repeating both processes several times. The resulting sirup was dissolved in 250 cc. of absolute methyl alcohol and shaken for two hours with 15 g. of silver carbonate. The colorless solution obtained by filtration was evaporated to dryness *in vacuo;* the addition of a little dry ether resulted in crystallization so that vacuum distillation became unnecessary.

The glucoside was dissolved in ether, evaporated to dryness, and the crystalline residue extracted with boiling petroleum ether to remove it from a small amount of gummy material. Concentration of the petroleum ether left about 5 g. of the glucoside, which upon recrystallization melted at 93–94°, and showed $[\alpha]_D$ −19.4° in water ($c = 2$). The physical constants and method of preparation identify it as the 2,3,4-trimethyl-β-methylglucoside.[8]

Grateful acknowledgment is made of a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences, which provided the microbalance, weights and palladium used in this work.

Summary

Populin, a glucoside occurring in certain species of poplar, has been methylated with methyl iodide and silver oxide. The resulting tetramethylpopulin was debenzoylated to a tetramethylsalicin, which on hydrolysis with hydrochloric acid yielded 2,3,4-trimethylglucose, identified by conversion to the crystalline 2,3,4-trimethyl-β-methylglucoside. This indicates that populin is 6-benzoylsalicin.

Evidence is presented that benzoylation of glucosides leads to the formation initially of the 6-monobenzoate.

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RECEIVED SEPTEMBER 18, 1934

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[8] See for example Oldham, THIS JOURNAL, 56, 1360 (1934).

NOTES

p-Nitrobenzyl Esters of Organic Acids

BY T. LEONARD KELLY AND MARNELL SEGURA

During the course of a research the following *p*-nitrobenzyl esters were prepared which do not appear in the literature. Since the melting points of these are an aid in the identification of acids they are of value. They were prepared according to the method of Reid and co-workers[1] and were recrystallized to constant melting point. All melting points are uncorrected but were taken in a Fisher melting point apparatus with a set of Anschütz thermometers which gave correct melting points with various pure reagents.

p-NITROBENZYL ESTERS

Acid	M. p., °C.	Nitrogen, % Calcd.	Nitrogen, % Found
o-Benzoylbenzoic	100.4	3.87	3.84
p-Cyanobenzoic	189.2	9.92	9.87
3,5-Dinitrobenzoic	156.8	12.06	12.14
Glutaric	69	6.93	6.81
Adipic	105.6	6.73	6.88
Suberic	85	6.30	6.26
Azelaic	43.8	6.11	6.18
Itaconic	90.6	7.00	7.10
Diphenic	182.6	5.46	5.63
		Halogen, %	
o-Bromobenzoic	109.8	23.78	24.17
m-Chlorobenzoic	107.2	12.16	12.14
o-Iodobenzoic	110.8	33.14	32.74
m-Iodobenzoic	121	33.14	33.47
p-Iodobenzoic	140.6	33.14	33.60

Caproic, caprylic, pelargonic and capric acids yielded oils which could not be induced to crystallize.

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RECEIVED APRIL 12, 1934

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[1] Reid and co-workers, THIS JOURNAL, 39, 124, 701, 1727 (1917).

The Thermal Decomposition of Acetone

BY F. O. RICE, EDWARD L. RODOWSKAS AND WARREN R. LEWIS

It has been shown experimentally that when acetone is decomposed in quartz or Pyrex vessels it yields ketene and methane;[1] furthermore, it has been demonstrated that as the percentage decomposition of the acetone is decreased the yield of ketene approaches more and more closely to 100%[2] and therefore the over-all decomposition of acetone must be represented by the equation $CH_3COCH_3 \longrightarrow CH_4 + CH_2{=}CO$.

This reaction may occur either by migration of a hydrogen atom or by rupture of the molecule into CH_3 and CH_3CO, followed by a chain reaction[3]

$$CH_3COCH_3 + CH_3 \longrightarrow CH_4 + CH_3COCH_2 \quad (1)$$

$$CH_3COCH_2 \longrightarrow CH_2{=}CO + CH_4 \quad (2)$$

In order to determine whether the addition of methyl groups brings about a chain reaction in

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[1] Rice and Vollrath, *Proc. Nat. Acad. Sci.*, 15, 702 (1929).

[2] Rice, Greenberg, Waters and Vollrath, THIS JOURNAL, 56, 1760 (1934).

[3] It is of course possible that both of these reactions proceed simultaneously.

gaseous acetone below its normal temperature of decomposition[4] we heated acetone containing approximately 1% of dimethylmercury in the range 350–400°. Under our conditions the dimethyl mercury was decomposed completely, whereas separate experiments showed that pure acetone was unaffected. We found that no ketene at all was produced, as would have been formed had reactions (1) and (2) taken place. Instead, a high boiling substance identified[5] as acetonylacetone $CH_3COCH_2CH_2COCH_3$ was formed in amounts approximately corresponding to the amount of dimethylmercury added. Furthermore, it was formed to a markedly smaller extent in acetone–dimethylmercury mixtures which had been heated for longer periods in the range 250–300°.

