86.6 (G) 54.0 (B)
Glyoxal efficiency = 90.6% (total) 1-Butanol efficiency = 77.2% (total)												
3	1.0	2-Ethylhexanol (5.0)	*p*-TsOH (2.2)	2.43			12.6	24.5	1.52	3.0	90.2	90.2 (G) 70.2 (E)
Glyoxal efficiency = 90.2% (total) 2-Ethylhexanol efficiency = 97.7% (total)												

[a] G = glyoxal (registry no., 107-22-2); B = 1-butanol (71-36-3); E = 2-ethylhexanol (104-76-7).

colate in yields of 90% or better. Thus, when 5 mol of cyclohexanol and 1 mol of glyoxal (40% aqueous) were heated to reflux in the presence of 0.006 mol of *p*-toluenesulfonic acid there appeared an azeotrope of water and cyclohexanol (101°) which removed both the water from the aqueous glyoxal and the water of reaction from the reaction system. After water evolution ceased the mixture was distilled. During the reduced-pressure distillation, large quantities of smoking vapor were given off and isolated in the traps. This material was cyclohexene in 43% yield. The distillate was cyclohexylcyclohexoxy acetate in 90% yield. Both of these materials were identified by comparison of their physical properties with those reported in the literature, carbon and hydrogen analysis, and their infrared and nmr spectra. No cyclohexene was observed prior to distillation.



The acetal product, as with other alkanols, was observed if the reaction was carried out at lower temperature. For example, refluxing a chloroform solution containing a 4:1 molar ratio of cyclohexanol to glyoxal in the presence of a catalytic amount of acid results in precipitation of crude product in 50% yield. Recrystallization of this material from heptane gave pure 1,1′,2,2′-tetrakis(cyclohexoxy)ethane. The structure of this material was demonstrated by its carbon and hydrogen analysis, molecular weight, and infrared and nmr spectra.



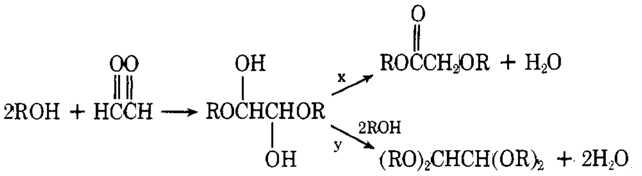
Preferential glycolate over acetal formation can be forced upon the other alcohols which normally give only low yields of glycolates at 100–120° by increasing the temperatures at which the reactions are run. Thus, if 2-ethyl-2-hexanol and 40% aqueous glyoxal were refluxed with 2.2% *p*-toluenesulfonic acid catalyst and the kettle temperature was allowed to approach 200°, glycolate was obtained in 90% yield. Table I lists the experiments that we have done, as well as the conditions, yields, and efficiencies to the various products. *tert*-Butyl alcohol was unreactive in this reaction, either to form glycolates or acetals.

Some of those glycolates which were only produced in low yields during the reaction of the alcohol with glyoxal were readily available *via* the high-temperature acid-catalyzed decomposition of the acetal itself. Thus, heating 1,1′,2,2′-tetrabutoxyethane with sulfuric acid at 181° gave a 90% yield of *n*-butyl butoxyacetate. Others, such as allyl and benzyl acetals, did not give any observable glycolates at all.

The acid-catalyzed hydrolysis of 1,1′,2,2′-tetrabutoxyethane gave mainly dimeric and trimeric acetals with little formation of glycolate. As with the neat acetal, glycolate formation was only observed at elevated temperatures. Interestingly, the cyclohexyl acetal hydrolyzed reversibly to the alcohol and glyoxal, with no other products being observed.

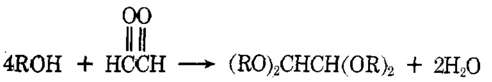
Discussion

There are several mechanisms which could be evoked to explain our results. Of these, there are two which were considered. The first involves formation of the hemiacetal followed either by further acetal formation or loss of water to give glycolate.



