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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Oxidative Ring Cleavage of Some Substituted Nitronaphthalenes[1]

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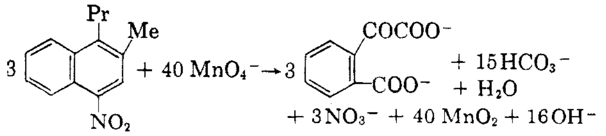
The oxidative ring cleavage of 2-methyl-1-propyl-4-nitronaphthalene, 1-bromo-5-nitronaphthalene, and 1,5-dinitronaphthalene by alkaline permanganate has been studied. The nitrated ring is cleaved preferentially by this reagent with the formation of substituted phthalonic acids. The hitherto unknown 3- and 6-bromophthalonic acids have been obtained in pure form and structures assigned. The data prove that 1-nitronaphthalenes are not cleaved by alkaline permanganate exclusively between carbons 1 and 2 or 3 and 4, but do not permit unequivocal designation of the point of ring cleavage.

As part of an investigation aimed at elucidation of satisfactory methods for selective ring cleavage of substituted naphthalenes, we became interested in the alkaline permanganate oxidation of naphthalene and certain of its derivatives. It is well known[2] that naphthalene is oxidized in good yield by that reagent to phthalonic acid. Under similar conditions alkylated naphthalenes are preferentially cleaved in the less-alkylated ring, but the degree of selectivity is not high.[3] An early report[4] states that 1-nitronaphthalene is slowly oxidized by permanganate but fails to specify conditions or products for the reaction. In view of the fact that 1-nitronaphthalene is cleaved by chromic anhydride to give 3-nitrophthalic acid,[4] it is interesting that Gardner[5] has reported the oxidation by alkaline permanganate of that compound to phthalonic acid in good yield. No further examples of this interesting oxidative cleavage have appeared. The high yield (74% as the aniline derivative), indicating a considerable degree of selectivity in this reaction, prompted a further investigation to determine its generality and hence utility for directed ring cleavage.

We have prepared and submitted to oxidation 1-bromo-5-nitronaphthalene and 2-methyl-1-propyl-4-nitronaphthalene. The results show that the nitro group does indeed direct the ring scission into the nitrated ring. In the case of 2-methyl-1-propyl-4-nitronaphthalene a mediocre yield of phthalic acid (36–40%) was obtained after isolation and purification. In this case no attempt was made to isolate the phthalonic acid undoubtedly formed in the alkaline medium, but the reaction mixture was acidified and permanganate added to a permanent color. The ether extraction employed for the isolation of phthalic acid permitted the recovery of substantially all of that substance from test solutions, but when phthalic acid was introduced in place of the naphthalene derivative only about 70% could be recovered under the normal oxidation conditions employed. However, no benzoic acid was found in such tests indicating probable destruction of the ring. For comparison purposes a sample of 2-methyl-1-propylnaphthalene was oxidized under identical conditions and only 13% of phthalic acid could be obtained. Thus the directive effect of the nitro group is indeed apparent but the presence of the alkyl groups reduced its effectiveness. The influence is also dependent on the alkalinity of the medium, for a run started in neutral solution produced only 20% phthalic acid despite the increasing *p*H of the medium as the reaction proceeds.



Oxidation of 1-bromo-5-nitronaphthalene under alkaline conditions gave a mixture of acidic products in good yield (76%). The crude product showed a wide melting range (*ca.* 125–165°), and contained no nitrogen as indicated by fusion tests and by Dumas analysis. That this mixture consisted substantially of the isomeric 3- and 6-bromophthalonic acids was denoted by its neutral equivalent

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[2] (a) J. Tcherniac, *Ber.*, **31**, 139 (1898). (b) F. Ullmann and J. B. Uzbachian, *Ber.*, **36**, 1797 (1903).

[3] R. B. Randall, M. B. Benger, and C. M. Groocock, *Proc. Royal Soc.* (*London*) **165A**, 432 (1938).

[4] F. Beilstein and A. Kurbatow, *Ann.*, **202**, 213 (1880).

[5] J. H. Gardner, *J. Am. Chem. Soc.*, **49**, 1831 (1927).

(calcd. 136.5, found 136.4). The opportune discovery that 3-bromophthalic acid is nearly insoluble in cold nitroethane, an excellent solvent for the bromophthalonic acids, permitted the separation of the former in nearly quantitative manner. A negligible amount of 3-bromophthalic acid (2%) was obtained from the crude oxidation product. Since the oxidation product here was nitrogen-free, the directive influence of the nitro group was dominant. Previous work[6] showed, by comparison, that with nitric acid as the oxidant a bromine atom can exert an important directive effect on ring cleavage.

