[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

CATALYTIC REDUCTION OF ALPHA-DIKETONES AND THEIR DERIVATIVES

BY JOHANNES S. BUCK AND SANFORD S. JENKINS[1]

RECEIVED FEBRUARY 23, 1929 PUBLISHED JULY 5, 1929

In order to obtain certain derivatives of α-diketones the authors investigated the catalytic reduction of benzils. The usual methods given in the literature are difficult and give poor yields. Five benzils were selected as starting materials: benzil made by the oxidation of benzoin with nitric acid;[2] anisil derived from anisoin after the method of Bösler;[3] piperil made from piperoin by oxidation with Fehling's solution;[4] veratril, obtained by oxidizing the crude reaction product of veratric aldehyde and alcoholic potassium cyanide;[5] and, finally, furil, prepared by oxidizing furoin in air.[6]

The catalytic reduction method of Adams[7] was selected, but as it was desired to work with quantities of the order of 0.005–0.01 mole, the apparatus was modified to this end. A second gage was inserted in the line between the reservoir and the bottle (Burgess–Parr Company's apparatus) as shown in the sketch. After the bottle was filled with hydrogen, it was cut off from the reservoir by means of the needle-valve. Under these conditions it functions as its own reservoir, the pressure in the bottle being read on the second gage. Since the capacity of the bottle is about 0.05 that of the tank, a correspondingly small amount of material will give about the same drop in pressure.

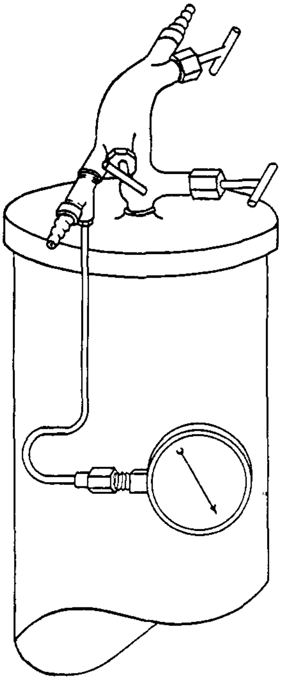

Fig. 1.

It is essential to guard carefully against leaks and to control the temperature within narrow limits. The authors find that benzoin is a very satisfactory material for calibrating the apparatus for one molecule of hydrogen, and benzil for two

---

[1] Presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at Duke University.

[2] Zinin, *Ann.*, **34**, 188 (1840).

[3] Bösler, *Ber.*, **14**, 327 (1871).

[4] Biltz and Wienands, *Ann.*, **308**, 11 (1899).

[5] Fritsch, *ibid.*, **329**, 53 (1903); Vanzetti, *Gazz. chim. ital.*, **57**, 162 (1927).

[6] Fischer, *Ann.*, 211, 221 (1882).

[7] Voorhees and Adams, THIS JOURNAL, **44**, 1397 (1922).

molecules of hydrogen. Heating the solution very often greatly speeds up the reduction and facilitates the solution of difficultly soluble compounds. The bottle was therefore heated by means of a thin copper cylinder, insulated and wound with resistance wire, current being supplied by a step-down transformer and controlled by a rheostat. It is necessary to calibrate the apparatus for each temperature and the temperature must be held sensibly constant throughout the run.

Benzil is readily reduced to benzoin and to hydrobenzoin. Usually an almost pure product was obtained after one recrystallization. When reduction was carried to completion the hydrobenzoin was obtained practically pure. The following equations represent the reaction

$$\mathrm{RCOCOR + H_2 = RCHOHCOR}$$
$$\mathrm{RCOCOR + 2H_2 = RCHOHCHOHR}$$

The solvent has an important effect on the reduction. Thus anisil reduces best in ethyl acetate, while piperil could only be reduced in pyridine. After many attempts under different conditions the authors failed to reduce veratril, but work is being continued on this compound. Furil readily takes up one molecule of hydrogen, but the action was not investigated beyond this stage as it has been dealt with by Adams.[8]

