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# A New Rearrangement. Catalytic Isomerization of *m*-Dioxanes to β-Alkoxy Aldehydes. II. Scope and Limitations[1]

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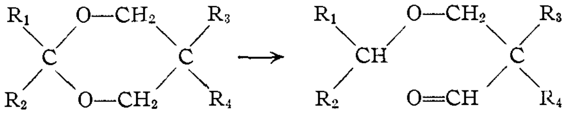
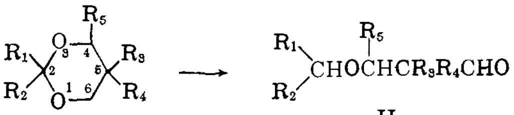
Rearrangement of *m*-dioxanes to β-alkoxy aldehydes is effected by pumice or certain forms of silica at 250–550°. Yields and conversions are generally good. The *m*-dioxanes from simple aliphatic aldehydes and ketones rearrange cleanly at about 400° on pumice; silica is active at 250–350°, but yields are slightly lower. Formals ($R_1 = R_2 = H$) are much more sluggish than other acetals and ketals. An acrolein acetal ($R_1 = CH_2{=}CH—$; $R_2 = H$) is inert to pumice but is rearranged smoothly by silica. A benzal ($R_1 = C_6H_5$, $R_2 = H$) is isomerized with astonishing facility, but ring substituents (*p*-Cl, *p*-$CH_3O$, *m*-$NO_2$, *p*-$Me_2N$) generally retard strongly the rearrangement. Even *p*-alkyl groups are slightly inhibitory. The aryl acetals on silica are converted in part also to the aromatic aldehyde and to the substituted toluene. An ether oxygen in the substituents $R_1$–$R_4$ retards rearrangement. If $R_3 = R_4 = H$, rearrangement occurs, but the product is cleaved to acrolein and an alcohol. Acetals with 5- and 7-membered rings do not undergo the rearrangement, but rather are cleaved. Diacetals are inert to hot pumice, but some of them are converted to diether-dialdehydes in fair yields by silica.



The discovery of the vapor-phase isomerization of *m*-dioxanes (I) to β-alkoxy aldehydes (II) catalyzed by weakly acidic surfaces was described in a preliminary communication.[3] This paper presents experiments with a wide variety of acetals which delineate the scope and limitations of this novel reaction. The effects of structure upon the reactivity of the acetal toward isomerization by the useable catalysts pumice and silica will be considered first. A variety of other catalysts was either inert or destructive. The side reactions and mechanism of this isomerization are discussed in the following paper. The experimental results are condensed into the tables and their footnotes. It will be convenient to refer to the individual acetals and products by the arabic numerals assigned in these tables, since their structures are at once apparent from the table format.[4]



I

II

**Effect of Acetal Structure upon the Rearrangement. Effect of Groups $R_1$ and $R_2$.**—The substituents elsewhere in the ring were held constant ($R_3 = R_4 = CH_3$; $R_5 = H$) while $R_1$ and $R_2$ were varied. The first pyrolysis of a new acetal was performed with pumice at about 400°. If the acetal was inert to pumice, the more active catalyst silica[5] was then tested.

1. Acetals from simple aliphatic aldehydes (3, 4, 7, 34), in which $R_2 = H$ and $R_1$ is methyl, isopropyl, 3-cyclohexen-1-yl and undecyl, are rearranged in good yield by pumice near 400°. Silica gel required a temperature of only 345° to give an 80% yield of 4. However, the long normal alkyl chain sensitized 34 toward a degradation by pumice at 450° or by silica at 355°; even at 305°, the product from silica was accompanied by a substantial quantity of degradation fragments. Our data are insufficient to allow a decision between chain length and chain branching as the cause of the difference between the isopropyl and undecyl acetals on silica, but this difference is less noticeable on pumice.

2. The formal 1 is much more sluggish than the acetals in paragraph 1. Conversions were poor on pumice even at 480° and, surprisingly, even on silica at 360°. At 400°, silica gave a good conversion, but cracking was pronounced. The activity of silica fell off quite rapidly as the run progressed.

3. Ketals (10, 11, 12) are isomerized readily on pumice at 350–400°. The conversion is better at the lower temperatures than with acetals. Cleavage to the starting ketone (acetone, cyclopentanone and cyclohexanone) was more prominent, especially at 400°, than with the acetals of paragraph 1.

4. A double bond attached to C-2, as in 2-vinyl- (6) or 2-isopropenyl-5,5-dimethyl-*m*-dioxane (III)[6] retards the rearrangement on pumice drastically; 6 is practically unaltered at 480°. However, it was isomerized on silica at 340° to allyloxypivalaldehyde in 80% yield. Some of the isopropenyl compound survived its passage through silica at 370°.

A double bond in $R_1$ not adjacent to the ring has no harmful effect (7).

5. Electron-withdrawing groups at C-2 impede the reaction. A chloromethyl group (8) prevents the reaction on pumice even at 480°. This acetal was largely destroyed by silica at 370°, though a low yield of β-chloroethoxypivalaldehyde was

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(1) Presented at the Gordon Research Conference on Organic Reactions and Processes, New Hampton, N. H., July 27, 1961.

(2) Present address: Spencer Chemical Co., Kansas City, Mo.

(3) C. S. Rondestvedt, Jr., and G. J. Mantell, *J. Am. Chem. Soc.*, **82**, 6419 (1960).

(4) The preparation and properties of the acetals have been described by C. S. Rondestvedt, Jr., *J. Org. Chem.*, **26**, 2247, 3024 (1961). Parallel numerals designate the acetals and the derived alkoxy aldehydes.

(5) Silica gel, Grade 70, "on 10 mesh," was supplied by the Davison Chemical Co.

(6) This acetal resulted from acetal 28 by loss of formaldehyde; see paragraph 7 of this section.

formed. The acetal with the trichloromethyl group (9) was recovered from pumice at 360° but it decomposed at 400°; silica at 380° was destructive.

6. Acetals from aromatic aldehydes are unique. The benzal (13) was rearranged completely by pumice at 350°, about 80% at 300°, and 12% at 225°. Silica was too destructive at 315°; no acetal survived, but only 46% of benzyloxypivalaldehyde was obtained, accompanied by 30% of benzaldehyde, and at least 6% of isobutyraldehyde, 3% of toluene and 2% of benzene (analysis by V.P.C.). Introduction of a methyl group into the *p*-position (14) lowered slightly the conversion on pumice at 300° and blocked the rearrangement almost completely at 225°. Silica was not tested with 14.

A *p*-isopropyl group (15) had a more profound effect on the rearrangement over pumice. At various temperatures between 285 and 330°, the first few drops of pyrolyzate were about 75% converted to *p*-isopropylbenzyloxypivalaldehyde containing a little *p*-isopropylbenzaldehyde, but the catalyst activity fell rapidly to conversions of 10–30% (depending on the temperature) in a very short time, and almost to zero when 30–50% of acetal (% of catalyst weight) had been fed. At 375°, however, conversion to products was complete, but 13% of *p*-isopropylbenzaldehyde (resulting from ring cleavage) accompanied the isomeric aldehyde. It appears that *p*-alkyl groups are somewhat inhibitory, and the retardation is more pronounced with increasing size of the alkyl group.

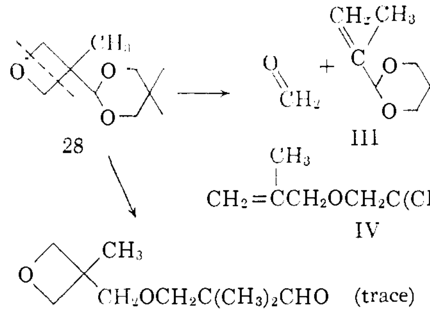
Other nuclear substituents are strongly inhibitory. On pumice at temperatures to 435°, the *p*-trifluoromethyl-, *p*-chloro-, *p*-methoxy-, *p*-dimethylamino-, and *m*-nitrophenyl acetals (16, 17, 21–23, respectively) gave at best only small amounts of the expected rearrangement products. The acetals were largely recovered. Silica was sufficiently more active to furnish isolable amounts of substituted-benzyloxypivalaldehydes from acetals 16–20. Several experiments had to be performed to find a satisfactory temperature for each acetal, otherwise unchanged starting material or by-products predominated.

The methoxyphenyl acetal (21) was degraded by silica at 375° to a nearly quantitative yield of isobutyraldehyde, together with anisole, anisaldehyde and *p*-methoxytoluene. The desired product was formed in low yield on a copper chromite catalyst and isolated only as a derivative. The *p*-dimethylamino acetal (22) was retained almost completely on silica at 285°; when the temperature was raised, slow desorption occurred to yield some *p*-dimethylaminotoluene and isobutyraldehyde, but most of the small amount desorbed was unrecognizable. On the other hand, copper chromite at 385° furnished 90% of practically pure *p*-dimethylaminotoluene from 22.

One experiment with the *m*-nitro acetal (23) on copper chromite at 345° gave a little amine, tentatively identified as *m*-(N-isobutylamino)-toluene, but most of the acetal simply disappeared. Evidently the nitro group functions as an oxidizing agent at the high reaction temperature. This acetal was not tried on silica.

All of the 2-aryl-5,5-dimethyl-*m*-dioxanes yielded the aromatic aldehyde ArCHO as the major by-product, together with a substantial amount of substituted toluene $ArCH_3$ and some of the substituted benzene ArH. The latter two materials were more abundant in pyrolyses conducted over silica catalyst. Isobutyraldehyde was the major by-product from the aliphatic portion of the ring, but small amounts of many other fragments were detected. The proportion of by-products increased at higher temperatures, especially with silica, so that good yields of isomeric aldehyde were obtained only in a rather narrow temperature range. The temperatures listed in the tables do not necessarily represent the optimum, since the study of a given acetal was pursued only to the point of obtaining a useable quantity of the product in question.[7]

7. An oxygen atom in group $R_1$ inhibits the rearrangement, as has already been noted for the *p*-methoxy compound 21. Where $R_1$ = tetrahydro-2-furyl (29), pumice at 470° yielded only about 30% of rearrangement product, and the balance of the acetal was recovered. Silica at 385° caused appreciable fragmentation to formaldehyde and other volatile products, but the alkoxy aldehyde was formed in fair yield. The 3-methyl-3-oxetanyl acetal (28) was likewise only partially converted by pumice at 460°. Silica at 370° caused extensive alteration of the molecule. The oxetane ring was split to formaldehyde and 2-isopropenyl-5,5-dimethyl-*m*-dioxane (III), and the latter rearranged normally to methallyloxypivalaldehyde (IV). A trace of III escaped rearrangement. Some of the starting acetal was recovered and a possible trace of its isomeric aldehyde was detected by infrared analysis. Some III and IV were perhaps formed also in the pyrolysis on pumice.



When the oxygen atom in $R_1$ is present as an acyclic ether, as in acetal 33, it apparently does not interfere and rearrangement proceeds normally. Perhaps the oxygen atom is sterically screened from the catalyst, or it may be that the acyclic ether is sufficiently less basic than the cyclic ethers so that it is not adsorbed on the catalyst.[8]

8. Diacetals derived from the dialdehydes $O{=}CH(CH_2)_nCHO$, $n$ = 0, 1, 2, 3 (41–44), were unchanged by pumice at temperatures to 575° in

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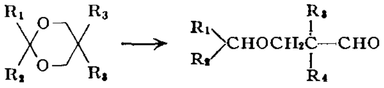
[7] The formation of by-products is considered in detail in the following paper, *J. Am. Chem. Soc.*, **84**, 3319 (1962).

