$PbCl_6$, by addition of ammonium chloride. This salt, when treated with concentrated sulfuric acid at 0°, separated out lead tetrachloride as a dense oily, yellow liquid, which was purified by washing with concentrated sulfuric acid. The liquid was kept at 0° while the Raman spectrum was being taken.

Germanium tetrachloride was made by boiling germanium dioxide with concentrated hydrochloric acid in a stream of hydrogen chloride gas.[8] The escaping hydrogen chloride gas carried the germanium tetrachloride through a water condenser into an acetone–Dry Ice-bath where germanium tetrachloride was frozen out of the gaseous mixture. The product was purified by distillation and treatment with sodium carbonate.

Discussion

Considerable difficulty was encountered in locating the Raman frequencies ν_2 and ν_4 in the case of lead tetrachloride since they lay close to the exciting line and were obscured by the background from it. Plate tracings showed a peak at 90 cm.$^{-1}$, but on only one plate were two separate lines resolved, these appearing at 85 cm.$^{-1}$ and 93 cm.$^{-1}$. The latter values are inclosed in brackets in Table I. The frequencies obtained for lead tetrachloride are in satisfactory agreement with those which would have been predicted by extrapolating the curves in Fig. 1.

TABLE I

RAMAN FREQUENCIES OF GERMANIUM TETRACHLORIDE

Investigator	ν_1	ν_2	ν_3	ν_4
Haun and Harkins[8]	397(10)	132(6)	451(1) or 508	171(6)
Schneider[9]	396	134	453	172
The authors	397(10) P	132(2) D	452(1) D	171(3) D

RAMAN FREQUENCIES OF LEAD TETRACHLORIDE

The authors	327(10) P	90(3) D [or 85]	348(3) D	90(3) D [or 93]

The Raman shifts obtained for germanium tetrachloride were found to be essentially the same as those found by the two previous investigators (Table I). With long overexposure, however, no trace of a line could be found in the region between 500 cm.$^{-1}$ and 600 cm.$^{-1}$, so it was concluded that the value of 452 cm.$^{-1}$ for ν_3 was the correct one rather than the possible alternate value listed by Haun and Harkins. The deviation of ν_3 may be explained by consideration of the masses of the atoms involved. ν_1 (A_1) and ν_2 (E) represent, respectively, a "breathing" and a bending frequency. Both are independent of the mass of the central atom, while $\nu_3(F_2)$ and $\nu_4(F_2)$ represent vibrations in which the central atom as well as the chlorine atoms are displaced. It would, therefore, be expected that the deviations in the latter two frequencies might occur, as shown by the ν_3 frequency of germanium tetrachloride. In an attempt to eliminate the effect of the mass of the central atom, force constants calculated by the method of Rosenthal[10] rather than frequencies were plotted against the central atom–chlorine distance as shown in Fig. 2. It will be noted that in this plot the germanium tetrachloride shows no marked deviations.

A more complete discussion of the correlation of the Raman spectra with metal–halogen distance is given by Hildebrand.[2]

Summary

For germanium tetrachloride, the correct value of ν_3 is 452 cm.$^{-1}$, and the deviation from the value predicted by plotting the metal–halide distance against Raman shift may be explained by consideration of the mass of the germanium atom. The Raman frequencies of lead tetrachloride are essentially what would have been predicted.

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(8) Foster, Drennan and Williston, THIS JOURNAL, **64**, 3042 (1942).

(9) K. W. F. Kohlrausch, "Der Smekal-Raman-Effect, Erganzungsband," 1931–1937, J. Springer, Berlin, 1938.

(10) J. E. Rosenthal, *Phys. Rev.*, **45**, 538 (1934); **46**, 730 (1934).

BERKELEY 4, CALIFORNIA RECEIVED JUNE 5, 1948

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT, MONSANTO CHEMICAL CO.]

Synthesis of Aromatic Phosphonic Acids and their Derivatives. II. Some Halobenzene Derivatives

BY GENNADY M. KOSOLAPOFF

Since the scientific literature contains the syntheses of only the *p*-chloro- and the *p*-bromo-benzenephosphonic acids,[1] it was felt advisable to prepare the possible isomers of halo-benzenephosphonic acids containing the principal halogens. This paper describes the syntheses of the *m*- and the *p*-isomers of the chloro-, bromo- and iodobenzenephosphonic acids, and includes the preparation of the related (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid.

