covered of which a sample yielded the same amount of pure semicarbazone as that given by the corresponding amount of pure aldehyde. From the thick, oily residue after distilling the ether, 7 g. of diphenylvinylglycol, m. p. 154°, was obtained. It was further identified by conversion to the diacetate, m. p. 119°. No further crystalline product could be obtained from the thick, oily residue, and efforts to obtain a crystalline diacetate or dibenzoate were fruitless. The oil combined with somewhat less than two molecular equivalents of bromine, but no crystalline bromide could be obtained.

Summary

1. Chromous chloride in aqueous or alcoholic solution has been found to be without effect at 25° on representative aliphatic aldehydes and ketones, aromatic ketones, saturated and unsaturated acids and esters, alcohols, ethylene or diphenylbutadiene.

2. Typical aromatic aldehydes, α,β unsaturated aldehydes, benzalacetophenone and certain other α,β unsaturated ketones are reduced by chromous chloride and vanadous chloride with the formation of dimolecular products. Mesityl oxide is not reduced. The amount of monomolecular reduction, if any, must be very small.

3. It seems probable that the dimolecular reduction process proceeds through an addition product of the carbonyl compound and the inorganic acid present and is analogous to the reduction of the halochromic salts of aryl carbinols.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

SYMMETRICAL DI-METHYLPHENYLMETHYL-HYDRAZINE AND RELATED COMPOUNDS[1]

BY W. A. SCHULZE AND H. L. LOCHTE

RECEIVED DECEMBER 29, 1925 PUBLISHED APRIL 5, 1926

Previous papers[2] have shown that aliphatic hydrazines which are not readily prepared by older methods may be obtained by catalytic reduction of the corresponding ketazines. The reduction of acetophenone ketazine has now been accomplished and various derivatives of the reduction product have been prepared.

Acetophenone ketazine was first prepared by Curtius and Thun[3] by the usual method. The yield, even after the reaction mixture had been heated under a reflux condenser for 12 hours, was evidently not good, as they reported the formation of a yellow oil which later was identified[4] as

---

[1] Constructed from a thesis submitted by W. A. Schulze in partial fulfilment of the requirements for the degree of Master of Arts at the University of Texas.

[2] (a) Lochte, Bailey and Noyes, THIS JOURNAL, **44**, 2556 (1922). (b) Harkins and Lochte, *ibid.*, **46**, 450 (1924).

[3] Curtius and Thun, *J. prakt. Chem.*, [2] **44**, 167 (1891).

[4] Curtius and Pflug, *ibid.*, [2] **44**, 540 (1891).

the hydrazone formed by the reaction between one molecular equivalent of the ketone and one of hydrazine hydrate. It has been found now that, although azines are readily hydrolyzed by *distilling* them in the presence of an acid, acetophenone ketazine may be prepared in a yield of over 90% of that calculated by adding two molecular equivalents of acetophenone to one molecular equivalent of hydrazine hydrochloride. The reaction proceeds even at room temperature and is complete in less than an hour. Preliminary tests show that a number of other azines may be prepared very easily if hydrazine hydrochloride instead of the hydrate is employed. Minunni and Carta-Satta[5] found that hydrazine sulfate readily reacts with furfuraldehyde and with nitrobenzaldehyde to give the corresponding azines, but their method apparently has not been employed by others in the preparation of azines.

The catalytic reduction of acetophenone ketazine according to the method used in the case of cyclohexanone ketazine[6] proceeds smoothly only in case freshly prepared ketazine is used. Careful purification by repeated recrystallizations is required to prepare an old sample for reduction.

Oxidation of the resulting symmetrical hydrazine yields a colorless crystalline solid melting at 74° to an oil with a very slight straw color. Hydrolysis of this product by means of acids yields primary methylphenylmethyl-hydrazine.

All attempts to prepare the hydrazone by direct synthesis from primary methylphenylmethyl-hydrazine and acetophenone failed. Inability to prepare this compound makes it impossible to establish definitely the structure of the product obtained on oxidizing the symmetrical hydrazine with hydrogen peroxide. A number of lines of evidence indicate that the oxidation product has the azo structure and not that of the isomeric hydrazone.

