quinone. The portion insoluble in alcohol was dissolved in 500 cc. of chloroform and precipitated with 1000 cc. of alcohol. The yield was 0.485 g. (11.3%) of greenish black microscopic needle-shaped crystals having metallic luster and purple streak and which appeared to be identical with those obtained from 2,6-dibenzamidophenol.

Anal. (Kjeldahl). Calcd. for $C_{40}H_{28}N_4O_6$: N, 8.49; quinoid O, 4.84. Found: N, 8.31; quinoid O (hydrazine), 5.22, 5.24.

The alkali salt of the hydroquinone formed by reduction of quinone from either source by hydrazine is yellow. Its yellow solution on acidification yields the colorless hydroquinone which rapidly becomes purple in the air. Reoxidized quinone from the above preparation contained 8.92% N which indicates some saponification of benzamido groups has occurred.

Summary

1. Iodine in the 2,6-position in phenols is about 37% as efficient as benzamido in favoring the cedriret reaction.

2. Placing iodine in the 4-position in 2,6-diiodophenol or 2,6-dibenzamidophenol does not prevent the cedriret reaction but decreases the yield by 83–86%.

3. The positions of the iodine atoms in the tetraiododiphenoquinone have been determined and 2,6-dibenzamido-4-iodophenol and 3,5,3′,5′-tetrabenzamidodiphenoquinone-4,4′ have been prepared.

UNIVERSITY, MISS.
RECEIVED MARCH 3, 1937

[CONTRIBUTION NO. 175 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

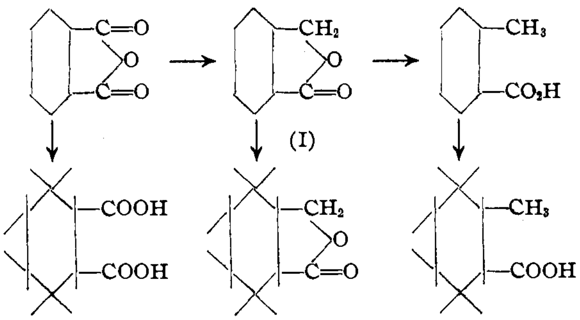
Phthalide. I. The Hydrogenation of Phthalic Anhydride

BY PAUL R. AUSTIN, E. W. BOUSQUET AND WILBUR A. LAZIER

Phthalic anhydride has been hydrogenated over nickel[1] and platinum[2] catalysts by a number of investigators, all of whom note the formation of phthalide (I) accompanied by varying amounts of toluic acid as well as ring-hydrogenated derivatives of the components of the reaction mixture (Chart I).

CHART I

HYDROGENATION OF PHTHALIC ANHYDRIDE



The complexity of the reaction may be illustrated by the recent work of Adkins, Wojcik and Covert[1d] who carried out the hydrogenation with nickel and isolated about equal amounts of phthalide, *o*-toluic acid and hexahydro-*o*-toluic acid. It was thought worth while to investigate further the optimum conditions for the catalytic synthesis of phthalide. Since early trials showed the presence of a solvent to be essential to high conversions, this factor was given primary consideration.

With nickel-on-kieselguhr catalyst yields of phthalide above 80% of the theoretical were realized using ethanol as the reaction medium. This process was carried out at 150–160°, a temperature at which the phthalic anhydride is converted readily to ethyl hydrogen phthalate and one might expect that the hydrogenation of this aromatic ester would be limited to the nucleus[1d] or inhibited completely by the action of the acid on the nickel catalyst.[3] The formation of phthalide which occurs in the presence of alcohol, leads us to postulate the hydrogenation of the tautomeric form of ethyl hydrogen phthalate (II), the course of the reduction proceeding by hydrogenolysis[4] in accordance with the following scheme (Chart II).

Furthermore, the closely related ester, *pseudo*-ethyl phthalaldehydate (III), hydrogenated smoothly to phthalide and *o*-toluic acid as predicted by this hypothesis. It is interesting to note that ester solvents, such as ethyl acetate, ethyl butyrate and butyl acetate may be employed satisfactorily in this process.

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[1] (a) Godchot, *Bull. soc. chim.*, [4] **1**, 829 (1907); (b) Eijkman, *Chem. Weekblad*, **4**, 191 (1907); (c) Lucius and Bruning, German Patent 368,414 (1923), *Friedl.*, **14**, 454; (d) Adkins, Wojcik and Covert, THIS JOURNAL, **55**, 1669 (1933).

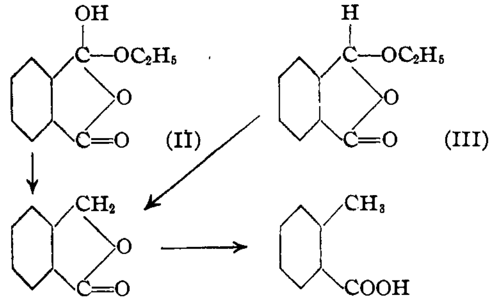
[2] Willstätter and Jaquet, *Ber.*, **51**, 767 (1918); Vavon and Peignier, *Bull. soc. chim.*, [4] **45**, 297 (1929).

