Reduction of Phthalic Acid and Its Derivatives by Zinc[1]

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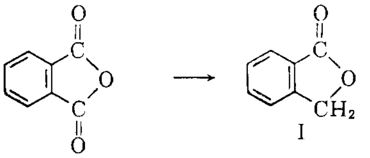
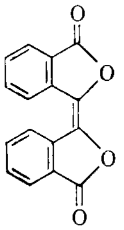
Phthalic acid is reduced cleanly to phthalide by zinc and acetic acid. Phthalic anhydride is reduced more rapidly but bimolecular reduction also occurs; phthalic anhydride is reduced cleanly to phthalide by zinc or zinc amalgam in the presence of hydrochloric acid. *N*-Alkylphthalimides are reduced under all of these conditions to phthalimidines; hydroxyphthalimidines appear to be intermediates and little or no bimolecular reduction occurs. It is suggested that these reactions occur by way of isobenzofuran or isoindole intermediates.

Although carboxylic acids and their derivatives can be reduced electrolytically,[2] or by means of sodium or sodium amalgam,[3] they are usually resistant to reduction by such less active metals as zinc or tin. Phthalic anhydride, however, can be reduced by zinc to phthalide (I) and a series of bimolecular products (II–V), the relative amounts of each depending on reaction conditions.[4–9] Phthalide (I) is the main product in acetic acid; formation of the bimolecular reduction products (II–V) is enhanced by the presence of acetic anhydride[5] and suppressed by the presence of hydrochloric acid.[7] Reduction in neutral medium (aqueous alcoholic calcium chloride) is reported to give only the keto acid, III,[6] possibly formed by hydrolysis of II.[8] Products IV and V can be prepared by reduction of II with zinc and acetic acid,[9] while the acid V can also be prepared by reduction of III with zinc and alkali.[8] We have further observed that phthalic acid itself is reduced cleanly, albeit slowly, to phthalide (I) by zinc and acetic acid. Dimethyl terephthalate and diethyl phthalate are not reduced; attempted reduction of benzoic anhydride led to recovery of benzoic acid, indicating that neither of these materials is reducible. Maleic anhydride is, however, reduced to succinic anhydride, which appears to resist further reduction. Hasselbach[9] reported that diphenic anhydride could be recovered quantitatively from attempted reductions by zinc and acetic acid and stated that H. Winzer had obtained similar results with camphoric anhydride. In view of the failure of these other compounds to undergo reduction it seems simpler to consider that phthalic acid is not reduced directly, but by way of the anhydride, generated *in situ* in hot glacial acetic acid. Under these circumstances the concentration of anhydride would always be low enough to prevent appreciable bimolecular reduction. On this basis, the effect of acetic anhydride in promoting bimolecular reduction[5] can probably be ascribed to its ability to prevent (or to reverse[5]) the hydrolysis of the anhydride which was observed by Graebe and Juillard[5] when the reduction was carried out simply in acetic acid under Wislicenus' conditions.[4]



I



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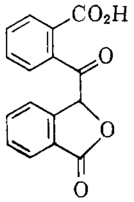

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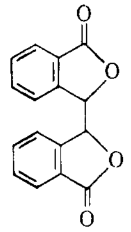

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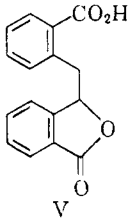

V

Phthalimide and several of its *N*-alkyl derivatives have been reduced to phthalimidines (VII) by tin and hydrochloric acid[10] and to hydroxyphthalimidines (VI) by zinc in cold basic solution[6] or by magnesium in methanol containing ammonium chloride[11]; phthalide (I) is formed by reduction with zinc in hot alkaline solution.[6] We have found that *N*-alkylphthalimides can be reduced cleanly to phthalimidines (VII) by zinc and acetic acid; in contrast to the reduction of phthalic anhydride, this process is not complicated by the formation of bimolecular products. When a deficiency of zinc is used, the corresponding hydroxyphthalimidine (VI) is formed; this can further be reduced to the phthalimidine (VII) and so is almost certainly an intermediate. *N*-Alkylphthalimides are also reduced to phthalimidines under Clemmensen conditions, the reaction being so fast and vigorous that no definitive evidence for the formation of hydroxyphthalimidine intermediates could be obtained.

