directly. It yielded 2.8 g. of *p*-dichlorobenzene, 0.5 g. of chlorobenzene, 0.6 g. of orange crystalline material (not identified) and 2.0 g. of α,p-dichlorohydrocinnamonitrile. The petroleum ether insoluble material on vacuum distillation gave 17.4 g. of orange oil, α,p-dichlorohydrocinnamonitrile, which boils at 128–132° (5 mm.).[3a] The oil, 4.1 g., was refluxed with 60 g. of 10% sodium hydroxide for two hours. The sodium salt was filtered, acidified with hydrochloric acid and recrystallized twice from absolute ethanol. The colorless needles (88%) melted at 249.5–250°.[4a,4b]

Cambridge, Massachusetts

[Contribution from the Chemical Laboratories of the University of Notre Dame]

The Methyl Esters of 3-Hydroxyphthalic Acid. Selective Reduction of Monomethyl Phthalates with Lithium Aluminum Hydride

By Ernest L. Eliel, Albert W. Burgstahler, Donald E. Rivard[1] and Louis Haefele

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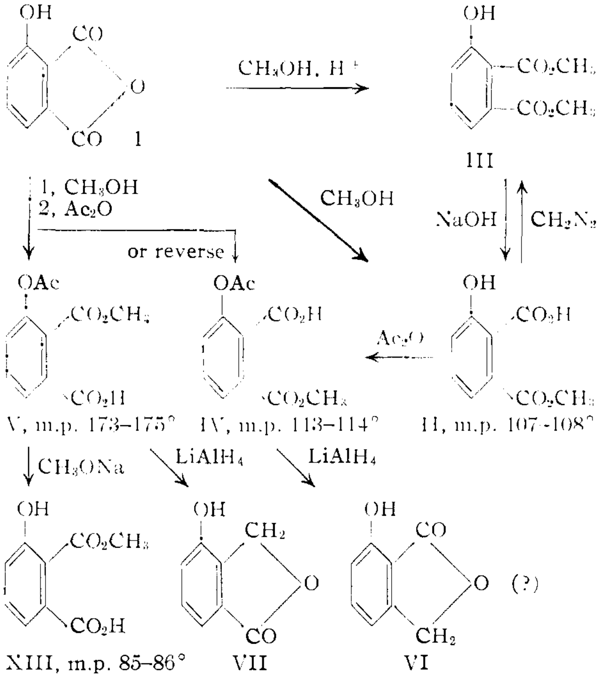
Reaction of 3-hydroxyphthalic anhydride with methanol gives the 1- and 2-methyl esters in about a 3:2 ratio. A method for reducing methyl phthalate to phthalide in good yield by means of lithium aluminum hydride is described.

In connection with another problem we were interested in the monomethyl esters of 3-hydroxyphthalic acid. Treatment of the anhydride I with hot methanol gave material melting over a wide range from which the pure half-ester II could be isolated only with considerable loss. The same material was obtained in very low yield by the saponification of the diester III with one equivalent of sodium hydroxide.

When the crude monomethyl ester was acetylated, a mixture resulted from which *both* monomethyl esters (IV and V) of 3-acetoxyphthalic acid could be isolated by crystallization. The lower melting of these (IV) proved to be identical with material obtained in good yield from the pure methyl 3-hydroxyphthalate (II) by acetylation. This ester IV was isolated in 44% yield, the yield of the higher melting isomer V being 25%. The formulas summarize the reactions so far outlined and some others described in the experimental part. Structures are assigned on the basis of the evidence given.



Attempts to prove the structures of the half-esters IV and V by decarboxylation failed, since saponification of the decarboxylation product of either IV *or* V appeared to give mainly 3-hydroxybenzoic acid.[2] A structure proof based on the selective reduction of the ester groups of IV and V by means of lithium aluminum hydride so as to obtain 7- (VI) and 4-hydroxyphthalide (VII), respectively, was then considered. The selective reduction of the ester group of an ester-acid with lithium aluminum hydride at low temperatures was first suggested in 1947.[3] Later, the reduction of methyl phthalate to phthalide was actually performed,[4] but no experimental details are available. The only other selective reduction of an ester-acid reported seems to be that of 1-methyl 3-chlorophthalate (VIII) to the corresponding phthalide IX,[5] but in this case steric factors may be partly responsible for the incomplete reduction, in view of the fact that an excess of the hydride was employed and that the isomeric 2-methyl 3-chlorophthalate (X), under the same conditions was reduced all the way to 3-chloro-*o*-xylylene glycol (XI).[5]

