Aniline and Raney Nickel.—(a) A stirred mixture of 9.3 g. (0.1 mole) of aniline, 100 ml. of 95% ethyl alcohol and about 30 g. of moist Raney nickel was heated under reflux for 2 hours. The nickel was removed by filtration and the filtrate was concentrated by heating on the steam-bath. The residue was distilled under reduced pressure and 9.5 g. (about 80% yield) of N-ethylaniline, b.p. 84° (10 mm.), $n^{25}\text{D}$ 1.5568, was obtained.

(b) A stirred mixture of 9.3 g. of aniline, 100 ml. of 95% ethyl alcohol and 1 g. of Raney nickel catalyst was treated as in procedure a. The product obtained (about 8 g.) was unchanged aniline.

Using procedure a as the general method, aniline and *n*-propyl, *n*-butyl, cyclohexyl and benzyl alcohols with Raney nickel (previously washed with the appropriate alcohol to remove ethanol) gave N-*n*-propyl, N-*n*-butyl, N-cyclohexyl and N-benzylaniline in 70, 81, 22 and 50% yields, respectively.

2-Naphthylamine and Raney Nickel.—A stirred mixture of 14.3 g. (0.1 mole) of 2-naphthylamine 100 ml. of 95% ethyl alcohol and about 40 g. of moist Raney nickel was heated under reflux for 4 hours. The nickel was removed by filtration and the filtrate distilled under reduced pressure. Following a forerun of alcohol 14 g. (82% yield) of N-ethyl-2-naphthylamine came over as a colorless oil, b.p. 162° (12 mm.), $n^{25}\text{D}$ 1.6402.

N-Ethyl-2,5-dimethoxyaniline.—A stirred mixture of 10 g. of 2,5-dimethoxyaniline, about 30 g. of moist Raney nickel and 100 ml. of 95% ethyl alcohol was heated under reflux for 4 hours. After removal of the nickel by filtration the filtrate was heated on the steam-bath to remove alcohol. The residue was distilled under reduced pressure. N-Ethyl-2,5-dimethoxyaniline came over as a colorless oil, b.p. 138° (15 mm.), $n^{25}\text{D}$ 1.5501. The yield was 7.3 g. (61%).

Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 66.23; H, 8.36; N, 8.05.

Aniline, Isopropyl Alcohol and Raney Nickel.—(a) A stirred mixture of 9.3 g. (0.1 mole) of aniline, about 30 g. of moist Raney nickel (washed with isopropyl alcohol to remove ethanol) and 100 ml. of isopropyl alcohol was heated overnight on the steam-bath. The nickel was removed by filtration and the filtrate distilled at atmospheric pressure. About 7.5 g. (50% yield) of N-isopropylaniline was obtained, b.p. 198–206° (lit.[10] b.p. 206–208°), $n^{25}\text{D}$ 1.5380.

Anal. Calcd. for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.72; H, 9.48; N, 10.63.

(b) A stirred mixture of 9.3 g. of aniline, about 30 g. of moist Raney nickel (washed with isopropyl alcohol) and 100 ml. of isopropyl alcohol was heated under reflux for 2 hours. After removal of the nickel by filtration 7 g. of aniline was recovered from the filtrate.

Aniline, Methyl Alcohol and Raney Nickel.—A stirred mixture of 9.3 g. of aniline, about 30 g. of moist Raney nickel (washed with methyl alcohol to remove ethanol) and 100 ml. of methyl alcohol was heated under reflux for 3 hours. After removal of the nickel by filtration, the filtrate was concentrated on the steam-bath. The residue was distilled and 8 g. of aniline recovered.

Attempted Alkylation of 2-Aminopyridine and 5-Aminotetrazole with Raney Nickel and Ethyl Alcohol.—(a) A mixture of 5 g. of 2-aminopyridine and about 15 g. of moist Raney nickel in 100 ml. of ethyl alcohol was heated under reflux for 4 hours. The nickel was removed by filtration and evaporation of the alcohol left 4 g. of starting material.