These results in conjunction with those of Gardner point to a relatively general ring activation by the nitro group in the case of alkaline permanganate cleavage. The *modus operandi* of this activation is then an open question. Intimately related to this latter problem is the question of the point at which cleavage of the nitrated ring occurs, a subject readily accessible to experimental study. Thus the unsymmetrical nitro substituted ring cleaves to give an unsymmetrical product, phthalonic acid, and if the other ring of the naphthalene were appropriately substituted the point of the ring opening should become apparent.

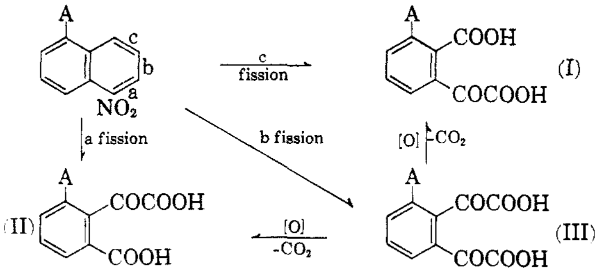

FIGURE I

As Figure I illustrates if a 5-substituted-1-nitronaphthalene is used, the isolation of only a 3-substituted phthalonic acid (I) denotes unequivocal cleavage at bond c, and similarly a 6-substituted phthalonic acid (II) cleavage at bond a. However, the isolation of a mixture of the two isomeric acids would not permit an *a priori* differentiation between oxidative scission at bond b or at both a and c. Two such cases have been studied in some detail as a part of this work, *i.e.* 5-bromo-1-nitronaphthalene and 1,5-dinitronaphthalene, these two being chosen because of their ease of preparation and the divergent electronic nature of the two labelling groups.

Oxidation of 1,5-dinitronaphthalene under the standard conditions employed gave rise to a good yield (75%) of a mixture of acids, m.p. 163–175°. Von Braun[7] has studied the 3- and 6-nitrophthalonic acids, developed a method of separation and assigned structures on the basis of isatin formation from 3-aminophthalonic acid, obtained from the corresponding nitro acid by reduction. Using the separation procedure of von Braun, we obtained 890 mg. of 6-nitrophthalonic acid, m.p. 185–186°, and 80 mg. of 3-nitrophthalonic acid, m.p. 192–193°, from 2 grams of the crude acidic mixture. The low recovery precludes any more certain conclusion than that the 6-nitrophthalonic acid is the more abundant product. Since the 6-nitrophthalonic acid is the less soluble isomer, it also seems safe to consider that the 11/1 ratio recovered constitutes a maximum and that the actual product contains a higher percentage of 3-nitrophthalonic acid.

As was noted above the oxidation of 1-bromo-5-nitronaphthalene also proceeds cleanly to give in good yield a mixture of acids which was shown to consist of the isomeric bromophthalonic acids. Though von Braun had in hand a sample of a similar mixture, he had failed to isolate the pure materials and no assignment of structure has been achieved. Partition chromatography on acidified silicic acid[8] failed to resolve the mixture using either 5% *n*-butanol in chloroform or pure chloroform as the eluant. All attempts to use the keto group for separation *via* preferential derivative formation at the less hindered position also proved fruitless. Although von Braun had found that Fischer esterification of the mixed bromophthalonic acids gave both acid and neutral esters, it was anticipated that the reaction product would be complex in view of the possibility for both normal and pseudoester formation.[9] Despite anticipated difficulties, the procedure offered the possibility of isolation of a pure substance from the acid ester so it was repeated.

Under the conditions employed (12 hr. at room temperature and one hr. at reflux) the mixed acids were readily esterified to give almost exactly half acid ester and half neutral ester. The results of four separate oxidations and esterifications were remarkably consistent showing less than 5% deviation from the 50–50 ratio in all cases. The neutral ester was a viscous yellow oil which was never induced to crystallize. Saponification gave a solid glassy material which when recrystallized from nitroethane gave a nicely crystalline pure white acid, m.p. 191.5–192.5°.

The basic extract of the esterification product yielded an acid ester which eventually crystallized. The solid acid ester, m.p. 111–119°, was repeatedly recrystallized from benzene but no improvement in the melting point was achieved. This material was saponified and the resultant acid recrystallized from nitroethane to give a light yellow crystalline acid, m.p. 185–186°. The melting point of a mixture of this acid and 3-bromophthalic acid, m.p. 186–186.5°, was 157–160°. A mixture of

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(6) V. Merz and W. Weith, *Ber.*, **15**, 2708 (1882).