Our attention was drawn to these reactions by their formal similarity to the Clemmensen reduction of

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(1) Reductions at Metal Surfaces, IV. Preceding paper, J. H. Brewster, J. Patterson, and D. A. Fidler, *J. Am. Chem. Soc.*, **76**, 6368 (1954).

(2) See F. Fichter, "Organische Elektrochemie," Steinkopff, Leipzig, 1942, pp. 251–275.

(3) Aliphatic esters are reduced to alcohols in hydroxylic media [L. Bouveault and G. Blanc, *Bull. soc. chim. France*, [3] **29, 787** (1903); [3] **31,** 666, 672 (1904)] and to acyloins in ether or liquid ammonia [reviewed by S. M. McElvain, *Org. Reactions*, **IV**, 256–264 (1948)]. Aromatic acids and their derivatives are reduced to benzoins by magnesium–magnesium iodide [M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **50**, 2762 (1928); R. C. Fuson, *et. al.*, *ibid.*, **62**, 600, 2091, 2962 (1940); **63**, 1500, 1679 (1941)] but commonly suffer nuclear reduction with sodium or sodium amalgam; thus phthalic acid gives a series of di- and tetrahydrophthalic acids [A. Baeyer, *Ann.*, **258**, 145 (1890); **260**, 145 (1892)].

(4) J. Wislicenus, *Ber.*, **17**, 2178 (1884).

(5) C. Graebe and P. Juillard, *Ann.*, **242**, 214 (1887).

(6) A. Reissert, *Ber.*, **46**, 1484 (1913). For details of the reduction of phthalimide to phthalide with the zinc-copper couple in alkaline solution, see J. H. Gardner and C. A. Naylor, Jr., "Organic Syntheses," Coll. Vol. II, 1943, p. 526, where references to preparations of phthalide by electrolytic or catalytic hydrogenation are also given.

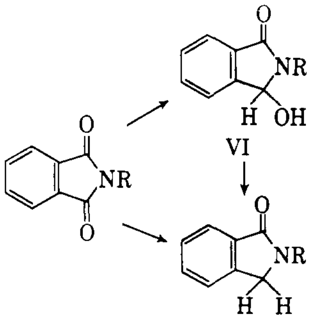
(7) V. M. Rodionov and E. L. Chukhina, *Zh. Prikl. Khim.*, **22**, 853 (1949). [*Chem. Abstr.*, **44**, 1068h (1950).]

(8) C. Graebe and H. Schmalzigaug, *Ann.*, **228**, 126 (1885).

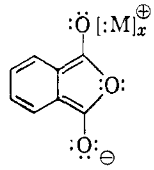
(9) E. Hasselbach, *ibid.*, **243**, 249 (1888).

(10) C. Graebe and A. Pictet, *Ber.*, **17**, 1173 (1884); *Ann.* **247**, 302 (1888).

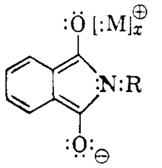
(11) A. Dunet and A. Willemart, *Bull. soc. chim. France*, [5] **15**, 1045 (1948).