(b) A mixture of 5 g. of 5-aminotetrazole, about 15 g. of moist Raney nickel and 100 ml. of 95% ethyl alcohol was treated as in procedure a. About 4 g. of unchanged starting material was recovered.

2-Phenylethylamine and Raney Nickel.—A stirred mixture of 20 g. of 2-phenylethylamine, about 50 g. of moist Raney nickel and 100 ml. of ethyl alcohol was heated under reflux for 0.5 hour. The nickel was removed by filtration and the filtrate concentrated by heating on the steam-bath. Following a forerun of 9 g. of 2-phenylethylamine, about 9 g. of di-(2-phenylethyl)-amine came over, b.p. 190° (15 mm.) (lit.[11] b.p. 335° (603 mm.)), $n^{25}\text{D}$ 1.5550.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.10; H, 8.47; N, 6.37.

A sample was converted to the hydrobromide salt and shown by infrared absorption to be identical with authentic material.

Benzylamine and Raney Nickel.—A stirred mixture of 10 g. of benzylamine, about 20 g. of moist Raney nickel and 100 ml. of 95% ethyl alcohol was heated under reflux for 2 hours. After removal of the nickel by filtration, the alcohol was evaporated on the steam-bath. The residue was distilled under reduced pressure. Following a forerun boiling between 70 and 120° (5 mm.) about 5 g. of constant boiling product came over, b.p. 160° (5 mm.). It was shown to be dibenzylamine by comparison of the infrared absorption curve with that of authentic material.

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[10] W. J. Hickinbottom, *J. Chem. Soc.*, **133**, 992 (1930).

[11] P. Spica, *Gazz. chim. ital.*, **9**, 555 (1879); *J. Chem. Soc. Ab.*, **38**, 241 (1880).

INDIANAPOLIS 6, INDIANA

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Hydrogenolysis of the Nitrogen–Nitrogen Bond with Raney Nickel

BY C. AINSWORTH

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Twelve compounds representing a variety of types but all containing nitrogen–nitrogen bonds have been subjected to the action of a large excess of Raney nickel in the absence of atmospheric hydrogen. In ten of the twelve examples the nitrogen–nitrogen bond was cleaved and the products were identified.

The conversion of carboxylic acid hydrazides to amides with excess Raney nickel was reported[1] recently from this Laboratory. Hydrogenolysis of some other compounds containing nitrogen–nitrogen bonds with excess Raney nickel is now reported.

Adkins,[2] in an early communication on Raney nickel, noted that the catalyst readily converted nitrobenzene into azo- and azoxybenzene. This observation is interesting since the over-all reaction represents the *formation* of a nitrogen–nitrogen bonded compound. Later[3] it was shown that the reaction of azoxybenzene and hydrazobenzene with excess Raney nickel in boiling ethyl alcohol gave rise to N-ethylaniline. This involved the *cleavage* of a nitrogen–nitrogen bonded compound, such reaction being followed by alkylation.[4–6]

Our interest in this cleavage reaction arose from the observation that treatment of 2-(β-benzamido-

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[1] C. Ainsworth, THIS JOURNAL, **76**, 5774 (1954). Also, S. Akabori and K. Narita, *Proc. Japan Acad.*, **29**, 264 (1953); *C. A.*, **49**, 864 (1955), employed Raney nickel in the conversion of L-glutamic γ-hydrazide to L-glutamine.

[2] L. W. Covert and H. Adkins, THIS JOURNAL, **54**, 4116 (1932).

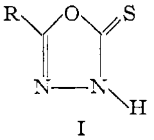
[3] R. Mozingo, C. Spencer and K. Folkers, *ibid.*, **66**, 1859 (1944).

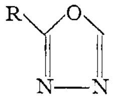
[4] K. H. Shah, B. D. Tilak and K. Venkataraman, *Proc. Indian Acad. Sci.*, **28A**, 145 (1948); *C. A.*, **44**, 3958 (1950).