(7) J. von Braun *et al.*, *Ber.*, **56**, 2332 (1923).

(8) C. S. Marvel and R. D. Rands, *J. Am. Chem. Soc.*, **72**, 2642 (1950).

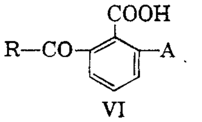
(9) A. Cornillot, *Ann. Chim.* [10] **7**, 275 and [10] **8**, 120 (1927).

the two bromophthalonic acids melted at 141–143°.

There remains then the problem of assigning structures to the two isolated acids, not a simple problem in view of the keto acid–lactol tautomerism superimposed on the problem of determining the position of the bromine atom with respect to the other substituents. Interestingly enough, however, this double problem ultimately proved to simplify the situation considerably. It was considered originally, in view of the well-established tendency of keto acids to form normal esters by the Fischer method,[9,10] that the acid derived from the neutral ester must be the 6-bromophthalonic acid (II). However, a study of the infrared spectra of the esters and their derived acids indicated that such could not be the case.

The infrared spectrum of the neutral ester shows peaks in the carbonyl region at 1790 cm.$^{-1}$ and 1730 cm.$^{-1}$ both showing up as part of a broad general absorption in the region from 1800–1720 cm.$^{-1}$. The crystalline acid derived from this ester shows two nicely resolved sharp absorption bands at 1790 and 1720 cm.$^{-1}$ along with a weaker broad band between 3480 and 3500 cm.$^{-1}$ (OH). The excellent paper of Grove and Willis[11] shows that the high frequency band at 1790 cm.$^{-1}$ can be attributed to the carbonyl of the five-membered ring lactol or pseudo-ester, whereas the 1720 and 1730 bands may be assigned to normal acid and ester groups respectively. The appearance of a normal hydroxyl absorption in the 3480 cm.$^{-1}$ region is also characteristic of lactols. Conversely the acid ester shows absorption in the carbonyl region at 1730 cm.$^{-1}$ and two inflections, one at 1715 cm.$^{-1}$, the other at 1690 cm.$^{-1}$. The acid derived therefrom absorbs at 1730 cm.$^{-1}$, and 1685 cm.$^{-1}$. The latter pair thus show only infrared bands characteristic of normal ester or acid groups and a ketone conjugated with an aromatic ring.[11] It is thus apparent that the neutral ester is a pseudo ester-normal ester and the acid obtained from it exists predominantly in the lactol form, whereas the acid ester is a normal ester and the acid it produced exists in the keto acid form.

The studies of Newman[10] on pseudo ester formation show that in acids of the type VI pseudo esters are formed only when A is a substituent other than H. Though that study involved mainly a methyl substituent, if it is assumed that this is a steric effect then the case in hand should be comparable because there is reasonable evidence that bromine is at least as bulky a group as methyl.[12] These data in combination with the infrared spectra reported above permit the unequivocal assignment of structure II (A = Br) to the acid melting at 185–186° and structure I(A = Br) to the acid melting at 191.5–192.5°. This assignment is also in accord with the fact that the low melting acid exhibits the characteristic yellow color of keto acids, whereas the high melting acid is pure white.



VI

The failure of 6-bromophthalonic acid to undergo more than monoesterification is interesting, and also raises the question of which carboxyl undergoes esterification. It is our opinion that the α-keto carboxyl group undergoes esterification and that the failure of the aromatic carboxyl to form an ester is merely a rate effect. Cornillot[9] has stated that phthalonic acid forms a diester in good yield only when the Fischer esterification utilizes alcoholic hydrochloric acid saturated in the cold. He also assigned the α-ketoester structure to the monoester in view of the pK_a of the free acid group. Effects of single ortho substituents on esterification rates cannot be correlated simply by steric considerations.[12] Thus an ortho hydroxyl decreases the rate by a factor of 21.9, nitro 32.2, but a bromine only 3.33, and a CH_3CO group increases the rate 27 times! If the effect in this last case is attributed to chelation, the similarity to the present case is removed because the added bromine ortho to the keto acid group would hinder the coplanarity appropriate for chelation.