In our hands, reduction of methyl phthalate in ether at −60° by the addition of the theoretical amount of ethereal lithium aluminum hydride failed to yield any phthalide. When the methyl phthalate was dissolved in tetrahydrofuran instead of ether at −60°, phthalide was formed in 32% yield. Satisfactory results were finally obtained by dissolving the half-ester in tetrahydrofuran and carrying out the reaction at −30°, the yield of the phthalide in this case being 72%. Apparently the success of the selective reduction goes hand in hand with the *absence* of the formation of a heavy precipitate in the reaction mixture. With ether as a sol-

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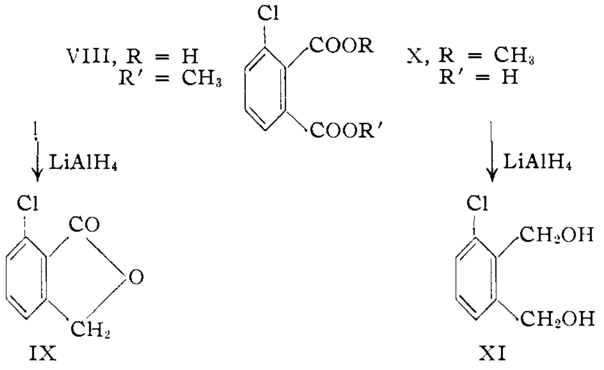
(1) Reilly Fellow, 1949–1951, National Institutes of Health Fellow 1951–1952.

(2) This acid was identified with certainty only in the case of V which should *not* have yielded 3-hydroxybenzoic acid by simple decarboxylation. Presumably, at the temperature required for decarboxylation, IV and V are interconvertible and the more labile carboxyl group *ortho* to the acetyl function is lost in either case.

(3) R. F. Nystrom and W. G. Brown, This Journal, **69**, 2548 (1947).

(4) G. Papineau-Couture, E. M. Richardson and G. A. Grant, *Can. J. Res., Sect. B*, **27**, 902 (1949).

(5) R. F. Bird and E. E. Turner, *J. Chem. Soc.*, 5050 (1952).



vent, such a precipitate appeared almost immediately at −60°, with tetrahydrofuran at −60° it did not appear until the mixture was allowed to warm to about −20° and with tetrahydrofuran at −30° it did not appear until about two-thirds of the requisite amount of hydride had been added.

Application of the selective reduction technique to the high-melting methyl 3-acetoxyphthalate gave 4-hydroxyphthalide (VII) in 68% yield, thus suggesting structure V for this half-ester. However, reduction of the low melting isomer IV gave only traces of what appeared to be 7-hydroxyphthalide (VI) along with appreciable amounts of 3-hydroxyphthalic acid; thus this proof of structure seemed somewhat unsatisfactory.

Conclusive proof that the low melting ester has structure IV was obtained through its reaction with *p*-toluidine and with N-*p*-nitrobenzoyl-α-phenylglycine (XII). Aspirin has been shown[6] to acetylate the former reagent to aceto-*p*-toluide and to give the blue anion of an azlactone with the latter in the presence of pyridine, but *m*-acetoxybenzoic acid and esters of acetylsalicylic acid do not respond to these tests.[6] Accordingly, compound IV with *p*-toluidine in pyridine solution gave aceto-*p*-toluide in 83% yield and with XII in pyridine solution containing a small amount of triethylamine it gave a deep blue color. In contrast, V failed to react with *p*-toluidine and gave but a faint blue color in the presence of XII.

The assignment of structure IV to the low melting and of structure V to the high melting half-ester is in agreement with other properties of these compounds. Thus while V is stable both on storage and on short boiling with water (the ferric chloride test for phenol remains negative), IV, while giving no color with ferric chloride in the cold when freshly purified, imparts a purple color to this reagent after short heating with water or after having been stored for some time. Moreover, IV on storage develops a strong odor of acetic anhydride. The phenolic half-ester II (which, on acetylation, yields IV) has an infrared absorption band at 5.82 μ (aromatic ester) and 6.02 μ (chelated carboxyl) while the isomeric ester XIII, obtained from V by treatment with sodium methoxide, absorbs at 5.92 μ (aromatic acid) with a shoulder at 6.01 μ (chelated carbomethoxyl).