[5] R. G. Rice and E. J. Kohn, THIS JOURNAL, **77**, 4052 (1955).

[6] C. Ainsworth, *ibid.*, **78**, 1635 (1956).

ethyl)-Δ^2-1,3,4-oxadiazoline-5-thione (I, R = $C_6H_5CONHCH_2CH_2$) with excess Raney nickel yielded β-benzamidopropionamide. This finding paralleled that of Hoggarth,[7] who obtained benzamide from 2-phenyl-1,3,4-oxadiazole-5-thiol [2-phenyl-Δ^2-1,3,-4-oxadiazoline-5-thione (I, R = C_6H_5)] and excess Raney nickel.


I


II

1,3,4-Oxadiazoles, of the type represented by II, recently[8] became available in this Laboratory. It seemed likely that such materials were intermediates in the conversion of compounds of type I with excess Raney nickel. Treatment of 2-phenyl-Δ^2-1,3,4-oxadiazoline-5-thione or 2-methylmercapto-5-phenyl-1,3,4-oxadiazole[7] with excess Raney nickel gave, in addition to benzamide, about a 20% yield of 2-phenyl-1,3,4-oxadiazole. The reaction of 2-phenyl-1,3,4-oxadiazole with excess Raney nickel formed benzamide. The hydrolysis product of II, namely, N-benzoyl-N′-formylhydrazine, when treated with excess Raney nickel also gave benzamide. 2-Phenyl-Δ^2-1,3,4-thiadiazoline-5-thione when treated with excess Raney nickel was converted in low yield to 2-phenyl-1,3,4-thiadiazole.

Next, the cleavage reaction of carboxylic acid hydrazides to amides was studied.[1] This reaction does not appear to be limited to this system, for the reaction of benzenesulfonic acid hydrazide and Raney nickel formed benzenesulfonamide. Other nitrogen–nitrogen systems that were studied included N,N′-dibenzoylhydrazine which yielded benzamide, and phenylhydrazine which in ethyl alcohol with Raney nickel formed a mixture of aniline and N-ethylaniline. Semicarbazide gave a small yield of urea, and N-nitrosodiphenylamine formed diphenylamine. Phthalhydrazide(2,3-dihydro-1,4-phthalazinedione) and maleic acid hydrazide were recovered unchanged when heated with excess Raney nickel.

Acknowledgments.—The microanalyses were performed by W. L. Brown, H. L. Hunter, G. M. Maciak and Gloria Beckmann. The physical data were obtained by H. E. Boaz and H. A. Rose.

Experimental[9]

β-Benzamidopropionic Acid Hydrazide.—A solution of 11 g. (0.05 mole) of ethyl β-benzamidopropionate,[10] 25 ml. of ethyl alcohol and 2.5 ml. (0.05 mole) of hydrazine hydrate was heated under reflux for 2 hours. The solvent was evaporated, and a quantitative yield of β-benzamidopropionic acid hydrazide remained. A sample was recrystallized from dioxane–ether, and the product was obtained as white needles, m.p. 152–153°.

Anal. Calcd. for $C_{10}H_{13}N_3O_2$: C, 57.96; H, 6.32. Found: C, 58.26; H, 6.36.

2-(β-Benzamidoethyl)-Δ^2-1,3,4-oxadiazoline-5-thione.—A solution of 10.4 g. (0.05 mole) of β-benzamidopropionic acid hydrazide, 3 g. (0.05 mole) of potassium hydroxide, 10 ml. of carbon disulfide and 100 ml. of ethyl alcohol was heated under reflux for 2 days. After removal of the alcohol by evaporation, the residue was dissolved in 50 ml. of water and then acidified with 6 *N* hydrochloric acid. The solid which separated was collected, washed with water and recrystallized from acetic acid–water. 2-(β-Benzamidoethyl)-Δ^2-1,3,4-oxadiazoline-5-thione separated as shiny platelets, m.p. 182–183°. The yield was 11.2 g. (90%).

