excess of the amine and if necessary heat was applied to start the reaction. Once started, the reaction proceeded rapidly with the evolution of heat. The excess of amine was washed out with acid and the product was filtered off and recrystallized from alcohol of the proper strength (Table I). The alternate procedure was to warm a mixture of the sulfonyl chloride, the amine and dil. sodium hydroxide solution until the reaction was complete. When a primary amine was used the solution was acidified and filtered and the product recrystallized. With secondary amines no acid was used.

The amides which have been characterized are given in Table I.

TABLE I

m-NITROBENZENE-SULFONAMIDES

Amine	M. p. of pure product °C.	Strength of alcohol for cryst. %	Analysis Calcd. %	Analysis Found %
Diethylamine	66	90	C, 46.15	46.13
Di-*n*-butylamine	61	90	N, 8.9	8.9
Methylaniline	100	60	N, 9.6	9.45
Ethylaniline	100.5	60	N, 9.15	9.10
n-Propylaniline	111.5	60	N, 8.75	8.63
n-Butylaniline	78.5	60	N, 8.38	8.31
α-Naphthylamine	166.5	90	N, 8.54	8.44
β-Naphthylamine	165.5	90	N, 8.54	8.50
o-Chloro-aniline	153	60	Cl, 11.34	11.0
p-Chloro-aniline	119.5	60	Cl, 11.34	10.93
p-Bromo-aniline	120.5	75	Br, 22.36	22.32

Summary

The *m*-nitrobenzenesulfonyl derivatives of several common amines have been characterized. The secondary amine derivatives are especially useful for identification purposes.

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

THE REDUCTION OF PHENYLHYDRAZONES

BY R. C. GOODWIN AND J. R. BAILEY

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Foster and Bailey,[1] employing the catalytic method of reduction with colloidal platinum as catalyst, succeeded in converting acetaldehyde phenylhydrazone to phenyl-hydrazo-ethyl, $C_6H_5NHNHC_2H_5$, a method of preparation of mixed aliphatic-aromatic hydrazo compounds which is a decided improvement over the processes described by earlier investigators.[2]

As shown in the present paper, acetone-phenylhydrazone can be reduced

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[1] Foster and Bailey, THIS JOURNAL, **44**, 1562 (1922).

[2] Fischer, *Ann.*, **190**, 102 (1877); **199**, 325 (1879). Tafel, *Ber.*, **18**, 1741 (1885). Knorr, *Ber.*, **39**, 3265 (1906). Knorr and Weidel, *Ber.*, **42**, 3523 (1909).

to the corresponding phenyl-hydrazo-*iso*propyl, $C_6H_5NHNHCH(CH_3)_2$, in a yield of 90%, and the phenylhydrazone of ketohexamethylene serves equally well for the preparation of phenyl-hydrazo-cyclohexyl, $C_6H_5NHNHC_6H_{11}$. The supposed methylene phenylhydrazone of J. W. Walker prepared from phenylhydrazine and formaldehyde[3] is not hydrogenated under the conditions employed for the reduction of other hydrazones. Walker regards his product, which melts at 146–155°, as monomolecular and the "true hydrazone of formaldehyde." This view, however, is not shared by Hans and Astrid Euler,[4] who claim that the "monomolecular form crystallizes from benzene in leaflets which melt at 128°." The fact that phenyl-hydrazo-acetonitrile, $C_6H_5NHNHCH_2C{\equiv}N$, which should result from the addition of hydrocyanic acid on the monomolecular phenylhydrazone of formaldehyde[5] is not reported in the literature may be explained, probably, by the assumption of an abnormal structure of Walker's supposed monomolecular methylene-phenylhydrazone.

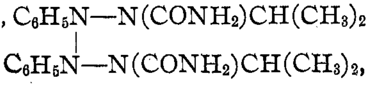
As was to be expected, phenyl-azo-*iso*propyl, $C_6H_5N{=}NCH(CH_3)_2$, is formed in practically quantitative yield by the action of various oxidizing agents on phenyl-hydrazo-*iso*propyl.

The hydrogen of the imino group adjacent to the *iso*propyl rather than the one adjacent to the phenyl in the hydrazo compound is reactive toward cyanic acid, acid chlorides, mustard oils and isocyanates.