These experimental facts prove that the chain reaction given above does not occur below 400°. They suggest[6] that in the range 350–400° reaction (1) occurs and is followed by the reaction

$$2CH_3COCH_2 \longrightarrow CH_3COCH_2CH_2COCH_3 \quad (3)$$

On the other hand, at lower temperatures the methyl groups do not attack the acetone, presumably recombining with themselves.

These experiments suggested that the acetonyl group CH_3COCH_2— might break chains by combining with one of the chain carriers; for example, $CH_3COCH_2 + CH_3 \longrightarrow CH_3COCH_2CH_3$. Accordingly we carried out some preliminary experiments on the rate of decomposition of acetone and acetaldehyde in the presence of small quantities of such substances as acetonylacetone $CH_3COCH_2CH_2COCH_3$, diallyl $CH_2{=}CHCH_2CH_2CH{=}CH_2$ and dibenzyl $C_6H_5CH_2CH_2C_6H_5$. These substances should dissociate[7] into CH_3COCH_2—, $CH_2{=}CHCH_2$— and $C_6H_5CH_2$—, and by combination with methyl groups should give the relatively stable molecules methyl ethyl ketone, 2-butene and ethyl benzene, respectively. However, we obtained only negative results in all the experiments we have performed so far and we have concluded that the activation energy of all radicals with molecules is sufficiently low, that rapid reaction occurs even at 400°. These experiments are pertinent in connection with Leermakers' suggestion[8] that acetone might be a chain breaker in other chain reactions involving methyl radicals.

We also tried to determine the stationary state concentration of methyl groups in acetone by allowing acetone vapor at 700° and 200 mm. to stream out through a small hole and pass over a cold tellurium mirror. Even after two hours we could not detect any effect on the mirror, indicating that the concentration of radicals must have been too low to detect in this manner. This is in agreement with the calculated concentration of methyl groups using the data of Rice and Herzfeld.[9]

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[4] Similar experiments have been performed (a) for butane by Frey, *Ind. Eng. Chem.*, **26**, 198 (1934); (b) for acetaldehyde by Sickman and Allen, THIS JOURNAL, **56**, 1251 (1934), and Leermakers, *ibid.*, **56**, 1537 (1934); (c) also for dimethyl and diethyl ethers, and acetone by Leermakers, *ibid.*, **56**, 1899 (1934).

[5] The method of identification used was that given by Knorr, *Ber.*, **19**, 46 (1886).

[6] See in this connection Leermakers, Ref. 4 c, p. 1902.

[7] All these compounds have a C–C bond in the β position to two double bonds; this bond should be relatively weak and rupture of the molecule would be expected to occur at this point.

[8] Ref. 3 c, p. 1903.

[9] Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

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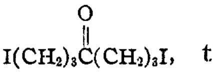
RECEIVED SEPTEMBER 19, 1934

The Structure of $C_7H_{12}O_2$ from the Hydrogenation of Furylacrolein

BY MARK FARLOW, HAROLD E. BURDICK AND HOMER ADKINS

Fittig and Strom[1] obtained a dibromide $C_7H_{12}Br_2O$ through the reaction of "oxetone" ($C_7H_{12}O_2$) with 48% hydrobromic acid. Apparently the same dibromide and also the corresponding diiodide were obtained in this Laboratory.[2] The facts noted below show that the diiodide is ω,ω'-diiodo-di-*n*-propyl ketone, a structure suggested but not established by Fittig and Strom for their dibromide. The diiodide reacted with piperidine to give ω,ω'-dipiperidinodipropyl ketone. The latter was identified by comparison of its dihydrochloride and semicarbazone with the derivatives for this ketone.[3] The diiodide was reduced with zinc and dry ethanol to dipropyl ketone, and the latter identified by its semicarbazone.



Since the diiodide is $I(CH_2)_3\overset{\overset{O}{\|}}{C}(CH_2)_3I$, the $C_7H_{12}O_2$ compound from which it was prepared cannot have the 1,5-dioxaoctohydroindene structure which was suggested by Burdick and Adkins. In all probability it is 1,9-dioxa-5-spirononane having the structure

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[1] Fittig and Strom, *Ann.*, **267**, 191 (1892).

[2] Burdick and Adkins, THIS JOURNAL, **56**, 348 (1934).

[3] Petit, *Bull. soc. acad. roy. Belg.*, [5] **12**, 775 (1926); Thomas and McElvain, THIS JOURNAL, **56**, 1806 (1934).