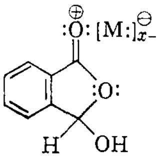
VII



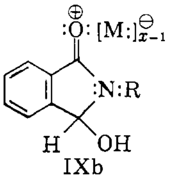
VIIIa



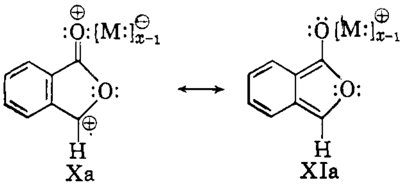
VIIIb



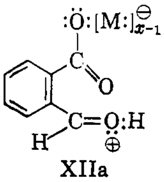
IXa



IXb



Xa XIa



XIIa

ketones[1,12]; our results indicate that they are mechanistically different. A five-membered unsaturated cyclic anhydride or imide structure appears to be required for easy reduction. Thus, phthalimides are reduced at the dropping mercury electrode in acidic medium but homophthalimide and several succinimides are not,[13] suggesting that this structure permits the formation of an especially stable intermediate in the electronation step. We suggest that this step involves the formation of an isobenzofuran (VIIIa)[14] or an isoindole (VIIIb), which, possessing ten *pi* electrons in two rings, should have appreciable aromatic character. In these intermediates negative charge would be concentrated on oxygen atoms; in the presence of acid these oxygen atoms would be protonated. Protonation prior to coördination with the metal surface would make electron addition easier; this may account for the effect of mineral acid in accelerating the reaction. It is clear that the electronated intermediates would lose their aromaticity were they linked to the metal surface by carbon–metal bonds. The easy reduction of *N-t*-butylphthalimide and the steric effect reported in the following paper[15] are consistent with an electronation step involving the formation of an oxygen-to-metal bond, but not with the sort of mechanism proposed for the Clemmensen reduction of ketones,[1,12] in which carbon-to-metal bonds are postulated. The formation of hydroxyphthalimidines as isolable products (presumably by protonation of VIIIb to form IXb) in basic,[6] neutral,[11] and acidic medium underscores this difference, for alcohols appear not to be intermediates in the Clemmensen reduction.[1,12] The preferential formation of monomolecular, as opposed to bimolecular, products in reductions of phthalimides is readily understood on the basis that radical intermediates are not required. Since there is no obvious reason why phthalic anhydride should differ appreciably from a phthalimide in this first stage of the reduction, we suggest that the bimolecular products (II–V) are formed at a later stage.

The chemisorbed intermediates IXa and IXb should lose water easily *in acidic medium* to form carbonium ions (Xa is one resonance form) stabilized by resonance with the benzene ring, with the cyclic oxygen atom (or nitrogen atom in the phthalimide system), and with the electron-rich massive metal (as in XIa). Protonation would then give phthalide (I) or a phthalimidine (VII). This would account for the effect of mineral acid in promoting the formation of phthalide and phthalimidines, while the inability of these products to form further isobenzofurans or isoindoles would account for the absence of further reduction.

We suggest that the pronounced differences in the anhydride and imide systems (in the absence of mineral acid) have their origin in the properties of the intermediates IXa and IXb. The first of these is simply the ring form of phthalaldehydic acid, chemisorbed on the metal surface; a simple shift of electrons would convert it to the open form XIIa. The aldehyde group of this substance would almost certainly be more easily reduced than the parent anhydride, giving a precursor for phthalide by monomolecular reduction and a precursor for IV by simple pinacolic reduction. Mixed bimolecular reduction with the anhydride would lead ultimately to II and III. This mode of reaction for IXa must compete with that involved in the formation of Xa. Since the latter requires acid while the former does not, reactions involving the aldehyde group of XIIa should become more important as the acidity of the medium decreases. It is to be recalled that mineral acid accelerates the formation of phthalide and suppresses the formation of bimolecular products and further that III appears to be the sole product of reduction in neutral medium, all consistent with this picture. In this regard it should be mentioned that although the ring form of phthalaldehydic acid appears to be the more stable in the solid state,[16] ultraviolet spectra of solutions indicate the presence of appreciable amounts of the open (aldehyde) form.[17] The fact that phthalaldehydic acid is not obtained as a reduction product of phthalic anhydride while hydroxyphthalimidines (VI) can be obtained from phthalimides indicates that IXb is more stable than IXa. This is to be expected.[18]

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[12] J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6364 (1954); T. Nakabayashi, *ibid.*, **82**, 3900, 3906, 3909 (1960).

[13] J. Tirouflet and R. Dabard, *Compt. rend.*, **242**, 2839 (1956); J. Tirouflet, R. Robin, and M. Guyard, *Bull. soc. chim. France*, **23**, 571 (1956).

[14] Addition of a single electron would produce a radical ion, of two electrons a dianion. We use here the formulation employed in our earlier papers,[1] involving coördination of a carbonyl oxygen atom to the metal surface, to cover both possibilities and to suggest that *at a metal surface* there may be no significant distinction between the two possibilities. Formulas VIII–XI each correspond, on this basis, to individual forms of resonance hybrids.

[15] J. H. Brewster and A. M. Fusco, *J. Org. Chem.*, **28**, 501 (1963).

