

1-Phenyl-3-benzoyloxy-5-pyrazolone Benzoylimide, XIII.—To a solution of 5 g. of 1-phenyl-3-hydroxy-5-pyrazolone imide, I,² and 4.4 g. of pyridine in 20 ml. of dioxane, on the steam-bath, was added 8 g. of benzoyl chloride, and the heating continued for one-half hour. The product crystallized on cooling, was washed on the filter with 50% ethanol and digested with 100 ml. of 95% ethanol; 7.7 g. (72%) of fine white needles, m. p. 193–194°, unchanged by recrystallization from ethanol.

Anal. Calcd. for C₂₃H₁₇N₃O₃: N, 10.97. Found: N, 11.03.

XIII⁹ was also obtained (69%) from 1-phenyl-3-benzoyloxy-5-pyrazolone imide, XI, or (88%) from 1-phenyl-3-hydroxy-5-pyrazolone benzoylimide, XII, following this procedure.

Summary

The acetylation and benzoylation of 1-phenyl-3-hydroxy-5-pyrazolone imide, I, is studied.

1 - Phenyl - 3 - hydroxy - 4 - acetyl - 5 - pyra-

zolone imide, II, 1-phenyl-3-acetoxy-4-acetyl-5-pyrazolone imide, V, 1-phenyl-2-acetyl-3-acetoxy-5-acetylimino- Δ_3 -pyrazoline, VII, 1-phenyl-3-hydroxy-5-pyrazolone acetylimide, VIIIa, 1-phenyl-3-benzoyloxy-5-pyrazolone imide, XI, 1-phenyl-3-hydroxy-5-pyrazolone benzoylimide, XII, 1-phenyl-3-benzoyloxy-5-pyrazolone benzoylimide, XIII, are prepared as new compounds, and their properties and structures established.

The C-acetylation in the formation of II is explained by the presence of the COCH₂C(NH)-system. When this is destroyed by O-acetylation, C-acetylation no longer occurs.

A suggestion is made for the course of the synthesis of anilinopyrazolones.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

The Preparation of Aldehydes and Ketones by Ozone Oxidation

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Specific directions for the preparation in 60 to 70% yields of aldehydes, ketones and acids by hydrolysis or oxidation of an olefin ozonide have been reported in a preceding paper.¹ In the present paper, the ozonide is decomposed by catalytic hydrogenation; the experimental factors are systematically investigated and a redesigned ozonizer is presented which operated well over a period of more than a year.

Equipment.—The reasons for redesigning the ozonizer were mainly the heating of the electrodes with consequent destruction of the ozone generated, and the fragility of an outfit made of Berthelot tubes sealed in series. The essential feature of the new design (Fig. 1) is the passage of the gas twice through the length of the tube, first through the annular space between the inner electrode A and tube B, and then between tube B and the outer electrode C. This construction gives a better ozone conversion than a single passage, and completely prevents the rupture of the Pyrex dielectric when tubing of no less than standard thickness is used. Tap water circulating through the outer jacket was used as one electrode; a mercury filled tube cooled only by conduction served as the inner electrode. The grounding of the outer electrode eliminated the necessity of shielding the apparatus for protection of the operator but made it necessary to use a high voltage transformer whose secondary could also be grounded at one end.

A single ozonizer of this type, operated with tap water at about 20°, and with its center electrode at 22 Kv., gave steadily 5.1% and 3.7% by weight of ozonized oxygen, at flow rates of 10 and 20 liters per hour, respectively. This corresponds to 0.64 and 0.93 g. of O₃ per hour. Higher concentrations are obtainable by more intense cooling. For instance, a similar but shorter ozonizer immersed in a dry-ice and acetone bath produced 12 and 10% of ozone at 5 and 10 liters per hour, respectively. Cooling of the inner electrode would undoubtedly help further but would also complicate the design. A second ozonizer mounted in series with the first did not improve the ozone output, but placing the two in parallel permitted a slightly higher net yield by decrease of the rate of gas flow through each tube.

The vessel in which ozonization of the olefin took place

was water jacketed and is shown in Fig. 2. Catalytic hydrogenation of the ozonide was performed in the same vessel, mounted on a rocking device similar in construction to the Parr outfit.³

An electric precipitator operating at 3 Kv. was mounted as shown in Fig. 2; it very effectively corrected the formation of uncondensed fogs and markedly improved the yields.