Failure to isolate the product which—to be identical with that obtained by oxidation—must have a melting point of 74° and must be insoluble in water, in itself indicates that the oxidation product probably has the azo structure. The fact that no derivative of the compound could be isolated indicates that the product probably has no imide nitrogen. Curtius and co-workers had no difficulty in preparing derivatives of their hydrazones, many of which were not as stable as our oxidation product.

However, the main reasons for assigning the azo structure as the most probable are its smooth decomposition, on simple heating, into nitrogen and pure 2,3-diphenylbutane and its rapid reduction by aluminum amalgam to the original hydrazo compound.

Decomposition into nitrogen and hydrocarbon has been repeatedly ob-

---

[5] Minunni and Carta-Satta, *Gazz. chim. ital.*, [2] **29**, 468 (1899).

[6] Harkins and Lochte, THIS JOURNAL, **46**, 452 (1924).

served in the case of azo compounds[7] but as far as we know, no such decomposition product has been established in the case of hydrazones of the type under discussion.

Thiele[7b] used reducibility by aluminum amalgam as a means of distinguishing between azo and hydrazone compounds. Fischer[8] evidently had the same difference in behavior in mind when he made tests which showed that azophenylethyl is readily reduced, while the corresponding hydrazone is not affected by sodium amalgam. Wieland[9] states that hydrazones are reducible only in case an aromatic or unsaturated group is adjacent to the methylene carbon atom. A study of accumulated data seems to show that the presence of an aromatic group does not make the hydrazone reducible by amalgams if an aliphatic group is also adjacent to the same methylene carbon atom. The azine and simple hydrazone of benzaldehyde and of benzophenone are reducible by amalgams, but the corresponding derivatives of acetone and of acetophenone are not affected. In the case of acetophenone, the ketazine is not affected on heating an alcoholic solution of it under a reflux condenser for 48 hours with aluminum amalgam. Our oxidation product, when treated in the same way, is reduced in less than an hour, as would be expected if it has the azo structure. The ease with which the compound is hydrolyzed by acids and even by moist air and the fact that only Perhydrol in alkaline solution appears to afford satisfactory yields of the oxidation product indicate that the compound changes to the isomeric hydrazone form more easily than the azo compounds described in previous papers from this Laboratory.

Experimental Part

Bis-methylphenyl-azimethylene (Acetophenone Ketazine).—The ketazine was prepared by adding one molecular equivalent of concd. hydrochloric acid to one molecular equivalent of 80% hydrazine hydrate.

The solution was cooled to 60° or less and 25 cc. of alcohol added. Finally, two molecular equivalents of acetophenone were added slowly during constant stirring. The mixture was then placed in a large flask and agitated in a mechanical shaker until no additional precipitate formed. The yield was practically equal to that calculated. Recrystallized from alcohol the bright yellow needles melt at 121°—identical with the melting point given by Curtius and Thun.[3]

Anal.[10] Calcd. for $C_{16}H_{16}N_2$: C, 81.36. Found: C, 81.28, 81.27.

Reduction of Acetophenone Azine.—Attempts to reduce this azine by means of aluminum amalgam failed completely. After heating an alcoholic solution of 1 g. of the azine with a large excess of aluminum amal-

---

[7] (a) Thiele, *Ber.*, **42,** 2579 (1909); (b) *Ann.*, **376,** 267 (1910). (c) Gomberg, *Ber.*, **30,** 2045 (1897).

[8] Fischer, *Ber.*, **29,** 793 (1896).

[9] H. Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, **1913.**

[10] When no analyses for hydrogen are given, carbon was determined by the bomb method of Wilde and Lochte, This Journal, **47,** 440 (1925).

gam under a reflux condenser for 48 hours the unchanged azine was recovered by extraction with ether. Attempts to reduce the azine catalytically according to the method used on the corresponding acetone derivative[11] without isolating the azine did not yield satisfactory results. If the azine was freshly prepared or carefully purified, reduction with colloidal platinum and hydrogen under a pressure of one atmosphere proceeded smoothly until two molecular equivalents of hydrogen had been absorbed. Reduction failed completely or proceeded only after using a total of 40 to 50 cc. of 10% chloroplatinic acid solution to furnish the catalyst in case the azine was several days old and had not been purified until its melting point showed that it was pure. In the case of freshly prepared azine, reduction offered no difficulties even though the product had not been recrystallized.