The formation of a mixture of esters from 3-hydroxyphthalic anhydride in which the 1-methyl ester IV predominates is another violation of Wegscheider's Rule.[7] According to this rule, in the reaction of a substituted phthalic (or other cyclic) anhydride with an alcohol, the more strongly acidic carboxyl group is esterified. Although there are a number of more or less well documented instances where the rule holds,[7,8] it is clearly violated in the case of 3-methylphthalic anhydride[9] and 4-chlorophthalic anhydride[10] in addition to the cases of the 3-hydroxy and 3-acetoxy (see Experimental) compounds described here.

A convenient synthesis of 3-hydroxyphthalic anhydride is described in the Experimental part.

Experimental[11]

3-Aminophthalic Anhydride.—A solution of 19.3 g. (0.10 mole) of 3-nitrophthalic anhydride, m.p. 163°, in 200 ml. of acetone was subjected to catalytic reduction at an initial hydrogen pressure of 60 p.s.i. in the presence of 3–5 g. of Raney nickel catalyst and 10 g. of anhydrous magnesium sulfate. The calculated amount of hydrogen was taken up in 2–3 hours. The solution was warmed to 50°, treated with Norite, filtered with suction with the aid of "Filter-Cel" and concentrated *in vacuo* at room temperature (the material tends to darken on warming). The residue was treated with 25 ml. of ethyl acetate, chilled and collected to give 11.4–12.7 g. (70–77%) of product melting at 192–193°. Recrystallization from ethyl acetate or acetone raised the melting point to 194–195°; lit.[12] 193–194°. The acetyl derivative melted at 185° as reported in the literature.[12,13]

3-Hydroxyphthalic Anhydride (I).—To 130 ml. of 15 *N* sulfuric acid cooled to 0°, 28.5 g. (0.175 mole) of 3-aminophthalic anhydride, m.p. 192–193°, was added gradually with good stirring. The material dissolved within one hour and a solution of 12.1 g. (0.175 mole) of sodium nitrite in 40 ml. of water was then added in about 30 minutes, the temperature being maintained below 5°. After another 30 minutes, the mixture was warmed to 79–80° and maintained at this temperature until nitrogen evolution ceased (*ca.* 1 hr.). The now dark orange solution was diluted with water to about 500 ml. and extracted continuously with ether for at least 30 hours. The ether layer was dried overnight with sodium sulfate, filtered and shaken for two hours with 30 g. of finely powdered barium chloride to remove traces of sulfuric acid. (Omission of this treatment leads to charring at the concentration stage.) The solution was filtered and concentrated and the resulting crude 3-hydroxyphthalic acid sublimed at about 160–180° (0.2 mm.) to give 22–26 g. (77–91%) of the anhydride melting at 196.5–197.5°. Recrystallization from acetone–benzene (Norite) raised the melting point to 199–200°; lit.[14] 199–201°. The acetyl derivative[15] melted at 115–116°; lit.[16] 115°.

1-Methyl 3-Hydroxyphthalate (II).—A solution of 6.5 g. (0.04 mole) of 3-hydroxyphthalic anhydride, m.p. 197–199°, in 50 ml. of absolute methanol was boiled under reflux for 36 hours in a system protected by a drying tube. Removal of the methanol at reduced pressure followed by crystalliza-

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[6] D. Davisdon and L. Auerbach, THIS JOURNAL, **75**, 5984 (1953).

[7] R. Wegscheider, *Monatsh.*, **16**, 144 (1895); **18**, 418, 631 (1897).

[8] R. Kahn, *Ber.*, **35**, 3872 (1902); C. Graebe and M. Leonhardt, *Ann.*, **290**, 225 (1896); R. Wegscheider and E. Bondi, *Monatsh.*, **26**, 1039 (1905); R. Wegscheider and R. Piesen, *ibid.*, **23**, 393 (1902); M. B. Chaudhari and K. S. Nargund, *J. Univ. Bombay*, **18**, Pt. 5, Sec. A, Sci. #27, 15 (1950); *C. A.*, **45**, 1975d (1951).

[9] N. Rabjohn and H. H. Farmer, THIS JOURNAL, **77**, 760 (1955).

[10] B. H. Chase and D. H. Hey, *J. Chem. Soc.*, 553 (1952); M. Hayashi, I. Furusawa and S. Tsuruoka, *J. Soc. Chem. Ind. Japan*, **44**, 436 (1941); *C. A.*, **44**, 7821h (1950).