[3] Covert, Connor and Adkins, THIS JOURNAL, **54**, 1661 (1932).

[4] Connor and Adkins, *ibid.*, **54**, 4678 (1932).

CHART II

HYDROGENATION OF ETHYL HYDROGEN PHTHALATE AND *pseudo*-ETHYL PHTHALALDEHYDATE



The use of Raney nickel catalyst in alcohol gave a relatively high conversion to phthalide and a low proportion of toluic acid, but the catalyst was found to promote considerable nuclear saturation. The effect of temperature on the distribution of the reaction products was rather marked. Hydrogenation in alcohol solution with nickel catalyst at 160° gave about 20% of toluic acid at the expense of a portion of the phthalide, while at 150° only 10% of toluic acid was obtained, and the yield of phthalide was above 80%. At 140° the hydrogen absorption was very slow. The conversion to hexahydrophthalide was little affected by the temperature in this range but, as indicated above, was largely dependent on the type of catalyst employed. Pressures varying from 700–2000 lb./ sq. in. (47–133 atm.) were about equally satisfactory in all of the hydrogenations using nickel.

Nuclear saturation and relatively high conversions to *o*-toluic acid are inherent disadvantages in the hydrogenation of phthalic anhydride with nickel, and to obviate these factors other types of catalysts were investigated. Copper chromite was the most effective in accomplishing this purpose. Benzene was found to be a suitable solvent, and hydrogenation carried out at 270° under 3000 pounds per sq. in. (200 atm.) of hydrogen pressure gave phthalide in a yield of 82.5%, while the conversion to *o*-toluic acid was about 10%. Alcohols were not useful as solvents for hydrogenations with copper chromite; for example, copper–barium chromite catalyst with ethanol and phthalic anhydride gave toluene, xylene and diethyl phthalate, but no phthalide. In hydrogenating phthalic anhydride in the absence of a solvent, copper–barium chromite and copper chromite catalysts gave 10 and 56% of phthalide, respectively.

By applying the hydrogenation technique to phthalide and some of its derivatives, a series of interesting compounds has been prepared. Thus Raney nickel catalyst with phthalide itself gave hexahydro-phthalide (82.5% conversion), 5-nitrophthalide was reduced over nickel-on-

TABLE I

HYDROGENATION OF PHTHALIC ANHYDRIDE AND PHTHALIDE DERIVATIVES

Run no.	Material hydrogenated	Grams	Catalyst	Grams	Solvent	Grams	Time, hrs.	Temp., °C.	Mean pressure, lb./sq. in.	Phthalide, %	*o*-Toluic acid, %
1	Phthalic anhydride	100	Ni-on-Kies.	11	Ethyl butyrate	176	1.0	170	1500	66.3	16.3
2	Phthalic anhydride	100	Ni-on-Kies.	10	Butyl acetate	100	2.5	160	2000	70.8	21.8
3	Phthalic anhydride	100	Ni-on-Kies.	10	Ethyl acetate	100	1.5	160	700	69.5	19.5
4	Phthalic anhydride	148	Ni-on-Kies.	15	Abs. ethanol	46	2.0	160	1500	72.4	16.5
5	Phthalic anhydride	148	Ni-on-Kies.	12	Methanol	32	4.75	150	1000	83.0[a]	10.8
6	Phthalic anhydride	148	Ni-on-Kies.	12	95% ethanol	50	4.0	150	1200	81.0[a]	12.5
7	Phthalic anhydride	148	Raney Ni	15	Abs. ethanol	50	4.0	160	2500	73.0[b]	10.3
8	Ethyl hydrogen phthalate	150	Ni-on-Kies.	11	None	..	5.25	150	1200	77.0[a]	12.7
9	Phthalic anhydride	150	Cu–Cr	12	None	..	5.0	270	3000	55.8[c]	3.6
10	Phthalic anhydride	150	Cu–Ba–Cr	12	None	..	8.0	270	3500	14.6[d]	8.7
11	Phthalic anhydride	8000	Cu–Cr	800	Benzene	8000	6.0	260	3000	82.5	9.8
12	*pseudo*-Ethyl phthalaldehydate	45	Ni-on-Kies.	3.6	95% ethanol	25	3.0	150	1200	50.4[e]	43.5
13	Phthalide	200	Raney Ni	20	None	..	2.0	140	2000	Hexahydrophthalide, 82.5%[f]	
14	5-Nitrophthalide	1000	Ni-on-Kies.	50	Abs. ethanol	3500	1.0	150	1500	5-Aminophthalide, 85%[g]	
15	Sodium-α-hydroxy-*o*-toluate	195	Ni-on-Kies.	20	Water	300	6.5	110	1500	*o*-Toluic acid, 80%	