The *p*-chloro derivative was prepared in the manner already described[2] and was used for the preparation of phosphanilic acid according to Bauer,[3] which was readily converted into the *p*-iodo-acid by the diazo-reaction. The preparation of the *p*-bromo-acid was conducted by our modified Michaelis reaction,[2] in the course of which it was found that considerable debromination took place, apparently through the action of the aluminum chloride catalyst.

The *m*-isomers were prepared from benzene-

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(1) Michaelis, *Ann.*, **293**, 193 (1896).

(2) Kosolapoff, THIS JOURNAL, **69**, 2020 (1947).

(3) Bauer, *ibid.*, **63**, 2137 (1941).

TABLE I

Compound	M. p., °C.	Analyses, %					
		Found			Calcd.		
		P	Hal	N	P	Hal	N
p-$ClC_6H_4PO_3H_2$	187–188	[1,2]					
p-$BrC_6H_4PO_3H_2$	198–199	[1]					
p-$IC_6H_4PO_3H_2$	228–229		44.5		10.9	44.8	
m-$ClC_6H_4PO_3H_2$	136–137		18.0		16.1	18.4	
m-$BrC_6H_4PO_3H_2$	152–153		33.1		13.1	33.8	
m-$IC_6H_4PO_3H_2$	182–183		44.3		10.9	44.8	
p,p'-$(NH_2C_6H_4)_2PO_2H$	216–218	11.74		11.0	12.5		11.3
p,p'-$(NH_2C_6H_4)(ClC_6H_4)PO_2H$	Dec. 196	11.1	12.9	5.2	11.6	13.3	5.25

phosphonic acid, which was nitrated in the *m*-position by a modified Nijk procedure,[4] the nitro-acid was reduced to the *m*-amino derivative by means of sodium sulfide and the latter was converted to the halo derivatives by diazotization.

bis-*p*-Chlorobenzene-phosphinic acid was aminated to yield a mixture of (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid and bis-(*p*-aminobenzene)-phosphinic acid.

Experimental Part

The properties of the products are summarized below.

p-**Bromobenzenephosphonic Acid.**—Bromobenzene (157 g., 1.0 mole), phosphorus trichloride (274 g., 2.0 moles) and aluminum chloride (133 g., 1.0 mole) were refluxed for eight hours with exclusion of moisture. The reaction mixture was converted to the phosphonic ester mixture,[2] in the course of which operation the evolution of much hydrogen bromide was noted. Distillation gave 17% of diethyl benzenephosphonate (b. p. 104–105° at 0.5 mm.) and 21% diethyl *p*-bromobenzenephosphonate, b. p. 126–128° at 0.5 mm., $n^{25}D$ 1.5188. Hydrolysis by refluxing for eight hours with 250 cc. of concentrated hydrochloric acid gave 93% *p*-bromobenzenephosphonic acid, which separated on cooling.

p-**Iodobenzenephosphonic Acid.**—Phosphanilic acid (5 g.) was dissolved in 75 cc. of 1:1 hydrochloric acid, diazotized at 0–5° by a solution of 2 g. of sodium nitrite, and treated with 6 g. of potassium iodide in 30 cc. of water. When the reaction subsided, the mixture was heated to 95° for thirty minutes, decolorized with sodium bisulfite and concentrated to 50 cc. On cooling, there was obtained 3.5 g. of crude *p*-iodobenzenephosphonic acid, which was dissolved in 100 cc. of boiling water, filtered, treated with 25 cc. of concentrated hydrochloric acid and concentrated to 50 cc. On cooling, the pure product separated in thin shiny plates in 36.5% yield (3.0 g.).

m-**Aminobenzenephosphonic Acid.**—Benzenephosphonic acid[2] (50 g.) was added in the course of fifteen minutes to 280 cc. of fuming nitric acid (d. 1.51) at 0–5° with vigorous stirring. After stirring for an additional forty minutes, the solution was poured on 500 g. of ice and the resulting solution was distilled with steam at constant volume until 1.5 liters of distillate was collected. The residual solution was evaporated to dryness under reduced pressure (water pump). The crude *m*-nitro acid was dissolved in 300 cc. water and was brought to *p*H 9 by addition of sodium hydroxide. The solution was treated with 160 g. sodium sulfide in 350 cc. of water and was heated to gentle reflux for two hours. The dark solution was cautiously acidified with concentrated hydrochloric acid, cooled, filtered, concentrated to 400 cc. and was carefully treated with 20% sodium hydroxide solution until just acid to congo red. The cooled solution was filtered to yield 30–35 g. (55–64%) of *m*-aminobenzenephosphonic acid in the form of greyish microcrystalline powder. After thorough washing with cold water and alcohol the product decomposed at 290° (Nijk[4] reports dec. 280°).

