We have attempted to isolate and analyze the pure potassium polysulfide from the alcohol solution. The yellow liquid was filtered and evaporated to dryness in a stream of dry nitrogen, and the residue was freed from sulfur by washing with carbon disulfide. Sulfur was determined by dissolving dried and weighed portions of the orange-brown material in water, oxidizing with bromine water, and precipitating as barium sulfate. Among many analyses several pairs of checks were obtained, but the checks were discordant with one another. Although the yellow alcohol solution did not smell of hydrogen sulfide, it was found that the vapors from its evaporation, even when the evaporation was carried out at laboratory temperature, contained hydrogen sulfide enough to blacken lead acetate paper. Alcoholysis evidently occurred, potassium ethylate was undoubtedly present in varying amounts in the residues from the evaporations—and an attempt at fractional crystallization of the polysulfide from alcohol was abandoned as impracticable.

## Summary

The reaction between potassium carbonate and sulfur in alcohol solution is essentially the same as in water solution but is very much more rapid. Alcohol dissolves an appreciable amount of both substances, while water dissolves a large amount of one and exceedingly little of the other. The solubilities of potassium carbonate, sodium carbonate and sulfur in absolute ethyl alcohol at 25° have been determined.

CAMBRIDGE, MASSACHUSETTS

---

[CONTRIBUTION FROM THE UNIVERSITY OF VERMONT]

# THE ODOR AND STRUCTURE OF CERTAIN CYCLIC ACETALS[1]

BY R. R. READ, HUBBEL LATHROP AND H. L. CHANDLER

RECEIVED APRIL 21, 1927 PUBLISHED DECEMBER 10, 1927

Verley[2] isolated an oil from jasmine blossoms that had as a principal constituent the cyclic acetal of phenylethyleneglycol and formaldehyde-1-phenyldioxolane. This compound was synthesized and found to have the same jasmine-like odor. The corresponding derivatives from acetaldehyde and valeraldehyde proved to have similar odors.

Shortly afterwards Hesse and Müller[3] reported that no trace of this acetal was to be found in jasmine oil and that the odor was due to two compounds of unknown nature in addition to phenylethyl acetate and a terpene alcohol ester.

---

[1] For the odor evaluation of the products described in this paper the writers are indebted to Burton T. Bush, Inc., of New York City, particularly to Dr. Ph. Chaleyer of that Company.

[2] Verley, *Compt. rend.*, **128**, 314 (1899).

[3] Hesse and Müller, *Ber.*, **32**, 565 (1899).

Whether or not the odor of jasmine oil is due to dioxolane derivatives, it was of interest to determine whether compounds related to those described by Verley were odorous and, if so, how the odor was affected by variations in structure.

Accordingly acetals based on the following glycols have been prepared: 1-phenoxy-2,3-propanediol, 1-phenyl-1,2-propanediol, 1-phenyl-2,3-propanediol, 1-*m*-methylphenyl-2,3-propanediol and 1-*p*-methylphenyl-2,3-propanediol, using as the other component formaldehyde, acetaldehyde and, in one case, heptaldehyde.

The following dioxolane derivatives were prepared: (*a*) 1-phenoxymethyl-, (*b*) 1-phenoxymethyl-4-methyl-, (*c*) 1-phenoxymethyl-4-*n*-hexyl-, (*d*) 1-phenyl-2-methyl-, (*e*) 1-phenyl-2,4-dimethyl-, (*f*) 1-phenyl-2-methyl-4-*n*-hexyl-, (*g*) 1-benzyl-4-methyl-, (*h*) 1-benzyl-, (*i*) 1-*m*-methylbenzyl-4-methyl-, (*j*) 1-*m*-methylbenzyl-, (*k*) 1-*p*-methylbenzyl-4-methyl-.

Conclusions were drawn as follows:

(*a*) Phenoxymethyldioxolanes have markedly less odor than the corresponding phenyl, benzyl and methylbenzyl derivatives.

(*b*) Methylbenzyldioxolanes are less odorous than the benzyl derivatives.

(*c*) A methyl group in the 4 position increases the original odor but not its persistence.

A summary of the character of the odors of the dioxolanes listed above is: (*a*) not agreeable or lasting, similar to (*b*) but weaker; (*b*) slight, not agreeable, somewhat like diphenyl or cresyl oxide; (*c*) very weak, oily; (*d*) when fresh reminiscent of Rumanian petroleum ether, on standing has faint sweet-pea character; (*e*) similar to phenylglycol acetate but milder; (*f*) slight, not floral; (*g*) when fresh similar to phenylglycol acetate, not lasting; (*h*) when fresh has a chemical odor, on standing reminiscent of phenylpropionaldehyde and lilac; (*i*) slight, similar to (*a*) and (*b*); (*j*) very similar to phenylglycol acetate, not lasting; (*k*) very slight.