[11] All melting and boiling points are uncorrected. Microanalyses by Micro-Tech Laboratories, Skokie, Illinois. Infrared spectra recorded by Mr. Rolland Ro.

[12] M. T. Bogert and F. L. Jouard, THIS JOURNAL, **31**, 483 (1909).

[13] C. H. Wang, R. Isensee, A. M. Griffith and B. E. Christensen, *ibid.*, **69**, 1909 (1947).

[14] Y. Miyasita, *J. Pharm. Soc. Japan*, **60**, 506 Abstracts 199 (1940); *C. A.*, **35**, 4009 (1941); see also O. Gisvold, *J. Am. Pharm. Assoc.*, **31**, 202 (1942).

[15] D. S. Pratt and G. A. Perkins, THIS JOURNAL, **40**, 228 (1918).

[16] H. Mühlemann, *Pharm. Acta Helv.*, **23**, 257 (1948); *C. A.*, **43**, 2984g (1949).

tion from benzene–petroleum ether (b.p. 30–60°) gave 5.5 g. (71%) of crystals melting over a range (98–104°). Apparently a mixture of II and XIII was at hand from which pure II, m.p. 107.5–108°, was isolated by repeated recrystallization.

Anal. Calcd. for $C_9H_8O_5$: C, 55.11; H, 4.11. Found: C, 55.34; H, 4.38.

Dimethyl 3-Hydroxyphthalate (III).—Treatment of 3.92 g. (0.02 mole) of 1-methyl 3-hydroxyphthalate, m.p. 106–107°, with excess ethereal diazomethane gave, after distillation of the ether and crystallization of the residue from petroleum ether (b.p. 30–60°) containing some benzene, 3.5 g. (83%) of dimethyl 3-hydrophthalate, m.p. 48–51°, b.p. 94–96° (0.1 mm.). Recrystallization from the above solvents raised the melting point to 51°.

Anal. Calcd. for $C_{10}H_{10}O_5$: C, 57.14; H, 4.79. Found: C, 57.15; H, 5.05.

The material gave a reddish purple color with aqueous alcoholic ferric chloride. The same material could be obtained in 63% yield by boiling 3-hydroxyphthalic anhydride (3.1 g.) under reflux for 12 hours with absolute methanol (40 ml.) saturated with hydrogen chloride gas.

Acetylation of the dimethyl ester by the Chattaway procedure[17] gave dimethyl 3-acetoxyphthalate, melting at 49–50° after two recrystallizations from benzene–petroleum ether (b.p. 30–60°). This material became liquid when mixed with dimethyl 3-hydroxyphthalate and is therefore distinct from the latter, despite the similarity in melting point.

Partial Saponification of Dimethyl 3-Hydroxyphthalate (III).—A solution of 1.05 g. (0.005 mole) of dimethyl 3-hydroxyphthalate, m.p. 50–51°, in 5 ml. of 1.00 *N* aqueous sodium hydroxide was warmed at 60° for two hours. Upon cooling, some unchanged diester solidified and more of this material was obtained by ether extraction of the aqueous solution, the total recovered being 0.31 g. (30%) melting at 49–51°. The aqueous phase was acidified and extracted with ether, which after drying and distillation left a residue weighing 0.37 g. Treatment of this residue with 20 ml. of warm benzene left undissolved 0.15 g. (16%) of 3-hydroxyphthalic acid, m.p. 161–163° (lit.[15] 161–163°). The benzene solution when concentrated to a volume of 5 ml. and treated with petroleum ether (b.p. 30–60°) deposited 0.12 g. (12%) of 1-methyl 3-hydroxyphthalate (II) melting at 103–106°. Recrystallization raised the melting point to 106–107°, undepressed by admixture of an analytical sample of II prepared as indicated above.

Saponification of dimethyl 3-hydroxyphthalate (III) with excess base gave 3-hydroxyphthalic acid, m.p. 163–164°, in 87% yield. Hydrolysis by warming with 25% hydrochloric acid at 90° for 15 minutes gave 60% of the acid and 9% of the crude half-ester II, m.p. 98–102°.