[16] D. D. Wheeler, D. C. Young, and D. S. Erley, *ibid.*, **22**, 547 (1957).

[17] Ng. Buu-Hoï and Che-Kin Lin, *Compt. rend.*, **209**, 221 (1939).

[18] Amides react with formaldehyde to give stable *N*-methylol compounds (analogous to IXb) [A. Einhorn, *et. al.*, *Ann.*, **343**, 207 (1905)], the further reactions of which involve cleavage of carbon–oxygen, rather than carbon–nitrogen bonds. The corresponding open-chain half esters of dihydroxymethane (analogous to IXa) are not, so far as the authors are aware, stable enough to be isolated.

The ring opening process would, however, be promoted by base and seems plausible as a step in the formation of phthalide (I) by reduction in hot alkali.[6]

Experimental[19]

Reduction of Phthalic Acid with Zinc Dust in Acetic Acid.—A mixture of 52 g. (0.317 mole) of phthalic acid and 500 ml. of glacial acetic acid was heated to reflux and 150 g. (2.29 g.-atoms) of zinc dust was added. The mixture was heated with mechanical stirring under reflux overnight and then filtered hot on a Büchner funnel. The unchanged zinc dust and the zinc acetate were washed on the funnel with three 100-ml. portions of glacial acetic acid. The combined filtrate and washings were concentrated to a small volume under vacuum and an excess of saturated sodium bicarbonate solution was added. The mixture was extracted four times with 100-ml. portions of ether, the ether extract was washed with water, dried over magnesium sulfate, and concentrated to a small volume on a steam plate. The residue was crystallized from ether–petroleum ether (35–37°) to give 34.5 g. (82%) of phthalide, m.p. 72.5–73.5° (lit.,[20] m.p. 73°).

Attempted Reductions.—Attempted reduction of diethyl phthalate under these conditions led to recovery of 96% of the starting material. Terephthalic acid under these conditions did not go into solution; dimethyl terephthalate did dissolve but was recovered in high yield (95%). Attempted reduction of benzoic anhydride led to recovery of benzoic acid (93%).

Clemmensen Reduction of Phthalic Anhydride.—To 100 g. of zinc amalgam[21] were added 40 g. of phthalic anhydride and 150 ml. of glacial acetic acid, all in a 500-ml. flask fitted with a condenser. During the course of 0.5 hr. 150 ml. of concd. hydrochloric acid was added in small portions through the top of the condenser. The reaction mixture warmed spontaneously to reflux and the anhydride dissolved; when the initial reaction had subsided the mixture was heated at reflux for 4 hr. The reaction mixture was decanted hot from unchanged amalgam and cooled to room temperature; 400 ml. of water was added and the solution was neutralized with sodium carbonate, at which point phthalide precipitated. The mixture was extracted four times with 150-ml. portions of ether; the combined ether extract was washed with 150 ml. of water, dried over magnesium sulfate, and concentrated on a steam plate. The phthalide was recrystallized from ether–petroleum ether (b.p. 35–37°) to give 23 g. (64%), m.p. 70.5–72°.

Reduction of Maleic Anhydride.—Forty grams (0.408 mole) of maleic anhydride (m.p. 57.5–60.2°) was placed in the thimble of a Soxhlet extractor over a flask fitted with a mechanical stirrer and containing 200 ml. of glacial acetic acid, 150 ml. of acetic anhydride, and 120 g. (1.83 g.-atoms) of zinc dust. The mixture was heated with stirring under sufficient reflux that the maleic anhydride was extracted into the reaction flask. After 4 hr. the reaction mixture was filtered hot with suction. The filtrate was kept in a cold room for 3 days; the succinic anhydride which crystallized was collected on a Büchner funnel, washed once with cold water, and dried under vacuum. There was obtained 31.3 g. (77%) of succinic anhydride, m.p. 118.7–120.4° (lit.,[22] m.p. 119.6°); this material did not depress the melting point of authentic succinic anhydride.