[8] **Oxygen atoms in $R_3$ and $R_4$ are also deleterious; see following section.**

TABLE I

β-ALKOXY TERTIARY ALDEHYDES BY REARRANGEMENT OF *m*-DIOXANES



A. Pyrolysis conditions, properties of products

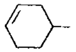
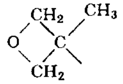
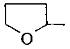
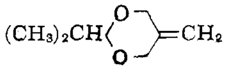
| From acetal | R¹ | R² | R³ | R⁴ | Catalyst | Temp., °C. | Yield, %[a] (recov. acetal) | B.p. °C. | B.p. Mm. | $n^{25}_D$ | Formula | Calcd., % C | Calcd., % H | Found, % C | Found, % H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | H | H | $CH_3$ | $CH_3$ | Pumice | 400–440 | 38 (37)[b] | 131.0–131.5 | Atm. | 1.4065 | $C_6H_{12}O_2$ | 62.03 | 10.42 | 61.8, 61.0 | 10.2, 10.4 |
| 2 | $CH_3$ | H | H | H | Pumice | 380–420 | [c] (46) | | | | | | | | |
| 3 | $CH_3$ | H | $CH_3$ | $CH_3$ | Pumice | 380–400 | 66 (9) | 145–147 | Atm. | 1.4037 | $C_7H_{14}O_2$ | 64.23 | 10.83 | 64.0, 63.8 | 10.3, 10.3 |
| 4 | $(CH_3)_2CH$ | H | $CH_3$ | $CH_3$ | Pumice | 410–416 | 69 (16) | 80.3 | 30 | 1.4078 | $C_9H_{18}O_2$ | 68.4 | 11.4 | 68.9, 68.5 | 11.5, 11.6 |
| | | | | | Silica | 337–352 | 80 (0)[d] | | | | | | | | |
| 5[e] | $(CH_3)_2CH$ | H | $CH_3$ | $CH_2CH_2CH_3$ | Pumice | 392–410 | 49 (low) | 113–114 | 44 | 1.4212 | $C_{11}H_{22}O_2$ | 71.0 | 11.8 | 71.3, 71.3 | 11.7, 11.7 |
| 6 | $CH_2{=}CH—$ | H | $CH_3$ | $CH_3$ | Silica | 343–354 | 80 (trace) | 106–107 | 104 | 1.4248 | $C_8H_{14}O_2$ | 67.57 | 9.92 | 67.7, 67.3 | 10.2, 10.1 |
| 7 |  | H | $CH_3$ | $CH_3$ | Pumice | 391–409 | High (0) | 104–105 | 6 | 1.4608 | $C_{12}H_{20}O_2$ | 73.42 | 10.27 | 73.6, 73.5 | 10.3, 10.1 |
| 8 | $ClCH_2$ | H | $CH_3$ | $CH_3$ | Pumice | 480–490 | 0 (80) | | | | | Compound not obtained pure | | | |
| | | | | | Silica | 363–375 | Low (low) | 113–117 | 47 | .... | $C_7H_{13}ClO_2$ | | | | |
| 9 | $Cl_3C$ | H | $CH_3$ | $CH_3$ | Pumice | 344–363[f] | 0 (82) | | | | | | | | |
| | | | | | Silica | 373–386[g] | 0 (0) | | | | | | | | |
| 10 | $CH_3$ | $CH_3$ | $CH_3$ | $CH_3$ | Pumice | 360–368 | 45 (12)[h] | 155 | Atm. | 1.4040 | $C_8H_{16}O_2$ | 66.62 | 11.19 | 65.4, 65.5 | 11.4, 11.3 |
| | | | | | Pumice | 400–410 | 31 (trace)[i] | | | | | | | | |
| 11 | $—(CH_2)_4—$ | | $CH_3$ | $CH_3$ | Pumice | 397–423 | 45 (trace)[j] | 93–97 | 18 | 1.4421 | | | | | |
| | | | | | Pumice | 357–366 | 51 (16)[j] | 116–118 | 45 | 1.4400 | $C_{10}H_{18}O_2$ | 70.55 | 10.66 | 70.0, 70.1 | 10.5, 10.9 |
| 12 | $—(CH_2)_5—$ | | $CH_3$ | $CH_3$ | Pumice | 380–390 | 80 (trace)[k] | 104–109 | 19 | 1.4461 | $C_{11}H_{20}O_2$ | 71.69 | 10.94 | 71.0, 71.1 | 10.8, 10.6 |
| 13 | $C_6H_5$ | H | $CH_3$ | $CH_3$ | Pumice | 340–360[l] | 75 (*ca.* 10)[m] | 139–140 | 21 | 1.4965 | $C_{12}H_{16}O_2$ | 74.96 | 8.39 | 74.9, 75.1 | 8.4, 8.5 |
| | | | | | $CuCrO_2$ | 271–282[n] | 8 | | | | | | | | |
| | | | | | Silica | 311–324 | 46 (0)[o] | | | | | | | | |
| 14 | $p$-$CH_3C_6H_4$ | H | $CH_3$ | $CH_3$ | Pumice | 284–310 | Good (low)[p] | 118–121 | 3.5 | .... | $C_{13}H_{18}O_2$ | 75.69 | 8.79 | 75.6, 75.6 | 8.7, 8.6 |
| 15 | $p$-$(CH_3)_2CHC_6H_4$ | H | $CH_3$ | $CH_3$ | Pumice | 372–383 | 62 (trace)[q] | 131–133 | 2 | 1.4951 | $C_{15}H_{22}O_2$ | 76.88 | 9.47 | 76.7, 76.5 | 9.4, 9.4 |
| 16[e] | $p$-$CF_3C_6H_4$ | H | $CH_3$ | $CH_3$ | Silica | 276–292 | 40 (low)[r] | 111–113 | 0.8 | 1.4535 | $C_{13}H_{15}F_3O_2$ | 60.0 | 5.8 | 58.4, 58.7 | 6.2, 6.1 |
| 17 | $p$-$ClC_6H_4$[s] | H | $CH_3$ | $CH_3$ | Silica | 246–256 | Good (trace) | 127–131 | 2.5 | 1.5099 | $C_{12}H_{15}ClO_2$[t] | 63.54 | 6.67 | 63.2, 63.1 | 6.7, 6.7 |
| 18 | 2,4-$Cl_2C_6H_3$ | H | $CH_3$ | $CH_3$ | Silica | 315–325 | 28 (trace)[u] | 128–133 | 1.4 | 1.5238 | $C_{12}H_{14}Cl_2O_2$[v] | 55.19 | 5.40 | 55.0; 55.4 | 5.5, 5.3 |
| 19 | 3,4-$Cl_2C_6H_3$ | H | $CH_3$ | $CH_3$ | Silica | 288–299 | 45 (trace)[w] | 146–148 | 2 | 1.5231 | $C_{12}H_{14}Cl_2O_2$[x] | 55.19 | 5.40 | 55.2, 55.0 | 5.5, 5.4 |
| 20 | 2,6-$Cl_2C_6H_3$ | H | $CH_3$ | $CH_3$ | Silica | 330–345 | 36 (0)[y] | 127–132 | 1 | 1.5266 | $C_{12}H_{14}Cl_2O_2$[z] | 55.19 | 5.40 | 55.9, 55.9 | 5.3, 5.2 |
| 21 | $p$-$CH_3OC_6H_4$ | H | $CH_3$ | $CH_3$ | $CuCrO_2$[aa] | 360–370 | Poor (poor) | 143–152 | 6[bb] | 1.5102[bb] | Compound not obtained pure | | | | |
| 22 | $p$-$(CH_3)_2NC_6H_4$ | H | $CH_3$ | $CH_3$ | $CuCrO_2$[cc] | 380–390 | 0[dd] | | | | | | | | |
| 23 | $m$-$NO_2C_6H_4$ | H | $CH_3$ | $CH_3$ | $CuCrO_2$[ee] | 338–354 | 0[ff] | | | | | | | | |
| 25a | $CH_3$ | H | $CH_3$ | $CH_2OSO_2C_6H_4CH_3$-$p$ | Pumice | 380–413 | 0[gg] | | | | | | | | |
| 26 | $(CH_3)_2CH$ | H | $—CH_2OCH_2—$ | | [hh] | [hh] | [hh] | | | | | | | | |
| 27 | $(CH_3)_2CH$ | H | $—OCH_2CH_2CH_2—$ | | Pumice | 453–468 | Poor (high)[ii] | | | | | | | | |
| 28 |  | H | $CH_3$ | $CH_3$ | Silica | 360–380 | 36 (low)[jj] | 60–62 | 6 | 1.4328 | $C_9H_{16}O_2$ | 69.19 | 10.30 | 69.0, 69.3 | 10.3, 10.4 |
| 29 |  | H | $CH_3$ | $CH_3$ | Silica[kk] | 372–399 | 42 (low) | 135–138 | 34 | 1.4488 | $C_{10}H_{18}O_3$ | 64.48 | 9.74 | 64.4, 64.5 | 9.6, 9.8 |
| 30 | $(CH_3)_2CH$ | H | $C_2H_5$ | $CH_2OCH_2CH{=}CH_2$ | Silica[ll] | 340–356 | Fair (fair)[ll] | *ca.* 109 | 5 | 1.4378 | $C_{13}H_{24}O_3$ | 68.38 | 10.59 | 68.2, 68.3 | 10.8, 10.7 |
| 31 | $CH_3CH_2CH_2$ | H | $CH_3$ | $CH{=}CH_2$ | Pumice | 402–417 | Poor (low)[mm] | *ca.* 95 | 12 | 1.4384 | $C_{10}H_{18}O_2$ | 70.54 | 10.65 | Not obtained pure | |
| 32 | $(CH_3)_2CH$ | H | $CH_3$ | $NO_2$ | Pumice | 372–400 | 0 (poor)[nn] | | | | | | | | |
| 33 | $(CH_3)_2CHCH_2OCH_2C(CH_3)_2$– | H | $CH_3$ | $CH_3$ | Pumice | 398–411 | 60 (low) | 127 | 18 | 1.4199 | $C_{14}H_{28}O_3$ | 68.81 | 11.15 | 68.7, 68.6 | 11.6, 11.7 |
| 34 | $n$-$(C_{11}H_{23})$ | H | $CH_3$ | $CH_3$ | Pumice[oo] | 410–440 | >58 (low) | 142–145 | 2.5 | 1.4380 | $C_{17}H_{34}O_2$ | 75.50 | 12.67 | 75.4, 75.4 | 12.8, 12.7 |
| 35 | From 2,4-diisopropyl-5,5-dimethyl-*m*-dioxane | | | | Pumice | 381–390 | [pp] | | | | | | | | |
| 36 | From 2-phenyl-4 isopropyl-5,5-dimethyl-*m*-dioxane[qq] | | | | | | | | | | | | | | |
| 37 | $(CH_3)_2CH$ | H | $—CH_2CH{=}CHCH_2CH_2—$ | | Silica | 342–346 | 46 (0) | | | | | | | | |
| | | | | | Pumice | 402–418 | 75 (trace) | 78–79 | 1 | 1.4610 | $C_{12}H_{20}O_2$ | 73.42 | 10.27 | 72.2, 72.2 | 10.2, 10.3 |
| 38 | $(CH_3)_2CH$ | H | $—CH_2CH_2CH_2CH_2CH_2—$ | | Pumice | 405–416 | 50 (trace) | 105–106 | 8 | 1.4508 | $C_{12}H_{22}O_2$ | 72.68 | 11.19 | 73.8, 74.1 | 11.2, 11.3 |
| 39 | $(CH_3)_2CH$ | H | $C_2H_5$ | $C_2H_5$ | Pumice[rr] | 450–459 | Low (good) | | | | Isolated only as semicarbazone | | | | |