Hydrochloride of Symmetrical Di-methylphenylmethyl-hydrazine.—The catalyst was precipitated by acetone, filtered off and the filtrate evaporated in vacuum on a steam-bath. The hydrochloride in a yield of 60 to 70% remained behind as a mass of white crystals which are very soluble in alcohol, soluble in water and slightly soluble in ethyl acetate and in benzene. Recrystallization from a mixture of ethyl acetate and alcohol yielded slender, white needles; m. p., 188°.

Anal. Calcd. for $C_{16}H_{21}N_2Cl$: C, 69.43; N, 10.13; Cl, 12.83. Found: C, 69.31; N, 10.28; Cl, 12.58, 12.63.

Symmetrical Di-methylphenylmethyl-hydrazine, $C_6H_5(CH_3)$-$CHNHNHCH(CH_3)C_6H_5$.—When the hydrochloride was treated with ammonium or sodium hydroxide solution, the base separated as a yellow oil layer. Distillation in a stream of nitrogen at a pressure of 30 mm. yielded, as the main fraction, a colorless liquid distilling at 110° to 115°. The fraction obtained between 115° and 118° was found to contain a considerable amount of 2,3-diphenylbutane, indicating that the first fraction was probably also contaminated with this decomposition product. When the 110° to 115° fraction was cooled to —50°, during rapid stirring, the substance changed between —35° and —40° to a glassy solid. Neither the cooling nor the heating curve gave any indication of a melting point. When an ether solution of the base was treated with hydrogen chloride, the hydrochloride melting at 188° was obtained. Both Fehling's and ammoniacal silver nitrate solutions were reduced slowly after the mixtures had been heated. This apparent weakness as reducing agent may be due to the slight solubility of the base in the alkaline solution. When left in contact with air the base was slowly oxidized to the compound melting at 74°, but the yield was poor. In view of the difficulty of purifying the poisonous and expensive base neither analyses nor physical constants were obtained.

NITROSO DERIVATIVE.—When a suspension of the hydrochloride in water was treated with sodium nitrite, a nitroso derivative was obtained as

---

[11] Lochte, Bailey and Noyes, THIS JOURNAL, **43**, 2600 (1921).

a straw-colored oil, slightly heavier than water. The moisture and impurities were removed by distillation at 100° and 5 mm. pressure. The portion remaining in the flask proved to be analytically pure.

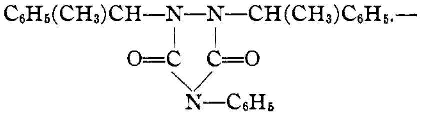
Anal. Calcd. for $C_{16}H_{19}ON_3$: C, 71.37; N, 15.61. Found: C, 71.10; N(micro), 15.77.

OXALATES OF THE HYDRAZO COMPOUND.—As in the case of a number of other symmetrical hydrazines[12] attempts to purify the oxalate showed that the product consists of a mixture of oxalates that were not completely separated.

1,2 - Bis - methylphenylmethyl - 4 - phenyl - semicarbazide, $C_6H_5(CH_3)CHNHN(CONHC_6H_5)CH(CH_3)C_6H_5$.—The phenylisocyanate derivative separated as a smear which gradually crystallized. Repeated recrystallization from absolute alcohol yielded slender, white needles; m. p., 108°.

Anal. Calcd. for $C_{23}H_{25}ON_3$: C, 76.88; N, 11.70. Found: C, 76.63; N (micro), 11.78.

1,2-Bis-methylphenylmethyl-4-phenylurazole,



When the phenylisocyanate derivative was heated to 155° with urea according to the method of Poth and Bailey[13] ammonia was liberated and a solid mass remained on cooling the mixture. The fraction that was insoluble in ammonium hydroxide was recrystallized from 50% alcohol. Thus purified, the beautiful white crystals melted at 105.5°.

Anal. Calcd. for $C_{24}H_{23}O_2N_3$: N, 10.91. Found (micro): 10.99.