A number of attempts to dehydrate the hydro compounds to the desoxy compounds by the use of acetic and hydrochloric acids were made. In the case of hydro-anisoin a good yield of desoxyanisoin was obtained, but from hydropiperoin a compound of melting point 114°, not identical with desoxypiperoin, was obtained but not further examined. Hydrobenzoin is known to dehydrate to an anhydride and diphenylacetaldehyde. One case of similar dehydration using sulfuric acid, (hydro-anisoin and isohydro-anisoin)[9] is recorded in the literature. Iso compounds, however, were never obtained in the present research. The desoxy compounds were prepared for this work by reducing the corresponding benzoins by means of tin and alcoholic hydrochloric acid.[10] Desoxybenzoin readily reduced to toluylene hydrate. Desoxyanisoin formed di-*p*-methoxytoluylene hydrate, and desoxypiperoin reduced with great difficulty to form di-*p*-methylenedioxytoluylene hydrate. Twenty-four runs were made on the desoxypiperoin using various solvents and otherwise modifying conditions; only one run gave the required product in satisfactory yield. The equation $\mathrm{RCH_2COR + H_2 = RCH_2CHOHR}$ represents the process. The toluylene hydrates readily lose water under the action of a mixture of acetic acid and hydrochloric acid to form the corresponding stilbenes, $\mathrm{RCH_2CHOHR = H_2O + RCH{=}CHR}$. Stilbenes so obtained are reduced more or less readily to form the corresponding diphenylethanes.

---

[8] Kaufmann and Adams, THIS JOURNAL, **45**, 3029 (1923).

[9] Rossel, *Ann.*, **151**, 42 (1869).

[10] I. Allen, private communication.

It will be seen that in one case the complete series of compounds from anisil to di-*p*-methoxydiphenylethane can be produced catalytically (acid or platinum oxide) in excellent yield.

The following scheme represents the process (anisil as example). Benzil and piperil are similar, but lack the stage *hydro to desoxy compound.*

$$\underset{\text{Anisil}}{\mathrm{CH_3OC_6H_4COCOC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}} \underset{\text{Anisoin}}{\mathrm{CH_3OC_6H_4COCHOHC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Hydro-anisoin}}{\mathrm{CH_3OC_6H_4CHOHCHOHC_6H_4OCH_3}} \xrightarrow[\mathrm{HAc}]{\mathrm{HCl}} \underset{\text{Desoxyanisoin}}{\mathrm{CH_3OC_6H_4COCH_2C_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Dimethoxytoluylene hydrate}}{\mathrm{CH_3OC_6H_4CHOHCH_2C_6H_4OCH_3}} \xrightarrow[\mathrm{HAc}]{\mathrm{HCl}} \underset{\text{Dimethoxystilbene}}{\mathrm{CH_3OC_6H_4CH{=}CHC_6H_4OCH_3}} \xrightarrow{\mathrm{H_2}}$$

$$\underset{\text{Dimethoxydiphenylethane}}{\mathrm{CH_3OC_6H_4CH_2CH_2C_6H_4OCH_3}}$$

The yields obtained in the foregoing reactions are excellent and would be practically quantitative if carried out on a larger scale. Compared with the usual methods of reduction (amalgam, tin and hydrochloric acid, etc.), the catalytic method is much superior, where applicable. It is interesting to note that many compounds usually described as yellow are obtained pure white by the catalytic method.

Experimental

In the following reductions 0.01 mole of substance, 50 cc. of solvent and 0.05 g. of platinum oxide were used. The product was usually identified by a mixed melting-point determination and comparison with an authentic specimen. The melting points of the crude products were usually within one or two degrees of the melting points given in the literature, indicating a high state of purity. Unless otherwise stated 0.01 mole of material was used for the reduction. The yields may be regarded as minimal in view of the small amounts of material used. For convenience the results are tabulated.

TABLE I

TABULATED RESULTS

Starting material	Product	Best solvent	Temp., °C.	Yield, %	M. p. of product, °C.
Benzil	Benzoin	Alcohol	Room	93	134
Anisil	Anisoin	Et. ac.	60	90	109–110
Piperil	Piperoin	Pyridine	60	87	118–120
Furil	Furoin	Alcohol	Room	86	135
Veratril	(Failed to reduce)				
Benzil	Hydrobenzoin	Alcohol	Room	90	134
Anisil	Hydro-anisoin	Et. ac.	60	88	168–170
Piperil	Hydropiperoin	Pyridine	60	80	200–202
Benzoin	Hydrobenzoin	Alcohol	60	90	134
Anisoin	Hydro-anisoin	Alcohol	60	89	168–170
Piperoin	Hydropiperoin	Alcohol	60	88	200–202

TABLE I (*Concluded*)

Starting material	Product	Best solvent	Temp., °C.	Yield, %	M. p. of product, °C.
Desoxybenzoin	Toluylene hydrate	Alcohol	Room	85	63
Desoxyanisoin	Di-*p*-methoxytoluylene hydrate	Acetic acid	Room	85	110.4
Desoxypiperoin	Di-*p*-methylenedioxytoluylene hydrate	Pyridine	Room	97	154–155
Stilbene	Diphenylethane	Alcohol	Room	86	53
Di-*p*-methoxystilbene	Di-*p*-methoxydiphenylethane	Et ac.	60	91	125
Di-*p*-methylenedioxystilbene	Di-*p*-methylenedioxydiphenylethane	Acetic acid	60	81	138

Desoxybenzoin, desoxyanisoin and desoxypiperoin (the latter not previously described) were produced by the reduction of the corresponding benzoins with tin and alcoholic hydrochloric acid. Desoxyanisoin may also be prepared by the action of acetic and hydrochloric acids on hydro-anisoin. Desoxypiperoin forms white crystals melting at 114.5° when crystallized from acetic acid. It is sparingly soluble in alcohol and moderately soluble in acetic acid.