Material Tested.—The catalytic hydrogenation of ozonides was proposed by F. G. Fischer,³ who recorded yields of aldehydes and ketones ranging from 50 to 70%. To obtain a direct comparison, cyclopentene and cyclohexene were first investigated; our results matched and slightly bettered Fischer's. Later, olefins variously branched were used, namely, 1-octene, 2-octene, 2-methyl-1-heptene, 2-methyl-2-heptene, and 2,3-dimethyl-2-heptene. This group included a representative of each of the five structural types of olefins.⁴ It is to be noted that the ozonization of the cyclic olefins yielded high boiling dialdehydes, which are easier to handle without losses than the volatile derivatives of the open chain olefins.

Solvent.—To minimize handling, ozonization and hydrogenolysis of the ozonide were carried out in the same solvent and the same container. Methylene chloride (the solvent used in the preceding paper) could not be used here because it prevents catalytic hydrogenation. Instead, ethyl acetate, methanol and absolute ethanol were used; all three were attacked appreciably by ozone but not enough to preclude their use. The concentration of olefin was in general 0.1 mole in 100 ml. of solvent and the temperature of ozonization was in the vicinity of 25°. Variations in concentrations from 0.05 to 0.25 mole per 100 ml. and changes of temperature from -78 to 55° did not significantly affect the yield of carbonyl compounds. Ethanol gave the best and ethyl acetate the worst yields of aldehydes; methanol was intermediate. This was attributed to the formation of acetals which protected the aldehydes against further oxidation. In the preparation of ketones the effect of the solvent was less noticeable, and it was in the opposite direction. The loss of solvents and of olefin was minimized by the use of the reflux condenser and electrical precipitator shown in Fig. 2.

(2) "Organic Syntheses," Coll. Vol. I, 1941, p. 65.

(3) Fischer, Düll and Ertel, *Ber.*, **65**, 1468 (1932).

(4) Boord in "The Science of Petroleum," Oxford University Press, London, 1938, Vol. II, p. 1353.

(1) Henne and Hill, *THIS JOURNAL*, **66**, 752 (1943).

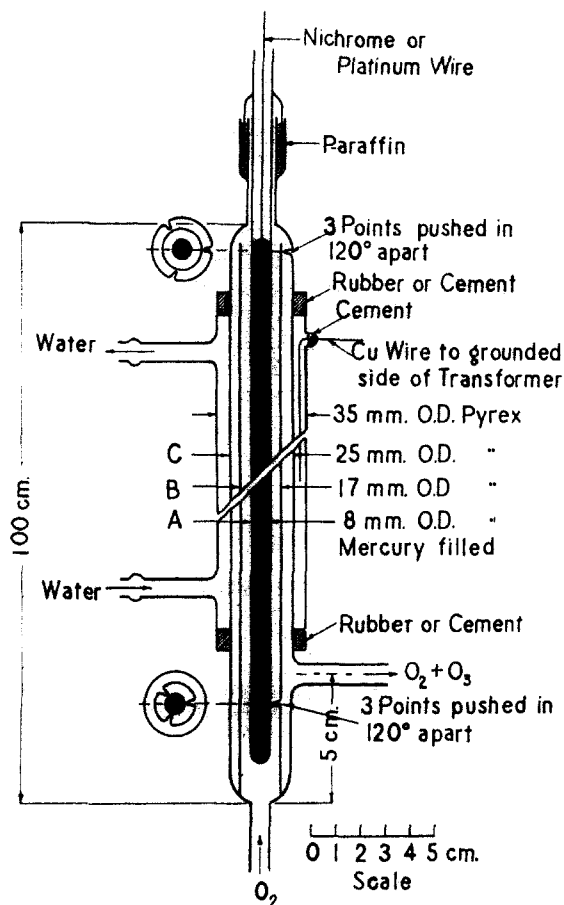


Fig. 1.—Ozonizer.

Spontaneous Decomposition of the Ozonide.—During the ozonization of 2-methyl-1-heptene and 1-octene a strong odor of formaldehyde was consistently noted in the effluent oxygen, and the gas reduced Tollens reagent; moreover, a white amorphous solid, which gave off formaldehyde when heated, collected in the condensing system. Acetaldehyde and acetone were similarly found to be liberated during ozonization of olefins containing ethylidene and isopropylidene groups, respectively. While this spontaneous decomposition of the ozonide has been recognized before,^{5,6} its importance in analysis for methylene, ethylidene, and isopropylidene groups in compounds of unknown structure has not always been appreciated.

To determine what proportion of the formaldehyde might be lost during ozonization, several attempts were made to measure it in the effluent gases by absorbing it in a known amount of standard alkali containing hydrogen peroxide. After destroying the excess peroxide, titration of the remaining alkali showed the amount of formaldehyde liberated. Results with ethyl acetate as the solvent were meaningless because some ester swept into the alkali. However, when 0.1 mole quantities of 2-methyl-1-heptene were ozonized in *n*-pentane and 3-methylpentane at 20°, analysis indicated that 26 and 29%, respectively, of the formaldehyde was liberated during ozonization.