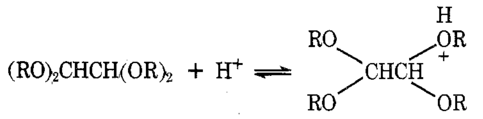
In order to explain different product formation one would have to consider that x is preferred over y at elevated temperatures. Two factors detract from this thesis. If the ability to lose water from the hemiacetal governs the formation of glycolate, the product distribution for all secondary or cyclic alcohols should be approximately of the same order. That this is not the case is evidenced by only cyclohexanol giving mainly glycolate under the same conditions that 2-butanol, 2-pentanol, 2-propanol, and cyclopentanol give mainly acetals. The other argument against this mechanism is that *tert*-butyl alcohol gives no glycolate nor acetal. The fact that *tert*-butylamine reacts with glyoxal[2] to give a diimine indicates that the *tert*-butyl group is not too hindered for reaction through the presumed aminal intermediate. Thus, if hemiacetal formation takes place, we would expect *only* glycolate formation rather than formation of a highly hindered tetra-*tert*-butoxyethane. The fact that no products except recovered *tert*-butyl alcohol were observed from this reaction weighs heavily against this pathway for the reaction.

A second mechanism requires initial formation of the bisacetal followed by a temperature- and acid-catalyzed decomposition of the acetal.

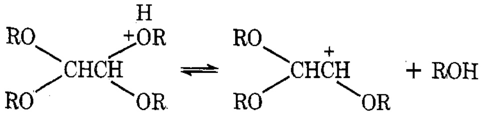


$$4ROH + \overset{OO}{\overset{\|\,\|}{HCCH}} \longrightarrow (RO)_2CHCH(OR)_2 + 2H_2O$$

(1)



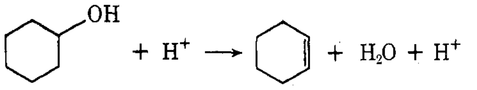
(2)



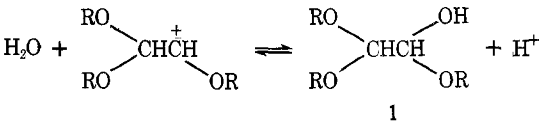
(3)

At this point two possible pathways are possible.

Path A



(4)



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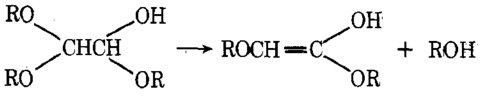

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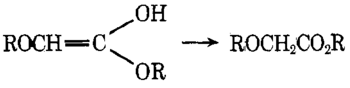
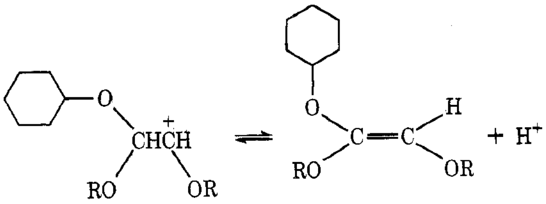
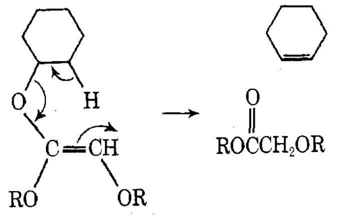


(7)

Path B



(8)



(9)

In order to test our conception of the initial portions of this mechanism (eq 1-3) and to distinguish between path A and path B, we studied the acid-catalyzed decomposition of acetals of glyoxal at elevated temperatures (130-225°). The results of these experiments are given in Table II. A similar type of decomposition is known over CeO_2 at 300-350°; however, lower yields were observed.[3-5]

There are three salient features which stand out in Table II. The first is that glycolates are, indeed, formed in this reaction. The second is that these reaction conditions were such that not all of the alcohol generated by the decomposition is converted to ethers or olefins. That is, there does not appear to be any overwhelming driving force for the alcohols going to these products, especially the olefins. The third feature is that the benzyl acetal and allyl acetal gave no glycolate products. These two facts lead us to the following conclusions concerning this reaction.