TABLE IA

B. Derivatives of products

| From acetal | Derivatives[ss] (crystn. solv.) | M.p., °C. | Formula | Calcd., % C | H | N | Other | Found, % C | H | N | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | DNP (M-A) | 135-137 | $C_{12}H_{16}N_4O_5$ | 48.64 | 5.44 | 18.91 | | 48.6, 48.3 | 5.4, 5.5 | 18.9, 18.7 | |
| 3 | DNP (M-A) | 130-132 | $C_{13}H_{18}N_4O_5$ | 50.32 | 5.85 | 18.06 | | 50.6, 50.4 | 6.0, 5.9 | 18.0, 17.9 | |
| 4 | DNP (E) | 123.8-124.8 | $C_{15}H_{22}N_4O_5$ | 53.2 | 6.55 | 16.5 | | 53.2, 53.1 | 6.6, 6.5 | 16.4, 16.4 | |
| | S (E-W) | 133.4-134.4 | $C_{10}H_{21}N_3O_3$ | 55.8 | 9.8 | 19.5 | | 56.3, 56.3 | 9.7, 9.7 | 19.3, 19.3 | |
| 5 | DNP (M) | 91 | $C_{17}H_{26}N_4O_5$ | 55.7 | 7.1 | 15.3 | | 56.0, 56.2 | 7.1, 7.1 | 15.7, 15.5 | |
| 6 | DNP (E) | 112.5-113.0 | $C_{14}H_{18}N_4O_5$ | 52.17 | 5.63 | 17.38 | | 52.1, 52.2 | 5.7, 5.7 | 17.7, 17.7 | |
| 7 | P (M-W) | 102.0-102.5 | $C_{18}H_{25}N_3O_3$ | 65.23 | 7.60 | 12.68 | | 65.1, 65.2 | 7.4, 7.5 | 13.1, 12.8 | |
| 8 | DNP (E) | 113-114 | $C_{13}H_{17}ClN_4O_5$ | 45.29 | 4.97 | 16.25 | Cl, 10.28 | 45.7, 45.4 | 5.0, 4.9 | 16.1, 16.4 | Cl, 10.3 |
| 10 | P (M-W) | 70-72 | $C_{14}H_{21}N_3O_3$ | 60.41 | 7.24 | 15.10 | | 60.2, 60.3 | 7.7, 7.6 | 15.1, 14.8 | |
| 11 | DNP (E) | 148.5-149.1 | $C_{16}H_{22}N_4O_5$ | 54.84 | 6.33 | 15.99 | | 55.1, 54.9 | 6.2, 6.4 | 15.9, 15.9 | |
| 12 | DNP (E) | 132.5-133.0 | $C_{17}H_{24}N_4O_5$ | 56.03 | 6.64 | 15.39 | | 55.9, 56.0 | 6.8, 6.8 | 15.4, 15.7 | |
| 13 | S (E-W)[tt] | 124.0-125.0 | $C_{13}H_{19}N_3O_2$ | 62.63 | 7.68 | 16.86 | | 62.7, 62.4 | 7.6, 7.6 | 17.1, 16.9 | |
| 14 | DNP (E) | 113.7-114.3 | $C_{19}H_{12}N_4O_5$ | 59.06 | 5.74 | 14.50 | | 59.1, 59.4 | 5.6, 5.7 | 14.5, 14.6 | |
| 15 | DNP (E) | 107.0-107.2 | $C_{21}H_{25}N_4O_5$ | 60.85 | 6.32 | 13.52 | | 60.7, 60.6 | 6.3, 6.2 | 13.5, 13.7 | |
| 16 | DNP (M) | 122.0-122.5 | $C_{19}H_{19}F_3N_4O_5$ | 51.8 | 4.3 | 12.7 | | 51.5, 51.9 | 4.8, 4.6 | 12.6, 12.7 | |
| 17 | DNP (E) | 144.5-146.0 | $C_{18}H_{19}ClN_4O_5$ | 53.14 | 4.71 | 13.77 | Cl, 8.72 | 53.3, 53.2 | 4.7, 4.6 | 13.9, 13.9 | Cl, 9.8, 9.5 |
| 18 | DNP (E-A) | 151-152 | $C_{18}H_{18}Cl_2N_4O_5$ | 48.99 | 4.11 | 12.70 | Cl, 16.07 | 49.0, 49.1 | 4.1, 4.1 | 12.7, 12.8 | Cl, 16.0, 16.4 |
| 19 | DNP (E) | 143-145 | $C_{18}H_{18}Cl_2N_4O_5$ | 48.99 | 4.11 | 12.70 | Cl, 16.07 | 49.0, 49.3 | 4.3, 4.2 | 13.1, 12.7 | Cl, 15.9, 16.1 |
| 20 | DNP (X) | 196-197 | $C_{18}H_{18}Cl_2N_4O_5$ | 48.99 | 4.11 | 12.70 | Cl, 16.07 | 49.7, 49.7 | 4.3, 4.4 | 12.8, 12.5 | Cl, 15.9, 15.9 |
| 21 | DNP (E) | 122.5-123.2 | $C_{19}H_{22}N_4O_6$ | 56.71 | 5.51 | 13.92 | | 56.4, 56.6 | 5.6, 5.5 | 13.7, 14.0 | |
| 28 | DNP (C)[uu] | 96.5-97.5 | $C_{15}H_{20}N_4O_5$ | 53.66 | 5.99 | 16.66 | | 53.5, 53.7 | 5.4, 5.6 | 16.9, 16.7 | |
| | Semi (E-W)[uu] | 120-121 | $C_{10}H_{19}N_3O_2$ | 56.31 | 8.98 | 19.70 | | 56.5, 56.6 | 8.9, 9.1 | 19.5, 19.6 | |
| 29 | DNP (E) | 109.1-109.8 | $C_{16}H_{22}N_4O_6$ | 52.45 | 6.05 | 15.29 | | 52.6, 52.5 | 5.8, 6.0 | 15.4, 15.6 | |
| 30 | DNP (E) | 127.2-128.0 | $C_{19}H_{28}N_4O_6$ | 55.87 | 6.91 | 13.72 | | 56.0, 56.1 | 7.5, 7.9 | 15.1, 14.8 | |
| 31 | DNP (E) | 97.0-97.6 | $C_{16}H_{22}N_4O_5$ | 54.84 | 6.33 | 15.99 | | 54.7, 54.7 | 6.6, 6.6 | | |
| 33 | DNP (E) | 119.8-120.4 | $C_{20}H_{32}N_4O_6$ | 56.58 | 7.60 | 13.20 | | 56.4, 56.5 | 7.6, 7.6 | 13.4, 13.4 | |
| 34 | DNP (E) | 85.0-85.8 | $C_{23}H_{38}N_4O_5$ | 61.31 | 8.50 | 12.44 | | 61.4, 61.2 | 8.2, 8.6 | 12.5, 12.4 | |
| 37 | DNP (E) | 106.3-106.7 | $C_{18}H_{24}N_4O_5$ | 57.43 | 6.41 | 14.89 | | 57.4, 57.5 | 6.3, 6.5 | 15.0, 14.7 | |
| 38 | Semi (M-W) | 147.3-148.3 | $C_{13}H_{25}N_3O_2$ | 61.14 | 9.87 | 16.45 | | 61.2, 61.1 | 9.8, 9.9 | | |

[a] Since in many cases, the product was not completely separated from unchanged acetal, some yields are given qualitatively: high = 80-100%; good = 60-80%; moderate = 40-60%; fair = 20-40%; poor = 20%. All yields are based on weight of acetal charged. [b] The acetal and aldehyde appear to form a constant-boiling mixture, b.p. 128° (atm.), $n^{25}_D$ 1.4161. [c] Plus 35% of acrolein and 40% of ethanol, and traces of acetaldehyde. [d] By infrared analysis of pyrolyzate, using the acetal band at 12.6 μ and the alkoxypivalaldehyde band at 12.9 μ. [e] Experiments with this acetal were performed by Harold W. Pier, to whom I am indebted. [f] The acetal was extensively destroyed at 390-400°. [g] The products were almost entirely volatile fragments. [h] Plus 27% of acetone, some $CH_2O$, a little isobutylene. [i] Plus 46% of acetone, 34% of isobutylene and considerable $CH_2O$. [j] Plus 38% (at 410°) or 17% (at 360°) of cyclopentanone, and also isobutyraldehyde and isobutylene. [k] Plus about 10% of cyclohexanone, and also isobutyraldehyde, formaldehyde and isobutylene; 7-10% of 3,3-dimethyloxetane was also formed. [l] At 400° the pyrolyzate (80% of acetal charged) was about 5% of benzaldehyde, balance benzyloxypivalaldehyde with almost no unchanged acetal. At 225° the pyrolyzate (98% recovery) was 1% benzaldehyde, 12% benzyloxypivalaldehyde, balance acetal. [m] A little benzaldehyde was also formed; semicarbazone, m.p. 218-220°. [n] At 350°, only half of the charge was recovered as a mixture of acetal and aldehyde; the trap contained benzene, toluene, isobutyraldehyde and isobutylene in substantial amounts. [o] Also 6% of isobutyraldehyde, 2% of benzene, 3% of toluene, 30% of benzaldehyde, based on acetal charged. When benzyloxypivaldehyde is passed through silica at 332-342°, the product is 7% of isobutyraldehyde, 4% of benzene, 13% of toluene, 57% of benzaldehyde and 23% unchanged aldehyde. [p] At 225° practically no isomerization occurred. The bulk of the charge was not desorbed from the catalyst until the temperature was raised to 290°. [q] Plus 13% of *p* isopropylbenzaldehyde. At 284-300°, the acetal was recovered quantitatively. [r] The acetal was essentially unchanged by pumice at 400-415°. [s] Pumice at 275, 375 and 435° gave almost entirely unchanged acetal. Silica at 355° gave considerable *p*-chlorotoluene, *p*-chlorobenzaldehyde and isobutyraldehyde; at 295°, very little cracking occurred, and the results were comparable to those at the lower temperature tabulated. [t] % Cl calcd. 15.64, found 15.2 and 15.3. [u] The acetal gave 40% of dichlorobenzaldehyde and dichlorotoluene in roughly equal amounts, plus isobutyraldehyde, methanol, isobutylene, a conjugated diene and apparently a conjugated carbonyl compound. [v] % Cl calcd. 27.15, found 27.3 and 27.7. [w] By-products were 30% of dichlorobenzaldehyde but very little dichlorotoluene; the smaller fragments were similar to those from acetal 18. [x] % Cl calcd. 27.15, found 26.9 and 26.8. [y] By-products were 7% of dichlorobenzaldehyde and 23% of dichlorotoluene, plus smaller fragments. [z] % Cl calcd. 27.15, found 27.5 and 27.6. [aa] The acetal was recovered unchanged from pumice at 275 and 375°. Silica at 375° gave a nearly quantitative yield of isobutyraldehyde, with some *p*-methoxytoluene, *p*-methoxybenzaldehyde and anisole. These by-products were also formed in the run tabulated. [bb] Contaminated with acetal. [cc] Unchanged by pumice at 390°; completely degraded by silica at 285°, in part to *p*-dimethylaminotoluene and isobutyraldehyde. [dd] *p*-Dimethylaminotoluene was obtained practically pure in 90% yield; picrate m.p. 124.5-125.5°, methiodide m.p. 220° dec. [ee] Unchanged by pumice at 275 and 375°, except for darkening. [ff] A low yield of an amine was obtained, identified tentatively as N-isobutylaniline by infrared. [gg] A low yield of toluene, arising by cleavage of the toluenesulfonyl group, was the only identifiable product. [hh] Unchanged by pumice at 400 or 480°. Silica at 340° at first produced a carbonyl compound, but the catalyst was rapidly deactivated and the remaining acetal passed through unchanged. At 385 and 425° with silica, the acetal was destroyed, and the pyrolyzate no longer contained an oxetane ring (absence of infrared band at 10.2 μ). [ii] Detection of isomeric product by infrared may be questionable. [jj] The product is not the isomeric aldehyde, but consists rather of methallyloxypivalaldehyde with some 2-isopropenyl-5,5-dimethyl-*m*-dioxane and formaldehyde polymer. A little unchanged acetal and possibly some of the expected isomeric aldehyde were also obtained. Pyrolysis on pumice at 460° returned mostly starting acetal, but some alkoxyaldehyde(s) were also detected. [kk] Pumice at 468-478° gives about 30% rearrangement. With silica, some isobutylene and formaldehyde were formed. [ll] Pumice at 415 or 455° caused considerable cracking, but no detectable alkoxyaldehyde was formed. An appreciable quantity of an unidentified, lower boiling aldehyde was formed by both pumice and silica, along with isobutyraldehyde. [mm] The product is accompanied by an isomer, b.p. 108-110°/(12 mm.), $n^{25}_D$ 1.4490, which gives a DNP (E), m.p. 139-143°. *Anal.* Found: C, 54.7, 54.6; H, 6.7, 6.5. [nn] The products resulted from cracking, and included methacrolein, isobutyraldehyde, $NO_2$, and an acetal of isobutyraldehyde, possibly



