

the unreacted thiocyanobenzene recovered in the form of phenyl disulfide was 0.041 mole (82%).

Results of Other Competitive Experiments.—*Nitration of thiocyanobenzene-benzene with nitric acid-sulfuric acid:* 94% yield of nitrobenzene. *Nitration of acetanilide-benzene with nitric acid in acetic acid:* 55% yield of *p*-nitroacetanilide

and 24% recovery of acetanilide. *Nitration of acetanilide-benzene with sulfuric acid-nitric acid:* 57% yield of nitrobenzene and 70% recovery of impure acetanilide. *Bromination of acetanilide-benzene:* 91% yield of *p*-bromoacetanilide.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

A Comparison of Raney Nickel and Raney Cobalt Catalysts for the Hydrogenation of Oximes

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A comparison of Raney cobalt and Raney nickel catalysts for the hydrogenation of six oximes has been made. Raney cobalt generally produced primary amines of as high purity and yield as did Raney nickel. In some cases, Raney cobalt produces best results in ethanol or dioxane solvent without addition of ammonia, whereas Raney nickel often requires an ammoniacal solvent for best results. With both catalysts, both the solvent and the presence or absence of ammonia have an important bearing on the yield and purity of the primary amine obtained.

The use of nickel as a catalyst for the hydrogenation of oximes and nitriles was introduced by Sabatier and his students in 1905.¹ They also used a cobalt catalyst for the hydrogenation of olefins, acetylene, benzene and some carbonyl compounds, but found its catalytic properties to be inferior to those of nickel.² Raney cobalt was prepared by Faucounau³ and used as a hydrogenation catalyst, but the hydrogenation of oximes was not studied. Schmidt in Germany, and later workers, demonstrated cobalt catalysts to be excellent for the hydrogenation of nitriles and dinitriles.⁴ Since powdered Raney cobalt alloy containing 40% cobalt and 60% aluminum is now commercially available, it seemed desirable to examine the use of Raney cobalt as a hydrogenation catalyst for oximes with the object of determining its merits relative to Raney nickel.

Six oximes have been hydrogenated over Raney cobalt and Raney nickel under comparable conditions. With three of the oximes, ethanol with and without added anhydrous ammonia, and dioxane likewise with and without ammonia, were employed as solvents, so that comparisons could be made under four different conditions. With the other three oximes, the Raney nickel was used with ammoniacal ethanol solvent and the Raney cobalt with ethanol and dioxane without ammonia. In all cases, the amines obtained were analyzed for secondary plus tertiary amine content by titrating with acid in the presence of salicylaldehyde, and for primary amine content by titrating with acid and making the necessary correction for non-primary amine content.⁵ The results are summarized in Table I.

Raney nickel has long been known to be an excellent catalyst for the hydrogenation of oximes.⁶

(1) A. Mailhe, *Compt. rend.*, **140**, 1691 (1905); P. Sabatier and J. B. Senderens, *ibid.*, **140**, 482 (1905).

(2) P. Sabatier and J. B. Senderens, *Ann. chim. phys.*, [8], **4**, 344 (1905).

(3) L. Faucounau, *Bull. soc. chim. France*, [5] **4**, 63 (1937).

(4) See ref. 1 of W. Reeve and W. M. Eareckson, *THIS JOURNAL*, **72**, 3299 (1950), for leading references.

(5) S. Siggia, J. G. Hanna and I. R. Kervenski, *Anal. Chem.*, **22**, 1295 (1950).

(6) H. Adkins, "Reactions of Hydrogen." University of Wisconsin Press, Madison, Wisconsin, 1937.