Anal. Calcd. for $C_{11}H_{11}N_3O_2S$: C, 52.99; H, 4.45; S, 12.86. Found: C, 52.92; H, 4.56; S, 13.01.

General Procedure.—A stirred mixture of 2 g. of the nitrogen compound, about 10 g. of moist Raney nickel and 50 ml. of 95% ethyl alcohol was heated under reflux for 2–3 hours. After removal of the nickel by filtration, the filtrate was concentrated by heating on the steam-bath. The residue was recrystallized from water.

In this way 2-(β-benzamidoethyl)-Δ^2-1,3,4-oxadiazoline-5-thione gave β-benzamidopropionamide, m.p. 171–172° (lit.[11] m.p. 170–171°), m.m.p. 171–172°; 2-phenyl-1,3,4-oxadiazole[8] yielded benzamide, m.p. 126–128°, m.m.p. 126–128°; N-benzoyl-N′-formylhydrazine[12] formed benzamide as did N,N′-dibenzoylhydrazine, all in about 50–60% yields. Similarly, N-nitrosodiphenylamine formed diphenylamine (identified by comparison of the infrared absorption curve with that of authentic material). Benzenesulfonic acid hydrazide was heated 0.5 hour only and yielded benzenesulfonamide (identified by comparison of X-ray diffraction pattern with that of authentic material). Semicarbazide gave urea in 20% yield, and phenylhydrazine gave rise to a mixture of aniline and N-ethylaniline as shown by infrared absorption studies. Both phthalhydrazide and maleic acid hydrazide treated according to the general procedure above were recovered unchanged.

2-Phenyl-Δ^2-1,3,4-oxadiazoline-5-thione and Raney Nickel.—A stirred mixture of 4 g. of 2-phenyl-Δ^2-1,3,4-oxadiazoline-5-thione,[7] 10 g. of moist Raney nickel and 100 ml. of ethyl alcohol was heated under reflux for 3 hours. The nickel was removed by filtration, and the filtrate was concentrated to 10 ml. After cooling, the benzamide (1.5 g.) which separated was collected, and the filtrate was evaporated on the steam-bath. The residue was extracted with ether. Evaporation of the ether left a new residue which was distilled under reduced pressure, and 0.65 g. (20% yield) of 2-phenyl-1,3,4-oxadiazole resulted. It was identified by comparison with authentic material prepared by an independent route.[8]

The use of 2-methylmercapto-5-phenyl-1,3,4-oxadiazole[7] in place of 2-phenyl-Δ^2-1,3,4-oxadiazoline-5-thione in the above reaction gave the same products in essentially the same yield.

2-Phenyl-1,3,4-thiadiazole.—A stirred mixture of 2 g. of 2-phenyl-Δ^2-1,3,4-thiadiazoline-5-thione,[13] 10 g. of moist Raney nickel and 100 ml. of ethyl alcohol was heated under reflux for 2 hours. The nickel was removed by filtration and the filtrate evaporated on the steam-bath. The residue was extracted with ether from which 0.5 g. of 2-phenyl-1,3,4-thiadiazole was obtained. It was identified by comparison with authentic material prepared by an independent method.[8]

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(7) E. Hoggarth, *J. Chem. Soc.*, 4811 (1952).

(8) C. Ainsworth, THIS JOURNAL, **77**, 1148 (1955).

(9) The Raney nickel used was "Raney Catalyst in Water" supplied by the Raney Catalyst Co., Chattanooga, Tennessee. The commercial material was slurried several times with 95% ethyl alcohol and stored under alcohol.

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(11) S. J. Kanewskaja, *Ber.*, **69**, 266 (1936).

(12) E. Muller and W. Kreutzmann, *Ann.*, **512**, 264 (1934).

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