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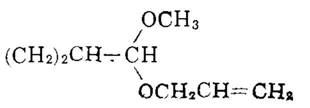
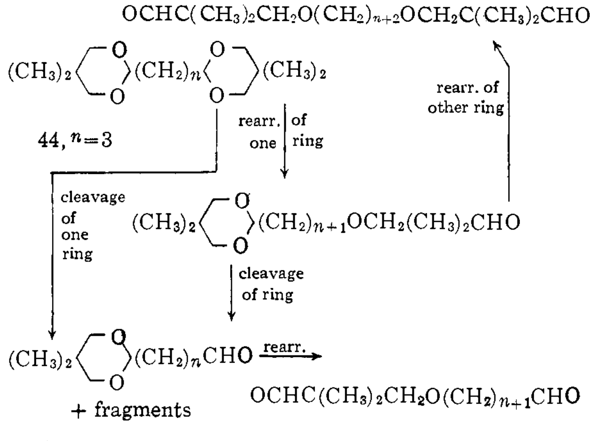


$(CH_2)_2CH-CH(OCH_3)(OCH_2CH=CH_2)$

Some starting material was recovered. [oo] Silica used as a catalyst at 350–362° caused complete degradation to dodecanal. At 305°, silica gave a moderate yield of dodecyloxypivalaldehyde, and considerable degradation. Fresh pumice at 450° caused considerable cracking to isobutyraldehyde, olefins and other products, but after brief use, it effectively isomerized the acetal with only a little cracking. [pp] The major product was 86% of isobutyraldehyde by ring cleavage. The other cleavage product was 53% of isobutyl isobutenyl ether; 23% of a mixture of acetal and (presumably) isomeric ketone $(CH_3)_2CHCOC(CH_3)_2CH_2OCH_2CH(CH_3)_2$ was obtained. Traces of methanol, isobutylene, formaldehyde, methacrolein and other fragments were also formed. [qq] Pumice at temperatures to 475° yielded initially a little benzaldehyde, toluene, isobutyraldehyde and another carbonyl compound. The catalyst activity fell very rapidly during the run, so that the acetal passed through unchanged after a few grams had been added. Silica at 330° caused almost complete fragmentation to toluene, isobutyraldehyde, a little benzaldehyde and several aliphatic compounds. The ether absorption in the infrared was so weak that it is unlikely that any of the normal rearrangement product was formed. [rr] On pumice at 400 or 455°, conversion was initially fair but fell off rapidly. The pyrolyzate was triturated with cold hexane to separate the insoluble acetal. [ss] DNP = 2,4-dinitrophenylhydrazone, S = semicarbazone, P = *p*-nitrophenylhydrazone, M = methanol, E = ethanol, A = ethyl acetate, W = water, X = xylene, C = cyclohexane. [tt] The molten derivative solidified abruptly at 206°, then remelted with gas evolution at 220°. [uu] These are the derivatives of methallyloxypivalaldehyde.

some cases, truly an unexpected stability. On silica, the susceptibility to reaction increased with the separation between the two *m*-dioxane rings. Acetal 41 was inert, or was destroyed at a sufficiently high temperature; 42 gave a low yield of dialdehyde. With two or three methylene groups between the two rings, satisfactory yields of dialdehyde $(CH_2)_{n+2}$–$[OCH_2C(CH_3)_2CHO]_2$ were formed. The wide variety of by-products includes the singly-rearranged aldehyde-dioxane, its cleavage products, the products of single and double cleavage of the starting acetal, and an arcane assortment of small fragments.

The glutaraldehyde acetal (44) was examined in some detail. About 46% was converted to the isomeric dialdehyde, 12% to a mixture of lower-boiling materials (including the once-rearranged aldehyde-acetal) and 12% to volatile fragments. The balance was lost as non-condensable gases, by retention on the catalyst, and as mechanical losses. The low-boiling fraction was mostly isobutyraldehyde, but the following constituents were separated by gas chromatography and identified by time-of-flight mass spectrometry: isobutylene, acetaldehyde, a butene, 1-propanol, 1,4-pentadiene, pivalaldehyde, a $C_6$-paraffin and a $C_6$-olefin. Though the other products can be rationalized,[7] the six carbon fragments are mysterious, for the acetal was built up of three five-carbon blocks. Obviously the catalyst can cause combination as well as cleavage.

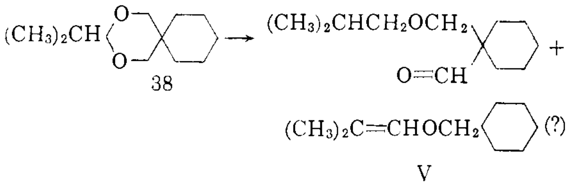


The 1,4-phenylene-bis-*m*-dioxane 45 was rearranged to some extent on pumice at 465° but only slightly at 410°. Separation of the small amount of product from the unchanged acetal was not accomplished; the evidence for the rearrangement is the infrared spectrum. This acetal was retained tenaciously on silica at 350°. When the catalyst was heated quickly to 435°, a small amount of acetal was desorbed, but most of the charge appeared as isobutyraldehyde and non-condensable gases. This acetal was not further investigated.

**Effect of Groups $R_3$ and $R_4$.**—These groups were varied with $R_1$ = isopropyl and $R_2$ = H.[9] The substitution at C-5 was not studied as extensively as substitution at C-2.

1. It is probable that any small alkyl group can occupy the 5-position. The results with 5,5-dimethyl (4) were essentially the same as with 5-methyl-5-*n*-propyl (5). The 5,5-diethyl compound was not studied, but since the 5,5-diethyloxathiane derivative (56) rearranges, the corresponding dioxane would probably undergo normal isomerization.

$R_3$ and $R_4$ may be combined into an unsaturated or saturated six-membered spirocyclic ring (37, 38). The unsaturated compound rearranged normally on pumice, in lower yield on silica. On the other hand, the saturated spiro acetal suffered extensive cracking to isobutyraldehyde and other small fragments, and an appreciable amount of a by-product not isolated in pure form. The infrared spectra of fractions rich in this by-product suggest it is a vinyl ether, perhaps V.[10]



2. When $R_3$ is a vinyl group, as in 2-*n*-propyl-5-methyl-5-vinyl-*m*-dioxane (31), isomerization took place to a limited extent at 380° on pumice. At 415°, conversion was improved, but the yield of pure product was low and other unidentified compounds were formed. This acetal was not tried with silica.

3. 2-Isopropyl-5,5-diphenyl-*m*-dioxane (39) was even more reluctant to rearrange on pumice, even at 455°. Although some of the expected 3-isobutoxy-2,2-diphenylpropanal was detected in the mixture with unchanged acetal by means of the infrared spectrum, it was not possible to isolate it in pure form. This acetal was retained on silica at

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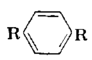
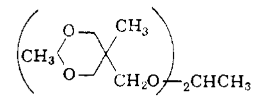
(9) Choice of $R_1$ and $R_2$ was indicated by the fact that isobutyraldehyde resulting from ring cleavage has a very easily recognized infrared spectrum.

(10) Vinyl ether was indeed a product from acetal 35, as discussed in the next section.

TABLE II

PYROLYSIS OF BIS-ACETALS

A. Pyrolytic conditions

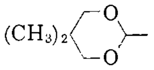
| No. | Acetal[a] | Catalyst | Temp., °C. | Yield, %[b] |
|---|---|---|---|---|
| 41 | R-R | Silica[c] | 381–408 | [d] |
| 42 | $RCH_2R$ | Silica[e] | 349–368 | Poor (low)[f] |
| 43 | $RCH_2CH_2R$ | MnNiCuCr[g] | 310–368[h] | Fair (low)[i] |
| 44 | $RCH_2CH_2CH_2R$ | Silica[j] | 339–363 | 46 (low)[k] |
| 45 |  | Pumice[l] | 459–479 | Low (high)[m] |
| 46 |  | Pumice | 385–391 | 0 (58)[n] |
| 47 | Pentaerythritol diformal | Pumice | 500 | 0 (high)[o] |
| 48 | Pentaerythritol diisobutyral | Silica[p] | 365–391 | [q] |
| 49 | Pentaerythritol dibenzal | Pumice | 419–444 | 0 (high)[r] |

B. Properties of $(O{=}CHCMe_2CH_2O)_2(CH_2)_n$

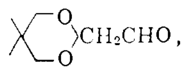
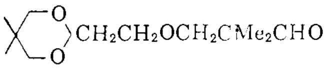
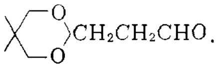
| No. | | B.p. | | | | Calcd., % | | Found, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | °C. | Mm. | $n^{25}_D$ | Formula | C | H | C | H |
| 42 | $n = 1$ | 115 | 1.2 | 1.4399 | $C_{13}H_{24}O_4$ | 63.90 | 9.90 | 63.7, 63.8 | 9.7, 9.5 |
| 43 | $n = 2$ | 136–138 | 3 | 1.4440 | $C_{14}H_{26}O_4$ | 65.08 | 10.18 | 65.2, 65.4 | 10.1, 10.1 |
| 44 | $n = 3$ | 150 | 1.2 | 1.4452 | $C_{15}H_{28}O_4$ | 66.14 | 10.34 | 66.1, 66.1 | 10.2, 10.3 |

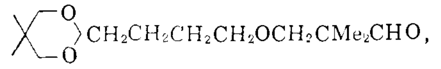
C. Bis-2,4-dinitrophenylhydrazones of dialdehydes

| No. | M.p., °C. | Crystn. solv.[s] | Formula | Calcd., % | | | Found, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| 42 | 175.4–176.1[t] | A | $C_{25}H_{32}N_8O_{10}$ | 49.66 | 5.34 | 18.54 | 50.3, 50.6 | 5.6, 5.7 | 17.5, 17.6 |
| 43 | 206–208 | X | $C_{26}H_{34}N_8O_{10}$ | 50.48 | 5.54 | 18.11 | 51.3, 51.1 | 5.7, 5.7 | 18.4, 18.4 |
| 44 | 150–151 | E-A | $C_{27}H_{36}N_8O_{10}$ | 51.21 | 5.74 | 17.71 | 51.3, 51.3 | 6.1, 6.1 | 18.3, 18.5 |

[a] In this section, R = 5,5-dimethyl-*m*-dioxan-2-yl, 

[b] See note *a*, Table I. [c] The acetal was recovered unchanged from pumice at 500–550°, though a little was decomposed at the beginning of the run. On silica at 350°, a trace of alkoxy aldehyde was produced (infrared absorption at 12.9 μ), but most of the acetal was recovered. Mixed metal chromites on silica at 370–389° caused extensive decomposition. [d] Some alkoxy aldehyde was perhaps produced (infrared), but recovery was low and considerable decomposition to isobutyraldehyde and olefins occurred. [e] Unchanged on pumice at 500–570°, high recovery. $ZnCl_2$ on pumice at 280 or 330° split the acetal into smaller fragments. Copper chromite at 350° caused extensive fragmentation to isobutyraldehyde and other products.

[f] Other products are isobutyraldehyde, an alcohol ,  and unchanged acetal. [g] Moderate recovery of acetal from pumice at 375–490°, considerable cracking. Cleaved by $ZnCl_2$–pumice at 285°. Destroyed by copper chromite at 345°, and by platinum–alumina at 285°. An experiment with silica gave results similar to these tabulated. [h] The temperature was varied deliberately during this run. At 320°, there was considerable gas evolution early in the run, and no liquid pyrolyzate was formed. The first liquid which appeared had substantial unchanged acetal. At 368°, fairly extensive degradation occurred. The optimum temperature was about 340°. [i] About 10% of isobutyraldehyde was formed, together with olefins. An unidentified aldehyde was obtained in low yield, b.p. 90–116° (3 mm.), $n^{25}_D$ 1.470–1.459, which may be .

