employed in the reduction of acetone-phenylhydrazone. It is a colorless oil which boils at 226° (100 mm.), and has solubilities similar to those of phenyl-hydrazo-*iso*propyl. Like the latter substance it is readily oxidized to the corresponding azo compound.

Anal. Calcd. for $C_{12}H_{18}N_2$: C, 75.79; H, 9.46; N, 14.74. Found: C, 75.87; H, 9.26; N, 14.84.

Summary

1. A process of preparing phenyl-hydrazo-*iso*propyl and phenyl-hydrazo-cyclohexyl by the catalytic reduction of the corresponding phenylhydrazones in the presence of colloidal platinum is described.
2. Phenyl-hydrazo-*iso*propyl on oxidation gives in quantitative yield phenyl-azo-*iso*propyl.
3. The two isomeric carbamyl derivatives of phenyl-hydrazo-*iso*propyl become readily available by the methods of preparation given. They both yield the same *iso*propyl-phenyl urazole.
4. A conclusive proof is furnished that the reactive imino group in phenyl-hydrazo-*iso*propyl joins the *iso*propyl radical.

AUSTIN, TEXAS

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

REARRANGEMENT OF DIPHENYL-PARA-TOLYL-ACETHYDROXAMIC ACID

BY CHARLES DEWITT HURD AND HENRY J. BROWNSTEIN

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It was the initial object of this investigation to secure additional material with which to test the hypothesis proposed by Jones and Hurd[1] as a result of experiments with derivatives of diphenyl-acethydroxamic acid and of triphenyl-acethydroxamic acid. When hydroxamic acids (Lossen), halogen amides (Hofmann), azides (Curtius) and other similar compounds rearrange, some radical, R, passes from carbon to nitrogen. In general terms, the equation is $R{-}CO{-}N{=}^{x}_{y} \longrightarrow O{=}C{=}NR + xy$. The hypothesis stated that if the radical, R, which "wanders" is potentially a free radical, the rearrangement will occur with greater ease than otherwise.

Thus far, there have been prepared but two sets of derivatives with which to test this hypothesis; one, in which the radical, R, was triphenyl methyl,[1] and the other in which it was diphenyl nitrogen.[2] Both of these cases confirmed the postulate, inasmuch as the rearrangements took place at room temperature with great readiness. The facile rearrangement in which diphenyl nitrogen was involved was made all the more striking when it was discovered that derivatives of the monophenyl analog, α-phenyl-β-

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[1] Jones and Hurd, THIS JOURNAL, **43,** 2426 (1921).

[2] Hurd, *ibid.*, **45,** 1472 (1923).

hydroxy-urea, could never be made to rearrange. A possible explanation of this non-rearrangement is reserved for a later paper.

For purposes of classification it will be mentioned that derivatives of diphenyl- and of dibenzyl-acethydroxamic acids[3] also were found to rearrange with great readiness. The fact that diphenylmethyl and dibenzylmethyl have not been isolated as free radicals does not invalidate the hypothesis. On the contrary, there is every reason to believe that the increase in the number of phenyl radicals, from none in methyl to three in triphenylmethyl, promotes the tendency for the radical to exist free. These results agree with such an assumption.

Since the isolation of triphenylmethyl, numerous other triarylmethyls have been prepared. Conceivably, these would all furnish a means for testing the hypothesis. However, the difficulty of preparation of the triaryl acetic acids, from which the triaryl acethydroxamic acids are produced, is such that only a few have been isolated.[4] Because of its comparative ease of preparation, diphenyl-*p*-tolyl-acetic acid was chosen as a starting point. The group in this case which is a potential free radical is diphenyl-*p*-tolylmethyl. Gomberg showed that this free radical could be easily prepared in solution by the interaction of diphenyl-*p*-tolylmethyl chloride with molecular silver.[5]