[a] About 3–4% of hexahydrophthalide also was obtained. [b] Seven per cent. of hexahydrophthalide was also isolated. [c] Phthalic acid 33.4% also was obtained. [d] Phthalic acid, 64.7%, predominated. [e] *pseudo*-Ethyl phthalaldehydate was prepared according to the procedure outlined by Meyer [*Monatsh.*, **25**, 491 (1904)]; it melted at 66°. [f] *o*-Toluic acid (1.0%) and hexahydro-*o*-toluic acid (6.0%) were also isolated. The hexahydrophthalide distilled at 103–105° (2 mm.). Einhorn [*Ann.*, **300**, 175 (1898)] gives the boiling range as 160–165° (60 mm.). [g] Nitrophthalide, m. p. 142°, was prepared as described by Teppema [*Rec. trav. chim.*, **42**, 30 (1933)]. 5-Aminophthalide was isolated by solution of the reaction mixture in dilute hydrochloric acid, filtration of the catalyst and precipitation of the free base with ammonium hydroxide. Crystallized from ethanol the aminophthalide melted at 182°. Tasman [*ibid.*, **46**, 661 (1927)] gives the melting point as 182°.

kieselguhr to 5-aminophthalide (85% conversion), and sodium-α-hydroxy-*o*-toluate (phthalide dissolved in aqueous sodium hydroxide) yielded *o*-toluic acid (80%) on hydrogenation over nickel-on-kieselguhr.

The hydrogenation of phthalic anhydride, pthalide and various phthalide derivatives is summarized in Table I.

Experimental Part

Apparatus.—The apparatus used in this work consisted of a shaking device, high pressure steel tubes connected to recording gages, electrical pyrometers for temperature control and a source of high pressure hydrogen. The tube capacity was approximately 400 cc. In operation, the material and catalyst were charged into the tube which was then made tight with a plug and a threaded nut. A thermocouple well extended through the plug into the inner space of the tube, and a hydrogen inlet line, valve and flexible line connected to the gas manifold completed the assembly. The tube was heated and agitated mechanically, and hydrogen absorption was measured by the pressure drop in the closed system. The time of reaction given in Table I was measured from the beginning of the hydrogenation to the conclusion of the run.

Catalysts.—Nickel-on-kieselguhr catalyst was prepared from the nitrate by precipitation of the carbonate followed by hydrogen reduction according to well-known methods[3] (p. 1651). Unsupported pyrophoric nickel was prepared according to the method of Raney,[5] and copper chromite and promoted copper chromite catalysts[6] were prepared according to the standard procedures.

Isolation of Products.—Water-soluble solvents were evaporated, replaced by benzene, and the acidic components extracted with aqueous sodium carbonate. The alkaline solution was separated and acidified to give *o*-toluic acid or hexahydro-*o*-toluic acid. Phthalide was obtained by evaporation of the organic solvent and may be further purified by crystallization from alcohol or benzene. Phthalic acid, when isolated, was found in the catalyst fraction and was recovered by solution and reprecipitation from sodium carbonate solution. All of the materials isolated were characterized by means of their melting points or boiling points and by comparison with authentic specimens.

Summary

Phthalide has been obtained in excellent yields by the hydrogenation of phthalic anhydride (a) with copper chromite in benzene, (b) with Raney catalyst in ethanol and (c) with nickel-on-kieselguhr in ester or alcohol solvents. The novel use of alcohol as a solvent for this reduction has been investigated and a mechanism for the hydrogenation has been proposed. Hexahydrophthalide, 5-aminophthalide and *o*-toluic acid have been obtained in high yields by further hydrogenation of phthalide or appropriate derivatives.

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[5] Raney, U. S. Patent 1,628,190; *C. A.*, **21**, 2116 (1927).

[6] Lazier, British Patent 301,806, June 12, 1926; *C. A.*, **23**, 4306 (1929); U. S. Patent 1,746,783, Feb. 11, 1930; *C. A.*, **24**, 1649 (1930); U. S. Patent 1,964,000, June 26, 1934; Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931); Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

WILMINGTON, DEL. RECEIVED FEBRUARY 16, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

The Ternary Systems $KClO_3$–KBr–H_2O, $KClO_3$–KI–H_2O and KIO_3–KI–H_2O at 25°

BY JOHN E. RICCI

The solubility isotherms reported in this paper were studied during the course of more extensive investigations; while no complex formation, in the form either of double compounds or of solid solutions, was found in all three systems, the results are nevertheless presented as solubility determinations which may have some interest and value. In connection with the system KIO_3–KI–H_2O, it may be mentioned that although a double compound or complex of some sort of these two salts might have been expected on the basis of the compounds known to form between sodium iodate and sodium iodide,[1] the results show no tendency at all toward compound formation between the potassium salts at 25°.

The experimental procedure was that usually employed for similar measurements. Definite mixtures of the components were stirred in a bath thermostatically controlled at 25 to ±0.02°, sufficient time (at least two days) being allowed for the attainment of equilibrium. The method of analysis of the saturated solution varied for the different systems, as follows: for the first system, the potassium bromide was determined by titration with standard silver nitrate solution, using Mohr's method; the total solid was determined by evaporation at 100° followed by 250°; and the potassium chlorate was then calculated by difference. In the second system, the potassium iodide was likewise titrated argentometrically, by Fajans' method, using eosin as the

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[1] Ricci, THIS JOURNAL, **56**, 295 (1934).