

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 $[\alpha]_D -19.4^\circ$ 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

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

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.

BRYN MAWR, PENNSYLVANIA

RECEIVED SEPTEMBER 18, 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-workers¹ 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.	Found
<i>o</i> -Benzoylbenzoic	100.4	3.87	3.84
<i>p</i> -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, %	
<i>o</i> -Bromobenzoic	109.8	23.78	24.17
<i>m</i> -Chlorobenzoic	107.2	12.16	12.14
<i>o</i> -Iodobenzoic	110.8	33.14	32.74
<i>m</i> -Iodobenzoic	121	33.14	33.47
<i>p</i> -Iodobenzoic	140.6	33.14	33.60

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

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

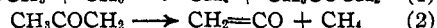
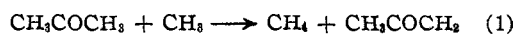
DEPARTMENT OF CHEMISTRY RECEIVED APRIL 12, 1934
HOLY CROSS COLLEGE
WORCESTER, MASS.

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 $\text{CH}_3\text{COCH}_3 \longrightarrow \text{CH}_4 + \text{CH}_2=\text{CO}$.

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 reaction³



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

(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 decomposition⁴ 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 identified⁵ as acetylacetone $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$ 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 suggest⁶ that in the range 350–400° reaction (1) occurs and is followed by the reaction



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

These experiments suggested that the acetyl group CH_3COCH_2 — might break chains by combining with one of the chain carriers; for example, $\text{CH}_3\text{COCH}_2 + \text{CH}_3 \longrightarrow \text{CH}_3\text{COCH}_2\text{CH}_3$. 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 acetylacetone $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$, diallyl $\text{CH}_2=\text{CHCH}_2\text{—CH}_2\text{CH}=\text{CH}_2$ and dibenzyl $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$. These substances should dissociate⁷ into $\text{CH}_3\text{—COCH}_2$ —, $\text{CH}_2=\text{CHCH}_2$ — and $\text{C}_6\text{H}_5\text{CH}_2$ —, 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,

(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.

that rapid reaction occurs even at 400°. These experiments are pertinent in connection with Leermakers' suggestion⁸ 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

(8) *Ref. 3 c*, p. 1903.

(9) Rice and Herzfeld, *This Journal*, **56**, 284 (1934).

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND RECEIVED SEPTEMBER 19, 1934

The Structure of $\text{C}_7\text{H}_{12}\text{O}_2$ from the Hydrogenation of Furylacrolein

BY MARK FARLOW, HAROLD E. BURDICK AND HOMER ADKINS

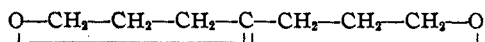
Fittig and Strom¹ obtained a dibromide $\text{C}_7\text{H}_{12}\text{Br}_2\text{O}$ through the reaction of "oxetone" ($\text{C}_7\text{H}_{12}\text{O}_2$) with 48% hydrobromic acid. Apparently the same dibromide and also the corresponding diiodide were obtained in this Laboratory.² The facts noted below 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 $\text{I}(\text{CH}_2)_3\overset{\text{O}}{\parallel}\text{C}(\text{CH}_2)_3\text{I}$, the $\text{C}_7\text{H}_{12}\text{O}_2$ 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-dioxo-5-spiroonane having the structure

(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 (1928); Thomas and McElvain, *This Journal*, **56**, 1806 (1934).



assigned by Fittig and Strom to their compound. This formulation was rejected by Burdick and Adkins because the resistance to hydrolysis of the compound did not seem in harmony with an acetal type of structure.

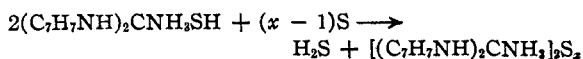
MADISON, WISCONSIN RECEIVED SEPTEMBER 24, 1934

Diphenyl- and Di-*o*-tolylguanidinium Polyselenides

BY R. L. McCLEARY AND W. CONARD FERNELIUS

Work conducted in this Laboratory¹ has proved the existence of diphenyl-, di-*o*-tolyl- and di-*p*-tolylguanidinium polysulfides. Furthermore, it has been possible to isolate the hydrosulfide of diphenylguanidine.²

These polysulfides were prepared by passing hydrogen sulfide through a suspension of the substituted guanidine in 95% ethanol until all the base had gone into solution as a hydrosulfide. After warming the solutions to about 60°, purified sulfur was added until no more went into solution. Hydrogen sulfide was evolved during the reactions as may be shown by the equation



Upon standing and allowing to cool, the red supernatant liquids soon deposited brick red micro-crystalline materials which proved to be the heptasulfides.

