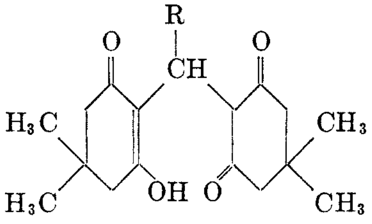
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

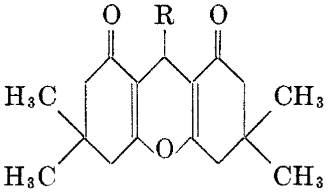
METHONE DERIVATIVES OF ALDEHYDES

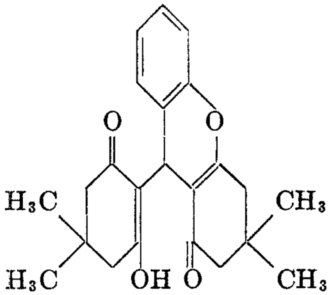
E. C. HORNING[1] AND M. G. HORNING[1]

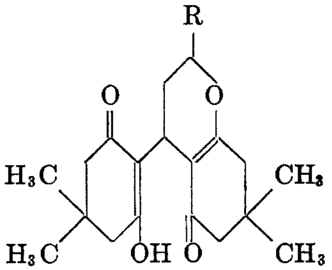
Received October 29, 1945

The use of methone (5,5-dimethyldihydroresorcinol) as a reagent for the identification and characterization of aldehydes is well known (1, 2, 3, 4, 5). A disadvantage attending the use of methone has been the lack of agreement on conditions recommended for the preparation of derivatives and a lack of data obtained by proposed general methods. A method for the characterization of aldehydes with methone, applicable to aliphatic and aromatic aldehydes, is described in the experimental section. The aldehyde is treated with methone in aqueous alcohol solution; a drop of piperidine is added as a catalyst, and a five minute reflux period suffices to complete the reaction. The crystalline methone derivatives (I) can be isolated readily and in good yield. The conditions described were satisfactory in all cases which were examined. The melting points of the derivatives are in Tables I and II. α,β-Unsaturated aldehydes and *o*-hydroxy aromatic aldehydes yield products differing in structure from the normal derivatives (I), but these products are formed in excellent yield, and serve equally well as derivatives. The structure assigned to the salicylaldehyde product is that of an octahydroxanthene (II, R = *o*-hydroxyphenyl) (6), although an alternate structure (III) has also been suggested (7). There is no proof of structure at hand for the compounds obtained with α,β-unsaturated aldehydes, but since they do not undergo a dehydration reaction under conditions suitable for the usual derivatives we believe they may have a pyran structure as in IV.


I


II


III


IV

---

[1] Present address, University of Pennsylvania.

It has been known for a long time that a variety of dehydration conditions will convert the normal derivatives (I) into octahydroxanthenes (II). Heating in acetic anhydride is the usual method; sulfuric acid and hydrogen chloride in alcohol have also been used. Prolonged heating in acetic acid alone has also been employed in some cases. An investigation of this reaction has shown that with one exception the cyclization can be effected through the relatively simple process of recrystallizing the methone derivative from aqueous alcohol to which a few drops of concentrated hydrochloric acid has been added. A routine procedure, described in the experimental section, has been applied to a number of derivatives, and the melting points of the products are listed in Tables I and II. All methone derivatives (I) yielded octahydroxanthenes except the compound derived from formaldehyde, which was recovered unchanged. Cyclization of this derivative requires more vigorous conditions (1, 2). It was also found that this cyclization procedure was not applicable to the products obtained from α,β-unsaturated aldehydes or to those from *o*-hydroxy aromatic aldehydes.

The cyclization requires a reaction period of approximately five minutes, and the yield is often very nearly quantitative. The octahydroxanthenes (II) are

TABLE I

ALIPHATIC ALDEHYDES

ALDEHYDE	DERIVATIVE I		DERIVATIVE II	
	M.P., °C	Ref.	M.P., °C	Ref.
Formaldehyde[a]	191–191.5	1, 2, 3, 4	—	1, 2
Acetaldehyde[a]	141–142	1, 2, 3, 4	176–177	1, 2, 3
Glyoxal[b]	228	2	170	2
Glyoxylic acid[b]	239	2	245	2
Acrolein[b]	192	1	162–163	1
	135	2	170–188	2
Propionaldehyde[a]	157–158	2, 4	141.5–143	1, 2
Crotonaldehyde[a]	193–194	1, 2, 8, 9	—	1, 2
Butyraldehyde[a]	134–135	2, 4	135–136	2
Isobutyraldehyde[a]	153–154.5	2, 10	154–155.5	2
Allylacetaldehyde[b]	98	11	—	—
n-Valeraldehyde[a]	107–109	4	112–113[c]	—
Isovaleraldehyde[b]	154–155	1	172–173	1
	137	2	168	2
Hexanal[b]	108.5	4	—	—
Heptanal[a]	101–103	1, 2, 4	110.5–112	1, 2
Octanal[b]	89.8	4	—	—
Nonanal[b]	86.3	4	—	—
Decanal[b]	91.7	4	—	—
Citronellal[b]	77–79	1	173	1
	70–71	3		

[a] Melting point values are from this work and are corrected.