The results show that in both cases studied a mixture of 3- and 6-substituted phthalonic acids is obtained from the oxidation. Thus the nitro group does not direct cleavage exclusively to either position a or c. This leaves three alternatives for consideration, fission at both bonds a and c in appropriate ratio, fission at bond b alone or some combination of these first two. No unequivocal decision can be reached on the basis of the evidence now available. However the rather considerable difference in proportions of the 3- and 6-substituted phthalonic acids obtained when the marking group is varied from nitro to bromine indicates a considerable influence of the substituent in the other ring on the nature of the product. This influence would not appear to be due to steric factors but rather to the difference of nitro and bromine in electronic character. The step or steps in this multistage process where this influence is exerted are not yet apparent.

Although any really significant discussion of this reaction process must await a more comprehensive study, the data accumulated here have limited in some degree the number of possibilities. There is, however, one simple assumption which provides a

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[10] M. S. Newman and C. W. Muth, *J. Am. Chem. Soc.*, **73**, 4627 (1951) and preceding papers.

[11] J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

[12] *Cf.* M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956, p. 215.

coherent explanation of the results. The activation of the nitrated ring can be accounted for by assuming addition of the hydroxyl ion to that ring with consequent formation of a 1,4-dihydronaphthalene derivative.[13] Addition products have been isolated[14] when polynitroaromatic compounds are treated with alkoxides. Thus the equilibrium formation of a minute quantity of the addition product cannot be *a priori* excluded here even though no adduct has been isolated from a mononitro compound. Oxidation of the isolated double bond in the dihydro form may be expected to be rapid and could lead to direct cleavage of the double bond.[15] This is cleavage at point b exclusively and would lead to the diketo dicarboxylic acid (III). Thus the ratio of 3- and 6-substituted phthalonic acids would be determined exclusively by the oxidative decarboxylation step, and thus, *via* the influence of the substituents on the other ring on this reaction.

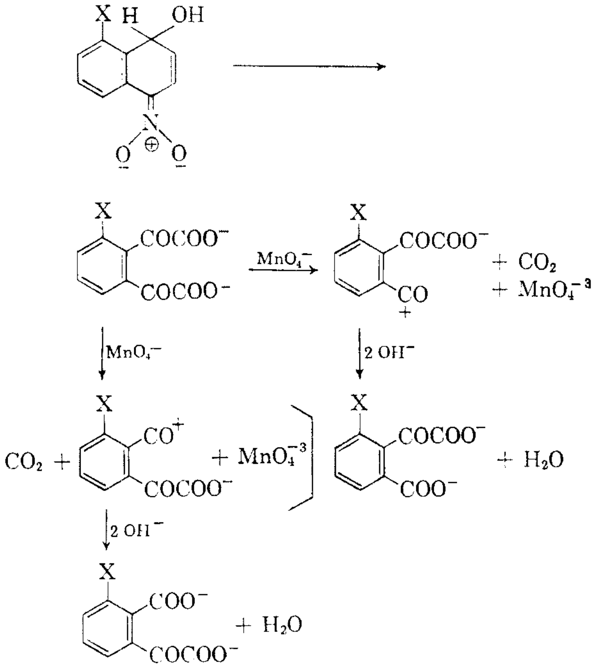

FIGURE II

If oxidative decarboxylation occurs by the simultaneous transfer of two electrons to MnO_4^- and loss of CO_2, a mechanism analogous to one considered by Wiberg and Stewart[16] for oxidation of formate ion, the reaction should be favored by electron releasing and hindered by electron attracting groups. Thus since the nitro group attracts electrons more effectively from the ortho and para positions the nitro substituted diacid should react more rapidly at the meta position and give a predominance of 6-nitrophthalonic acid. The experimental observations accord with this result. The bromo diacid should conversely produce a predominance of the 3-bromophthalonic acid since bromine attracts electrons more effectively from the meta position. However, the data show that the bromine has little influence on the reaction. This may be explained in two ways. Either the steric effect favors reaction at the meta position in both cases augmenting the electronic influence in the nitro case and masking it in the bromo, or the strong electron attraction of the two alpha keto groups swamps the weaker electronic effect of the bromine and only a powerful attracting force such as the nitro group supplies can influence the course of the reaction.

EXPERIMENTAL

1-Allyl-2-methylnaphthalene. This substance was prepared from 1-bromo-2-methylnaphthalene[17] essentially according to the directions of Fieser and Hershberg[18] for the preparation of 1-allylnaphthalene. The product, b.p. 129–130° (6 mm.), n_D^{20} 1.6133, was obtained in 76% yield after distillation through a 30 in. Vigreux column.