A very conclusive proof of the structure of the semicarbazide formed in the reaction of cyanic acid with phenyl-hydrazo-*iso*propyl as $C_6H_5NHN(CONH_2)CH(CH_3)_2$ (1) is furnished in the reduction of acetone-2-phenyl semicarbazone where the product obtained must be assigned the formula $C_6H_5N(CONH_2)NHCH(CH_3)_2$ (2). Products 1 and 2, in conformity with the structures given, are isomeric.

That benzoyl chloride forms with phenyl-hydrazo-*iso*propyl $C_6H_5NHN(COC_6H_5)CH(CH_3)_2$ is proved by the unexpected reaction of the benzoyl derivative with cyanic acid to form a semicarbazide that is identical with the product obtained in benzoylating 1-*iso*propyl-2-phenyl semicarbazide. The product obtained by either method is accordingly 1-*iso*propyl-2-phenyl-1-benzoyl semicarbazide, $C_6H_5N(CONH_2)N(COC_6H_5)CH(CH_3)_2$.

Either of the above phenyl-*iso*propyl semicarbazides, like the parent hydrazo compound, gives on oxidation phenyl-azo-*iso*propyl, among other products as yet unidentified, a result certainly anomalous in view of the ordinary stability of the carbamyl radical at room temperature in the presence of hydrolytic agents. The semicarbazide of Structure 1 might logically be expected to oxidize to the tetrazine,



$$\begin{array}{l} C_6H_5N{-}N(CONH_2)CH(CH_3)_2 \\ \quad\;\; | \\ C_6H_5N{-}N(CONH_2)CH(CH_3)_2, \end{array}$$

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[3] Walker, *J. Chem. Soc.*, **69**, 1282 (1896).

[4] Hans and Astrid Euler, *Ber.*, **39**, 50, Footnote 1 (1906).

[5] Compare von Miller and Plöchl, *Ber.*, **25**, 2058 (1892).

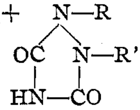
and the one of Structure 2 to acetone-2-phenyl semicarbazone, from which it is obtained by reduction.

Our failure to establish conditions for effecting the normal oxidation in the latter case led to an investigation of the behavior of acetone-2-phenyl semicarbazone itself toward oxidizing agents. We find that this semicarbazone reacts readily in acetone solution with permanganate, giving an excellent yield of a beautifully crystallizing, yellow product which will be reported on in a subsequent communication.

Poth and Bailey[6] in their investigation of the behavior of 1-hexahydrophenyl semicarbazide at elevated temperatures isolated the corresponding carbazide, urazole and urazine, whereas Pinner[7] showed that 1-phenyl semicarbazide on decomposition forms the corresponding urazole and urazine. The only product we succeeded in isolating from the decomposition of phenyl-*iso*propyl semicarbazide (1) was the urazole. It may be that here the carbazide precedes the urazole formation and that the carbazide undergoes decomposition, since the most plausible explanation of the formation of a urazole involves the following reactions.

$$2\text{R—NHN(R}')\text{CONH}_2 \longrightarrow (\text{R—NHN—R}')_2\text{CO} + \text{CO(NH}_2)_2$$

$$\text{R—NHN(R}')\text{CONH}_2 + \text{CO(NH}_2)_2 \longrightarrow 2\text{NH}_3 +$$



This view finds support in the work of Poth and Bailey referred to above. While, in repeating the experiment of Pinner, their attempt to isolate diphenyl carbazide, $(\text{C}_6\text{H}_5\text{NHNH})_2\text{CO}$, among the decomposition products of 1-phenyl semicarbazide was unsuccessful, they by the very characteristic color reactions of this carbazide quite definitely established its formation, at least in small amount.

Pinner has shown that the yield of urazole is increased by heating 1-phenyl semicarbazide along with urea. Poth and Bailey made a similar observation in the case of hexahydrophenyl semicarbazide, obtaining in this way a yield of 74.5%. From a mixture of phenyl-*iso*propyl semicarbazide (1) and urea we obtain a yield of 88% of the urazole and, as was to be expected, the isomeric semicarbazide (2) gives the same urazole. To test further the value of the urazole reaction in characterizing semicarbazides, *iso*propyl urazole was made from 1-*iso*propyl semicarbazide[8] by the Pinner method. The above results make it probable that all semicarbazides, where a 2-imino hydrogen is present, can be converted with good yield to the corresponding urazoles.

[6] Poth and Bailey, This Journal, **45**, 3008 (1923).