Preparation of Diphenylguanidinium Polyselenide.—Ethanol was freed of air by boiling and cooling in a stream of nitrogen. Hydrogen selenide, generated by the hydrolysis of aluminum selenide, was passed through a drying tower and into a suspension of diphenylguanidine in the above ethanol. A solution, slightly orange in color, resulted. On adding powdered selenium, the solution became dark red. When selenium was no longer dissolved, the solution was decanted from the excess selenium. After standing for some time (a much longer period than for the guanidinium polysulfides) a fine crystalline material separated from the solution which when dry exhibited a dark gray-purple color: decomposition range 152–156°.

Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_6\text{Se}_4$: Se, 42.7; N, 11.3. Found: Se,³ 42.9, 40.7; N, 11.4, 11.3.

Preparation of Di-*o*-tolylguanidinium Polyselenide.—Identical results were obtained substituting di-*o*-tolylguanidine for the diphenyl compound in the above operations; decomposition point of the tetraselenide 170–174°.

Anal. Calcd. for $\text{C}_{30}\text{H}_{26}\text{N}_6\text{Se}_4$: Se, 39.7; N, 10.5. Found: Se, 39.5, 40.2; N, 10.4, 10.2.

(1) M. C. Reed (with C. E. Boord), Dissertation, The Ohio State University, 1925. D. E. Strain (with C. E. Boord), Dissertation, The Ohio State University, 1927.

(2) M. Achterhof, R. F. Conaway and C. E. Boord, *THIS JOURNAL*, **53**, 2682–2688 (1931).

(3) Determined by the method of E. H. Shaw, Jr., and E. B. Reid, *THIS JOURNAL*, **49**, 2330–2334 (1927).

These tetraselenides are decomposed with extreme ease by dilute acids to yield amorphous black selenium and hydrogen selenide. A portion of the latter seems to be either decomposed or oxidized at the moment of its liberation.

Anal. On treatment with dilute HCl, 0.4344 g. of diphenylguanidinium tetraselenide deposited 0.1766 g. or 40.8% Se. Calcd.: 3 Se, 32.1; 4 Se, 42.7. H_2Se identified by its odor. Neutralization of the filtrate gave crystals of diphenylguanidine, m. p. 148°.

Attempts were made to isolate an amine hydroselenide in a system closed to the air but were unsuccessful because of the continual decomposition of the hydrogen selenide.

CHEMICAL LABORATORY

THE OHIO STATE UNIVERSITY

COLUMBUS, OHIO

RECEIVED SEPTEMBER 27, 1934

α -Oximino and α -Amino Derivatives of *o*-Hydroxypropiophenone

BY HAROLD L. MASON

In 1931 Hartung, Munch, Miller and Crossley¹ described the preparation of a series of phenolic arylisonitroso ketones. They did not succeed, however, in obtaining *o*-hydroxyphenyl- α -oximinoethyl ketone because the ortho phenolic group interfered in some way. This compound has now been prepared through the intermediacy of *o*-benzoyloxypropiophenone and *o*-benzoyloxyphenyl α -oximinoethyl ketone. The latter has been reduced to the corresponding amine. It should be easily possible by means of obvious reactions to convert this ketone amine to *o*-hydroxyphenylpropanolamine. The investigation has not been carried that far, and, since it cannot be continued, the results are presented at this time.

Experimental

***o*-Benzoyloxypropiophenone.**—This was prepared from *o*-hydroxypropiophenone and benzoyl chloride by the Schotten-Baumann reaction. After recrystallization from petroleum ether it melted at 58–59°.

***o*-Benzoyloxyphenyl α -Oximinoethyl Ketone.**—The nitrosation of *o*-benzoyloxypropiophenone was carried out as described by Hartung¹ and his associates. Sixty grams of *o*-benzoyloxypropiophenone partially dissolved in 150 cc. of ether was treated with 24.6 g. of butyl nitrite while bubbling in hydrogen chloride. After completion of the reaction the ether was removed under reduced pressure. The partially crystalline residue was dissolved in 35 cc. of benzene and petroleum ether added slowly with rapid stirring. The product crystallized slowly. After drying at 60° it weighed 49 g., a yield of 73%. It melted at 100–101°.

(1) Hartung, Munch, Miller and Crossley, *THIS JOURNAL*, **53**, 4149 (1931).

Anal. Calcd. for $C_{16}H_{13}O_4N$: C, 67.82; H, 4.63. Found: C, 67.54; H, 4.88.

