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.

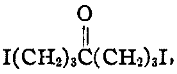
(9) Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

DEPARTMENT OF CHEMISTRY
THE JOHNS HOPKINS UNIVERSITY
BALTIMORE, MARYLAND 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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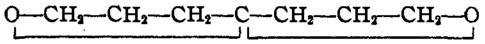
(1) Fittig and Strom, *Ann.*, **267**, 191 (1892).

(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).



$$O{-}CH_2{-}CH_2{-}CH_2{-}C{-}CH_2{-}CH_2{-}CH_2{-}O$$

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 Laboratory[1] 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

$$2(C_7H_7NH)_2CNH_3SH + (x-1)S \longrightarrow H_2S + [(C_7H_7NH)_2CNH_3]_2S_x$$

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 $C_{26}H_{28}N_6Se_4$: 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 $C_{30}H_{36}N_6Se_4$: Se, 39.7; N, 10.5. Found: Se, 39.5, 40.2; N, 10.4, 10.2.

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.

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RECEIVED SEPTEMBER 27, 1934

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[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. E. Reid, THIS JOURNAL, **49**, 2330–2334 (1927).

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

BY HAROLD L. MASON

In 1931 Hartung, Munch, Miller and Crossley[1] 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 Hartung[1] 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°.

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