[7] Pinner, *Ber.*, **21**, 1224 (1888).

[8] Neighbors and Bailey, This Journal, **44**, 1557 (1922).

Experimental Part

Phenyl-hydrazo-*iso*propyl, $C_6H_5NHNHCH(CH_3)_2$.—For the preparation of the colloidal platinum solution a mixture of 0.6 g. of gum arabic in 10 cc. of water, 10 cc. of chloroplatinic acid, and 20 cc. of 95% ethyl alcohol, together with a few drops of seeding solution is agitated for a few minutes with hydrogen under two atmospheres' pressure. There is now added 50 g. of freshly distilled acetone-phenylhydrazone, dissolved in a mixture of 30 cc. of hydrochloric acid (d., 1.19) and 400 cc. of 50% ethyl alcohol. The reduction, which requires five hours, is carried out under an initial pressure of $3^{1}/_{3}$ atmospheres and is continued for an hour after the calculated amount of hydrogen has been absorbed. At the end of the experiment the gas pressure may sink as low as one atmosphere. For isolation of the hydrazo compound the colloid is broken in the usual way with acetone, the platinum filtered off, and the solution concentrated in a vacuum at water-bath temperature to the point of crystallization. From the dry hydrochloride, mixed with the calculated amount of finely ground potassium hydroxide in a Claisen flask, the hydrazo base distils at 162° (25 mm.) in a yield of about 90%, calculated from the acetone-phenylhydrazone used. When in the vacuum distillation only a limited amount of air is admitted, the distillate is colorless. However, on exposure to air it soon acquires a light yellow color and the characteristic odor of the azo compound. Phenyl-hydrazo-*iso*propyl is readily soluble in organic solvents but practically insoluble in water; d., 0.9720; n^{20}, 1.5463. It is readily oxidized by Fehling's solution, ammoniacal silver solution, and other oxidizing agents such as mercuric oxide, nitrous acid and permanganate. In boiling acetic acid solution the hydrazo compound is reduced with zinc dust to aniline and *iso*propyl amine. It has a specific gravity of 0.9720 and a refractive index of 1.5463 at 20°. The sample used in analysis was dried over potassium carbonate and redistilled.

Anal. Calcd. for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.67. Found: C, 71.97; H, 9.11; N, 18.79.

THE HYDROCHLORIDE.—This salt may be isolated directly after the reduction of acetone-phenylhydrazone as described above. It also precipitates from an alcoholic solution of the base upon the addition of dil. hydrochloric acid or can be prepared by passing hydrogen chloride into an ethereal solution of the base. Recrystallized from alcohol, it is obtained in flat prisms; m. p., 202°. The salt is more difficultly soluble in water than in alcohol.

Anal. Calcd. for $C_9H_{15}N_2Cl$: N, 14.95; Cl, 15.82. Found: N, 15.13; Cl, 19.01.

THE OXALATE.—The hydrazo base and anhydrous oxalic acid in ether solution produce a heat of reaction sufficient to boil the solvent, and the oxalate precipitates. It can be recrystallized in lustrous, flaky leaves; m. p., 189°. This salt, like the hydrochloride, is less soluble in water than in alcohol or acetone.

Anal. Calcd. for $C_{11}H_{16}O_4N_2$: C, 55.00; H, 6.67; N, 11.67. Found: C, 55.09; H, 6.51; N, 11.77.

Phenyl-azo-*iso*propyl, $C_6H_5N{=}NCH(CH_3)_2$.—To a cold solution of phenyl-hydrazo-*iso*propyl in dil. hydrochloric acid is slowly added 10% sodium nitrite solution until a starch iodide test reveals the presence of free nitrous acid. Probably an unstable nitroso derivative is first formed which decomposes with the evolution of nitrous oxide. The reddish-brown solution is extracted with ether and, after the solvent has been distilled, the residue is fractionated in a vacuum. The azo compound boils at 110° (28 mm.). Phenyl-azo-*iso*propyl, in contrast to the isomeric acetone-phenylhydrazone, is readily reduced with either sodium or aluminum amalgam to phenyl-hydrazo-*iso*propyl. It is reddish-yellow, possesses a characteristic, not unpleasant, ethereal odor and is readily soluble in organic solvents but insoluble in water; d., 0.9443; n^{20}, 1.5249.