1-Methyl 3-Acetoxyphthalate (IV) and 2-Methyl 3-Acetoxyphthalate (V). (a) **From Crude Methyl 3-Hydroxyphthalates.**—The crude material remaining after the removal of solvent in the reaction of 15 g. (0.091 mole) of 3-hydroxyphthalic anhydride (I) with methanol was dissolved in a mixture of 50 g. of crushed ice and a solution of 7.28 g. (0.182 mole) of sodium hydroxide in 30 ml. of water. The solution was shaken vigorously with 8.7 ml. (0.91 mole) of acetic anhydride for about 3 minutes[17] and then acidified with cold, dilute hydrochloric acid. A white solid precipitated and was extracted with three 30-ml. portions of ether. The combined ether extracts were washed with water, dried over sodium sulfate and the solvent removed *in vacuo*. The residue was taken up in 30 ml. of warm (60°) benzene which on cooling deposited 3.3 g. (25% yield, taking into account recovered 3-hydroxyphthalic acid—see below) of 2-methyl 3-acetoxyphthalate (V) melting at 167–170°. Two recrystallizations from water raised the melting point to 175–177°. The compound did not give a color with ferric chloride even after storage or short boiling with water.

Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.23; neut. equiv., 238. Found: C, 55.40; H, 4.50; neut. equiv., 232, 239.

Addition of petroleum ether (b.p. 60–90°) to the benzene filtrate from which V had been removed gave 5.9 g. (44% considering recovered 3-hydroxyphthalic acid) of 1-methyl 3-acetoxyphthalate (IV) melting at 106–109°. Recrystallization from benzene–petroleum ether (b.p. 60–90°) raised the melting point to 112–113°.

Removal of solvent from the mother liquor remaining after collection of IV followed by boiling of the residue with 50 ml. of 10% hydrochloric acid for two hours and distillation of the aqueous acids at reduced pressure gave 6.2 g. (after drying) of crude 3-hydroxyphthalic acid melting at 146–148° (lit.[15] 161–163°) which was taken into account in the computation of the above yields.

(b) **From 3-Acetoxyphthalic Anhydride.**—A solution of 2.1 g. (0.01 mole) of 3-acetoxyphthalic anhydride, m.p. 113–114.5°, in 25 ml. of absolute methanol was boiled under reflux for 16 hours. The excess methanol was then removed under reduced pressure and the residue was treated with 15 ml. of ether and chilled to yield 0.7 g. (23%) of 2-methyl 3-acetoxyphthalate (V) which melted at 175–177° after two recrystallizations and did not depress the melting point of the sample described above on admixture. From the filtrate 0.7 g. (23%) of crude 1-methyl-3-acetoxyphthalate melting at 81–86° was obtained. One recrystallization raised the melting point to 103–105°.

(c) **1-Methyl 3-Acetoxyphthalate (IV) from the Pure Hydroxy Ester II.**—1-Methyl 3-acetoxyphthalate (IV) could be obtained from 1-methyl 3-hydroxyphthalate (II), m.p. 105–107°, by the Chattaway method in 85% yield (product melting at 112–113°) or by acetylation in cold pyridine in 74% yield. This establishes the structural correlation of II and IV and also the fact that the isomeric acetoxy ester V is *not* formed from II in the acetylation step. IV obtained by the Chattaway method melted at 113.5–114°, after two recrystallizations from benzene. The material gave no color with ferric chloride when freshly prepared, but on standing developed an odor of acetic anhydride and then gave a purple color with ferric chloride. The same color was obtained with material which had been briefly boiled with water.

Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.47; H, 4.23. Found: C, 55.70; H, 4.48.

When the acetylation was carried out in *hot* pyridine the product, melting at 116–116.5°, proved to be 3-acetoxyphthalic anhydride, undepressed in melting point by admixture of an authentic sample. Admixture of IV depressed the melting point to 92–97°.

Anal. Calcd. for $C_{10}H_6O_5$: C, 58.26; H, 2.94. Found: C, 58.42; H, 3.10.