These acetals are not extremely stable, apparently regenerating aldehyde on long standing although repeated distillation does not affect the boiling range.

## Experimental

References, methods of preparation, constants and other data on the glycols used are given in the following table.

**Preparation of Dioxolanes.**—These were all prepared in the same way[4] by heating equal molal fractions of the glycol and aldehyde on a steam-bath under a reflux condenser with stirring for six hours. Five drops of 40% sulfuric acid was used as a catalyst. An excess of solid sodium carbonate was added, the oil taken up in ether, washed once with dilute carbonate solution, twice with water and then dried over sodium sulfate. After the removal of the ether the product was vacuum distilled.

---

[4] Fischer and Giebe, *Ber.*, **30**, 3053 (1897).

TABLE I

DATA ON GLYCOLS USED

| Name | Prepared from | B. p., °C. | $d_4^{20}$ | Formula | Calcd. | | Found | |
|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | C | H |
| Phenylglycerin ether[a] | ...... | 176 (16 mm.) | ... | .... | .. | ... | .. | ... |
| 1-Phenyl-1,2-propanediol[b] | ...... | .... | ... | .... | .. | ... | .. | ... |
| 1-Phenyl-2,3-propanediol[c] | Chlorohydrin[d] | 160–163 (13 mm.) | 1.115 | $C_9H_{12}O_2$ | 71.1 | 7.9 | 70.9 | 7.7 |
| 1-*o*-Methylphenyl-2,3-propanediol | Chlorohydrin[e] | .... | ... | .... | .. | ... | .. | ... |
| 1-*m*-Methylphenyl-2,3-propanediol[f] | Chlorohydrin[g] | 165–166 (10 mm.) | 1.090 | $C_{10}H_{14}O_2$ | 72.3 | 8.4 | 72.3 | 8.3 |
| 1-*p*-Methylphenyl-2,3-propanediol | Chlorohydrin[h] | 170–172 (13 mm.) | 1.074 | $C_{10}H_{14}O_2$ | 72.3 | 8.4 | 71.8 | 8.5 |

[a] M. p. (from ether) 63°. Fourneau [*J. Pharm. Chem.*, [7], **1**, 55 (1910); *C. A.*, **4**, 3070 (1910)] gives b. p. 200° (22 mm.); m. p. 69°.

[b] Zincke and Zahn, *Ber.*, **43**, 849 (1900). Both alpha and beta forms. The crude dibromide is remarkably irritant on the eyes.

[c] By the method of Brooks and Humphrey, *J. Ind. Eng. Chem.*, **9**, 750 (1917); a viscous oil of faint, agreeable odor.

[d] Fourneau and Tiffeneau, *Bull. soc. chim.*, [4], **1**, 1227 (1907); *C. A.*, **2**, 1273 (1908), prepared the chlorohydrin by the action of phenylmagnesium bromide on epichlorohydrin (yield, 33%), 1-chloro-3-bromo-2-propanol also being formed in 30% yield; b. p. 88–90° (20 mm.), $d_4^{20}$ = 1.726 [*Ann. Suppl.*, **1**, 225 (1861)].

[e] Prepared according to method of ref. *d;* ratio of chlorohydrin to chlorobromopropanol, 1:9; b. p. 144–146° (20 mm.), $d_4^{20}$ = 1.150.

[f] Viscous liquid with faint, agreeable odor.

[g] Prepared by method of ref. *d* (yield, 30%); ratio to chlorobromopropanol, 1:1; b. p. 135–150° (11 mm.).

[h] Prepared by method of ref. *d;* products in same ratio as in ref. *e*.

With the hope that acetals might be formed when the corresponding oxide and aldehyde were treated with sulfuric acid, as in the case of the mixed glycol and aldehyde, benzylethylene oxide was prepared from 1-phenol-3-chloro-2-propanol added to an