m-**Chlorobenzenephosphonic Acid.**—*m*-Aminobenzenephosphonic acid (5 g.) in 50 cc. of 1:1 hydrochloric acid was diazotized at 0–5° with 2 g. of sodium nitrite and the solution was treated with 5.7 g. of cuprous chloride in concentrated hydrochloric acid. When the reaction subsided, the mixture was heated to 95° for thirty minutes, and after dilution to 150 cc., the solution was treated with hydrogen sulfide to remove the bulk of copper. The filtered solution was concentrated to incipient crystallization, cooled and filtered. The crude product, after washing with 5 cc. of cold hydrochloric acid, was recrystallized from 1:1 hydrochloric acid, when it was isolated in the form of colorless fine needles; yield, 2.5 g. (45%).

m-**Bromobenzenephosphonic Acid.**—The diazonium solution of 5 g. of *m*-aminobenzenephosphonic acid was prepared as above in 100 cc. of 30% hydrobromic acid and was treated with a solution of 3 g. of cupric sulfate pentahydrate, 2.5 g. of sodium bromide and 1.6 g. of copper turnings in 50 cc. of 40% hydrobromic acid. The mixture was worked up as above to yield 4.5 g. (66%) of *p*-bromobenzenephosphonic acid, which formed large thin colorless plates.

m-**Iodobenzenephosphonic Acid.**—The procedure was identical to that used for the *p*-isomer; yield, 3.4 g. (42%).

bis-(*p*-Aminobenzene)-phosphinic Acid and (*p*-Aminobenzene)-(*p*-chlorobenzene)-phosphinic Acid.—Chlorobenzene (675 g., 6 moles), phosphorus trichloride (1375 g., 10 moles) and aluminum chloride (400 g., 3 moles) were heated to gentle reflux for seventy-two hours. The mixture was worked up as described earlier[2] to yield 490 g. (52%) of crude ethyl bis-*p*-chlorobenzenephosphinate, b. p. 166–178° at 0.2–0.4 mm. This gave, upon crystallization from hexane, 368 g. (39%) of the pure ester, which melted at 75–77°. The ester (88 g.) was refluxed overnight with 250 cc. of concentrated hydrochloric acid, cooled and the aqueous solution was decanted from the precipitated acid. The latter was dissolved in 150 cc. of concentrated ammonium hydroxide, the solution was made up to one liter with concentrated ammonium hydroxide, treated with cuprous oxide from 1.2 moles of cupric sulfate pentahydrate and charged into a hydrogenation bomb liner. The mixture was heated to 150° for six hours. The cooled reaction mixture was diluted to two liters with water and was treated with a warm solution of 288 g. of sodium sulfide hydrate in 400 cc. of water. After filtration, the clear solution was concentrated to 400 cc. and made just acid to congo red by means of 1:1 hydrochloric acid. The crude acid mixture was filtered off, dissolved in the least amount of 1:1 hydrochloric acid, treated with charcoal, filtered and cautiously treated with 20% sodium hydroxide until just acid to congo red. The sandy microcrystalline precipitate of (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid was filtered off and washed with cold water and alcohol; yield, 11.0 g. (15%).

The filtrate from the above was treated further with 20% sodium hydroxide until just acid to Alkacid paper (*p*H 5-5.5). The microcrystalline precipitate of bis-(*p*-aminobenzene)-phosphinic acid was filtered off and washed with cold water and alcohol; yield, 33 g. (49%).

Summary

The preparation of *m*- and *p*-isomers of chloro-,

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[4] Nijk, *Rec. trav. chim.*, **41**, 461 (1922).

bromo- and iodo-benzenephosphonic acids is described and the syntheses of the related bis-(*p*-aminobenzene)-phosphinic acid and (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid are presented.

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[CONTRIBUTION FROM GENERAL MILLS, INC.]