[j] Not tried on pumice. Copper chromite at 375–400° caused extensive degradation to isobutyraldehyde, isobutylene and other fragments. [k] Good recovery by weight. Some isobutyraldehyde and isobutylene, possible vinyl ether. There is also a fraction, b.p. 126–128° (1.2 mm.), $n^{25}_D$ 1.4485, believed to be , the product of half rearrangement. [l] The result on pumice at 402–414° was similar. Silica at 267–272° retained the charge completely; when it was heated to 350°, nothing was desorbed. When further heated to 465°, some isobutyraldehyde was driven out, but no aromatic material was desorbed. [m] Though infrared showed some rearrangement (mono and/or di), the unchanged starting material could not be cleanly separated by crystallization. [n] The product was cracking fragments plus unchanged acetal. [o] Mostly unchanged, but some cracking to formaldehyde and other products. At 400° the acetal was unchanged. [p] Pumice at 450-565° gave some isobutyraldehyde, but 83% was recovered unchanged. [q] No acetal survived. The products were isobutyraldehyde, gaseous fragments, and other small molecules. [r] Mostly acetal, a trace of benzaldehyde. [s] For abbreviations, see Table IB, note *ss*. [t] If immersed at 140°, it melts, resolidifies immediately, and remelts at 175.4-176.1°. Immersed at 122°, m.p. 175.4–176.1°.

305° as a black zone at the top of the catalyst bed; nothing emerged from the tube except a few drops of water.

4. $R_3$ may not be hydrogen. In acetal 2,

rearrangement apparently occurred to the extent of about 50% over pumice at 400°. The predicted product, β-ethoxypropionaldehyde, will be recognized as the adduct of ethanol to acrolein. Under the conditions of the experiment, it dissociated to its components, both of which were isolated and identified. It is probable that only β-alkoxy tertiary aldehydes can be prepared by this catalytic pyrolysis.

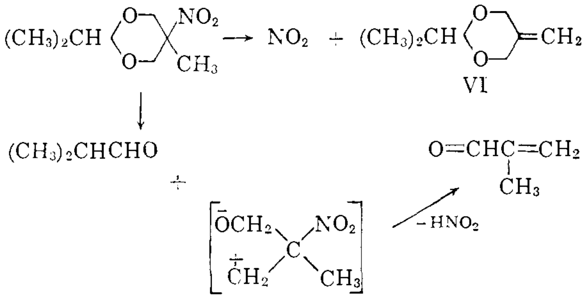
5. Substituents containing oxygen appear to be as harmful at C-5 as they are at C-2. An acyclic ether function, as in acetal 30, is moderately inhibitory; pumice caused considerable cracking at 400°, but it was possible to obtain a fair yield of isomeric aldehyde from silica, along with unchanged acetal and an unidentified impurity. The tris-acetal "trimethylolethane sesquiacetal" (46) was partly cracked but mostly unchanged by hot pumice.

The *spiro*-ethers 26 and 27 were unaffected by pumice until the temperature became high enough to cause extensive decomposition. The same was true with silica catalyst, although the destruction threshold temperature was lower than with pumice.

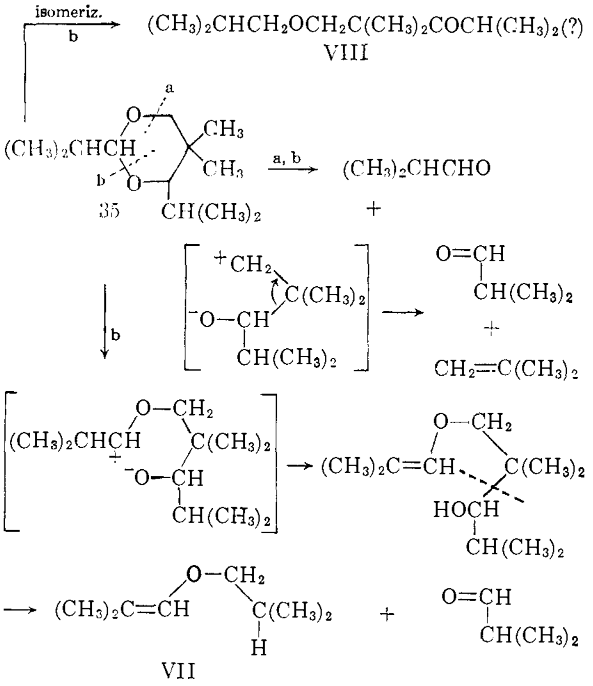
The *spiro*-bis-acetals derived from pentaerythritol (47–49) were extremely inert, and were recovered almost quantitatively from pumice at temperatures to 500°. Pentaerythritol diisobutyral (48) was degraded by silica at 365–391° to isobutyraldehyde and other small liquid and gaseous fragments. This behavior is in sharp contrast to the similarly constructed *spiro*-acetals 37 and 38, which lack the additional oxygen atoms.

When $R_3$ was *p*-toluenesulfonatomethyl (24), the molecule was disrupted, and the only product identified was toluene resulting from aromatic desulfonation. Most of the remainder was retained on the catalyst.

A nitro group at C-5 was no better. Acetal 32 was in part recovered from pumice at 390°, and the remaining material did not contain nitro groups. Brown fumes of nitrogen dioxide were liberated in the early stage of the pyrolysis. Other fragments identified included methacrolein, isobutyraldehyde and an acetal of isobutyraldehyde which may be VI.



**Effect of Substituents Elsewhere in the *m*-Dioxane Ring.**—No systematic study was made of groups in the 4- and 6-positions. 4,4-Dimethyl-*m*-dioxane (59) was unaffected by pumice at 325°, but it was cleaved in part to formaldehyde at 375°. 2,4-Diisopropyl-5,5-dimethyl-*m*-dioxane (35) was converted to isobutenyl isobutyl ether (VII) (53% yield) and isobutyraldehyde, though a small amount of material believed to be the isomeric ketone VIII was also formed.



The path by which 35 is transformed to VII and isobutyraldehyde is proposed by analogy to the well-known acid-catalyzed conversion of acyclic acetals to vinyl ethers and alcohols. The intermediate mono-ether of a 1,3-diol should undergo cleavage by acidic reagents as do the diols themselves.[11]

2-Phenyl-4-isopropyl-5,5-dimethyl-*m*-dioxane (36) cannot form a vinyl ether. When it was passed through pumice at 400° or 470°, a little cleavage to toluene, isobutyraldehyde and other aliphatics occurred early in the run. The catalyst activity rapidly dropped and the remainder of the charge passed through unchanged. On silica at 330°, fragmentation to the above-mentioned products was almost complete. There appeared to be no unchanged acetal or isomeric aldehyde or ketone.

It has not been determined whether other 4-substituted *m*-dioxanes can be isomerized, so that the question whether an aldehyde or a ketone would be formed preferentially remains unanswered. The preceding results suggest that fragmentation is apt to predominate.

**Effect of Ring Size.**—One 5-membered cyclic acetal was examined. 2,4,4-Trimethyl-1,3-dioxolane (51) was cleaved to acetaldehyde and a fragment which rearranged to a mixture of isobutyraldehyde and methyl ethyl ketone. No α-ethoxyisobutyraldehyde was detected. This cleavage is analogous to that reported by Neish, Haskell and MacDonald,[12] who split assorted 2-alkyl-4,5-dimethyl-1,3-dioxolanes to the same products by passage of the acetal over phosphoric acid on pumice at 400°. No other dioxolane was examined in the present work.

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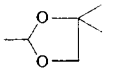
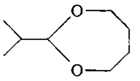
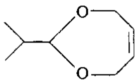
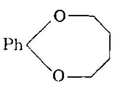
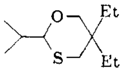
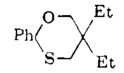
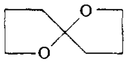
(11) See for example, R. W. Brown and G. Dougherty, *J. Org. Chem.*, **13**, 173 (1948); J. English and F. V. Brutcher, *J. Am. Chem. Soc.*, **74**, 4279 (1952). Compare also the formally analogous conversion of 2-(hydroxy-*t*-butyl)-5,5-dimethyl-*m*-dioxane to 2-isopropyl-5,5-dimethyl-*m*-dioxane by loss of formaldehyde.[3]

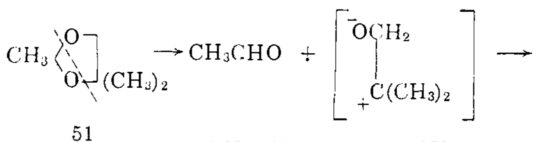
(12) A. C. Neish, V. C. Haskell and F. J. MacDonald, *Can. J. Res.*, **B25**, 266 (1947).

TABLE III

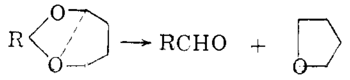
PYROLYSIS OF OTHER MONO-ACETALS

| No. | Acetal | | Catalyst | Temp., °C. | Products |
|---|---|---|---|---|---|
| 51 | 2,4,4-Trimethyl-1,3-dioxolane |  | Pumice | 351–358 | [a] |
| 52 | 2-Isopropyl-1,3-dioxepane |  | Pumice | 390–400 | [b] |
| 53 | 2-Isopropyl-1,3-dioxep-5-ene |  | Pumice | 390–403 | [c] |
| 54 | 2-Phenyl-1,3-dioxepane |  | Pumice | 403–416 | [d] |
| 55 | 2-Isopropyl-5,5-diethyl-1,3-oxathiane |  | Silica | 350 | [e] |
| 56 | 2-Phenyl-5,5-diethyl-1,3-oxathiane |  | Pumice | 415 | [f, g, h] |
| 57 | 1,6-Dioxaspiro[4,4]nonane |  | Silica[i] | 349–354 | [j k] |
| 58 | 2,2-Dimethoxypropane | | Pumice | 405–437 | [l] |
| 59 | 4,4-Dimethyl-*m*-dioxane | | Pumice | 367–382 | [m] |

[a] A high recovery of cracking fragments was obtained. These consisted largely of acetaldehyde, paraldehyde, isobutyraldehyde and some methyl ethyl ketone. [b] The product was a mixture of isobutyraldehyde and tetrahydrofuran. Very little unchanged acetal was recovered. [c] Essentially unchanged acetal. [d] Quantitative conversion to benzaldehyde and tetrahydrofuran. At 314–325°, mostly unchanged acetal, with a little cleavage. [e] No starting material recovered; none of the expected product was obtained. On pumice at 415°, most of the pyrolyzate was starting material, with some $Et_2C{=}OH_2$, and other cracking fragments with OH and C=O absorption. [f] At 360°, the conversion was less complete. At 415°, the trap contained largely 2-ethyl-1-butene, with a little benzene and toluene, and a foul-smelling thioaldehyde(?). The oxathiane boils higher and has a lower refractive index than the product. [g] The product, 3-(α-toluenethio)-2,2-diethylpropanal, b.p. 140° (3 mm.), $n^{25}_D$ 1.5455, was not obtained pure. [h] The DNP melted at 112–113° (E). *Anal.* Calcd. for $C_{20}H_{24}N_4O_4S$: C, 57.67; H, 5.81; N, 13.45; S, 7.70. Found: C, 57.4, 57.6; H, 5.8, 5.7; N, 13.4, 13.2; S, 7.4, 7.1. [i] The acetal was recovered unchanged from pumice at 400 or 450°. On silica at 315° the acetal was only slightly altered; at 385° it was mostly destroyed. [j] The product was partly unchanged ketal, and some cracking occurred as well. Both β-(tetrahydro-2-furyl)-propionaldehyde and 3-(3,4-dihydro-2-furyl)-1-propanol were formed, the latter identified by infrared bands for cyclic vinyl ether and primary OH. [k] β-(Tetrahydro-2-furyl)-propionaldehyde, b.p. 107° (40 mm.), $n^{25}_D$ 1.4585. *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.3, 65.4; H, 9.4, 9.1. Its DNP melted at 94.5–95.0° (E). *Anal.* Calcd. for $C_{13}H_{16}N_4O_5$: C, 50.64; H, 5.23; N, 18.17. Found: C, 50.5, 50.3; H, 5.2, 5.2; N, 18.3, 18.3. [l] About half the acetal was recovered unchanged. The other identified products were methanol, acetone and $CH_2{=}C(CH_3)OCH_3$. [m] Considerable formaldehyde was formed, but the balance was unchanged acetal. At 318–329°, the acetal was unchanged.