(A) Glycolates observed in the reaction of alcohols and glycols can be obtained *via* a direct decomposition of the acetals.

(B) Water is available *via* both eq 4 and from ether formation, and may react as in eq 5.

(C) The fact that benzyl and allyl acetals do not react to give glycolate products is not explicable in terms of eq 6 and 7, but is supported by a mechanism in which eq 8 and 9 are dominant, since neither of these acetals has easily removable hydrogens available for a hydride shift.

We therefore propose eq 2, 3, 8, and 9 as the most probable mechanism for the acid-catalyzed decomposition of acetals of glyoxal.

The formation of glycolates in alcohols with glyoxal may or may not simply consist of adding eq 1. While we feel that our mechanism (eq 1, 2, 3, 8, and 9) probably explains the major portion of glycolate formation in the reactions of alcohols with glyoxal at 100-120° (and totally at 175-200°), and with cyclohexanol at 100-120°, we could not eliminate eq 5-7 completely because the reactions of 40% aqueous glyoxal with all of the alcohols are carried out in the presence of a large excess of water which was removed at varying rates. Therefore, the following pair of experiments was carried out in which the concentration of water, the temperature, and the time of reaction were kept constant. If, in fact, the difference between cyclohexanol and the other alcohols lies in differences in rate of water removal, concentration, or temperature, then the following experiment should give equivalent results with any alcohol.

We have, therefore, run similar reactions of glyoxal with 1-butanol and cyclohexanol in dioxane at 94°. In these homogeneous systems, the concentration of water and the temperature were the same. Furthermore, water was not removed from the system; therefore eq 5-7 should be favored in any case. The results of these two experiments are given in Table III.

Our conclusion from the above is that the rate of water removal or water concentration does not have an important effect on the formation of products as would be expected if eq 5-7 were operative in the mechanism. Further evidence for the nonintermediacy of structures such as 1 in eq 5 lies in the experiments given in Table IV.

In expt 4 and 5, the tetrabutoxyethane is indeed hydrolyzed with water and under mild conditions forms mainly the dimeric and trimeric products. However, only a very small amount of acetal goes to the glycolate even though the trialkoxyhydroxyethane 1 is most likely present. The effect of temperature is once again illustrated by expt 6 and 7. In those cases, the reaction temperature was allowed to reach 175°. We notice with great interest the corresponding increase in glycolate formation to the detriment of other products.

The reaction of tetracyclohexoxyethane with water (expt 8) gives *no* products except tarry residue (polymeric glyoxal) and cyclohexanol in 86% yield. It is difficult to understand why no glycolate was formed in this case from the hydrolysis product, trialkoxyhydroxyethane, if it really were an intermediate to the glycolate, when the reaction of cyclohexanol with glyoxal gives exclusively glycolate at this same temperature.

Experimental Section[6]

Cyclohexyl Cyclohexoxyacetate. A mixture of 500.0 g (5.0 mol) of cyclohexanol and 145.0 g (1.0 mol) of 40% glyoxal was heated to reflux (121°) in the presence of 1.0 g of *p*-toluenesulfonic acid. The water from glyoxal and also water of reaction was removed azeotropically (101°) with cyclohexanol. The kettle tem-

Table II
Acid- and Thermally Catalyzed Decomposition of Glyoxal Acetals[e]

$$(RO)_2CHCH(OR)_2 \xrightarrow[\Delta]{H^+}$$

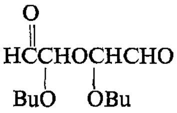
R	Equiv H+/N-acetal	Temp, °C[b]	Products, % yield[c] ROCH2CO2R	R-H[d]	ROH	ROR	
2-Butyl (37160-62-6)	0.010	220	45 (39635-98-8)	*a*	36 (78-92-2)		
Cyclopentyl (37406-80-7)	0.010	135	95+ (39635-97-7)	16 (142-29-0)	15 (96-41-3)	9	
2-Ethylhexyl (37160-56-8)	0.750	211	54 (10397-23-6)	42 (1632-16-2)		11 (10143-60-9)	23% unreacted
Butyl (6284-81-7)	0.380	225	83 (10397-22-5)	8	22	16 (142-96-1)	5% unreacted
Butyl	0.380	181	90	*a*	33	17	19% unreacted
Cyclohexyl (51122-92-0)	0.082	182	68 (51122-93-1)	42 (110-83-8)	14 (108-93-0)		
Allyl (16646-44-9)	0.036	190			25 (107-18-6)		46% unreacted
Allyl	0.190	130					Polymerized to char
Benzyl (51175-61-2)	0.370	180–190					No recognizable products

