

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE NITRATION OF THE METHYL, ETHYL AND TERTIARY-BUTYL ESTERS OF PHENYLACETIC ACID

BY DAVID L. YABROFF AND C. W. PORTER

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This paper deals with the nitration of three of the esters of phenylacetic acid. The work reported here is a continuation of an investigation of the orienting influences of various groups in the benzene ring. The purpose of the research was formulated in an earlier paper.¹ In general it is an attempt to evaluate the orienting influences of atoms and groups not directly attached to the ring. The residual charge on the key atom in phenylacetic acid and its esters as estimated by Latimer and Porter² is zero; that in toluene is also zero. In benzoic acid and its esters the residual charge on the atom attached to the ring is +1.4.

Table I gives our results for the nitration of phenylacetic acid¹ and its esters and Zaki's results³ for the three esters of benzoic acid. The values for toluene⁴ and for benzoic acid⁵ are those of Holleman.

TABLE I

Nitration of	Meta, %	Nitration of	Meta, %
$C_6H_5CH_2COOH$	14.4	C_6H_5COOH	80.2
$C_6H_5CH_2COOCH_3$	12.1	$C_6H_5COOCH_3$	72.6
$C_6H_5CH_2COOC_2H_5$	10.3	$C_6H_5COOC_2H_5$	69.9
$C_6H_5CH_2COOC(CH_3)_3$	5.6	$C_6H_5COOC(CH_3)_3$	59.4
$C_6H_5CH_3$	4.4		

As may be seen in Table I the percentage of the meta derivative is highest in the case of the free acid. Replacement of the hydrogen by alkyl groups causes a successive diminution in the percentage of the meta isomer. This was explained by Zaki³ for the benzoic esters as due to the electron affinity of the various alkyl groups as compared with that of hydrogen. In our language we should say that the replacement of hydrogen by the various alkyl groups must modify the residual charge on the key atom. In the case of the esters the effective residual charge must be slightly more negative than that of the free acid, since less of the meta derivative is formed.

Methyl phenylacetate and tertiary-butyl phenylacetate heretofore have not been nitrated although nitro derivatives of the methyl ester have been obtained by esterification of the corresponding nitrophenylacetic

¹ Yabroff and Porter, *THIS JOURNAL*, **54**, 1199 (1932).² Latimer and Porter, *ibid.*, **52**, 206 (1930).³ Zaki, *J. Chem. Soc.*, 983 (1928).⁴ Holleman, *Rec. trav. chim.*, **33**, 1 (1914).⁵ Holleman, *ibid.*, **18**, 278 (1899).

acids.^{6,7,8} Tertiary-butyl phenylacetate was included in order to ascertain the accentuated effect of the three methyl groups in the alcohol residue. Ethyl phenylacetate has been nitrated by Baker and Ingold,⁹ who found that approximately 9% of the meta derivative was formed and by Flürscheim and Holmes,¹⁰ who obtained about 12% of the meta isomer.

The analytical method used for determining the percentage of the meta derivative for the three esters of phenylacetic acid was the same as that described for phenylacetic acid itself.¹

Experimental Section

Reagents.—Eastmans ethyl and methyl phenylacetates were purified by fractional distillation under reduced pressure. The preparation and purification of tertiary-butyl phenylacetate has been described.¹¹

Nitration.—The methyl and ethyl esters were nitrated by adding approximately 5 g. of the purified ester in small amounts to 30 cc. of nitric acid (*d* 1.495) freed from oxides of nitrogen. The temperature was maintained at 0° and the flask was thoroughly shaken after each small addition of the ester. The mixtures were allowed to stand for four hours longer at 0°.

Attempts to nitrate the tertiary-butyl ester in the same manner led to a great amount of hydrolysis (60–80%). Nitration was finally accomplished by allowing a mixture of 25 cc. of nitric acid (*d* 1.52) and 25 cc. of acetic anhydride to run slowly into a solution of the ester (about 7 g.) in 30 cc. of acetic anhydride. The temperature was maintained at 0°. The nitric acid solution was added at a steady rate of about 1 cc. per minute and the mixture was stirred vigorously during the entire time of addition. The mixture was then allowed to stand for one and one-half hours longer at 0°.¹²

After the period of nitration was over the nitration mixture obtained from each ester was poured into cracked ice and just neutralized with potassium hydroxide solution. The temperature was maintained at 0° by the further addition of ice. The nitro bodies which separated as a semi-solid oil were taken up with ether and the aqueous layer was extracted twice with ether. The ether extracts were combined, washed with ice water and dried over anhydrous sodium sulfate. Evaporation of the ether left a very pale yellow oil which became semi-solid upon standing. Equivalent weight determinations and analyses were made as described in the earlier paper.¹

The results of the nitrations and analyses are given in Tables II, III and IV where the figures for the molecular weights, the titrations and the brominations represent averages of three determinations made with aliquot

⁶ Maxwell, *Ber.*, **12**, 1764 (1879).

⁷ Bedson, *J. Chem. Soc.*, **37**, 90 (1880).

⁸ Borsche, *Ber.*, **42**, 3596 (1909–1910).

⁹ Baker and Ingold, *J. Chem. Soc.*, 832 (1927).

¹⁰ Flürscheim and Holmes, *ibid.*, 1607 (1928).

¹¹ Yabroff and Porter, *THIS JOURNAL*, **54**, 2453 (1932).