51

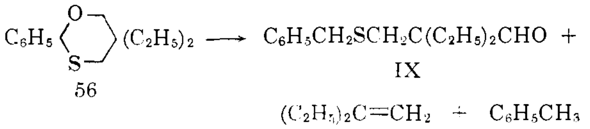
2-Isopropyl- and 2-phenyl-1,3-dioxepane (52, 54) were cleaved to isobutyraldehyde (or benzaldehyde) and tetrahydrofuran, the extent of cleavage increasing with increasing temperature of the catalyst bed. 2-Isopropyl-1,3-dioxep-5-ene (53) was unchanged, bespeaking its relatively rigid structure.



These results indicate that the rearrangement is limited to six-membered ring acetals.

**Miscellaneous Acetals.**—2,2-Dimethoxypropane (58) was passed through pumice at 410°. Over half of the ketal was recovered unchanged, and the balance appeared as acetone and methanol in the mole ratio 1:1.36. A little methyl isopropenyl ether was detected by its infrared spectrum. Evidently the ring structure of the *m*-dioxanes furnishes a powerful impetus to the rearrangement, since the cyclic acetone ketal (10) was completely isomerized (and cleaved to some extent) at this temperature.

Two oxathianes have been studied briefly. The 2-isopropyl derivative (55) was largely destroyed by pumice or silica. Rearrangement of the phenyl derivative (56) to 2,2-diethyl-3-(α-toluenethio)-propanal (IX) proceeded on pumice, but degradation to 2-ethyl-1-butene and toluene occurred at the same time.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One atypical ketal undergoes this rearrangement. 1,6-Dioxaspiro[4,4]nonane (57) in which the two

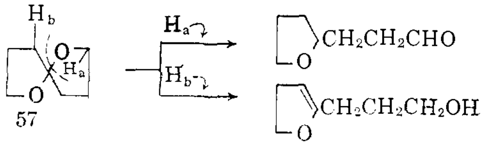
TABLE IV

CATALYST SCREENING

| Catalyst | Temp., °C. | Products |
|---|---|---|
| A. Catalysts causing essentially no rearrangement | | |
| Pyrex glass fragments | 450 | |
| Cast iron turnings | 400 | |
| 10% $CoCl_2$ on pumice | 295 | |
| 5% $H_3BO_3$ on pumice | 295 | |
| 10% anh. $MgCl_2$ flakes (Dow) on pumice | 295 | |
| 10% $Cu(OAc)_2$ on pumice | 315 | |
| Sintered copper (Girdler T-601) | 320 | |
| $Cr_2O_3$ gel | 315, 415 | |
| $Cr_2O_3$–$Al_2O_3$ (Girdler G-41) | 340 | |
| Cr-promoted $Fe_2O_3$ (Girdler G-3A) | 350 | |
| Diisopropyl sulfate[a] | 270, 350[b] | |
| Ni powder (Girdler G-49) | [c] | |
| Di-*tert*-butyl peroxide | 155[d] | |
| Various manganese chromites on $Al_2O_3$ (A. B. Stiles) | 320–390 | |
| Various MnCuCrNi on $Al_2O_3$ (A. B. Stiles) | 340–388 | |
| B. Catalysts with weak activity | | |
| Aluminum sulfate | 270[e] | |
| Bentonite clay | 300, 355 | |
| Silica–alumina–ammonia | [f] | |
| C. Catalysts causing cleavage | | |
| Silica, Davison Grade 04 | 250, 325 | $H_2O$, aromatic hydrocarbon, $(CH_2O)_x$, isobutyraldehyde, isobutylene |
| 10% $H_3PO_4$ on $SiO_2$ | 255 | $H_2O$, isobutyraldehyde, isobutylene |
| Attapulgite clay | 300, 400 | Isobutyraldehyde, methyl ethyl ketone, unsatd. hydrocarbons, unidentified; a little isobutoxy pivalaldehyde |
| Alumina, Alcoa F-20 | 355 | Quant. isobutylene, + other hydrocarbons, $H_2O$; no isobutyraldehyde |
| Boron phosphate[g] | 255, 325 | Unsatd. hydrocarbons, water, methyl ethyl ketone; no isobutyraldehyde |
| Silica–alumina[h] | 250, 280 | Aromatic hydrocarbons, isobutylene, water, isobutyraldehyde |
| D. Catalysts causing extensive fragmentation | | |
| Charcoal[i] | 370 | $H_2O$, olefins, non-condensable gas |
| BTS Katalyzator[j] | 250 | No reaction |
| | 300 | Isobutyraldehyde, isobutylene, $H_2O$, hydrocarbons |
| | 335 | $CO_2$, $H_2O$ |
| CoO–Kieselguhr (Girdler T-300) | 380 | $CO_2$, $H_2O$, isobutylene, propylene, ethylene |
| NiO–Kieselguhr (Girdler T-316)[k] | 330 | Retained on catalyst |
| NiO–Kieselguhr (Girdler T-316)[l] | 355 | Gas; cat. shattered and plugged tube |
| Ni hydrog. cat. (Girdler G-12)[l] | 375 | Gas; cat. shattered and plugged tube |
| MnCuCrNi on microcel (A. B. Stiles) | 325 | Hydrocarbons |
| MnCuCrNi on $SiO_2$–$Al_2O_3$ (A. B. Stiles) | 320, 235 | Gas, $H_2O$, olefins and paraffins; some acetal at 235° |
| MnCuCrNi on $TiO_2$ (A. B. Stiles) | 320, 380 | Gas, $H_2O$, olefins; some unidentified C=O compound |
| Ni powder (Girdler G-49B) on pumice | 295 | Gas, a little unchanged acetal, isobutyraldehyde |
| Pt–$Al_2O_3$ (Houdry "platforming")[l] | 250 | Isobutyraldehyde, a little unchanged acetal |
| Nickel chromite (A. B. Stiles) | 310, 380 | Combustion to $CO_2$; a little acetal recovered |

[a] R. H. Hall and E. S. Stern, *J. Chem. Soc.*, 3383 (1954), dealcoholated acetals to vinyl ethers by passing a mixture of acetal and isopropyl sulfate through a hot tube at 300°. [b] In these experiments, a 1% solution of isopropyl sulfate in the acetal was passed through a heated column of Pyrex glass fragments. [c] Refluxed 4 hours (160°) with 5% of this nickel powder. [d] 1% of peroxide in the acetal in vapor phase over glass fragments at 155° gave no reaction; refluxing the acetal for 16 hours with the peroxide formed no isobutoxypivalaldehyde. [e] At 355°, extensive formation of a malodorous sulfur compound occurred. At 270$^a$, low recovery with extensive cracking occurred, but some isobutoxypivalaldehyde was produced. [f] Houdry S-90 was saturated at 300° with gaseous ammonia, swept with nitrogen, and the acetal added. At 200 or 230°, the pyrolyzate was acetal with a little isobutoxypivalaldehyde and considerable isobutyraldehyde; the recovery was low. At 250°, the product contained amines (odor, infrared) and isobutyraldehyde. [g] See U. S. Patents 1,895,238; 1,924,763–8. [h] Houdry synthetic cracking catalyst, S-46. [i] Norite A and coconut-shell char. 6–10 mesh, gave equivalent results. [j] Supplied by Badische Anilin-und-Soda Fabrik; it contains copper oxide, with minor amounts of other metals. [k] Conditioned with methanol as described above. [l] Reduced at 350–400° in a hydrogen stream.

ketal oxygens are in separate five-membered rings, was unchanged by pumice. In the narrow temperature range 340–360°, it was partially converted by silica to β-(tetrahydro-2-furyl)-propionaldehyde and a product tentatively identified as 3-(4,5-dihydro-2-furyl)-1-propanol (a vinyl ether). This



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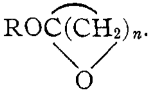
result suggests that the structural requirement for rearrangement of an acetal may be only



$ROC(CH_2)_n$. Experiments with 2-alkoxytetrahydro-furan and -pyran are planned, though it is anticipated that dealcoholation to dihydro-furan and -pyran will predominate.

**Catalysts.**—The hypothesis that this rearrangement is acid catalyzed led to testing of various acidic materials. 2-Isopropyl-5,5-dimethyl-*m*-dioxane (4) as the model acetal was passed through the subject catalyst and the effluent was examined by infrared spectroscopy supplemented, as required, by distillation and gas chromatography. Results of runs on the various catalysts are given in the Experimental section and in Table IV.

The acidic catalysts may be classified as hyperactive or inactive. The former cause cleavage of the model acetal to isobutyraldehyde, isobutylene, formaldehyde and gaseous fragments. Silica gel (Davison Grade 04 high-surface), alumina (Alcoa F-10), silica-alumina cracking catalysts (Houdry Process Corp.) and supported phosphoric acid fall into this classification.

Weakly acidic salts deposited on pumice, such as magnesium chloride, boric acid, cobalt chloride and copper acetate belong in the inactive category. Zinc chloride on pumice at 300° was quite effective with 4, but the yields were low because of concurrent cleavage. With the bis-acetal 42, zinc chloride yielded a mixture of fragmentation products, but no isomeric carbonyl compound could be detected.

Copper chromite (Girdler G-13, reduced with methanol) was considerably more active than pumice, both toward 4 and the resistant 2-vinyl (6) and 2-*p*-methoxyphenyl (21) compounds. However, the bis-acetals 42 and 43 were fragmented. As noted above, two aryl-*m*-dioxanes (21 and 22) yielded the substituted toluenes as well.

Desultory attempts to effect the rearrangement in the liquid phase were unsuccessful. When 4 was refluxed (160°) with catalytic amounts (1–10%) of diisopropyl sulfate, aluminum isopropoxide, *t*-butyl peroxide, *p*-toluenesulfonic acid or sulfuric acid, no isomeric aldehyde was produced. The latter two reagents caused some cracking to isobutyraldehyde and tarry products.

**Infrared Spectra.**—Several characteristic infrared absorptions proved very valuable in identification of the compounds encountered. The *m*-dioxanes exhibit a strong fundamental ether stretching frequency near 9.0 $\mu$, flanked in most cases by bands near 8.7 and 9.6 $\mu$ of slightly lower intensity. It is believed that these side bands result from coupling effects involving both cyclic oxygen atoms; such an effect has been noted with straight-chain multiple ether functions and with branched-chain aliphatic ethers.[13] As the amount of substitution at the 2-position increases, the side bands become weaker and the fundamental increases in intensity.

An absorption of medium intensity at 12.6–12.7 $\mu$ has been observed in the 5,5-di*alkyl*-*m*-dioxanes, with very few exceptions. In the spiroketals 11 and 12, this band is attenuated but still visible; 11 exhibits a broad band at 11.8 $\mu$, and 12 shows two sharp bands of medium intensity at 11.8 and 12.1 $\mu$. In acetal 21, the band is at 12.78 $\mu$, and in acetal 43, it is at 12.55 $\mu$. This absorption is provisionally attributed to a deformation frequency of the $CH_2$ group in the unit $-OCH_2CR_2-$; it is shifted by deuteration.[7] The necessity of the 5,5-disubstituted structure is shown by the absence of this absorption in 2-methyl-*m*-dioxane and 4,4-dimethyl-*m*-dioxane. When the substituents at C-5 are not simple alkyl, the band shifts or disappears. The 5,5-diphenyl compound (39) has a band at 13.84 $\mu$ which may represent the shift of the 12.7 $\mu$ band; the 12–13 $\mu$ region is completely barren. The acetal 24, with a hydroxymethyl group at C-5, absorbs at 12.62 $\mu$, but its low- and high-melting toluenesulfonates, respectively, absorb in this region at 12.80 $\mu$ weak, and not at all. The allyl ether (acetal 30) absorbs at 12.91 $\mu$. When the 5-position is bridged by an oxetane ring (acetal 26), an absorption appears at 13.3 $\mu$; when the bridging ring is tetrahydrofuran (acetal 27), the band is at 12.95 $\mu$. In the spirocyclic acetal with a 6-membered carbocyclic ring at C-5 (38), a very weak band is observed at 12.7 $\mu$, and other bands are found at 11.8 and 12.1 $\mu$. These three are absent from the unsaturated analog 37, which does absorb at 12.8 $\mu$. A nitro group at C-5 (acetal 25) causes the band to disappear.