[a] Not isolated. [b] Maximum temperature before reaction was terminated by neutralization. This does not represent any specific temperature requirement, but only temperature reached during the experiment. [c] The yields of ROH, ROR, and R-H (olefin) are based on possible 4 mol of alcohol or olefin/mol of acetal. The yields based on our mechanism (1 mol of alcohol and 1 mol of olefin/mol of starting acetal) are actually much higher. [d] Olefin. [e] Registry numbers are in parentheses.

Table III
Comparison of Alcohol Reactions[a]

		Products, % yield			
			Acetals		
Alcohol	Time, days	Glycolate	Monomeric	Dimeric	Trimeric
Cyclohexanol	10	19.4	0.90		
1-Butanol	10	7.9	1.4	6.2 18.8[b] (51175-73-6)	3.3

[a] In these reactions, 4.0 mol of alcohol, 1.0 mol of 40% glyoxal, 2.0 g of *p*-toluenesulfonic acid, and 200 g of dioxane were heated at 94° for the indicated time, and the products were isolated by distillation. [b] This compound appears to be a linear dialdehyde that polymerized on standing. Microanalysis and nmr indicate a structure such as shown below. Registry number is in parentheses.



$$\underset{}{H\overset{O}{\overset{\|}{C}}}\underset{\substack{|\\BuO}}{C}HO\underset{\substack{|\\OBu}}{C}HCHO$$

Table IV
Reaction of Acetals With Water

	Reactants						Products, % yield				
Expt	Acetal	H2O	Temp, °C	Acid	Wt %	Equiv H+/N-acetal	Glycolate	Acetal	Dimer	Trimer	Alcohol
4	Butyl	H_2O	116	P-Ts	1.30	0.032	3.4	38.8	37.0[a]	5.4	26.4
5	Butyl	H_2O	120	H_2SO_4	0.73	0.069	2.9	53.9	30.2		14.0
6	Butyl	H_2O	175	P-Ts	3.35	0.084	23.4	21.5	42.1 (0.4)[b]	13.4	37.0
7	Butyl	H_2O	175	P-Ts	1.30	0.032	25.6	42.1	22.8 (0.3)		26.0
8	Cyclohexyl	H_2O	100	P-Ts	2.19	0.079					86.0

[a] Registry no., 51174-84-6. [b] The dimer in parentheses in this column is the same as that described in Table III.

perature was maintained at 121° by reducing the pressure as distillation proceeded (Monostat). When water ceased to be evolved (116.9 g total) the solution was distilled under reduced pressure to give two main fractions. The first was cyclohexanol, bp 40–68° (3 mm), 174.7 g (1.75 mol). The second fraction was cyclohexyl cyclohexoxyacetate, bp 130–137° (3 mm) [lit.[7] bp 130–132° (8 mm)], $n^{25}D$ 1.4700, 216.7 g 90.3% yield. A residue remained from this distillation (65.0 g).

Anal. Calcd for $C_{14}H_{24}O_3$: C, 70,00; H, 10.00; mol wt, 240. Found: C, 69.69; H, 10.25; mol wt, 240 (mass spectrum).

Inspection of the traps from the above distillation afforded cyclohexene, 35.0 g, 43% yield, $n^{25}D$ 1.4445, whose infrared and mass spectra were identical with those of an authentic sample.