TABLE II

CONSTANTS AND DATA ON DIOXOLANES

| | Dioxolane | B. p., °C. | M. p., °C. | $d_4^{20}$ | Formula | Calcd., % | | Found, % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | C | H |
| (*a*) | 1-Phenoxymethyl | 138-139 (11 mm.) | 40-43 | ... | $C_{10}H_{12}O_3$ | 66.6 | 6.7 | 66.2 | 6.7 |
| (*b*) | 1-Phenoxymethyl-4-methyl | 152–154 (11 mm.) | 24 | ... | $C_{11}H_{14}O_3$ | 68.0 | 7.2 | 68.2 | 7.1 |
| (*c*) | 1-Phenoxymethyl-4-*n*-hexyl | 201–203 (12 mm.) | ... | ... | $C_{16}H_{14}O_3$ | 72.7 | 9.1 | 72.6 | 9.1 |
| (*d*)[a] | 1-Phenyl-2-methyl | 104–105 (11 mm.) | ... | ... | $C_{10}H_{13}O_2$ | 73.2 | 7.3 | No analysis | |
| (*d*)[b] | 1-Phenyl-2-methyl | 105–107 (12 mm.) | ... | ... | $C_{10}H_{12}O_2$ | 73.2 | 7.3 | 73.3 | 7.6 |
| (*e*) | 1-Phenyl-2,4-dimethyl | 116–118 (19 mm.) | ... | 1.032 | $C_{11}H_{14}O_2$ | 74.1 | 7.9 | 74.2 | 7.7 |
| (*f*) | 1-Benzyl-4-methyl | 120–124 (16 mm.) | ... | 1.092 | $C_{11}H_{14}O_2$ | 74.1 | 7.9 | 72.8 | 7.5 |
| (*g*) | 1-Benzyl | 125–128 (16 mm.) | ... | 1.098 | $C_{10}H_{12}O_2$ | 73.2 | 7.3 | 71.0 | 6.8 |
| (*h*) | 1-*m*-Methylbenzyl-4-methyl | 123–125 (13 mm.) | ... | 1.028 | $C_{12}H_{16}O_2$ | 75.0 | 8.3 | 74.6 | 8.5 |
| (*i*) | 1-*m*-Methylbenzyl | 128–130 (15 mm.) | ... | 1.032 | $C_{11}H_{14}O_2$ | 74.1 | 7.9 | 73.1 | 7.8 |
| (*j*) | 1-*p*-Methylbenzyl-4-methyl | 135–142 (17 mm.) | ... | 1.032 | $C_{12}H_{16}O_2$ | 75.0 | 8.3 | 73.5 | 8.3 |

[a] From the α-glycol.

[b] From the β-glycol.

equal molal quantity of trimethylene oxide with 5 drops of 40% sulfuric acid and heated for six hours on the steam-bath. The benzylethylene oxide was recovered unchanged. This is in accordance with the results obtained by Wurtz with ethylene oxide and acetaldehyde.[5]

## Summary

1. Few of the dioxolanes based on phenyl-, methylphenyl- and phenoxypropanediol have a marked agreeable odor.
2. None of the compounds has a jasmine-like odor.

BURLINGTON, VERMONT

---

[CONTRIBUTION FROM THE MEDICAL RESEARCH DIVISION, CHEMICAL WARFARE SERVICE, EDGEWOOD ARSENAL]

# CHLORINATION OF β,β-DICHLORO-ETHYL SULFIDE. I[1]

BY W. E. LAWSON AND T. P. DAWSON

RECEIVED JUNE 7, 1927 PUBLISHED DECEMBER 10, 1927

The only feasible methods for the destruction of Mustard Gas, or β,β-dichloro-ethyl sulfide, involve the use of chlorine. Small amounts in the laboratory may be oxidized with nitric acid to the sulfoxide, which is non-vesicant, that is, does not cause blistering of the skin, and under certain conditions clothing may be demustardized with live steam, but these are practically the only instances of other means for its destruction.

The ease and rapidity with which β,β-dichloro-ethyl sulfide is chlorinated suggests a preliminary addition of the chlorine followed by a molecular rearrangement involving substitution of one atom of chlorine and elimination of one molecule of hydrogen chloride[2] according to the equations

$$(ClCH_2CH_2)_2S + Cl_2 \longrightarrow (ClCH_2CH_2)_2SCl_2$$
$$(ClCH_2CH_2)_2SCl_2 \longrightarrow ClCH_2CHClSCH_2CH_2Cl + HCl$$

Certain facts that give support to this view have already been published. The sulfide is promptly oxidized to the sulfoxide by nitric acid;[3] it reacts with chloramine-T to form an addition product, $(ClCH_2CH_2)_2S = NSO_2$-$C_6H_4CH_3$;[4] and it adds bromine to form a dibromide and perbromide.[5]

One paper on the chlorination of β,β-dichloro-ethyl sulfide has appeared, besides a number of chemical warfare studies. Mann and Pope[6] chlorinated the compound to different stages with gaseous chlorine and

[5] Wurtz, *Ann.*, **120**, 328 (1861).

---

[1] Published by permission of the Chief of the Chemical Warfare Service.

[2] It is with pleasure that we acknowledge that this suggestion was first made by Professor E. Emmet Reid of Johns Hopkins University in a discussion with one of us on the chlorination of Mustard Gas.

[3] Helfrich and Reid, THIS JOURNAL, **42**, 1208 (1920).

[4] Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922).

[5] Gibson and Pope, *ibid.*, **117**, 271 (1920).

[6] Mann and Pope, *J. Chem. Soc.*, **121**, 594 (1922).