When the structure $-OCH_2CR_2-$ is in a 5-membered ring, this band is still recognizable, but it is shifted to 12.54 $\mu$ (acetal 51). This structural unit is not present in the 7-membered ring compounds examined here; the 2-isopropyl- and 2-phenyl-dioxepanes (acetals 52 and 54) absorb at 12.45 and 12.35 $\mu$, respectively. This band is not found in neopentyl alcohol, neopentyl glycol or 2,2-diethyl-1,3-propanediol.

After the rearrangement has proceeded, with destruction of the ring, the unit $-OCH_2CR_2-$ finds itself less constrained, and its absorption shifts to longer wave lengths. In the alkoxy aldehydes listed in the tables, a medium absorption is found in the range 12.81–12.93 $\mu$, with all but three in the narrower range 12.86–12.91 $\mu$. In the 2,6-dichlorobenzyl compound (20), it is masked by a very broad intense band from the aromatic ring. This band is completely absent from the spectra of the 1-alkylcyclohexanal and cyclohexenal (38, 37).

A second band in the alkoxy aldehydes appears at 11.2 $\mu$. Though usually less distinct than that at 12.9 $\mu$, it is nevertheless useful in recognizing the system.

On the Perkin–Elmer Infracord or model 21 spectrophotometer the acetal and alkoxy aldehyde bands are distinct; in a few cases quantitative

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(13) L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 114. See also E. D. Bergmann and S. Pinchas, *Rec. trav. chim.*, **71**, 161 (1952), and G. Lagrange and P. Mastagli, *Compt. rend.*, **241**, 1947 (1955).

analysis of incompletely rearranged mixtures was performed. The sensitivity limits appear to be about 10–90%. If the carbonyl compound resulting from ring cleavage is removed first, the carbonyl absorption of the alkoxy aldehyde can also be used in quantitative analysis.[14]

**Synthetic Utility.**—β-Alkoxy aldehydes are generally prepared by conjugate addition of alcohols to α,β-unsaturated aldehydes. This reaction is not applicable to tertiary aldehydes, $R_3OCH_2CR_1R_2CHO$, those having no α-hydrogen atom. It should be possible to etherify the hydroxy aldehydes $HOCH_2CR_1R_2CHO$ (which are available from $HCR_1R_2CHO + CH_2O$), but there apparently is no such attempt reported.

The boron fluoride-catalyzed addition of acetals to vinyl ethers yields β-alkoxy acetals, and the method has been recently applied by Brannock to tertiary aldehyde acetals (eq. 1).[15] We have extended Brannock's method to the addition of

$$R_4CH(OR_3)_2 + R_1R_2C{=}CHOR_5 \xrightarrow{BF_3} R_3OCHR_4CR_1R_2CH(OR_3)OR_5 \xrightarrow{\text{hydrolysis}} R_3OCHR_4CR_1R_2CHO \quad (1)$$

formals ($R_4$ = H) to isobutenyl alkyl ethers (see Experimental), and obtained ethoxypivalaldehyde after hydrolysis.[3]

Aldehydes themselves can be induced to add to vinyl ethers under the influence of boron fluoride. This unusual reaction was applied to the preparation of one unsaturated tertiary aldehyde (eq. 2)

$$CH_3CH{=}CHCHO + (CH_3)_2C{=}CHOCH_3 \xrightarrow{BF_3} CH_3CH{=}CHCH(OCH_3)C(CH_3)_2CHO \quad (2)$$

in moderate yield.[16]

These two appear to be the only methods in the literature for β-alkoxy tertiary aldehydes. In comparison to our new method, they offer one advantage, that a new carbon–carbon bond is formed from smaller molecules. In our method, the carbon skeleton must be first built up by aldol condensation (or other procedure) into the 1,3-diol required for acetal preparation. Secondly, both published methods can yield β-alkoxy ketones, which our method at present cannot do.

On the other hand, there are drawbacks to the reactions in eq. 1 and 2. Brannock's method yields a new acetal which can add to a second mole of vinyl ether. This consecutive addition could doubtless be suppressed by use of a large excess of original acetal which must later be separated; in our hands a 50% excess of diethyl formal was not sufficient to eliminate poly-addition to ethyl isobutenyl ether. A further, though minor disadvantage to this method is the necessity for having $R_3 = R_5$. If the alkoxy groups are different, there is a rapid interchange of alkoxyls and a mixed product is obtained. We found that dimethyl formal and ethyl isobutenyl ether gave a mixture of methoxy- and ethoxy-pivalaldehyde.

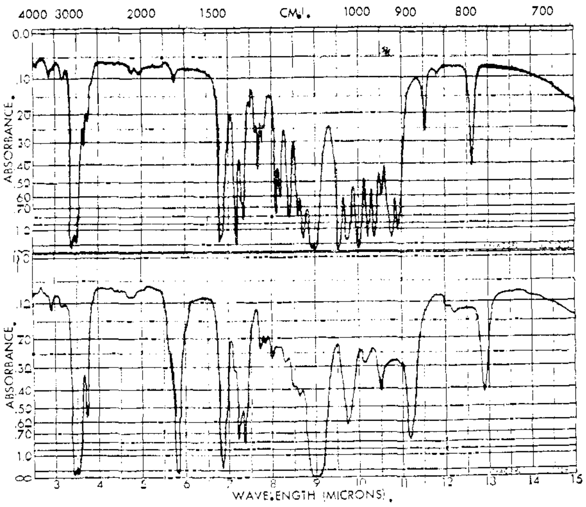

Fig. 1.—Infrared Spectra: upper curve, 2-isopropyl-5,5-dimethyl-*m*-dioxane; lower curve, isobutoxypivalaldehyde.

The method of Hoaglin, Kubler and Leech (eq. 2) can also give poly-addition, as they noted, but there is no problem with alkoxyl interchange. Neither of these methods has been studied in enough detail to establish the yields, scope and limitations. Although their methods do not require a vapor-phase, high-temperature apparatus in the final step, the requisite vinyl ethers are prepared either by catalytic vapor-phase (or liquid-phase in lower yield) dealcoholation of an acetal, or the use of acetylene under pressure.

At the present time, our method is probably the procedure of choice for synthesizing $ROCH_2CR_2CHO$. The other methods will permit preparation of β-substituted compounds $ROCHRCR_2CHO$ (and perhaps $ROCR_2CR_2CHO$ from ketals or ketones) which cannot be made from *m*-dioxanes at the present time.

## Experimental

**Procedure for Pyrolysis.**—In scouting experiments, two 12″ "clamshell" commercial furnaces were mounted vertically. However, the temperature profile along the 24″ length was very uneven, especially where the two furnaces were in contact. In most of the pyrolyses reported, home-made furnaces were used. These were built from 1.25″ (1.75″) o.d. stainless steel pipe wrapped with asbestos and insulated with a 2.5″ layer of steam-pipe insulation. Three heating units controlled by variable transformers heated the middle half and the top and bottom quarters of the tube independently. The heated zones were 34″ (28″) long. Four iron–constantan thermocouples in a 6 mm. well inside the pipe were spaced 7″ apart, the top one 1″ below the top of the catalyst bed, and connected to a recording potentiometer. The top and bottom of the pipe were closed by pieces of asbestos board with holes cut to fit the pyrolysis tubes, thereby minimizing convection currents through the furnace. The furnaces were mounted vertically.

An 18 or 20 mm. o.d. (occasionally 12 or 25 mm.) Pyrex tube with standard taper joints was fitted with indented prongs to support the catalyst. About 45 g. of catalyst was introduced into the tube to a height of 24″ (usually), and the catalyst was baked at the operating temperature for 30–60 min. in a nitrogen stream to remove water. Liquid acetals were added from a graduated dropping funnel with

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[14] The authors are indebted to Mrs. Dorothy Pfahler Miller, formerly of this Laboratory, for helpful discussions of the infrared spectra. The spectra of 2-isopropyl-5,5-dimethyl-*m*-dioxane and of isobutoxypivalaldehyde are reproduced as typical examples in Fig. 1.

[15] K. C. Brannock, *J. Org. Chem.*, **25**, 258 (1960).

[16] R. I. Hoaglin, D. G. Kubler and R. E. Leech, *J. Am. Chem. Soc.*, **80**, 3069 (1958). Dr. Kubler, private communication, predicted that saturated aldehydes would react similarly.

a constant-head device. The rate of addition was controlled by a Teflon-tipped needle valve operated through a Teflon[17] bushing. The acetal was added directly to the top of the catalyst bed in most cases, though occasionally a layer of 0.25″ Berl saddles was placed on top to serve as a preheater. Solid acetals were added from a similar needle-valve funnel without the constant-head device, and maintained molten by heating tapes. In most experiments, the rate of addition was 10–20 ml./hr. The acetals 41 and 49 melt too high for convenient addition as a liquid, so these were added manually at about the same rate from a glass "hopper" device provided with a scraper passing through a rubber sleeve. This obviously requires continuous attention from the operator.

A stream of nitrogen was passed through the tube along with the acetal. The rate was estimated from a flowmeter on the input side and calculated from a wet test meter at the end of the exhaust gas line. The nitrogen flow rate was normally 40–60 ml./min.

The pyrolyzate was collected in a receiver without external cooling. More volatile components were caught in two traps in series cooled to −80°. The exit gas was led through a mineral oil bubbler into a tared Ascarite tower, thence to the wet test meter. The tube was swept with nitrogen for about 1 hour after addition was complete.

The bulk pyrolyzate (dried with calcium chloride, potassium carbonate, or Linde Molecular Sieve 4A if water was visible as a separate layer) was examined by infrared spectroscopy. In the later work, infrared samples of the effluent were taken at intervals during the run to check on the changing activity of the catalyst with use. It was thus found that both pumice and silica possessed an initial high activity (essentially no acetal left, some cracking), which diminished rapidly to a still high plateau almost unchanged after long use with the simpler acetals. In several cases, especially with 2-aryl-*m*-dioxanes at lower temperatures, the activity fell rapidly to zero. Catalyst regeneration was not studied.

The pyrolyzate was distilled through a 100-mm. micro-Vigreux column for separation from cracking fragments. In many cases where conversion was high, later cuts from these distillations were free from acetal (infrared) and were used directly for analysis and for the preparation of derivatives. In all cases examined in this work, the alkoxy aldehyde boiled somewhat higher than the isomeric acetal, and its refractive index was about 0.015 lower. The refractive index of mixtures of acetal and aldehyde is approximately a linear function of composition, so that in some of the cases reported in the tables, the numerical yield was calculated from the refractive indices of various cuts. Infrared absorption can also be used for estimation, most conveniently by using the ratio of absorptions of the 12.6 and 12.9 $\mu$ bands to avoid interference from extraneous carbonyl compounds.

Semicarbazones were prepared by the procedure of Shriner, Fuson and Curtin.[18] Dinitrophenylhydrazones were prepared either by the phosphoric acid method of Johnson[19] or the "diglyme" method of Shine[20]; a few were made by the sulfuric acid method of Brady.[21] The Brady reagent is potent but its shelf life is limited. The phosphoric acid–ethanol reagent of Johnson has a shelf life of at least one year, but it had the drawback of frequently giving difficultly filterable derivatives in our hands. The Shine reagent (dinitrophenylhydrazine in "diglyme") appears to be stable indefinitely, and it has the advantage of control of the quantity of acid catalyst employed. Thus acetals react only slowly in the presence of a trace of concentrated hydrochloric acid, while the aldehydes encountered in this work react rapidly. By using an excess of crude aldehyde, the DNP reagent is consumed before the contaminating acetal reacts appreciably. However, most of the monoaldehyde DNP derivatives encountered did not precipitate from the "diglyme" solution, and dilution with water or ethanol was necessary. The Shine procedure is preferred and is highly recommended.