Reduction of Phthalimides with Zinc and Acetic Acid. *N-t*-Butylphthalimidine.—A solution of 40.6 g. (0.200 mole) of *N-t*-butylphthalimide[23] (m.p. 59–60°) in 500 g. of glacial acetic acid was heated to 60° and 70 g. (1.10 g.-atoms) of zinc dust was added all at once with mechanical stirring (Teflon paddle). The reaction mixture was heated at reflux with stirring for 4 hr. and then filtered hot on a sintered glass Büchner-type funnel with suction. The filter cake was washed with three 50-ml. portions of glacial acetic acid. The combined filtrate was evaporated to a small volume under vacuum at room temperature and 350 ml. of saturated sodium bicarbonate solution was added. The mixture was extracted with four 100-ml. portions of chloroform. The combined extract was washed once with 50 ml. of saturated sodium bicarbonate solution and once with 50 ml. of water, then dried and concentrated. The residue was distilled at 155–161°/5 mm. and the distillate was crystallized four times from ligroin (b.p. 60–70°) to give 34.8 g. (92% yield) of colorless crystals of *N-t*-butylphthalimidine, m.p. 53.5–54°.

Anal. Calcd. for $C_{12}H_{15}NO$: C, 76.15; H, 7.99; N, 7.40. Found: C, 76.46; H, 8.09; N, 7.24.

***N*-Isopropylphthalimidine.**—*N*-Isopropylphthalimide[24,25] (37.8 g.) was similarly reduced to give 32.0 g. (91%) of *N*-isopropylphthalimidine, b.p., 125–133°/2 mm., m.p., 101–101.5°.

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.62; H, 7.70; N, 8.03.

***N*-Methylphthalimidine.**—(a) *N*-Methylphthalimide[10,24] (32.2 g.) was reduced in the same way to give 25.4 g. (86%) of *N*-methylphthalimidine, b.p., 131–135°/2 mm.; m.p. 114.5–115.5° (lit.[10] 117°). (b) In the same way, *N*-methyl-3-hydroxyphthalimidine[11] (25.6 g.) was reduced to 18.5 g. (80%) of *N*-methylphthalimidine, m.p. 116–117°. (c) In the same way, *N*-methyl-3-methoxyphthalimidine[11] (13.4 g.) was reduced to 9.2 g. (82%) of *N*-methylphthalimidine, m.p. 114.5–115°.

The infrared spectra of the three products were identical.

Reduction of *N*-Methylphthalimide with Insufficient Zinc.—A mixture of 32.2 g. (0.200 mole) of *N*-methylphthalimide and 500 g. of glacial acetic acid was warmed to 65° with mechanical stirring (Teflon paddle). Then 13.1 g. (0.200 g.-atom) of zinc dust was added all at once and the mixture was heated at reflux for 4 hr. The hot mixture was filtered on a Büchner-type funnel with a sintered glass disk and the residue was washed on the funnel with three 50-ml. portions of glacial acetic acid. The filtrate was concentrated to a small volume under vacuum. The residue was treated with 350 ml. of saturated sodium bicarbonate solution and the mixture was extracted with four 100-ml. portions of chloroform. The chloroform extract was washed with 100 ml. of water, dried over magnesium sulfate, and concentrated to about 150 ml. Petroleum ether (b.p. 30–60°) was added to turbidity and the solution was let stand overnight in the cold room. The fine, colorless precipitate was collected with suction, washed three times with 25-ml. portions of petroleum ether, and dried in air. There was obtained 17.6 g. (54%) of *N*-methyl-3-hydroxyphthalimidine, m.p. 126–127° (lit.,[11] m.p. 129°); the infrared spectrum was identical with that of a sample prepared by the method of Dunet and Willemart.[11] From the filtrate there was recovered 7.9 g. (24%) of *N*-methylphthalimide, m.p. and m. m.p. 132–132.5°.

Clemmensen Reductions

Phthalimidinoacetic Acid.—One hundred grams (1.55 g.-atoms) of mossy zinc was amalgamated with a solution of 8 g. of mercuric chloride, 15 ml. of concentrated hydrochloric acid, and 200 ml. of water; the suspension was shaken for 5 min. and the aqueous solution discarded. The zinc was covered with 75 ml. of water and to this was added 47 g. (0.201 mole) of phthalimidoacetic ester[24,26] and 100 ml. of concd. hydrochloric acid. When the mixture was heated to boiling a vigorous reaction ensued and external cooling was needed to keep the reaction under control. After all the organic material had dissolved the mixture was boiled under reflux for 4 hr. The hot solution was decanted from undissolved zinc and allowed to cool. A white crystalline solid precipitated and was collected; another crop was obtained by evaporating the mother liquor to half volume. In all 29 g. (76%) of material, m.p. 208–215° (dec.) was obtained. Recrystallization from a mixture of acetic acid and ether raised the melting point to 213–215° (dec.).

