

of tetralin are: f. p. -35.80° ; b. p. (760 mm.) 207.57° ; n_{D}^{20} 1.54135; d_{4}^{20} 0.9702.

Both naphthalene and tetralin were completely hydrogenated to decalin under all the conditions tried (Tables I and II). The liquid catalyzate gave no temperature rise when 2 cc. of it was shaken for three minutes in a test-tube with 2 cc. of nitrating mixture (1 vol. sulfuric acid d. 1.84 plus 2 vols. nitric acid d. 1.42), this qualitative test showing the absence of more than 3% of naphthalene or tetralin. The physical constants (n_{D}^{20} , d_{4}^{20} , δ (specific dispersion)⁹) of the catalyzates agreed with those of mixtures of *cis*- and *trans*-decalin.¹⁰ The catalyzate composite boiled at $187.1-194.1^{\circ}$ at 760 mm.

TABLE I

VAPOR PHASE HYDROGENATION OF NAPHTHALENE OVER NICKEL CATALYST

Hrs.	Pressure, mm.	Inlet H ₂ , hr./- 25°C.	Mole ratio H ₂ /C ₁₀ H ₈	Catalyst temp., °C.	g.	Liquid catalyzate		
						n_{D}^{20}	d_{4}^{20}	δ
15	755	1.4	26.0	123	3.7	1.4735	0.880	97
16	741	1.7	25.5	149	5.6	1.4729	.878	98
16	740	1.7	24.5	176	5.6	1.4732	.879	98
16	740	1.7	24.5	199	5.3	1.4719	.876	97

TABLE II

VAPOR PHASE HYDROGENATION OF TETRALIN OVER NICKEL CATALYST

Hrs.	Pressure, mm.	Inlet H ₂ , hr./- 25°C.	Mole ratio H ₂ /C ₁₀ H ₈	Catalyst temp., °C.	g.	Liquid catalyzate		
						n_{D}^{20}	d_{4}^{20}	δ
3	735	5.2	14.6	126	4.9	1.4740	0.881	98
3	735	5.1	14.6	151	5.4	1.4749	.883	98
3	735	4.8	14.6	175	4.7	1.4740	.881	98
3	735	5.2	14.6	200	5.1	1.4792	.892	98

(9) $\delta = (nF - nC)/d \times 10^4$.

(10) Seyer and Walker (THIS JOURNAL, 60, 2125 (1938)) reported d_{4}^{20} 0.8963 and 0.8699, b. p. (760 mm.) 194.6 and 185.5 and n_{D}^{20} 1.48113 and 1.46968 for *cis*- and *trans*-decalins, respectively. The specific dispersion of decalin mixtures has been reported as about 98 (Ward and Fulweiler, *Ind. Eng. Chem., Anal. Ed.*, 6, 396 (1934); Fuchs and Anderson, *Ind. Eng. Chem.*, 29, 319 (1937); Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, 10, 559 (1938); Grosse and Wackher, *ibid.*, 11, 614 (1939); Bloch and Thomas, THIS JOURNAL, 66, 1589 (1944)).

KOPPERS MULTIPLE FELLOWSHIP ON TAR SYNTHETICS
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The Reduction of Diphenylnitrosamine in the Presence of Raney Nickel Catalyst and Platinum Catalyst¹

BY GERALD F. GRILLOT

Paal and Yao² published in 1930 the results that they had obtained in reducing diphenylnitrosamine with hydrogen at about one atmosphere pressure and at room temperature in the presence of palladium deposited on calcium carbonate and barium sulfate. They had expected to obtain *unsym*-diphenylhydrazine, but instead diphenylamine and nitrogen were formed almost quantitatively.

(1) Original manuscript received June 21, 1944.

(2) Paal and Yao, *Ber.*, 63B, 57 (1930).

In the hope that *unsym*-diphenylhydrazine might nevertheless be obtained by the use of a suitable catalyst, the author carried out the reduction using as catalyst both Raney nickel³ and Adams platinum oxide.⁴

Thus, using diphenylnitrosamine prepared according to the method of Fischer,⁵ melting after recrystallization at 66.5° as given by Witt,⁶ reduction with hydrogen in the presence of Raney nickel catalyst at 35 lb. pressure in alcoholic solution at room temperature was substantially complete in an hour, 89% of the theoretical quantity of hydrogen was absorbed and an 83% yield of crude diphenylamine, melting at 53° , was obtained. The odor of ammonia was quite evident in the reduced solution. The benzoyl derivative of the diphenylamine was prepared and it melted at 179° as compared with the recognized melting point of 180° .⁷ The mother liquor from the crystallization of the diphenylamine, with the addition of a few drops of acetic acid, gave no precipitate with benzaldehyde, indicating the absence of any *unsym*-diphenylhydrazine.

Using a somewhat more dilute solution containing in addition 5% of acetic acid by volume, four hours was required for the completion of the reaction, 85% of the theoretical amount of hydrogen was absorbed. Treatment of the solution with sodium hydroxide yielded ammonia equivalent to a 92% reduction.

Similar results were obtained using Adams platinum oxide catalyst in a slightly more dilute alcoholic solution.

These results confirmed the findings of Paal and Yao above mentioned, except that under our conditions a substantially quantitative yield of ammonia rather than of nitrogen resulted from the reduction.

(3) Adkins, "Reactions of Hydrogen, etc.," University of Wisconsin Press, Madison, Wis., 1937, p. 20.

(4) Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 452.

(5) Emil Fischer, *Ann.*, 190, 174 (1878).

(6) Witt, *Ber.*, 8, 856 (1875).

(7) Shriner and Fuson, "Identification of Organic Compounds," Sec. Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 196.

UNIVERSITY OF KENTUCKY

LEXINGTON, KY.

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Interaction between Sodium Triphosphate and Salts of Polyvalent Cations as Shown by pH Measurements

BY LEA FRANKENTHAL

In the course of an investigation on sodium triphosphate an instantaneous acid shift was detected in solutions of this compound to which Mg^{++} , Ca^{++} , Mn^{++} or Al^{+++} salts were added. A similar qualitative observation of the decrease in pH has been made by H. Rudy¹ in a study of the dissolving effect of sodium triphosphate on calcium soaps. Accepted concepts concerning the

(1) H. Rudy, *Angew. Chem.*, 54, 447 (1941).