1,1′,2,2′-Tetrakis(cyclohexoxy)ethane. A mixture of 886.8 g (8.87 mol) of cyclohexanol and 320.5 g (2.21 mol) of 40% glyoxal was heated to reflux in 1 l. of chloroform in the presence of 2.0 g of *p*-toluenesulfonic acid. Water from the glyoxal and from reaction was removed azeotropically by the chloroform (49° in the head, 68° in the kettle). When no more water was evolved (242.8 g) the pressure was reduced in the system and the chloroform was stripped. After standing overnight the solution had turned solid. The mass was filtered to give 354.3 g of crude product (50% yield). Dissolution of the solid in *n*-heptane and cooling at −80° gave, upon filtration, 218.0 g of white solid, mp 56–61°.

Anal. Calcd for $C_{14}H_{46}O_4$: C, 73.93; H, 10.90; mol wt, 424. Found: C, 72.58, 73.01; H, 10.84, 10.53; mol wt, 398 (osmometry).

The infrared spectrum (KBr) showed no OH or C=O bands. The nmr spectrum (CS_2) showed peaks at 4.2 ppm from TMS (s, 2.2 H) and a complex multiplet at 1.5 (40.0 H).

2-Ethylhexyl 2-Ethylhexoxyacetate (Expt 3). A mixture of 2-ethylhexanol, 40% glyoxal, and *p*-toluenesulfonic acid (amounts given in Table I) was heated at reflux and water was removed azeotropically. During this operation the head temperature was 90° and the kettle was 155°. After all of the water had been removed the temperature had reached 200° and heating and distillation was continued while a mixture of 2-ethylhexene and di-2-ethylhexyl ether (identified by glpc, mass spectrum, and comparison with authentic samples) was isolated overhead. Continued distillation at reduced pressure gave the product, bp 126–130° (1 mm), $n^{22}D$ 1.4381.

Anal. Calcd for $C_{18}H_{30}O_3$: C, 72.00; H, 12.00; mol wt, 294. Found: C, 72.10; H, 11.93; mol wt, 294 (mass spectrum).

***n*-Butyl Butoxyacetate (Expt 1 and 2).** A mixture of 1-butanol, 40% glyoxal, and acid (amounts and type given in Table I) was heated to reflux and water was removed azeotropically (head 96°, kettle 97°). After all of the water had been removed the distillation was continued at atmospheric pressure, allowing the temperature to rise and reach 140°. During this time olefins and di-*n*-butyl ether (identified by comparison of infrared spectrum) distilled. The temperature of the kettle was maintained at 160–170° for 1 hr and then distillation was continued at reduced pressure to recover the product, bp 95° (10 mm), $n^{25}D$ 1.4234 [lit.[8] bp 113–115° (17.5 mm), $n^{25}D$ 1.4160].

1,1′,2,2′-Tetrakis(benzyloxy)ethane. A mixture of benzyl alcohol (4.0 mol, 432.0 g), 40% aqueous glyoxal (1.0 mol, 145.0 g), 500 ml of benzene, and 2.0 g of *p*-toluenesulfonic acid was charged to a flask equipped with an automatic azeotrope head. The mixture was brought to reflux and water was removed. When no more water came off, the benzene and any other low boilers were removed at reduced pressure (150 mm) and the contents of the reaction flask were allowed to stand overnight at room temperature. The resultant solid crystals were filtered (464.0 g) and recrystallized from 500 ml of heptane. Filtration gave 261.8 g of product, mp 71°. Cooling of the mother liquors gave 89.2 g of additional material. The yield was 77%.

Anal. Calcd for $C_{30}H_{30}O_4$: C, 70.30; H, 6.61. Found: C, 79.49; H, 6.57.

The nmr spectrum (CCl_4) showed peaks at 4.55 (s, 7.8 H), 4.65 (s, 2.3 H), and 7.13 ppm (s, 20.0 H).