The results of the present investigation are as follows. First of all, the rearrangement of diphenyl-*p*-tolyl-acethydroxamic acid derivatives, in conformity with the hypothesis, was observed to take place at room temperature. The isocyanate, $CH_3—C_6H_4—C(C_6H_5)_2—NCO$, was the product of rearrangement. It reacted with alcohol to give the urethan, $Ar_3C—NH-COOC_2H_5$,[6] and with aniline to produce the urea, $Ar_3C—NH—CO—NH-C_6H_5$. It was shown that the isocyanate would not react with water to form the symmetrical disubstituted urea, $CO(NH-CAr_3)_2$; in this respect it resembles triphenylmethyl isocyanate.[7]

Another interesting result of the present work is worthy of mention because of its unusual nature and because similar facts were noticed in each of the other series of hydroxamic acids[8] to which the hypothesis applies. Neither the sodium nor the potassium salt of the acetyl ester of diphenyl-*p*-tolyl-acethydroxamic acid could be precipitated in a pure state when the customary methods were employed. Ordinarily, it is only necessary to add sodium (or potassium) ethylate to an alcoholic solution of the ester, and dilute it with a little ether to produce a copious precipitate of the salt.

[3] (a) Ref. 1. (b) Jones and Scott, THIS JOURNAL, **44,** 411 (1922).

[4] Note, for example, the difficulty in the preparation of tribenzylacetic acid. Ref. 3 b, p. 409.

[5] Gomberg, *Ber.*, **37,** 1633 (1904).

[6] $Ar_3C—$ represents the radical $CH_3—C_6H_4—C(C_6H_5)_2—$.

[7] Ref. 1, p. 2428.

[8] Ref. 1, pp. 2434, 2435, 2436, 2440. Ref. 3 b, p. 418. Ref. 2, p. 1488.

However, in this case, a dilution with 40 volumes of petroleum ether in addition to ordinary ether, caused the separation of only a small fraction of the total amount of dissolved material. In addition, its appearance was gelatinous instead of crystalline. These results undoubtedly show how weakly acidic are the compounds (the acetyl or benzoyl esters) in question.

Experimental Part

Diphenyl-*p*-tolyl-acetic acid was prepared from benzilic acid, toluene, and stannic chloride by the method of Bistrzycki and Wehrbein.[9]

Diphenyl-*p*-tolyl-acetyl Chloride, $CH_3—C_6H_4—C(C_6H_5)_2—COCl$.—Three g. of diphenyl-*p*-tolyl-acetic acid and 10 cc. of thionyl chloride were placed in a small flask fitted with an air-cooled condenser, which was then warmed gently until solution was complete. In five minutes, when the evolution of sulfur dioxide and hydrogen chloride had ceased, the contents of the flask were poured into a beaker containing crushed ice, where the unchanged thionyl chloride was decomposed. The solid acid chloride was collected upon a filter, washed with a little cold water, pressed on a porous plate and dried in a vacuum desiccator. With no further purification, it melted at 89–90°. The yield was practically quantitative.

Bistrzycki and Landtewing[10] prepared this compound with phosphorus pentachloride as the chlorinating agent and phosphorus oxychloride as the solvent. There is danger in this method of failing to obtain the desired product because of its decomposition at higher temperatures into diphenyl-*p*-tolylmethyl chloride and carbon monoxide. This decomposition occurs at 120°, and the boiling point of phosphorus oxychloride approaches that temperature too closely for a safe margin.

Diphenyl-*p*-tolyl-acethydroxamic Acid, $CH_3C_6H_4C(C_6H_5)_2CONHOH$.—A solution of 2.5 g. of the acid chloride in 40 cc. of petroleum ether (60–70°) was poured into a flask which contained 2.5 g. of free hydroxylamine.[11] The flask was stoppered and shaken at frequent intervals during an hour. It was then put aside until the next day, at which time the solid was collected upon a filter. It consisted of diphenyl-*p*-tolyl-acethydroxamic acid, hydroxylamine hydrochloride and some unused hydroxylamine. The hydroxamic acid was dissolved in carbon tetrachloride, in which the other two compounds are quite insoluble. After filtration, the solvent was evaporated to a point where, upon cooling, beautiful white crystals of the hydroxamic acid appeared. This product melted sharply at 146.5°.