While this procedure indicates the amount of formaldehyde swept from the solution, it does not show the extent of the spontaneous decomposition. The values obtained are too low because some formaldehyde is quickly oxidized to less volatile formic acid, and some polymerizes in the condensing system.

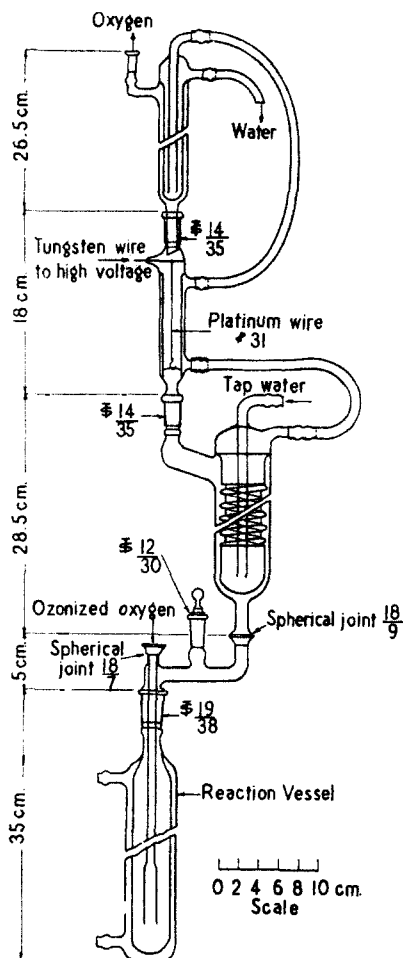
(5) Briner and de Nimitz, *Helv. Chim. Acta*, **21**, 748 (1938).

Fig. 2.—Reaction and condensing system.

Since Fischer reported that cyclopentene and cyclohexene ozonides consumed as much as 90% of the theoretical quantity of hydrogen, it was felt that hydrogenation could be used to determine the ozonide content of the solutions, and by difference the amount of spontaneous decomposition. When 0.1 of a mole of 2-methyl-1-heptene was ozonized in 100 ml. of ethyl acetate at 25°, the samples consumed from 35 to 55% of the theoretical volume of hydrogen. When alcohols were used as solvents, the hydrogen consumption was as high as 68%. No formaldehyde was detected in the gases; this was attributed to the formation of formals.

Hydrogenolysis.—After completion of the ozonization, the jacketed vessel containing the ozonide solution was transferred to a low-pressure hydrogenator operating at about three atmospheres. The catalyst in most cases was 1% palladium supported on calcium carbonate, prepared according to Busch and Stöwe.⁶ The most satisfactory results were obtained when the palladium oxide was reduced prior to use on the ozonide. Platinum oxide and palladium black catalysts were tried, but without satisfactory results.

The solvent affected the speed of hydrogenation considerably. In ethyl acetate, which was used in the majority of the experiments, hydrogenation required twelve to twenty-four hours for completion. In methanol, the reaction was completed in two to four hours and the time was only slightly longer in ethanol. When ethyl acetate was

(6) Busch and Stöwe, *Ber.*, **49**, 1064 (1916).

used, the addition of 5 to 15 ml. of methanol before hydrogenation increased the rate appreciably.

Final Products.—The aldehydes and ketones were isolated as oximes, semicarbazones or dinitrophenylhydrazones. Ketones were obtained in better yields. This was attributed to the fact that ozonides yielding aldehydes by spontaneous decomposition give the corresponding acid as well.⁸ Aldehydes subjected to a stream of ozonized oxygen are oxidized to acids and peracids.⁷ In alcohol solutions, isolation of the aldehydes was complicated by the formation of higher boiling neutral fractions, probably acetals. Boiling these with dilute hydrochloric acid yielded additional quantities of the aldehydes which were included in the yields reported.

The table summarizes the yields obtained in experiments in which 0.1 mole quantities of olefin were ozonized at 25°.