TABLE I
HYDROGENATION OF OXIMES OVER RANEY NICKEL AND RANEY COBALT^a

| Catalyst | Solvent | Yield, % | °C. | B.p. Mm. | Amine, % Sec. and tert. | |
|--|-----------------------------------|----------|---------|----------|----------------------------|----|
| <i>n</i> -C ₃ H ₇ CH:NOH ^b | | | | | | |
| Co | Ethanol | 95 | 78-81 | 760 | 97 | 5 |
| Ni | Ethanol | 92 | 79-84 | 760 | 82 | 5 |
| Co | Ethanol with 3% NH ₃ | 86 | 79-85 | 760 | 96 | 5 |
| Ni | Ethanol with 3% NH ₃ | 97 | 79-83 | 760 | 95 | 5 |
| Co | Dioxane | 86 | 79-85 | 760 | 96 | 1 |
| Ni | Dioxane | 87 | 79-83 | 760 | 91 | 11 |
| Co | Dioxane with 1.2% NH ₃ | 92 | 79-86 | 760 | 89 | 15 |
| Ni | Dioxane with 1.2% NH ₃ | 96 | 79-83 | 760 | 94 | 6 |
| C ₆ H ₅ CH:NOH ^{b,c} | | | | | | |
| Co | Ethanol | 84 | 89-91 | 15 | 96 | 2 |
| Ni | Ethanol | 76 | 179-183 | 760 | 96 | 1 |
| Co | Ethanol with 3% NH ₃ | 91 | 89-98 | 15 | 97 | 0 |
| Ni | Ethanol with 3% NH ₃ | 81 | 90 | 20 | 98 | 0 |
| Co | Dioxane | 78 | 177-181 | 760 | 96 | 0 |
| Ni | Dioxane | 88 | 90 | 15-20 | 99 | 0 |
| Co | Dioxane with 1.2% NH ₃ | 89 | 182-186 | 760 | 96 | 0 |
| Ni | Dioxane with 1.2% NH ₃ | 68 | 181-183 | 760 | 97 | 1 |
| 2-Furaldoxime ^{b,c} | | | | | | |
| Co | Ethanol | 39 | 63-67 | 30 | 96 | 1 |
| Ni | Ethanol with 3% NH ₃ | 51 | 145-150 | 760 | 96 | 1 |
| Co | Dioxane | 43 | 147-151 | 760 | 97 | 1 |
| C ₆ H ₅ (CH ₃)C:NOH ^{b,c} | | | | | | |
| Co | Ethanol | 93 | 65-68 | 760 | 97 | 2 |
| Ni | Ethanol with 3% NH ₃ | 92 | 65-68 | 760 | 95 | 3 |
| Co | Dioxane | 96 | 64-68 | 760 | 97 | 4 |
| <i>t</i> -C ₄ H ₉ (CH ₃)C:NOH ^d | | | | | | |
| Co | Ethanol | 59 | 103-105 | 760 | 97 | 0 |
| Ni | Ethanol with 3% NH ₃ | 63 | 103-106 | 760 | 99 | 0 |
| Co | Dioxane | 50 | 102-105 | 760 | 99 | 0 |
| C ₆ H ₅ (CH ₃)C:NOH ^e | | | | | | |
| Co | Ethanol | 91 | 182-188 | 760 | 83 | 4 |
| Ni | Ethanol | 88 | 79-80 | 21 | 93 | 3 |
| Co | Ethanol with 3% NH ₃ | 86 | 185-189 | 760 | 90 | 3 |
| Ni | Ethanol with 3% NH ₃ | 86 | 185-189 | 760 | 95 | 2 |
| Co | Dioxane | 87 | 179-189 | 760 | 80 | 3 |
| Ni | Dioxane | 95 | 74-78 | 10 | 96 | 2 |
| Co | Dioxane with 1.2% NH ₃ | 87 | 185-186 | 760 | 96 | 1 |
| Ni | Dioxane with 1.2% NH ₃ | 75 | 183-186 | 760 | 94 | 2 |

^a All hydrogenations were carried out in a 300-ml. steel reaction vessel under an initial hydrogen pressure of 200-220 atm. with 0.25 teaspoon (about 2 g.) of the Raney catalyst and 25 or 30 g. of the oxime dissolved in 100 ml. of solvent. The reaction temperature was chosen so that the hydrogenation was substantially complete in 10 to 30

minutes, and was between 80 and 125° in all cases. ³L. Beregi (*Magyar Kém. Folyóirat*, **56**, 257 (1950); *C.A.*, **46**, 8000 (1952)) reports a 56% yield of *n*-butylamine, a 33% yield of benzylamine, a 51% yield of furfurylamine, and a 75% yield of 2-aminobutane from the oximes over Raney nickel with dioxane as a solvent at 15–18°. ⁶R. Paul (*Bull. soc. chim. France*, [5] **4**, 1121 (1937)) reports a 20% yield of benzylamine and a 44% yield of furfurylamine over Raney nickel with alcohol as a solvent at 15–18° and 1 atm. pressure. At 60 atm. hydrogen pressure and 70–85°, a 79% yield of 2-aminobutane and a 97% yield of α -phenethylamine were reported. ⁴M. Smith and H. Adkins (*THIS JOURNAL*, **60**, 660 (1938)) report a 40% yield with methanol as the solvent. ⁵C. Winans and H. Adkins (*ibid.*, **55**, 2051 (1933)) report a 77% yield of benzylamine using a nickel-on-kieselguhr catalyst. In ref. 6, page 92, the same authors report a 78% yield of α -phenethylamine from acetophenone oxime.