Anal. Calcd. for $C_9H_{12}N_2$: C, 72.91; H, 8.11; N, 18.92. Found: C, 72.72; H, 7.84; N, 19.14.

Reduction of Phenyl-azo-*iso*propyl to Phenyl-hydrazo-*iso*propyl.—The azo body, dissolved in absolute alcohol to which a few drops of water are added, is allowed to react with aluminum or sodium amalgam until the solution is a light yellow. The filtered solution is then acidified with hydrochloric acid and evaporated to dryness in a vacuum at water-bath temperature. The salt obtained in this way is identical with the hydrochloride of phenyl-hydrazo-*iso*propyl formed in the catalytic reduction of acetone-phenylhydrazone.

Di-*iso*propyl-diphenyl Tetrazine.—Phenyl-hydrazo-*iso*propyl reacts with formaldehyde similarly to the hydrazo compounds of this type,[9] yielding a product that is either 1,5-di-*iso*propyl-2,4-diphenyl-1,2,4,5-tetrazine or the isomeric, symmetrical 1,4-di-*iso*propyl-2,5-diphenyl-1,2,4,5-tetrazine. One g. of phenyl-hydrazo-*iso*propyl suspended in 5 cc. of water is shaken with a slight excess of 40% formaldehyde. The emulsion of oily globules is broken by the addition of alcohol; the supernatant liquid is decanted; and, by long standing with alcohol, the oil is brought to crystallization in the form of radiating groups of needles. This substance is insoluble in water, difficultly soluble in alcohol, and is best purified by recrystallization from acetone; m. p., 163°.

Anal. Calcd. for $C_{20}H_{28}N_4$: C, 74.07; H, 8.64; N, 17.28. Found: C, 73.82; H, 8.77; N, 17.43.

Benzoyl-phenyl-hydrazo-*iso*propyl, $C_6H_5NHN(COC_6H_5)CH(CH_3)_2$.—With equivalent amounts of hydrazo base, benzoyl chloride and sodium bicarbonate in benzene, reaction takes place with an evolution of heat sufficient to boil the solvent, and part of the original base separates as hydrochloride. To complete benzoylation the solution is refluxed for one hour and the benzoyl derivative precipitated with petroleum ether, after the filtered solution has been concentrated to a small volume. It is readily soluble in organic solvents with the exception of ether and petroleum ether and can be purified by recrystallization from 70% ethyl alcohol. It crystallizes in thin plates; m. p., 113.5°.

Anal. Calcd. for $C_{16}H_{18}ON_2$: C, 75.59; H, 7.09; N, 11.02. Found: C, 75.74; H, 7.02; N, 11.22.

Dibenzoyl-phenyl-hydrazo-*iso*propyl, $C_6H_5N(COC_6H_5)N(COC_6H_5)CH(CH_3)_2$.—A mixture of 12.5 cc. of benzoyl chloride and 5 g. of phenyl-hydrazo-*iso*propyl is heated at 140° until a homogeneous liquid results and the evolution of hydrogen chloride ceases. The viscous residue is warmed with a solution of sodium carbonate and the dibenzoyl compound filtered off. Recrystallized from 70% alcohol, it is obtained in the form of slender rods; m. p., 140°. The compound is very soluble in acetone and alcohol, less so in ether and acetic ether and difficultly soluble in water.

Anal. Calcd. for $C_{23}H_{22}O_2N_2$: C, 77.09; H, 6.14; N, 7.82. Found: C, 77.23; H, 5.96; N, 7.66.

2-*iso*Propyl-1,4-diphenyl Semicarbazide, $C_6H_5NHN(C_3H_7)CONHC_6H_5$.—When equivalent quantities of hydrazo base and phenyl isocyanate are dissolved in ether, a vigorous reaction ensues with boiling of the solvent and precipitation of the isocyanate derivative. This product is readily soluble in alcohol and acetone and insoluble in water. From alcohol it crystallizes in prisms; m. p., 146°.

Anal. Calcd. for $C_{16}H_{19}ON_3$: C, 71.37; H, 7.06; N, 15.61. Found: C, 71.15; H, 7.09; N, 15.56.