**Catalysts.**—Granular pumice was obtained from the James H. Rhodes Co. and screened. Either 10–12 mesh or 12–20 mesh gave equivalent results; 4–8 mesh was slightly inferior, and coarser lumps gave much poorer conversions. Grade 70 silica gel was obtained from the Davison Chemical Co. as "on 10" mesh lumps, and used as received after baking out in the tube. This silica has a stated pore volume of 1.16 ml./g., pore diameter 140 Å., and a surface area of 340 sq. m./g.[22] Copper chromite was supplied by Girdler Catalysts as their "G-13 catalyst" in the form of $^1/_8 \times {^3/_{16}}''$ pellets. As furnished, however, it contained a very active oxidizing agent (copper oxide?) which was eliminated by heating it to about 350° and adding methanol slowly in a nitrogen stream until the violent exothermic reaction was completely spent (about 40 ml. for a standard volume of catalyst). Such "conditioned" catalyst still possessed some oxidizing power, since in pyrolyses with it, moderate amounts of carbon dioxide were always collected in the Ascarite absorber. The mixed metal chromite catalysts on various supports were supplied through the courtesy of Mr. A. B. Stiles, Belle, W. Va. The catalysts of this type found active in this rearrangement were supported on a Davison silica gel similar in properties to Grade 70. It was necessary to "condition" them with methanol before use, but after the violent oxidation had proceeded, a still exothermic decomposition of methanol to gaseous products continued at a steady rate. In use, the mixed chromite on silica catalysts were slightly more active than silica alone in transforming acetals, but this activity was offset by their greater destructiveness and consequent lower yields.

The four catalysts pumice, silica, copper chromite and mixed chromites on silica were the only materials found in this work to have any synthetic value in rearranging acetals to alkoxy aldehydes. A wide variety of other materials was screened for catalytic activity toward alkoxy aldehyde production, using 4 as the model acetal. The pyrolyzates were examined by infrared spectroscopy and refractive index, but no detailed study was made unless warranted. The catalysts studied are listed in Table IV with brief details of the unsuccessful experiments.

**Isobutoxypivalic Acid. A. By Oxidation of Isobutoxypivalaldehyde.**—A stirred suspension of 15.8 g. of pure isobutoxypivalaldehyde in 100 ml. of water and 4 g. of 10% sodium hydroxide solution was treated with a solution of 32.0 g. of potassium permanganate in 200 ml. of warm water during 1.5 hours. The temperature increased gradually to 62°. The manganese dioxide was reduced with sodium bisulfite and dilute sulfuric acid, and the aqueous solution was extracted with ether. The acid was extracted into sodium carbonate solution and again into ether. The residue after evaporation of the ether deposited 1.2 g. of dimethylmalonic acid (9.4% yield), m.p. 194° dec. after crystallization from benzene; its infrared spectrum was identical to that of authentic dimethylmalonic acid. The liquid acid was distilled through a short Vigreux column, the center cut boiling at 84.0–84.5° (0.7 mm.), $n^{25}_D$ 1.4207, $d^{25}_{25}$ 0.9463, *MR* 46.59 (calcd. 46.95). The same acid was formed by bubbling air into the aldehyde containing a little cobalt butyl phthalate.

**B. By Independent Synthesis.**—**Ethyl hydroxypivalate** was prepared from the acid and ethanol (hydrogen chloride) in 60% yield, b.p. 83.0–83.5° (16 mm.), $n^{25}_D$ 1.4245, $d^{20}_4$ 0.9976. The ester was accompanied by 22% of ethyl hydroxypivaloyloxypivalate formed by self-esterification, b.p. 134.5° (9.5 mm.), $n^{25}_D$ 1.4373.

Sodium hydride (50% in mineral oil, 12.4 g., 0.26 mole) was suspended in a solution of 250 ml. of dry ether and 27.5 g. (0.304 mole) of distilled methallyl chloride. Ethyl hydroxypivalate (27.7 g., 0.19 mole) was added dropwise during 9 hours. An additional 0.54 g. of sodium hydride and 10.0 g. of methallyl chloride were added and the mixture was refluxed for 2 hours. Absolute ethanol was added to destroy any unreacted hydride, the mixture was refluxed for 45 minutes, and then poured into an ice-cold mixture of 300 g. of water and 10 g. of sulfuric acid. The aqueous layer was extracted with 100 ml. of ether, the combined ether layers were washed with sodium bicarbonate solution and water, and dried with sodium sulfate. The residue, 45.5 g., was fractionated through a 27″ spinning brush column.

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(17) du Pont's trademark for its polytetrafluoroethylene resin.

(18) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Identification of Organic Compounds," Fourth Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 218.

(19) G. D. Johnson, *J. Am. Chem. Soc.*, **75**, 2720 (1953).

(20) H. J. Shine, *J. Org. Chem.*, **24**, 252 (1959).

(21) W. Brady, *J. Chem. Soc.*, 756 (1931).

(22) In contrast, Davison Grade 04 silica gel has the following respective properties: 0.45 m./g., 22 Å., and 832 sq. m./g. Grade 04 is highly destructive to acetals, as discussed above.

The desired ethyl **methallyloxypivalate** was obtained in only 17% yield, b.p. 91–94.5° (16 mm.); the later fraction, b.p. 94.5° (16 mm.), had $n^{25}{}_D$ 1.4268, $d^{25}{}_{25}$ 0.9203, *MR* 55.77 (calcd. 52.85).

*Anal.* Calcd. for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0. Found: C, 65.9, 66.1; H, 10.2, 10.2.

The unsaturated ester was hydrogenated in methanol at atmospheric pressure over platinum oxide. The reduction was complete in 15 minutes. Most of the methanol was removed from the filtered solution, and the residue was refluxed with methanolic potassium hydroxide for 2.75 hours. The acid was isolated by evaporating the methanol, acidifying, and extracting with ether. **Isobutoxypivalic acid** was obtained in 55% yield, b.p. 78° (0.9 mm.), $n^{25}{}_D$ 1.4200, $d^{25}{}_{25}$ 0.9472.

*Anal.* Calcd. for $C_9H_{18}O_3$: C, 62.1; H, 10.3; neut. equiv., 174. Found: C, 62.2, 61.8; H, 10.3, 10.5; neut. equiv., 173, 174.

The amides were prepared from the two acids A and B; m.p. 35–36° and 36.5–38°, respectively, mixture m.p. 36–37°.

*Anal.* Calcd. for $C_9H_{19}NO_2$: N, 8.1. Found: amide A, N, 7.9, 7.9; amide B, N, 8.1, 8.0.

An attempt to alkylate ethyl hydroxypivalate with isobutyl iodide failed owing to competitive dehydroiodination. Since this technique had been used successfully to prepare ethoxypivalic acid[23] (the only previously known alkoxypivalic acid), this failure must be ascribed to the known low reactivity of isobutyl halides in $S_N2$ displacement reactions and to their pronounced tendency to undergo elimination of hydrogen halide.

**Addition of Diethyl Formal to Ethyl Isobutenyl Ether.**—Ethyl isobutenyl ether was prepared by the liquid-phase de-ethanolation of isobutyraldehyde diethyl acetal.[15] In our hands, the published directions yielded an ether heavily contaminated with unchanged acetal. Perhaps the head temperature limit given (72–84°) should have been 72–74°. A small distillation column did not achieve complete separation.[24] The ether was added dropwise to a 50% excess of diethyl formal containing a little boron fluoride etherate according to Brannock's method for addition of higher acetals to this ether. Crude 1,1,3-triethoxy-2,2-dimethylpropane was obtained in 60% yield. A higher-boiling fraction is probably the 2:1 adduct resulting from addition of this new acetal to a second mole of vinyl ether, and if so, its formation could be suppressed by use of a larger excess of diethyl formal. The redistilled 1:1 adduct, b.p. 100° (33 mm.), $n^{25}{}_D$ 1.4100, was analyzed.

*Anal.* Calcd. for $C_{11}H_{24}O_3$: C, 64.66; H, 11.84. Found: C, 64.8, 64.7; H, 11.6, 11.4.

A sample was exposed to the Johnson DNP reagent[19] and yielded ethoxypivalaldehyde 2,4-dinitrophenylhydrazone identical with that prepared from aldehyde obtained by pyrolysis of acetal 3. A second sample was hydrolyzed[15] to ethoxypivalaldehyde, the physical properties and infrared spectrum of which were identical with those of the pyrolysis product.

Addition of dimethyl formal to ethyl isobutenyl ether in the presence of boron fluoride etherate led to a complicated mixture of products because of the rapid interchange of methoxy and ethoxy groups, and because of poly-addition. The mixture of 1:1 adducts was separated by distillation, and hydrolysis gave an inseparable mixture of alkoxy aldehydes. The presence of methoxy- and ethoxy-pivalaldehyde was detected in the infrared spectrum. A dinitrophenylhydrazone prepared from the mixture could not be purified by crystallization; chromatography was not attempted. Methyl isobutenyl ether was no longer available; hence the addition of dimethyl formal was not attempted.

**Isobutyl Isobutenyl Ether.**—The pyrolyzate of acetal 35 was fractionated. After a large forerun of isobutyraldehyde the ether was collected at 129.0–130.5°, $n^{25}{}_D$ 1.4139.[25] Continued distillation of the remainder yielded a small amount of a mixture boiling at 144–152° (135 mm.), $n^{25}{}_D$ 1.4250, exhibiting the spectrum of the acetal plus a very strong band at 5.85 μ. There was only a faint absorption at 3.7 μ; hence the carbonyl compound is probably a ketone. An attempt to prepare a DNP yielded a mixture heavily contaminated with the derivative of isobutyraldehyde.

The isobutenyl ether was identified by its analysis (Calcd. for $C_8H_{16}O$: C, 75.0; H, 12.5. Found: C, 74.7, 74.8; H, 12.0, 12.1) and by hydrolysis in aqueous acid to isobutyraldehyde (DNP m.p. 183–184°, mixed m.p. 183–184°) and isobutyl alcohol (3,5-dinitrobenzoate m.p. 85.5–86.8°, mixed m.p. 86.5–87.5°).

**Acknowledgment.**—The author is indebted to James L. Chestnut and Wallace Buskirk for efficient and imaginative technical assistance.

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[23] L. Marcilly, *Bull. soc. chim. France*, [3] **31**, 119 (1904).

[24] Preparation of methyl isobutenyl ether for another purpose was accomplished quantitatively by passing isobutyraldehyde dimethyl acetal through a bed of Grade 70 silica at 200°. It is believed that this procedure would be preferred for future preparation of the ethyl ether because of the simplicity and ease of operation; no attention is required once the drop rate has been set. This vapor phase method was not tried with the diethyl acetal since sufficient material was available from the other preparation.

[25] J. L. E. Erickson and M. Z. Woskow, *J. Org. Chem.*, **23**, 670 (1958), report b.p. 131–132°, $n^{25}{}_D$ 1.4138. They state that their series of vinyl ethers shows C=C stretch frequencies at 5.9–6.1 μ and C–O–C stretch at 8.1–9.0 μ. Our product absorbs at 5.91, 8.4, 8.8 and 12.1 μ, all strong. The 12.1 μ band is curiously distorted on the short wave length side. The methyl and ethyl isobutenyl ethers have the same band patterns.

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[CONTRIBUTION NO. 323 FROM THE JACKSON LABORATORY, ORGANIC CHEMICALS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON 98, DEL.]

# A New Rearrangement. Catalytic Isomerization of *m*-Dioxanes to β-Alkoxy Aldehydes. III. Reaction Mechanism and By-products

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The rearrangement is portrayed by a four-stage process: 1. Adsorption on the catalyst; both oxygens of the acetal coördinate with acidic sites on the catalyst surface. 2. The oxygen–carbon bond is weakened to yield a carbonium ion center stabilized by the groups on C-2. 3. Hydrogen migrates from C-6 to C-2, assisted by the ring geometry. 4. Desorption. The by-products of the reaction are rationalized by ring cleavage to a carbonyl compound and a dipolar ion $^-O-CH_2-CMe_2-CH_2{}^+$. Subsequent reactions of this dipolar ion can account for the wide variety of fragments produced.

The effects of acetal structure upon the catalytic isomerization of *m*-dioxanes to β-alkoxy aldehydes were described in the preceding paper.[1] The present article discusses the mechanism of the rearrangement and attempts to account for some of the unexpected by-products of the reaction.

Acyclic acetals are dealcoholated by acid catalysts to vinyl ethers.[2] By analogy, conversion of

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[1] C. S. Rondestvedt, Jr., and G. J. Mantell, *J. Am. Chem. Soc.*, **84**, 3307 (1962).

[2] A few examples of this reaction are found in the work of L. Claisen, *Ber.*, **31**, 1019 (1898); **29**, 1006 (1896); F. Sigmund, *Monatsh.*,