Anal. Calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.33; neut. equiv., 191. Found: C, 62.66; H, 4.74; N, 7.28; neut. equiv., 190.

***N*-Methylphthalimidine.**—Similar reduction of *N*-methylphthalimide gave a solid containing much zinc and chloride ion. The material was dissolved in water and treated with a large excess of dilute sodium sulfide solution; the white precipitate was removed by filtration and washed with water and alcohol. The filtrate was evaporated until a white solid was obtained;

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[19] Microanalyses cited in this work were carried out by Mrs. C. S. Yeh and Mrs. D. W. Margerum. Infrared spectra were determined by Miss M. M. Haley.

[20] J. Hessert, *Ber.*, **10**, 1445 (1877).

[21] E. L. Martin, *Org. Reactions*, **I**, 163 (1942).

[22] K. Kraut, *Ann.*, **137**, 254 (1866).

[23] L. I. Smith and O. H. Emerson, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N.Y., 1955, p. 151.

[24] Prepared by reaction of potassium phthalimide with the appropriate halide in dimethylformamide, by the general method of J. C. Sheehan and W. A. Bolhofer, *J. Am. Chem. Soc.*, **72**, 2786 (1950).

[25] S. Gabriel, *Ber.*, **24** 3104 (1891).

[26] C. Goedeckemeyer, *ibid.*, **21**, 2684 (1888).

this on recrystallization from chloroform–petroleum ether gave 28% of *N*-methylphthalimidine, m.p. 114–116°, undepressed on admixture with an authentic sample,[10] m.p. 115–118°. The infrared spectra of the two samples were identical.

***N*-Ethylphthalimidine.**—Ten grams (0.057 mole) of *N*-ethylphthalimide[10,24] was mixed with 40 ml. of water, 50 ml. of conc. hydrochloric acid, and 25 g. (0.38 g.-atom) of amalgamated zinc. The mixture was boiled under reflux for 2 hr. The hot solution was decanted and diluted with an equal volume of water; the mixture deposited a colorless oil upon standing overnight. The mixture was extracted with chloroform; the chloroform solution was dried and evaporated. The residue was distilled to give 5.4 g. (59%) of *N*-ethylphthalimidine, b.p. 120–121°/2 mm. When chilled in an icebox this material crystallized, m.p. 44–45° (lit.,[10] 45°).

***N*-Benzylphthalimidine.**—Under similar conditions there was obtained, from 20 g. of *N*-benzylphthalimide,[24,27] 12.4 g. (66%) of *N*-benzylphthalimidine, m.p. 88–90° (lit.,[28] 90–91°).

Acknowledgment.—We wish to thank the Continental Oil Company for a free-grant fellowship given to L.E.C. and the Purdue Research Foundation for additional financial support of this work.

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[27] S. Gabriel, *Ber.*, **20**, 2224 (1887).

[28] S. Gabriel, *ibid.*, **45**, 724 (1912).

Steric Effect in the Reduction of *N*-Methyl-1,2-naphthalimide with Zinc[1]