The compound is also soluble in ether, ethyl acetate, chloroform, alcohol and benzene; it is insoluble in water and ligroin. An alcoholic solution gave the customary color reaction with ferric chloride.

Anal. Subs., 0.3957: N, 16.35 cc. (over 40% KOH; 26.5°, 737.1 mm.). Calcd. for $C_{21}H_{19}O_2N$: N, 4.41. Found: 4.48.

ACETYL ESTER, $CH_3C_6H_4C(C_6H_5)_2CONHOCOCH_3$.—One g. of diphenyl-*p*-tolyl acethydroxamic acid was placed in an excess (5 cc.) of acetic anhydride and was warmed. In about two minutes, a test with ferric chloride showed that the reaction was complete. In order to stop any further action which might lead to the formation of the diacetyl ester, 20 cc. of cold water was added to decompose the excess of anhydride. The ester appeared as an oil, but in the course of a few hours it solidified. The yield was quantitative. It was recrystallized from a mixture of 15 cc. of ligroin and 3 cc. of benzene.

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[9] Bistrzycki and Wehrbein, *Ber.*, **34**, 3080 (1901).

[10] Bistrzycki and Landtewing, *Ber.*, **41**, 686 (1908).

[11] This was prepared by a crystallization method; butyl alcohol was the solvent.

One crystallization gave a product that melted at 135°. The ester was soluble in most organic solvents. It was difficultly soluble in cold ligroin and water.

Anal. Subs., 0.1913: N, 7.08 cc. (over 40% KOH; 27°, 743.3 mm. (26°)). Calcd. for $C_{23}H_{21}O_3N$: N, 3.90. Found: 4.04.

POTASSIUM SALT, $CH_3C_6H_4C(C_6H_5)_2CONKOCOCH_3$.—To a solution of 0.38 g. of the acetyl ester in 3 cc. of absolute alcohol, there was added 0.52 cc. of alcoholic potassium hydroxide (1 cc. ≈ 0.115 g. of KOH). No precipitate appeared upon the addition of 20 cc. of absolute ether, but a very small amount of a gelatinous solid did form when 40 cc. of ligroin was added. The addition of more ligroin caused no further precipitation. The solid was collected upon a filter, and dried in a desiccator over sulfuric acid. The filtrate was evaporated in an open dish. A white solid remained which was washed with water to remove the inorganic material. The residue proved to be a mixture of substances which contained the urethan and the isocyanate. The details for the separation of these substances are similar to those given below for the sodium salt.

The precipitated potassium salt was dissolved in 2 cc. of water. In about 30 seconds, a definite turbidity appeared and bubbles of a gas, probably carbon dioxide, were noticeably evolved when the solution was heated slightly. The quantity of material was too small for further investigation.

SODIUM SALT.—To a solution of 0.31 g. of the acetyl ester in 4 cc. of absolute alcohol was added the calculated amount (0.85 cc. containing 0.0195 g. of dissolved sodium) of sodium ethylate solution. Nothing precipitated from solution when the two were mixed. Twenty cc. of absolute ether was then added and following it, 20 cc. of petroleum ether. A small quantity of gelatinous precipitate formed gradually during the course of 15 minutes. This was removed by filtration. Further dilution to 200 cc. with petroleum ether caused an almost imperceptible precipitation. As before, the liquid was filtered and the filtrate was then evaporated. The treatment of the precipitate and of the residue from the filtrate will be discussed separately.

THE PRECIPITATE.—The solid was dissolved in 3 cc. of water. Almost instantly, bubbles of a gas were produced and an oil was formed. No further change was apparent after several hours, so the mixture was extracted with ether, following which the ether was set aside to evaporate upon a watch glass. A small quantity of an oily residue failed to evaporate. It solidified after a time. It melted between 60° and 68°. In a free flame, the liquid distilled up the melting-point tube, with apparent decomposition. This solid may have been the isocyanate, but the quantity of it was too minute to permit certain determination.