¹² The use of a solvent, such as acetic anhydride, may change the total rate of nitration, but if the solvent does not react with the compound which is being nitrated, the ratios between the ortho, meta and para derivatives remain constant. For evidence relating to this assumption see Holleman, *Chem. Rev.*, **1**, 224 (1925), and Francis, *ibid.*, **3**, 257 (1927).

parts of the sample. The weights referred to in the tables are in grams. For a complete explanation of the headings used in the following tables see our first paper.¹ To avoid unnecessary duplication the details of the procedure are not presented here.

TABLE II
METHYL PHENYLACETATE

Nitration number.....	1	2	3
Weight nitrated.....	4.83	5.64	4.93
Weight of nitro compounds obtained.....	5.70	7.04	6.01
Nitration yield, %.....	91	96	94
Molecular weight of nitration product.....	195.3	195.7	195.0
Weight oxidized by KMnO_4	4.57	4.82	4.61
Weight of oxidation products obtained (benzoic and nitrobenzoic acids).....	3.56	3.67	3.55
Oxidation yield, %.....	91	89	90
Weight of benzoic acid sublimed.....	0.024	0.021	0.051
Benzoic acid present in product, %.....	0.7	0.6	1.4
Molecular weight of oxidation products.....	167.1	167.0	167.4
0.2485 <i>N</i> TiCl_3 required to reduce the sample, cc.	30.60	30.83	29.33
Total nitrobenzoic acids present, g.....	0.2117	0.2133	0.2029
Tribromoaniline formed from reduced sample including solubility correction, g.....	0.367	0.372	0.351
<i>o-p</i> -Nitrobenzoic acids present, g.....	0.1859	0.1884	0.1778
Meta compound, %.....	12.2	11.7	12.4

Average percentage of meta compound, 12.1

TABLE III
ETHYL PHENYLACETATE

Nitration number.....	1	2	3
Weight nitrated.....	4.63	5.21	4.97
Weight of nitro compounds obtained.....	5.62	6.45	5.82
Nitration yield, %.....	95	97	92
Molecular weight of nitration product.....	207.0	209.3	208.6
Weight oxidized by KMnO_4	4.60	4.53	4.56
Weight of oxidation products obtained (benzoic and nitrobenzoic acids).....	3.30	3.27	3.20
Oxidation yield, %.....	90	90	88
Weight of benzoic acid sublimed.....	0.016	0.037	0.029
Benzoic acid present in product, %.....	0.5	1.1	0.9
Molecular weight of oxidation products.....	167.2	166.9	166.8
0.2485 <i>N</i> TiCl_3 required to reduce the sample, cc.	30.12	31.61	27.98
Total nitrobenzoic acids present, g.....	0.2084	0.2187	0.1936
Tribromoaniline formed from reduced sample including solubility correction, g.....	0.370	0.386	0.343
<i>o-p</i> -Nitrobenzoic acids present, g.....	0.1874	0.1955	0.1737
Meta compound, %.....	10.1	10.6	10.3

Average percentage of meta compound, 10.3

TABLE IV
TERTIARY-BUTYL PHENYLACETATE

Nitration number.....	1	2	3
Weight nitrated.....	6.46	6.88	6.56
Weight of nitro compounds obtained.....	7.39	7.55	7.90
Nitration yield, %.....	93	89	98
Molecular weight of nitration product.....	239.3	238.1	237.8
Weight oxidized by KMnO ₄	5.13	4.86	4.75
Weight of oxidation products obtained (benzoic and nitrobenzoic acids).....	3.15	3.04	3.10
Oxidation yield, %.....	87	89	93
Weight of benzoic acid sublimed.....	0.038	0.027	0.016
Benzoic acid present in product, %.....	1.2	0.9	0.5
Molecular weight of oxidation products.....	166.9	167.3	167.1
0.2507 <i>N</i> TiCl ₃ required to reduce the sample, cc.	32.48	30.81	32.83
Total nitrobenzoic acids present, g.....	0.2267	0.2151	0.2292
Tribromoaniline formed from reduced sample including solubility correction, g.....	0.421	0.400	0.429
<i>o-p</i> -Nitrobenzoic acids present, g.....	0.2133	0.2026	0.2173
Meta compound, %.....	5.9	5.8	5.2

Average percentage of meta compound, 5.6

Summary

As a continuation in the study of the influences of remote atoms on the residual charge of the key atom in benzene derivatives, the quantitative nitration of the methyl, ethyl and tertiary-butyl esters of phenylacetic acid has been accomplished. The percentages of the meta derivatives formed were 12.1, 10.3 and 5.6, respectively.

BERKELEY, CALIFORNIA

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NITRATION OF META-DIPHENYLBENZENE AND DERIVATIVES OF NITRO-META-DIPHENYLBENZENE¹

BY C. ARTHUR WARDNER WITH ALEXANDER LOWY

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In the process for the preparation of diphenyl from benzene, considerable amounts of high boiling products are produced. *m*-Diphenylbenzene is one of the constituents of this high boiling material. Since the trinitro compound is the only nitro derivative of *m*-diphenylbenzene which has been recorded, a study of the nitration of this hydrocarbon was undertaken with the object of synthesizing the mono and dinitro compounds and some of their derivatives.

¹ Abstracted from a thesis presented by C. Arthur Wardner to the Graduate School in partial fulfilment of the requirement for the Ph.D. degree.