2-Methyl 3-Hydroxyphthalate (XIII).[18]—Since this ester could not be isolated from the mixture resulting from the treatment of 3-hydroxyphthalic anhydride (I) with methanol, it was prepared by transesterification of the acetyl group in 2-methyl 3-acetoxyphthalate (V). To a solution of sodium methoxide prepared by adding 0.16 g. (0.0070 g.-atom) of sodium to 5 ml. of absolute methanol was added 0.55 g. (0.0023 mole) of 2-methyl 3-acetoxyphthalate (V) dissolved in 10 ml. of absolute methanol and the mixture was heated at 50° for one half hour. Excess methanol was distilled *in vacuo*, dilute (1:1) hydrochloric acid was added to the residue and the latter was extracted with two 10-ml. portions of ether. The combined ether solutions were washed with 5 ml. of water, dried over sodium sulfate and concentrated. The residue weighed 0.41 g. (89%) and melted at 65–69°. Several recrystallizations from petroleum ether (b.p. 30–60°) raised the melting point to 73–74°, but this is apparently the melting point of a hydrate, since after drying in an Abderhalden drier over phosphorus pentoxide at room temperature and 0.01 mm. for 24 hours the sample melted at 85–86°. The material is hygroscopic and good analytical data were obtained only on freshly dried material.

Anal. Calcd. for $C_9H_8O_5$: C, 55.11; H, 4.11. Found: C, 54.87; H, 4.22.

Phthalide from Methyl Phthalate.—To a solution of 18.0 g. (0.1 mole) of methyl phthalate in 250 ml. of dry tetrahydrofuran cooled to −30° was added 75 ml. (0.075 mole) of a standardized[19] 1.00 *M* ethereal solution of lithium aluminum hydride dropwise and with good stirring, the temperature being maintained at −30° by external cooling. There was little precipitation until about two-thirds of the hydride solution had been added, at which point a white solid separated. After addition of all the hydride, a small amount of ethyl acetate was added to the reaction mixture to destroy

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[17] F. D. Chattaway, *J. Chem. Soc.*, 2495 (1931).

[18] This experiment was carried out by Mr. Arthur E. Oberster.

[19] H. Felkin, *Bull. soc. chim. France*, 347 (1951).

any excess hydride. The mixture was allowed to warm and the solvent was removed by distillation at reduced pressure. The residue was treated with 100 ml. of water and 150 ml. of 10% sulfuric acid and extracted with 250 ml. of ether. The ether solution was dried over magnesium sulfate and concentrated. The residue was boiled for one hour with 50 ml. of 20% sodium hydroxide solution and the resulting solution extracted twice with ether, treated with Norite, filtered, acidified with concentrated hydrochloric acid, and boiled for one hour. On chilling in an ice-bath the solution deposited 9.62 g. (72%) of slightly yellow crystals of phthalide melting at 58–65°. One recrystallization from water raised the melting point to 71.5–73°, undepressed by admixture of an authentic specimen of phthalide. (Phthalide is reported to melt at 73°.)

Reduction of 2-Methyl 3-Acetoxyphthalate (V).—A solution of 2.38 g. (0.01 mole) of 2-methyl 3-acetoxyphthalate (V), m.p. 175–177°, in 50 ml. of dry tetrahydrofuran was reduced at −60° by the slow addition of 12.5 ml. (0.013 mole) of a 1.04 *M* solution of lithium aluminum hydride in ether. The reaction was exothermic and the mixture had to be cooled and the hydride added slowly (over about 30 minutes). After the addition of 2.5 ml. of ethyl acetate the mixture was allowed to warm to room temperature, concentrated *in vacuo*, treated with 20 ml. of 10% sulfuric acid and 20 ml. of water and extracted twice with 20-ml. portions of ether. The combined ether extracts were dried over sodium sulfate, concentrated, and the residue boiled for 1.5 hour with 20 ml. of 20% hydrochloric acid. On cooling a white solid precipitated which weighed 1.00 g. (68%) and melted at 240–245°. Three recrystallizations from water raised the melting point to 252–254°, undepressed by admixture of an authentic sample[20] of 4-hydroxyphthalide (VII), m.p. 255–256°. The two samples had identical infrared spectra. The acetyl derivative of the 4-hydroxyphthalide formed in the above reduction melted at 96–97° and did not depress the melting point of an authentic specimen.[20]

Reduction of 1-Methyl 3-Acetoxyphthalate (IV).—This was carried out as described for the isomer V, starting with 1.12 g. (0.0047 mole) of IV. Only 50 mg. of solid precipitated from the hydrochloric acid solution; this melted over a range (204–218°). Fractional sublimation at 100° (0.05 mm.) gave two compounds. The more volatile one melted at 119–122° and was probably 7-hydroxyphthalide (VI) since its melting point was not depressed by admixture of an authentic sample of VI[20] melting at 135–136.5° and the infrared spectra of the two samples were very similar. Identification cannot, however, be considered as conclusive. The less volatile component melted above 250° and showed a carbonyl band at 5.82 μ but no hydroxyl band in the infrared. It was not identified.