[b] Melting point values are from the literature.

[c] *Anal.* Calc'd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.31; H, 9.35.

TABLE II

AROMATIC ALDEHYDES

ALDEHYDE	DERIVATIVE I		DERIVATIVE II	
	M.P., °C	Ref.	M.P., °C	Ref.
Benzaldehyde[a]	194–195	6, 7, 12	204–205.5	6, 7, 12
Salicylaldehyde[a]	205–206	1, 3, 6, 7	—	6, 7
p-Hydroxybenzaldehyde[b]	188–190	1	246	1
	184	7	208–209	7
2,4-Dihydroxybenzaldehyde[b]	225–226	7	—	—
3,4-Dihydroxybenzaldehyde[b]	145 dec.	7	—	—
m-Nitrobenzaldehyde[a]	197–198[c]	7	171.5–172.5	7
p-Nitrobenzaldehyde[b]	188–190	7	222	7
o-Chlorobenzaldehyde[b]	205	1	224–226	1
o-Tolualdehyde[a]	166–167[d]	—	213.5–215[e]	—
m-Tolualdehyde[a]	171–172.5[f]	—	205–207[g]	—
Phenylacetaldehyde[b]	164–165	13	125–126	13
o-Methoxybenzaldehyde[a]	187–188	6	190–191	6
Anisaldehyde[a]	142–143	1, 3, 7	241–243	1, 7
Piperonal[a]	175.5–177	1, 3, 7	218.5–220	1, 7
2-Hydroxy-3-methoxybenzaldehyde[a]	232–234[h]	—	—	—
Vanillin[a]	195.5–196.5	1, 3, 7	226–228	1
Cinnamaldehyde[a]	215–217	1, 7	—	1, 7
2,3-Dimethoxybenzaldehyde[a]	149–150[i]	—	168–169[j]	—
Veratraldehyde[a]	173–174[k]	—	184–185.5[l]	—
p-Dimethylaminobenzaldehyde[a]	194.5–195.5	1, 14	220–222	14
Acetylvanillin[b]	167	3	148–149	7
Cuminal[b]	170–171	1	172–173	1

[a] Melting point values are from this work and are corrected.

[b] Melting point values are from the literature.

[c] *Anal.* Calc'd for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58.
Found: C, 67.09; H, 6.59.

[d] *Anal.* Calc'd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91.
Found: C, 75.41; H, 8.02.

[e] *Anal.* Calc'd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74.
Found: C, 79.23; H, 7.83.

[f] *Anal.* Calc'd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91.
Found: C, 75.21; H, 7.90.

[g] *Anal.* Calc'd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74.
Found: C, 78.85; H, 7.81.

[h] *Anal.* Calc'd for $C_{24}H_{28}O_5$: C, 72.70; H, 7.12.
Found: C, 72.82; H, 7.27.

[i] *Anal.* Calc'd for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53.
Found: C, 70.35; H, 7.74.

[j] *Anal.* Calc'd for $C_{25}H_{30}O_5$: C, 73.14; H, 7.37.
Found: C, 73.14; H, 7.25.

[k] *Anal.* Calc'd for $C_{25}H_{32}O_6$: C, 70.07; H, 7.53.
Found: C, 70.14; H, 7.65.

[l] *Anal.* Calc'd for $C_{25}H_{32}O_5$: C, 73.14; H, 7.37.
Found: C, 72.68; H, 7.32.

colorless crystalline products, varying considerably in melting point with variations in the R group. For purposes of identification of aldehydes, a combination of the two reactions offers the advantage that two derivatives may be obtained from one reaction of the original aldehyde. The methone derivative (I) may be prepared and after the melting point determination a cyclization can be carried out to yield a second derivative (II). This procedure may be of particular value when only small amounts of aldehyde are available.

EXPERIMENTAL

Reagents. Methone and piperidine were obtained from the Eastman Kodak Co. Aldehydes were commercial or laboratory preparations; liquid aldehydes were distilled before use.

Melting Points. Melting points up to 230° were taken in a stirred bath and are corrected. A metal block was used for higher temperatures.