From the data, it is apparent that Raney cobalt is likewise an excellent catalyst for this reaction. In the case of the six oximes studied, the two catalysts were about equally effective in three cases as far as yield and purity of product were concerned. In the other three cases, the Raney nickel may have been slightly superior in two cases and the Raney cobalt in one. The advantage of using a Raney cobalt catalyst is that sometimes it is as good or better than Raney nickel even when it is used with a dioxane or ethanol solvent containing no ammonia, whereas Raney nickel may require an ammoniacal solvent for best results in hydrogenating nitriles,⁷ and probably also oximes. The hydrogen-

(7) E. J. Schwoegler and H. Adkins, *THIS JOURNAL*, **61**, 3499 (1939).

ation of butyraldoxime illustrates this advantage of Raney cobalt.

Experimental

Hydrogenations.—A standard 300-ml. Aminco steel hydrogenation vessel and standard accessory equipment were used. Conditions are in the footnote to Table I. High boiling amines were isolated by distillation. The *n*-butylamine, 2-aminobutane and pinacolylamine were converted to their hydrochlorides, the solvent removed by distillation under water-pump pressure, a saturated solution of sodium hydroxide in diethylene glycol added, and the amine distilled off. Pinacolylamine formed an azeotrope with water, b.p. 84–85°, consisting of about 80% amine. The water was removed by treatment with solid potassium hydroxide, and the amine layer separated and distilled.

Catalysts. Solvents and Compounds.—The Raney catalysts were prepared by the W-7 procedure of Adkins and Billica.⁸ The age of the catalysts at the time of use varied from a few days to three months. Catalyst age within these limits did not appear to affect the yields obtained.

The absolute ethanol used as a solvent was shaken with Raney nickel under the usual hydrogenation conditions at 125° for 2 hours, the nickel filtered off, the ethanol distilled from calcium oxide, and the middle half collected and stored for future use. The dioxane was purified by refluxing over sodium, distilling, and the middle third of the distillate used. The ammoniacal solvents were prepared by bubbling ammonia gas through the cooled solvent for several hours.

All of the oximes were prepared by standard methods and had the physical constants reported in the literature. The benzaldoxime was a mixture of the *syn* and *anti* forms, b.p. 132° at 20 mm.

(8) H. Adkins and H. R. Billica, *ibid.*, **70**, 698 (1948).

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The Rearrangement and Condensation of Reissert Compounds with Grignard Reagents¹

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A series of 1-acyl-1,2-dihydroquinaldonitriles and 2-acyl-1,2-dihydroisoquinaldonitriles (Reissert compounds) have been rearranged and condensed with a variety of Grignard reagents. The mechanism of the rearrangement has been investigated, and it has been demonstrated that the rearrangement proceeds by an intramolecular process.

In a previous communication it was reported that 1-benzoyl-1,2-dihydroquinaldonitrile (Ia) reacts with methylmagnesium bromide in benzene or dioxane solution to give methylphenyl-2-quinolylcarbinol (IIa).⁴ A similar rearrangement to form 2-benzoylquinoline (III) occurs when Ia is treated with sodium hydride in boiling xylene.⁵ The Grignard reaction has now been extended to a variety of Reissert compounds and a variety of Grignard reagents, and the mechanism of the rearrangement has been investigated.

In the first series of reactions an ether solution of methylmagnesium bromide was added to a dioxane solution of the Reissert compound. The temperature was kept below 60° at all stages of the reac-

(1) (a) A portion of this paper was abstracted from a thesis submitted by Robert H. Glazier in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Kansas University, 1952; (b) work performed in part under the auspices of the U. S. Atomic Energy Commission.

(2) Brookhaven National Laboratory, Upton, Long Island, N. Y.

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(4) W. E. McEwen, J. V. Kindall, R. N. Hazlett and R. H. Glazier, *THIS JOURNAL*, **78**, 4591 (1951).

(5) V. Boekelheide and J. Weinstock, *ibid.*, **74**, 660 (1952).