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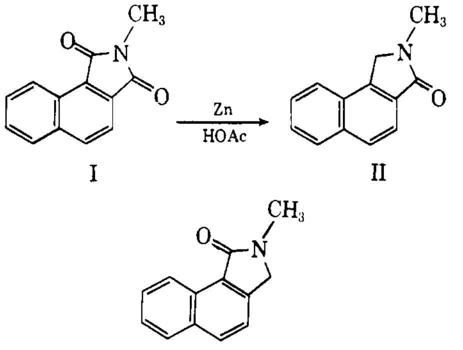
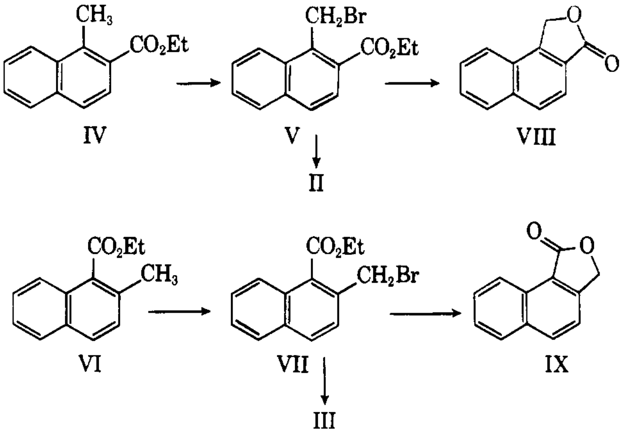
The more hindered carbonyl group of *N*-methyl-1,2-naphthalimide is selectively reduced by zinc and acetic acid. The *N*-methylated 4,5- and 6,7-benzophthalimidines have been prepared by independent syntheses. The reduction of 1,2-naphthalic anhydride under similar conditions gives both of the possible benzophthalides.

It seemed important to determine whether an unsymmetrical phthalimide such as I would be reduced by zinc and acetic acid at the less hindered carbonyl group (as might be expected if the reaction is analogous to the Clemmensen reduction of ketones[2]) or at the more hindered group (as would be possible under the mechanism considered in part IV[1]). Reduction of I gave a 79% yield of a single compound having the composition of an *N*-methyl-1,2-naphthalimidine. The two possible products (II and III) were prepared by independent methods; direct comparisons showed the reduction product to have structure II.



Ethyl 1-methyl-2-naphthoate[3] (IV) was photobrominated[4] in carbon tetrachloride. The product (V) was added to liquid methylamine to give the phthalimidine II[5]; this substance produced no melting point depression on admixture with the reduction product and had a superimposable infrared spectrum. The other phthalimidine (III) was similarly prepared by photobromination[4] of ethyl 2-methyl-1-naphthoate[6] (VI) followed by reaction with methylamine. This substance depressed the melting point of the reduction product; its infrared spectrum differed in the "fingerprint" region and showed a small shift (*ca.* 5 cm.$^{-1}$) of the carbonyl band to lower wave numbers.



In the course of this work the two benzophthalides (VIII and IX) were also prepared. The second of these (IX) had previously been prepared by reduction of 1,2-naphthalic anhydride with lithium aluminum hydride[7] and also by heating the methyl ester analog of VII.[8] The isomeric bromo ester (V) failed to give the latter reaction, perhaps because the *peri* hydrogen atom prevents the necessary alignment of the bromine atom for internal displacement. It could, however, be hydrolyzed by base to a product which lactonized to VIII on treatment with acid. A mixture from which each of these lactones could be isolated was obtained in 82% yield by reduction of 1,2-naphthalic anhydride with zinc and acetic acid; it is hoped that the precise composition of this mixture can be established in future work.

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[1] Reductions at Metal Surfaces, V. Preceding paper, J. H. Brewster, A. M. Fusco, L. E. Carosino, and B. G. Corman, *J. Org. Chem.*, **28**, 498 (1963).

[2] (a) J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6364 (1954); J. H. Brewster, J. Patterson, and D. A. Fidler, *ibid.*, **76**, 6368 (1954). (b) T. Nakabayashi, *ibid.*, **82**, 3900, 3906, 3909 (1960).

[3] H. Gilman and J. E. Kirby, *ibid.*, **51**, 3475 (1929).

[4] See E. L. Eliel and D. E. Rivard, *J. Org. Chem.*, **17**, 1252 (1952).

[5] Phthalimidine itself has been prepared by reaction of ethyl *o*-bromomethylbenzoate with aqueous alcoholic ammonia. The bromo ester gives phthalide on heating. W. Davies and W. H. Perkin, Jr., *J. Chem. Soc.*, **121**, 2202 (1922).

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[7] F. Weygand, K. G. Kinkel, and D. Tietjen, *Chem. Ber.*, **83**, 394 (1950).

[8] Y. Hirshberg, D. Lavie, and E. D. Bergmann, *J. Chem. Soc.*, 1030 (1951).