Anal. Calcd. for $C_{14}H_{14}$: C, 92.31; H, 7.69. Found: C, 92.00; H, 7.60.

The *picrate* of the product was isolated from methanol and recrystallized from that solvent, m.p. 95.5–96.5°.

Anal. Calcd. for $C_{20}H_{17}N_3O_7$: C, 58.39; H, 4.13. Found: C, 58.25; H, 4.12.

2-Methyl-1-propylnaphthalene. Ten grams (0.055 mole) of 1-allyl-2-methylnaphthalene was dissolved in 30 ml. of absolute ethanol, mixed with approximately one gram of Raney nickel and shaken with hydrogen at two atmospheres pressure for 2 hr. The reduction product was isolated by distillation after removal of the catalyst and solvent, b.p. 138–139° (9 mm.), n_D^{20} 1.5960. Smith and Lo[19] have reported this compound to boil at 102–105° (5 mm.) and to have n_D^{20} 1.5961. The picrate prepared in ethanol melted at 118–119°, which agrees with the melting point previously reported.[19]

2-Methyl-1-propyl-4-nitronaphthalene. A solution of 3 ml. of nitric acid (*d* 1.42) in 2 ml. of nitromethane was added dropwise to a cold, well stirred solution of 2.0 g. (0.001 mole) of 2-methyl-1-propylnaphthalene in 2 ml. of nitromethane. During the course of the reaction the temperature was maintained below −10° by the addition of Dry Ice directly to the reaction mixture. As the nitration progresses a yellow precipitate of the nitration product is formed. After all the acid had been added the mixture was stirred for 1 hr., and the product isolated then by filtration. After recrystallization from methanol the product melted at 69.5–70.5°, yield 51%.

Anal. Calcd. for $C_{14}H_{15}NO_2$: C, 73.41; H, 6.55. Found: C, 73.25; H, 6.50.

General oxidation procedure. The aromatic compound was suspended in sufficient 0.5*N* NaOH to make the initial concentration after addition of permanganate solution approximately 0.1*N* NaOH. The calculated amount of potassium

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(13) A 1,2-dihydro form is also conceivable, but since it is eliminated as the sole form by the experimental results whereas the 1,4-dihydro derivative as a single entity is permitted by the present data, we have chosen to simplify the discussion by reference to the latter derivative only.

(14) J. Meisenheimer, *Ann.*, **323**, 205 (1902).

(15) K. B. Wiberg and K. A. Saegebarth, *J. Am. Chem. Soc.*, **79**, 2822 (1957).

(16) K. B. Wiberg and R. Stewart, *J. Am. Chem. Soc.*, **78**, 1213 (1956).

(17) R. Adams and L. O. Binder, *J. Am. Chem. Soc.*, **63**, 2773 (1941).

(18) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 1658 (1938).

(19) L. I. Smith and C. P. Lo, *J. Am. Chem. Soc.*, **70**, 2209 (1948).

permanganate was dissolved in enough hot water to adjust the total reaction mixture concentration to 5–6%. The permanganate solution was added to the reaction flask in one batch and the reaction heated under reflux with vigorous stirring until the oxidation was effectively complete as indicated by color. Enough ethanol was added to reduce any remaining permanganate and the manganese dioxide removed by filtration. The dioxide was washed with 0.1*N* NaOH and water, and the combined filtrates then concentrated to about 1/7 the volume of the reaction mixture. After having been acidified the concentrate was repeatedly extracted with ether. The crude oxidation product was obtained upon evaporation of the ether.

Oxidation of 2-methyl-1-propyl-4-nitronaphthalene was carried out as described above. Under these conditions 10 hr. was required to effect complete reaction. The isolation procedure was modified slightly in that the acidified concentrate was cooled in an ice bath and treated dropwise with 5% permanganate until the color persisted. This solution was extracted with ether for 40 hr., and the ethereal solution evaporated to dryness. The residue was triturated with a small amount of ice water and the insoluble phthalic acid collected on a Buchner funnel, m.p. 203–205°, yield 35–40%. The *p*-bromophenacyl ester was prepared and recrystallized from acetone, m.p. 154.5–155.5.[20] The *p*-phenylphenacyl ester was also prepared and, after recrystallization from ethanol, melted at 168–169°.[21]

Oxidation of 1-propyl-2-methylnaphthalene was effected as described above except that 4% permanganate was employed. Phthalic acid was isolated in 13% yield as crude acid, m.p. 196–200°. It was identified by derivative formation as noted above.