2-*iso*Propyl-1,4-diphenyl Thiosemicarbazide, $C_6H_5NHN(C_3H_7)CSNHC_6H_5$.—The

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[9] Knorr and Weidel, *Ber.*, **42**, 3525 (1909).

thiocarbamyl derivative is prepared similarly to the preceding substance by the action of phenylmustard oil on the hydrazo base in ether solution. The reaction product is readily soluble in acetone and alcohol but in water even more insoluble than the corresponding isocyanate compound. From alcohol it crystallizes in prisms with dome-shaped end faces; m. p., 153°.

Anal. Calcd. for $C_{16}H_{19}N_3S$: N, 14.74. Found: 14.99.

2-*iso*Propyl-1-phenyl Semicarbazide, $C_6H_5NHN(C_3H_7)CONH_2$.—To 35 g. of phenyl-hydrazo-*iso*propyl, or 43.5 g. of its hydrochloride, in 70 cc. of glacial acetic acid is added at a temperature below 40°, 20 g. of potassium cyanate in small portions over a period of 45 minutes. The temperature is then allowed to rise to 60°, and after a half hour the semicarbazide is precipitated in a yield of 85%, by dilution of the solution with water to thrice its volume. A further small amount separates on neutralization of the filtrate with ammonium hydroxide. This semicarbazide dissolves readily in the common solvents, petroleum ether excepted. It dissolves in concd. hydrochloric acid but is precipitated on dilution of the solution. On oxidation it passes to phenyl-azo-*iso*propyl and heated alone, or better with urea, yields the corresponding urazole. Very characteristic for this semicarbazide is its crystallization from water in sheaves of long, slender needles which melt at 119°.

Anal. Calcd. for $C_{10}H_{15}ON_3$: C, 62.12; H, 7.77; N, 21.76. Found: C, 62.05; H, 7.89; N, 21.74.

1-Nitroso-2-*iso*propyl-1-phenyl Semicarbazide, $C_6H_5N(NO)N(C_3H_7)CONH_2$.—The nitroso compound, prepared by the addition of a 10% solution of sodium nitrite to 2-*iso*propyl-1-phenyl semicarbazide in dil. hydrochloric acid and purified by recrystallization from acetone, melts at 156°. It is soluble in the common organic solvents with the exception of petroleum ether.

Anal. Calcd. for $C_{10}H_{14}O_2N_4$: C, 54.05; H, 6.31; N, 25.23. Found: C, 54.32; H, 6.18; N, 25.32.

1-*iso*Propyl-2-phenyl Semicarbazide $(CH_3)CHNHN(C_6H_5)CONH_2$.—Twenty-five g. of acetone-2-phenyl semicarbazone[10] is added to a colloidal platinum solution prepared in the usual way from 10 cc. of 10% chloroplatinic acid, 200 cc. of 50% ethyl alcohol and 0.2 g. of gum arabic. The reduction is carried out as in the case of acetone-phenylhydrazone and the isolation of the semicarbazide effected as in the case of phenylhydrazo-*iso*propyl. It has solubilities similar to the isomeric semicarbazide, but it is more difficultly soluble in all solvents and, in contrast to its isomer, dissolves readily in aqueous ferric chloride and dilute mineral acids. From either alcohol or water it crystallizes in diamond-shaped, rhombic plates; m. p., 209°.

Anal. Calcd. for $C_{10}H_{15}ON_3$: C, 62.12; H, 7.77; N, 21.76. Found: C, 61.98; H, 7.82; N, 21.98.

Widman[11] calls attention to the fact that as a rule alpha derivatives of phenylhydrazine melt much lower than the corresponding beta derivatives. Here the rule is reversed, since $C_6H_5NHN(C_3H_7)CONH_2$, that is, β-*iso*propyl-β-carbamyl-phenylhydrazine melts 90° lower than its isomer, $C_6H_5N(CONH_2)NHCH(CH_3)_2$, β-*iso*propyl-α-carbamyl-phenylhydrazine. However, in the case of the semicarbazides, $C_6H_5N(CONH_2)NH_2$ and $C_6H_5NHNHCONH_2$, the α-carbamyl-phenylhydrazine melts at 120° and the beta derivative at 172°.

Oxidation of 1-*iso*Propyl-2-phenyl Semicarbazide.—Onto 5 g. of the semicarbazide was poured 2.8 g. of potassium permanganate in 50 cc. of water and after 12 hours the

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[10] Goodwin and Bailey, THIS JOURNAL, **46**, 2827 (1924).