The aqueous solution from which these compounds had precipitated was extracted twice with 15 ml. portions of ether which after drying and concentration yielded 0.42 g. (49%) of impure 3-hydroxyphthalic acid, converted to the anhydride, m.p. 188–192°, by sublimation. The anhydride was identified by mixture melting point and infrared spectrum. The presence of 3-hydroxyphthalyl alcohol was suspected by analogy with the case of the half-esters of 3-chlorophthalic acid,[5] but the compound was not isolated, perhaps due to its water solubility.

Reaction of the Methyl 3-Acetoxyphthalates with *p*-Toluidine.—A solution of 1.19 g. (0.005 mole) of the ester and 0.85 g. of *p*-toluidine in 1 ml. of pyridine was allowed to stand for one hour. Water (10 ml.) was then added and the precipitated solid collected after chilling.

In the case of the low-melting half-ester IV, an exothermic reaction ensued and there was obtained 0.62 g. (83%) of aceto-*p*-toluide melting at 144–146°, undepressed by admixture of an authentic sample. In contrast, the high-melting half-ester V did not produce an exothermic reaction and led only to the recovery of 0.80 g. (94%) of unchanged *p*-toluidine melting at 42–43°.

Azlactone Tests.[6]—These tests were performed as described for aspirin.[6] The 1-methyl 3-acetoxyphthalate (IV) gave an intense blue color whereas the 2-methyl isomer V gave only a faint blue color, even on prolonged standing.

NOTRE DAME, INDIANA

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[20] E. L. Eliel, D. E. Rivard and A. W. Burgstahler, *J. Org. Chem.*, **18**, 1679 (1953).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

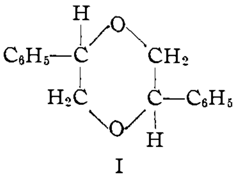
The Structure of Styrene Oxide Dimers.[1] II. Chemical Evidence

BY R. K. SUMMERBELL AND M. J. KLAND-ENGLISH

RECEIVED MAY 5, 1955

Polymerization of styrene oxide with acid catalysts results in a mixture, the dimer fraction of which yields three compounds: *cis*- and *trans*-2,5-diphenyl-1,4-dioxane (1), previously prepared by the reaction of 2,5-dichloro-1,4-dioxane with phenylmagnesium bromide, and the cyclic acetal, 2-benzyl-4-phenyl-1,3-dioxolane (II).

In the previous paper,[2] the reaction of 2,5-dichloro-1,4-dioxane with phenylmagnesium bromide to give two isomeric 2,5-diphenyl-1,4-dioxanes (I) was described. However, the proof of structure of the products was not entirely satisfactory, since ether cleavage experiments gave phenylethylene glycol in yields too low to exclude the possibility of an acetal II or ketal III structure. Also, hydrogenation experiments of Baker[3] and co-workers on the isomers I failed to give the anticipated high yields of 2-phenylethanol, and three moles of hydrogen rather than two were absorbed. If the reaction were halted when only two moles of hydrogen had been absorbed, one-third of the unchanged starting material was recovered. This behavior is anomalous if the compounds in question do have the assumed dioxane structures. Recently, Stumpf[4] has briefly described similar hydrogenation experiments in which high yields of the expected alcohol were obtained, but no details are given as to hydrogen uptake.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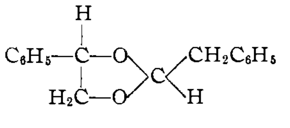
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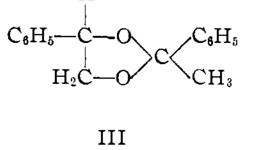
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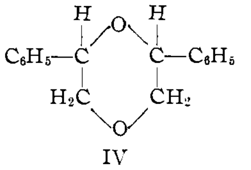
IV

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[1] Abstracted from the Ph.D. thesis of Mathilde J. Kland-English, Northwestern University, 1948.

[2] L. A. Bryan, W. M. Smedley and R. K. Summerbell, THIS JOURNAL, **72**, 2206 (1950).

[3] R. H. Baker, K. Cornell and M. Cron, *ibid.*, **70**, 1490 (1948).

[4] W. Stumpf, *Z. Elektrochem.*, **57**, 690 (1953).