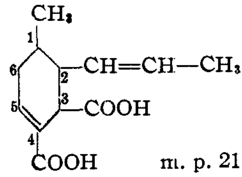
The Dimers of Methyl Sorbate

BY D. H. WHEELER

The structure of the dimer of methyl sorbate, the simplest of the conjugated diene esters, has been of interest as a model whereby structures of some probability might be assigned to the dimers formed during the thermal polymerization of drying oils and the simpler esters of the corresponding acids.

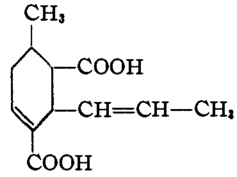
Farmer and Morrison-Jones[1] obtained dimers of methyl sorbate in 81% yield by heating the monomer at 180–230° for about three hours. By an elaborate fractionation they separated the crude dimer ester into fraction A ($n^{18}D$ 1.47720 to 1.47870) and fraction B ($n^{18}D > 1.4900$), estimating the percentages of A and B to be 13 and 12%, respectively, of the total dimer. By saponification of A they obtained acids from which, by fractional crystallization, they isolated four different crystalline disorbic acids. One of these acids, m. p. 216°, isolated in 2–4.5% yield (0.3 to 0.6% of total dimer), was definitely shown to have structure I, 1-methyl-2-propenyl-4-cyclohexene-3,4-dicarboxylic acid. A second acid, m. p. 191°, isolated in a similarly small yield, was shown to have structure II, 1-methyl-3-propenyl-4-cyclohexene-2,4-dicarboxylic acid. A third acid, m. p. 200°, apparently was a *cis–trans* isomer of II, and a fourth acid, m. p. 164–169°, was not characterized. They could isolate no crystalline dimeric acid from mixture B, except traces of the same acids as from A and B was not investigated further.

As was pointed out by these workers, the structures shown for these acids differ from those expected as a result of the usual Diels–Alder reaction in that the ring double bond is α-β or conjugated to the carboxy group rather than β-γ to it. Thus, the normal structure instead of I would be III, 1-methyl-2-propenyl-5-cyclohexene-3,4-dicarboxylic acid, and the normal structure instead of II would be IV, 1-methyl-3-propenyl-5-cyclohexene-2,4-dicarboxylic acid.

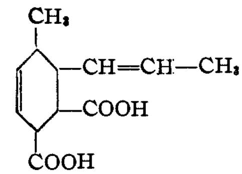


m. p. 216°

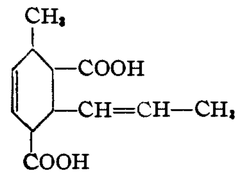
I



II



III



IV

These authors did not definitely comment upon the stage at which the shift of the double bond occurred, but they apparently believed that the esters had the same structure as the acids from which they were derived. Bradley[2] has suggested that the dimeric methyl esters had the normal structure, and that the β-γ to α-β shift of the double bond occurred during the alkaline saponification of the ester.

The present work indicates that the esters composing mixture A have the normal structure, and that mixture B is composed largely of dimers with a double bond in the α-β position to a carbomethoxy group. The conjugated acids isolated by the English workers from mixture A of the esters must therefore have been formed by a β-γ to α-β shift of the cyclic double bond during the alkaline saponification. These conclusions are based largely on considerations of the ultraviolet absorption characteristics of the dimeric methyl esters, and of the acids obtained from them by alkaline saponification.

Iodine values of the esters and acids were in accord with the indicated structures, but molecular refractions of the conjugated forms did not show as much exaltation as was expected.

The high yield of crude dimeric methyl esters reported by Farmer was confirmed. However, a single efficient fractional distillation afforded 43% of dimeric ester A, and 32.5% of dimeric ester B, corresponding in n_D to the fractions separated by Farmer in 13% and 12% yield, respectively. The boiling point of fraction B was 16–18° above that of fraction A. Refractionation of A afforded 47% of a lower boiling fraction, A-1, with a lower n_D and 27% of a higher boiling fraction, A-2, with a higher n_D. Fraction A-2, when crystallized from petroleum ether at −40°, yielded 25% of a crystalline dimeric ester, A-2-p, m. p. 64.5–65.5°. No crystalline methyl ester could be isolated from A-1 or B by similar treatment. Alkaline saponification of A-2-p afforded the dimer of sorbic acid m.

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(1) Farmer and Morrison-Jones, *J. Chem. Soc.*, 1339–1346 (1940).

(2) Bradley, Symposium on Vegetable Drying Oils, Univ. of Minnesota, March 28, 1947.