[11] Widman, *Ber.*, **27**, 2964 (1894).

reaction mixture was extracted with ether. The ether was washed with dil. hydrochloric acid and then dried over calcium chloride. The small amount of phenyl-azo-*iso*propyl, which remained as a yellow oil on evaporation of the solvent, was distilled over barium oxide in a vacuum and purified by fractional distillation.

Anal. Calcd. for $C_9H_{12}N_2$: N, 18.92. Found: 19.18.

An entirely different oxidation product which consisted of a white, beautifully crystallized solid was obtained by oxidizing in boiling acetone solution 5 g. of the semicarbazide with 2.8 g. of permanganate. This product will be reported on later.

2-*iso*Propyl-1-phenyl-1-benzoyl Semicarbazide, $C_6H_5N(COC_6H_5)N(CONH_2)$-$CH(CH_3)_2$.—As in benzoylating phenyl-hydrazo-*iso*propyl, equivalent quantities of 2-*iso*propyl-1-phenyl semicarbazide, benzoyl chloride and sodium bicarbonate are allowed to react in boiling benzene. The product is obtained as a gelatinous mass and can be recrystallized from 70% alcohol in flat prisms with domed-shape end faces; m. p., 162°. It is readily soluble in alcohol, benzene and acetic ether and difficultly soluble in water.

Anal. Calcd. for $C_{17}H_{19}O_2N_3$: C, 68.68; H, 6.39; N, 14.14. Found: C, 68.75; H, 6.45; N, 14.34.

1-*iso*Propyl-2-phenyl-1-benzoyl Semicarbazide, $C_6H_5N(CONH_2)N(COC_6H_5)$-$CH(CH_3)_2$.—This derivative can be prepared by benzoylating 1-*iso*propyl-2-phenyl semicarbazide under the same conditions as given in the preceding preparation. It can also be made in excellent yield by dissolving 1 g. of β-benzoyl-phenyl-hydrazo-*iso*propyl in 10 cc. of glacial acetic acid and adding 0.5 g. of potassium cyanate. After the reaction mixture has stood for a few hours, practically all of the semicarbazide crystallizes. It differs from the isomer described in being more difficultly soluble in all solvents. Recrystallized from dil. alcohol it is obtained in slender rods; m. p., 181°. Neither of the benzoyl-*iso*propyl-phenyl semicarbazides condenses to a triazole when boiled in potassium hydroxide solution.

Anal. Calcd. for $C_{17}H_{19}O_2N_3$: C, 68.68; H, 6.39; N, 14.14. Found: C, 68.83; H, 6.24; N, 14.29.

1-*iso*Propyl-2-phenyl Urazole.—Both of the semicarbazides described above when heated with urea give the same urazole in a yield of about 88%; 2 g. of either semicarbazide mixed with 0.7 g. of urea in a test-tube is placed in a glycerol bath at 200°, the temperature raised to 240°, and the heating continued for 15 minutes. At first there is a rapid evolution of gas, but this almost ceases toward the end of the process. The melt is dissolved in dil. ammonium hydroxide and the urazole precipitated with hydrochloric acid. It can be recrystallized from hot water, with the addition of a little Filtchar, forming long rods; m. p., 165°. The urazole is soluble in the common organic solvents, petroleum ether excepted.

Anal. Calcd. for $C_{11}H_{13}O_2N_3$: C, 60.27; H, 5.94; N, 19.18. Found: C, 60.76, 60.42; H, 5.70, 6.30; N, 19.06.

1-*iso*Propyl Urazole.—Two g. of 1-*iso*propyl semicarbazide and 1.5 g. of urea are heated for one-half hour at 200°, the melt is dissolved in dil. ammonium hydroxide and the product obtained on acidifying the solution with hydrochloric acid is recrystallized from water in thin plates. The urazole is readily soluble in water and alcohol, more difficultly soluble in acetic ether, and very difficultly soluble in the other common solvents; m. p., 190°. Micro-analysis of the substance gave the following results.

Anal. Calcd. for $C_5H_9O_2N_3$: C, 41.96; H, 6.29; N, 29.37. Found: C, 42.48; H, 6.49; N, 29.48.

Phenyl-hydrazo-cyclohexyl, $C_6H_5NHNHC_6H_{11}$.—This hydrazo compound results from the reduction of cyclohexanone-phenylhydrazone under conditions similar to those 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 $R—CO—N{=}^{x}_{y} \longrightarrow O{=}\dot{C}{=}NR + xy$. 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).