Aliphatic aldehydes: Methone derivatives (I). To 4 cc. of 50% ethanol-water were added 400 mg. of methone and 0.10 cc. of the aliphatic aldehyde. One drop of piperidine[2] was added, and the mixture was heated under reflux on a steam-bath for 5 minutes. In cases where the solution was still clear at the end of this period, water was added dropwise to the cloud point. After chilling the reaction mixture, the derivative was separated by filtration, and washed with 50% ethanol-water.

The time required for crystallization of the product varied with individual aldehydes. In some cases crystalline derivatives separated during the reflux period; in other cases the addition of a little water was necessary; and in a few cases the derivative separated as an oil which crystallized readily on cooling and stirring. The yield was usually above 300 mg. Recrystallization, which was necessary in most cases, was effected from aqueous methanol. All derivatives were colorless.

Aliphatic aldehydes: Cyclization to 2,2,7,7-tetramethyl-4,5-diketo-9-alkyloctahydroxanthenes (II). One hundred milligrams of the methone derivative (I) was dissolved in 3 to 4 cc. (as required) of hot 80% ethanol-water, and one drop of conc'd hydrochloric acid was added. The solution was heated under reflux for 5 minutes. Water was added dropwise to the cloud point, and after cooling and chilling, the xanthenes were obtained by filtration and washing with aqueous ethanol.

These derivatives crystallized readily, and were obtained in good yield (usually over 80 mg.). They were of a high degree of purity, and usually did not require recrystallization. Where necessary, recrystallization was effected from aqueous methanol. All derivatives were colorless.

Aromatic aldehydes: Methone derivatives (I). The general procedure for aliphatic aldehydes was followed except that the amount of methone used was 300 mg. The amount of aldehyde was 0.10 cc. for liquids and 100 mg. for solids.

The derivatives usually appeared in crystalline form during the addition of water; oiling occurred in very few instances. Yields were usually nearly quantitative. Recrystallization, where necessary, was effected from aqueous methanol. All derivatives were colorless, except that from *p*-dimethylaminobenzaldehyde, which was bright yellow.

Aromatic aldehydes: Cyclization to 2,2,7,7-tetramethyl-4,5-diketo-9-aryloctahydroxanthenes (II). The procedure for aliphatic aldehydes was followed, but slightly larger amounts of solvent were required in some cases. These derivatives crystallized readily, in a high degree of purity, and usually were obtained in nearly quantitative yield. Recrystallization, where necessary, was effected from aqueous methanol. All derivatives were colorless.

---

[2] The use of piperidine as a catalyst in dihydroresorcinol-aldehyde condensations was apparently first suggested by Desai (6).

In the case of the octahydroxanthene from *p*-dimethylaminobenzaldehyde, the solution was buffered with 4 *M* sodium acetate solution after cyclization was completed. This derivative was soluble in dilute hydrochloric acid.

SUMMARY

A general procedure for the preparation of methone derivatives of aldehydes has been applied to a number of aliphatic and aromatic aldehydes. It has been found that the cyclization of the derivatives to octahydroxanthenes may be accomplished readily by crystallization from aqueous alcohol containing a little hydrochloric acid, and that this procedure may be utilized for the preparation of a second set of derivatives.

Ann Arbor, Mich.

REFERENCES

(1) Vorländer, *Z. anal. Chem.*, **77**, 241 (1929).
(2) Klein and Linser, *Mikrochem., Pregl Festschr.*, **1929**, 204.
(3) Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).
(4) Kao and Yen, *Science Repts. Natl. Tsing Hua Univ., Ser. A*, **1**, 185 (1932). *Chem. Abstr.*, **26**, 5924 (1932).
(5) Leffmann and Pines, *Bull. Wagner Free Inst. Sci.*, **4**, 15 (1929).
(6) Desai, *J. Indian Chem. Soc.*, **10**, 663 (1933).
(7) Chakravarti, Chattopadhyaya, and Ghosh, *J. Indian Inst. Sci.*, **A14**, 141 (1932).
(8) Späth, Lorenz, and Freund, *Ber.*, **75**, 1029 (1942).
(9) Kasuya, *J. Am. Chem. Soc.*, **59**, 2742 (1937).
(10) Cairns and Fletcher, *J. Am. Chem. Soc.*, **63**, 1034 (1941).
(11) Hurd and Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938).
(12) Vorländer and Strauss, *Ann.*, **309**, 379 (1899).
(13) Lin and Robinson, *J. Chem. Soc.*, 2005 (1938).
(14) Desai and Wali, *J. Indian Chem. Soc.*, **13**, 735 (1936).