Oxidation Product of Symmetrical Di-methylphenylmethyl-hydrazine.—Oxidation by mild oxidizing agents changed the hydrazine to a product melting at 74°. Although any oxidizing agent gave more or less of the product, the only agent that gave satisfactory yields was Perhydrol in alkaline solution which yielded 70 to 90% of hard white crystals, insoluble in water and fairly stable in air. One recrystallization from alcohol yielded the pure product. While the solid was white, the melted substance had a slight but definite straw color. Prolonged exposure to moist air decomposed the substance to a smear with a pronounced acetophenone odor. Hydrolysis by boiling with dil. hydrochloric acid yielded acetophenone and the primary hydrazine. As the compound has either the azo or the hydrazone structure, attempts were made to prepare derivatives by reaction with phenylisocyanate, phenylmustard oil, hydrocyanic acid and cyanic acid, but no derivatives of the hydrazone could be isolated. Attempts to synthesize the hydrazone directly by reaction between primary methylphenylmethylhydrazine and acetophenone failed to yield crystalline products even though numerous attempts were made under various conditions including the use of absolute alcohol, zinc chloride, sodium acetate and iodine as condensing agents. The high melting point and the insolubility of the oxidation product in water should have made the isolation of it from any of the above reaction mixtures an easy operation, had the product been identical with the one obtained by oxidation.

Anal. Calcd. for $C_{16}H_{18}N_2$: C, 80.66; H, 7.56; N, 11.76. Found: C, 81.01; H, 7.42; N (micro), 11.51.

---

[12] Ref. 2 a, p. 2560.

[13] Poth and Bailey, THIS JOURNAL, **45**, 3009 (1923).

REDUCTION OF THE OXIDATION PRODUCT.—One g. of the oxidation product melting at 74° was treated with an excess of aluminum amalgam and 3 cc. of 95% alcohol. A few drops of water were added from time to time while the reaction proceeded at room temperature. At the end of an hour extraction with ether yielded a solution which, on treatment with hydrogen chloride, deposited a mass of white flakes. The ether was removed by being warmed in a vacuum and the residue recrystallized from ethyl acetate. One recrystallization yielded a product melting at 180° and another the pure hydrochloride; m. p., 188°. When this product was mixed with known hydrochloride the melting point was not reduced.

DECOMPOSITION OF THE OXIDATION PRODUCT.—When an attempt was made to distil the oxidation product in a vacuum, 2,3-diphenylbutane distilled between 205° and 215° (40 mm.) or between 180° and 195° (30 mm.). The product was analytically pure; m. p., 123.5°. Engler and Bethge[14] reported the same melting point.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.43. Found: 91.31.

Oxalate of Primary Methylphenylmethyl-hydrazine, $C_6H_5(CH_3)CHNHNH_2\cdot(COOH)_2$.—The oxidation product was readily hydrolyzed by boiling for 15 minutes with 1:3 hydrochloric acid and then distillng the volatile products in a vacuum. The base obtained on treating the residue with sodium hydroxide decomposed rapidly. An ether solution of the base when treated with an ether solution of one molecular equivalent of oxalic acid reacted, with heat evolution. The oxalate precipitated as a fine, white powder which melted at 172°, with decomposition. The salt is slightly soluble in water, fairly soluble in alcohol and insoluble in ethyl acetate, benzene and in ether.

Anal. Calcd. for $C_{10}H_{14}O_4N_2$: C, 53.09; N, 12.39. Found: C, 52.92; N, 12.65.

Dibenzoyl Derivative of the Primary Hydrazine.—The dibenzoyl derivative was recrystallized by adding water to the hot saturated alcoholic solution until a permanent cloudiness appeared, and then cooling as usual; m. p., 193°. The compound is soluble in the common organic solvents, but insoluble in water.

Anal. Calcd. for $C_{22}H_{20}O_2N_2$: C, 76.74; N, 8.14. Found: C, 76.87; N, 8.08.

Summary

1. An improved method of preparing acetophenone ketazine is described.

2. This ketazine has been reduced catalytically, and a number of derivatives of the resulting symmetrical hydrazine are described.

3. Pure 2,3-diphenylbutane is obtained in good yield by vacuum distillation of the product obtained on oxidizing the symmetrical hydrazine.

AUSTIN, TEXAS

---

[14] Engler and Bethge, *Ber.*, **7**, 1127 (1874).