The residue on the watch glass, from which the sample had been taken for determination of the melting point, dissolved in two drops of concd. sulfuric acid forming a yellow solution. Dilution with water caused the precipitation of a white solid. There was no apparent decomposition.

The Residue from the Filtrate.—This was a taffy-like solid. It resisted the ordinary methods of inducing crystallization, such as cooling, scratching, or desiccation. Quite accidentally, it was found that when ether was poured over the mass, within two seconds the viscous material changed to a white solid. This solid possessed the properties anticipated for the urethan, $CH_3C_6H_4C(C_6H_5)_2NHCOOC_2H_5$, whereas the ether filtrate was shown to contain diphenyl-*p*-tolylmethyl isocyanate. These two compounds are rearrangement products, and it may be pointed out that no application of heat was employed in their preparation.

Diphenyl-*p*-tolylmethyl Urethan.—The white solid was redissolved in benzene and decanted from the admixed sodium acetate. The urethan could not be precipitated by petroleum ether, so the solution was evaporated. A transparent oil remained, which was again instantly converted into round, white, crystalline clumps when ether was poured upon it. The solid was pressed on a porous plate and washed with a little ether; m. p., 116–118°, with preliminary softening at 114°. The physical properties of this compound are very similar to those of diphenylmethyl urethan,[12] prepared similarly.

Anal. Subs., 0.1267: N, 4.69 cc. (over 40% KOH; 24°, 746.7 mm.). Calcd. for $C_{23}H_{23}O_2N$: N, 4.06. Found: 4.10.

Diphenyl-*p*-tolylmethyl Isocyanate, $CH_3C_6H_4C(C_6H_5)_2NCO$.—The ether solution was shown to contain the isocyanate, by allowing it to react with aniline. Neither the urethan, nor the amine, $CH_3C_6H_4C(C_6H_5)_2NH_2$, which are other possible solutes due to rearrangement, exhibited any change with aniline. The isocyanate should, however, form the disubstituted urea, $CH_3C_6H_4C(C_6H_5)_2NHCONHC_6H_5$. Such was found to be the case. A high-melting solid remained when the solvents were evaporated. It was recrystallized from ether.

Phenyl Diphenyl-*p*-tolylmethyl Urea.—This compound melted at 213–215°. It is insoluble in ligroin and water; only slightly soluble in ether, cold alcohol, or cold benzene; it is very soluble in ethyl acetate.

Summary

Diphenyl-*p*-tolyl-acethydroxamic acid and certain of its derivatives have been prepared. They undergo the Lossen rearrangement with great readiness, and thus afford affirmative evidence for the hypothesis of Jones and Hurd.

The preparation of the pure alkali metal salts of the esters of this acid was not possible. It is a striking fact that the same circumstance has been encountered with every other series of hydroxamic acid derivatives to which the hypothesis applies.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES. V. THE BROMINATION OF 2-AMINO-PARA-CYMENE AND CERTAIN NEW AZO DYES

SECOND PAPER[1]

BY ALVIN S. WHEELER AND HAYWOOD M. TAYLOR

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The first work on the bromination of 2-amino-*p*-cymene was reported by Wheeler and Smithey.[2] In that work it was found that the bromination was most successfully carried out by treating a carbon tetrachloride solution of aceto-amidocymene with bromine. The free base was obtained as a colorless oil, soon turning yellow and then red, similar to the behavior of aniline. Its hydrochloride, hydrobromide and certain diazo deriva-

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[12] Ref. 1, p. 2434.

[1] This paper is an abstract of a thesis submitted by Haywood M. Taylor in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of North Carolina in June, 1924.

[2] Wheeler and Smithey, THIS JOURNAL, **43,** 2611 (1921).