Anal. Calcd. for $C_{16}H_{12}O_5$: C, 67.61; H, 4.24. Found: C, 67.48; H, 4.40.

Di-*p*-methoxytoluylene hydrate was found to melt at 110.4°. It forms white diamond-shaped crystals.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.49; H, 6.97. Found: C, 74.32; H, 6.81.

Wiechell[11] obtained this compound in another way and reports the melting point as 170°. As a check, the authors reduced desoxyanisoin with sodium amalgam and acetic acid and found the same melting point of 110°. Their specimen, prepared catalytically, gave dimethoxystilbene in 90% yield when heated with acetic and hydrochloric acids.

Di-*p*-methylenedioxytoluylene hydrate was obtained only once out of 24 runs, and then in a yield of 97%. The compound forms white crystals from alcohol and melts at 154–155°.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.89. Found: C, 66.95; H, 5.09.

The same compound was obtained in moderate yield by the reduction of desoxypiperoin with sodium amalgam and acetic acid. Prepared by either method, it was convertible into di-*p*-methylenedioxystilbene in 90% yield.

The stilbenes listed were obtained in 85–90% yield by heating the corresponding toluylene hydrates for ten minutes with a mixture of 80% acetic acid and 20% concentrated hydrochloric acid.

Summary

1. Benzoins are readily produced from benzils by catalytic reduction.
2. Hydrobenzoins are similarly produced from benzils or benzoins.
3. Desoxybenzoins reduce to toluylene hydrates.
4. Stilbenes, conveniently prepared by dehydrating the toluylene hydrates, give on reduction diphenylethanes.
5. Veratril failed to reduce.
6. Desoxypiperoin reduced once out of 24 trials.

---

[11] Wiechell, *Ann.*, **279**, 340 (1894).

7. The catalytic method, when applicable, gives excellent yields and is superior to other methods.
8. A convenient method for reducing 0.01 to 0.0025 mole is described.
9. Benzoin is recommended as a standard for calibrating the apparatus for one mole of hydrogen and benzil for two moles.
10. The complete series of reduction products of anisoin may be prepared catalytically.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM THE DEPARTMENT OF RESEARCH IN PURE CHEMISTRY, MELLON INSTITUTE OF INDUSTRIAL RESEARCH, UNIVERSITY OF PITTSBURGH]

THE PREPARATION OF ALLOMUCIC ACID AND CERTAIN OF ITS DERIVATIVES

BY C. L. BUTLER AND LEONARD H. CRETCHER

RECEIVED MARCH 1, 1929 PUBLISHED JULY 5, 1929

While engaged in the investigation of certain sugar acids, it was desired to prepare allomucic acid in comparatively large amounts. This is one of the less common dibasic acids in the sugar group and but few of its derivatives have been described. The only published method of preparation is that of Fischer,[1] who obtained the acid by epimerization of mucic acid with excess of pyridine at 140°. The yield was 14%.

The present authors have been able to prepare pure allomucic acid from mucic acid in yield of 33%. This was accomplished under the conditions of epimerization previously employed in this Laboratory for the preparation of *d*-talonic acid from *d*-galactonic acid.[2]

It was shown by Fischer[1] that allomucic acid is partially converted into a monolactone on boiling or evaporation of a water solution. Fischer did not isolate this lactone and we were not able to prepare it in crystalline form. A solution of the lactone was used in the present work for the preparation of the mono-amide.

Diethyl allomucate was prepared by the method employed by Malaguti[3] for the esterification of mucic acid, namely, the use of a comparatively large amount of concd. sulfuric acid and alcohol. The yield was 42% of the theoretical. It was found that it was also possible to esterify with alcohol containing 1% of hydrochloric acid. This method gives a better yield (58%) of ester and is somewhat simpler in manipulation. The ester was easily converted into the diamide by addition of concd. ammonia water.

It was shown by Kiliani[4] that *l*-mannosaccharic dilactone reduces

---

[1] Fischer, *Ber.*, **24**, 2136 (1891).

[2] Hedenburg and Cretcher, THIS JOURNAL, **49**, 478 (1927).

[3] Malaguti, *Ann. chim. phys.*, [2] **63**, 86 (1836).

[4] Kiliani, *Ber.*, **20**, 339, 2710 (1887).