Acid-Catalyzed Decompositions of Acetals. A. In a typical reaction, the acetal was introduced to a magnetically stirred reaction flask equipped with a thermometer and a short Vigreux column with a take-off head. The appropriate amount of acid (either *p*-toluenesulfonic or sulfuric) was added and the mixture was heated to reflux. The resulting low-boiling azeotrope of water and organic product was removed until no more came off, or until a maximum yield of glycolate was produced (usually 45–60 min of reaction). The mixture was cooled, neutralized with sodium bicarbonate, and distilled. The products were identified either by mass spectra and glpc, or by isolation and identification in the usual manner (C, H analysis, nmr, and comparison with known physical properties).

B. A mixture of acetal (1.0 mol) and water (4.8 mol) was heated under conditions of temperature and acid shown in Table IV. After 4–5 hr, the reaction mixture was neutralized and analyzed by glpc and mass spectroscopy.

Acknowledgment. We thank Mr. B. E. Wilkes for the mass spectra.

Registry No.—Benzyl alcohol, 100-51-6.

References and Notes

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Thermal Decomposition and Dehydration of Tri-*tert*-butylcarbinol. Competing Free Radical and Carbonium Ion Reactions

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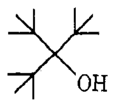
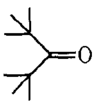
Since its synthesis in 1945, tri-*tert*-butylcarbinol[1] has received little attention, despite widespread interest in steric effects on reactivity. We wish now to report the results of an investigation of the dehydration of this compound in a variety of media, undertaken as part of a continuing study on the reactivity of tertiary alcohols and the synthesis of encumbered olefins.[2-4]

Treatment with hexamethylphosphorus triamide (HMPT) at 215–240° has proved to be a particularly convenient and mild method of dehydrating alcohols (in the sense that little or no rearrangement occurs).[3,5] For secondary alcohols, an E2 mechanism involving alkyl tetramethyldiamidate intermediates has been proposed[5] whereas, for tertiary alcohols and, exceptionally, for di-*tert*-butylcarbinol, a carbonium ion mechanism seems to be operative.[3]

This method fails, however, for the title compound **1**. When samples of **1** in HMPT were heated at temperatures between 180 and 240° (Table I), only hexamethylacetone (**2**) and the corresponding secondary alcohol **3** were obtained, in a ratio which varied from 0.5:1 to 1.2:1 as the temperature was increased. At 240°, alcohol **3** is partially dehydrated with rearrangement to 2,3,4,4-tetramethylpent-1-ene (**4**). Subsequently it was found that alcohol **1** is decomposed when heated *alone* for 5 min at 240°, giving again ketone **2** and alcohol **3** in the ratio 1.5:1. In the presence of α-methylstyrene the product ratio is slightly different (Table II) and two new compounds, identified by nmr, ir, and mass spectroscopy as **5b** and **6**, are obtained in very nearly the same ratio as **2** and **3**. The addition of styrene and of *trans*-β-methylstyrene was also examined; only the corresponding saturated adducts, **5a** and **5c**, could be isolated.



1



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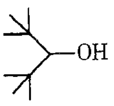

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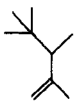

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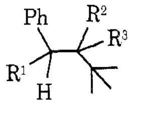
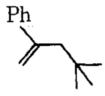


5a, $R^1 = R^2 = R^3 = H$
b, $R^1 = Me; R^2 = R^3 = H$
c, $R^1 = R^2 = H; R^3 = Me$



6

Since the same adducts **5** and **6** are formed also in HMPT solution, it is clear that, in HMPT or alone, alcohol **1** reacts by the same *free radical* mechanism. The formation of **2** and **3** would appear to be consistent with the following mechanism for the decomposition of **1**.

$$t\text{-Bu}_3\text{COH} \xrightarrow{\Delta} t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot$$

$$2\ t\text{-Bu}_2\text{COH}\cdot \longrightarrow \mathbf{2} + \mathbf{3}$$

$$t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot \longrightarrow \mathbf{2} + [\text{C}_4\text{H}_{10}]$$

$$\text{or}\quad t\text{-Bu}_2\text{COH}\cdot + t\text{-Bu}\cdot \longrightarrow \mathbf{3} + [\text{C}_4\text{H}_8]$$