***o*-Hydroxyphenyl α -Oximinoethyl Ketone.**—*o*-Benzoyloxyphenyl α -oximinoethyl ketone (8.4 g.) in alcoholic solution was treated with 15 cc. of 5 *N* sodium hydroxide solution. After fifteen minutes the solution was diluted with water and made just acid to litmus with acetic acid. The yellow oil which separated was dissolved in ether. The ether solution was washed with a solution of sodium carbonate and dried over sodium sulfate. After removal of the ether the partially crystalline residue was dissolved in hot petroleum ether. The large yellow plates which separated on cooling melted at 85–88°. Another recrystallization did not change the melting point. Ferric chloride produced a deep red color in alcoholic solution.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 60.31; H, 5.07. Found: C, 60.19; H, 5.23.

***o*-Benzoyloxyphenyl α -Aminoethyl Ketone.**—The oximino ketone was reduced catalytically in absolute alcohol solution following the conditions of Hartung and Munch.² The uptake of hydrogen did not stop completely when two moles had been absorbed but the rate fell off quite sharply at that point. However, much of the hydrogen was used up in side reactions since the yield of amine was only 30%. A large proportion of the oximino ketone was recovered unchanged. This was accompanied by a small amount of oil which was not investigated.

After removal of the catalyst the solution was evaporated under reduced pressure to about 25 cc. and an equal vol-

ume of dry ether added. The hydrochloride of the amine separated as long interlacing needles which decomposed at about 180° without melting. For recrystallization it was dissolved in hot alcohol containing 1 cc. of concd. hydrochloric acid. After filtration acetone was added slowly. The crystals which separated apparently contained one-half molecule of water. However, loss of weight at 120° was negligible. After two hours at 125–130° there was some loss of weight but there was also evidence of some decomposition.

Anal. Calcd. for $C_{16}H_{13}O_3NCl$: C, 62.83; H, 5.82. Calcd. for $C_{16}H_{13}O_3NCl \cdot 0.5H_2O$: C, 61.03; H, 5.45. Found: C, 61.00, 61.35; H, 5.50, 5.48.

The free base was prepared by neutralization of an aqueous solution of the hydrochloride with sodium carbonate. It precipitated as fine needles. After recrystallization from petroleum ether they melted at 112–114°. They reduced Fehling's solution.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.34; H, 5.62. Found: C, 71.32; H, 5.75.

Summary

o-Benzoyloxy α -oximinoethyl ketone has been prepared. It has been converted into *o*-hydroxyphenyl α -oximinoethyl ketone by hydrolysis and into *o*-benzoyloxyphenyl α -aminoethyl ketone by catalytic hydrogenation.

DIVISION OF CHEMISTRY
THE MAYO FOUNDATION
ROCHESTER, MINN.

RECEIVED OCTOBER 1, 1934

(2) Hartung and Munch, *THIS JOURNAL*, **51**, 2262 (1929).

COMMUNICATIONS TO THE EDITOR

A BENZALDEHYDE ELECTRODE

Sir:

In "the difficult alkaline range" of *pH* we have substituted benzaldehyde for quinhydrone in a regular quinhydrone *pH* determination apparatus, and, using a saturated calomel electrode as reference, have made reproducible determinations between *pH* 7 and 13.64. Checked against a hydrogen electrode, the deviations in *pH* units in a large number of measurements were: 0.00–0.09 unit, 44.36%; 0.10–0.19 unit, 33.12%; 0.20–0.29 unit, 14.57%; 0.30–0.39 unit, 5.30%; 0.40–0.49 unit, 2.65%; above 0.50 unit, 0.00%. Comparable to colorimetric readings, therefore, the benzaldehyde electrode gave accuracy within 0.2 *pH* in 77.48% of the determinations.

The determinations were carried out in 50-cc. Pyrex beakers, with 40 cc. of the solution and 0.4

cc. of benzaldehyde mixed by a stirrer at 1200 r. p. m. The electrode was a 10-cm. coil of platinum wire. The connection was through a salt bridge into saturated potassium chloride, into which the calomel electrode tip dips.

From the data a master curve has been plotted, smoothed mathematically, which presents potentials as ordinates against *pH* values as abscissas. The coefficient of correlation between the *pH* values obtained with the benzaldehyde electrode and with the hydrogen electrode between *pH* 7 and 14 is 0.996 ± 0.0006 . The most reproducible region is between *pH* 9 and 14.

A linear relationship was found to exist between the common logarithm of the absolute potential of the benzaldehyde electrode (found by adding 0.5266, the so-called absolute potential of the saturated calomel electrode, to the observed po-