3- and 6-Nitrophthalonic acids. Oxidation of 1,5-dinitronaphthalene[22] by the general procedure required 2 hr. and gave 75.5% of crude acids, m.p. 163–175°. Two grams of the mixed acids were separated according to the procedure of von Braun[7] giving 890 mg. of 6-nitrophthalonic acid, m.p. 185–186°, and 80 mg. of 3-nitrophthalonic acid, m.p. 192–193°. The melting points are in excellent agreement with those reported by von Braun.

3- and 6-Bromophthalonic acids. When 1-bromo-5-nitronaphthalene is oxidized under the general conditions herein employed a mixture of acids, m.p. 124–164°, was obtained in 65% yield. Neutral equivalent: calcd. for $C_9H_5BrO_5$, 136.5; found, 136.4. This acid mixture was dissolved in a minimum amount of nitroethane, and a small amount (2%) of insoluble 3-bromophthalic acid, m.p. 186–186.5° (lit.[7] 188°), was recovered.

The acid mixture, 8.1 g. (3.0 mmol.), was dissolved in 50 ml. of ethanol containing approximately 12 g. of HCl. This solution was allowed to stand at room temperature for 12 hr. and heated then to boiling for 1 hr. The solvent and hydrogen chloride were removed under reduced pressure and the oily residue taken up in ether. The ether solution was extracted with 5% sodium bicarbonate solution. The ether solution was dried over anhydrous sodium sulfate, and the ether removed *in vacuo*. A pale yellow viscous oil remained, 4.10 g. (44%), which was not further purified. The ester shows broad absorption at 1725–1800 cm.$^{-1}$ with a strong peak at 1800 cm.$^{-1}$ (five membered lactone) and a weaker peak at 1730 cm.$^{-1}$ (normal ester.)

The bicarbonate solution was made acid to Congo Red and extracted several times with ether. The ether solution was dried and the ether removed leaving a pale yellow oil which slowly crystallized. The light tan crystalline acid ester, 4.22 g. (46%), melted at 111–119° and repeated crystallization failed to improve the melting range.

Anal. Calcd. for $C_{11}H_9BrO_5$: C, 43.87; H, 3.08; neut. equiv., 301. Found: C, 44.27; H, 3.25; neut. equiv., 297.

This ester shows absorption in the infrared at 3100–3300 cm.$^{-1}$ (COOH) and 1730 cm.$^{-1}$ (COOEt) with shoulders at 1715 cm.$^{-1}$ (aromatic COOH) and 1690 cm.$^{-1}$ (aromatic ketone).

The neutral ester, 3.2 g. (10 mmol.), was stirred for 10 hr. then heated for 0.5 hr. at reflux with 60 ml. of aqueous sodium hydroxide solution containing 1.0 g. (25 mmol.) of the base. After acidification the solution was extracted with ether, the combined extracts dried over anhydrous sodium sulfate, and the ether removed *in vacuo*. The white crystals of 3-bromophthalonic acid melted at 191.5–192.5° after recrystallization from nitroethane. Yield 2.12 g. (80%).

Anal. Calcd. for $C_9H_5BrO_5$: C, 39.42; H, 1.85; Br, 29.3; neut. equiv., 136.5. Found: C, 39.60; H, 2.03; Br, 29.3; neut. equiv., 136.9.

This acid absorbs at 1790 cm.$^{-1}$ (five membered lactone) and 1720 cm.$^{-1}$ (COOH) with broad general absorption between 3480–3520 cm.$^{-1}$ (OH) and 2500–3200 cm.$^{-1}$ (COOH).

The acid ester was hydrolyzed in similar fashion. The 6-bromophthalonic acid was obtained as light yellow crystals, m.p. 185.0–186.0° (from nitroethane), in 69% yield.

Anal. Calcd. for $C_9H_5BrO_5$: Br, 29.3; neut. equiv., 136.5. Found: Br, 28.9; neut. equiv., 136.8.

3-Bromophthalonic acid shows infrared peaks at 1730 cm.$^{-1}$ (COOH), 1685 cm.$^{-1}$ (ketone conjugated with aromatic ring), and 3200 cm.$^{-1}$ (COOH).

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(20) T. L. Kelly and P. A. Kleff, *J. Am. Chem. Soc.*, **54**, 4444 (1932).

(21) N. L. Drake and J. P. Sweeney, *J. Am. Chem. Soc.*, **54**, 2059 (1932).

(22) C. C. Price and S. T. Voong, *J. Org. Chem.*, **14**, 111 (1949).