PER CENT. YIELD OF ALDEHYDES AND KETONES

Product	EtOAc	Solvent MeOH	EtOH
Pentanal	..	49	..
Hexanal	8	24	37
Heptanal	26	30	35
2-Hexanone	61
2-Heptanone	44	35	40

To obtain aldehydes and ketones, hydrogenolysis of the ozonides is safe and convenient. Except for dialdehydes the yields are lower than those reported for hydrolysis by concentrated acetic acid in the presence of zinc.¹

Experimental Details

Pentanal.—A solution of 11.2 g. (0.1 mole) of 2-methyl-2-heptene in enough methanol to make a total volume of 100 ml. was ozonized at 25° for 4.2 hours. When hydrogenated over 0.5 g. of the catalyst (1% palladium on calcium carbonate) the ozonide solution consumed 55% of the theoretical quantity of hydrogen. After filtering to remove the catalyst, the solution was distilled through a short Vigreux column. Acetone and solvent were collected up to 66° and discarded. Distillation was continued to 115°, when the flask was nearly dry. The 2,4-dinitrophenylhydrazone of pentanal was isolated from the distillate in 49% yield.

Hexanal.—A solution of 11.2 g. (0.1 mole) of 2-octene in sufficient ethyl acetate to make a total volume of 100 ml. was ozonized at 25° for 4.8 hours. On hydrogenation, the solution absorbed only 16% of the theoretical amount of hydrogen. Distillation yielded 8% hexanal (isolated as semicarbazone), 38% hexanoic acid, and 15% high boiling residue. The total recovery was 61% of theoretical, assuming that the residue had the same empirical formula as the acid.

The ozonide solution from a similar run made in methanol consumed 52% of the theoretical quantity of hydrogen. The distillate collected between 66 and 148° was boiled with 0.1 *N* hydrochloric acid before isolating the aldehyde. The yield of hexanal semicarbazone was 24%.

Two runs in ethanol were conducted in the same way as the one in methanol. In both cases the yield of hexanal semicarbazone was 37%.

Heptanal.—A solution of 11.2 (0.1 mole) of 1-octene in sufficient ethyl acetate to make a volume of 100 ml. was ozonized at 25° for 4.9 hours. On hydrogenation, the solution took up 38% of the theoretical amount of hydrogen. Distillation yielded 26% heptanal (as semicarbazone), 28% heptanoic acid, and 1% high-boiling residue. Total recovery was 71%.

In a second run, made in methanol, the hydrogen consumption was 54% of theoretical. On distillation, the product was separated into two fractions, one boiling from 66 to 160° (heptanal boils at 155°) and the other from 160 to 180°, mostly at 180°. The latter fraction, after boiling with 0.1 *N* hydrochloric acid, yielded 14% of heptanal semicarbazone. The lower fraction gave 16% for a total yield of 30%.

After hydrolyzing with 0.1 *N* hydrochloric acid, the 80 to 180° cut from a run in ethanol gave a 35% yield of heptanal as semicarbazone.

2-Hexanone.—A solution of 12.6 g. (0.1 mole) of 2,3-dimethyl-2-heptene in sufficient ethyl acetate to make 100 ml. was ozonized at 25° from 4.6 hours. The ozonide solution was hydrogenated, taking up 41% of the theoretical quantity of hydrogen. After distillation, 2-hexanone was isolated as its semicarbazone in 61% yield. There remained 20% of high boiling residue, making a total recovery of 81%.

Shortly after starting the ozonization of 2,3-dimethyl-2-heptene in methanol a violent explosion destroyed the reaction and condensing systems. No further work on this compound was done.

2-Heptanone.—In four separate runs, 11.2 g. (0.1 mole) of 2-methyl-1-heptene dissolved in enough ethyl acetate to make a volume of 100 ml. was ozonized at 25° for approximately 4.5 hours. On hydrogenation, the average hydrogen consumption of the ozonide solution was 41%. After distilling off the solvent up to 80°, the ketone fraction was collected to 155°. The average yield of 2-heptanone semicarbazone was 44%. An average of 22% of high boiling residue gave a total recovery of 66%. Similar runs in methanol and ethanol gave 2-heptanone in yields of 35 and 40%, respectively.

Glutaric Aldehyde.—A solution of 3.5 g. (0.05 mole) of cyclopentene in 100 ml. of ethyl acetate was ozonized at dry-ice temperature for four hours. After hydrogenating the ozonide suspension, the ethyl acetate was distilled off. Glutaric aldehyde was isolated from the residue as its dioxime in 71% yield.

Adipic Aldehyde.—From 4.2 g. (0.05 mole) of cyclohexene treated in the same way as the cyclopentene, a 51% yield of adipaldehyde dioxime was obtained. One-fourth of a mole in 100 ml. of ethyl acetate yielded only 21%.

Summary

1. A new ozonizer is presented, which proved dependable in continuous operation. It is sturdily built of Pyrex glass and features a water cooled electrode.

2. The various factors influencing the preparation of aldehydes and ketones by catalytic reduction of an ozonide have been investigated.

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(7) Fischer, Düll and Volz, *Ann.*, **486**, 80 (1931).