[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, COMMUNICABLE DISEASE CENTER, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

The Preparation of Some Carboxynitrophenylphosphonic Acids and Related Compounds

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The preparation of eight of the ten possible isomeric carboxynitrophenylphosphonic acids is described. The compounds were prepared by oxidation of nitrotolylphosphonic acids, by nitration of carboxyphenylphosphonic acids, or from the diazonium fluoborate.

The *in vitro* antitreponemal activity of several substituted arylphosphonic and diarylphosphinic acids has been described.[1] In the course of further screening, it was found that 2-carboxy-5-nitrophenylphosphonic acid was considerably more active than any phosphonic acid previously tested. This result prompted us to investigate other carboxynitro-substituted compounds. The present paper describes the preparation of eight of the ten possible isomeric carboxynitrophenylphosphonic acids as well as a number of related acids. The compounds prepared, together with their analyses, yields and melting points, are listed in Tables I and II. The chemotherapeutic results will be reported elsewhere.

p-tolylphosphonic acids were readily oxidized when eight moles of potassium permanganate were used per mole of tolyl compound. Larger amounts of permanganate were needed, however, for the complete oxidation of the methyl group in the nitro-*o*-tolylphosphonic acids. Thus, one mole of 4-nitro-2-tolylphosphonic acid required about fourteen moles of permanganate, and 5-nitro-2-tolylphosphonic acid required about eleven moles; if smaller amounts of oxidizing agent were used, it was possible to isolate starting material from the reaction mixture. In all the oxidations studied a side reaction occurred which resulted in the formation of significant amounts of inorganic phosphate. This was demonstrated by the precipitate of magnesium ammonium phosphate obtained when magnesia mixture was added to an aliquot of the cold reaction mixture after the manganese dioxide had been removed. The magnesium ammonium phosphate was reprecipitated and finally weighed as magnesium pyrophosphate. The results obtained in this manner indicated that the amount of inorganic phosphate formed depended on the starting material and the reaction conditions; as little as 2% to as much as 40% of the phosphorus was converted to phosphate during the course of the permanganate oxidation. No information was obtained concerning the mechanism of the conversion of the arylphosphonic acid into inorganic phosphate.

TABLE I

NITROTOLYLPHOSPHONIC AND PHOSPHINIC ACIDS

Compound	Yield, %	M.P.	P		N		Neut. Equiv.	
			Calcd.	Found	Calcd.	Found	Found	Calcd.
$2\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3PO_3H_2$	44	225–228	14.27	14.19	6.45	6.48	108.6	108.8
$2\text{-}CH_3\text{-}5\text{-}O_2NC_6H_3PO_3H_2$[a]	55	222–225	14.27	14.28	6.45	6.32	108.6	109.2
$3\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3PO_3H_2$	42	173–176	14.27	14.00	6.45	6.35	108.6	108.6
$5\text{-}CH_3\text{-}2\text{-}O_2NC_6H_3PO_3H_2$	100	128–146	14.27	14.03	6.45	6.31	108.6	108.0
$4\text{-}CH_3\text{-}3\text{-}O_2NC_6H_3PO_3H_2$[b]	100	156–158	14.27	14.11	6.45	6.34	108.6	109.3
$(2\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3)_2PO_2H$	3	228–229	9.21	9.41	8.33	8.27	336.2	339.6
$(2\text{-}CH_3\text{-}5\text{-}O_2NC_6H_3)_2PO_2H$	7	243–245	9.21	9.17	8.33	8.20	336.2	335.1
$(3\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3)_2PO_2H$	1	240–250	9.21	9.29	8.33	8.05	336.2	331.6
$(4\text{-}CH_3\text{-}3\text{-}O_2NC_6H_3)_2PO_2H$[c]	70	235–237.5	9.21	9.21	8.33	8.13	336.2	336.8

[a] Previously prepared by A. Michaelis, ref. 6, by the nitration of *o*-tolylphosphonic acid; m.p. 174°. [b] Previously prepared by A. Michaelis, ref. 6; m.p. 191°. [c] Prepared by nitration of di-*p*-tolylphosphinic acid with fuming nitric acid at 30–35°; recrystallized from aqueous alcohol. Previously reported by A. Michaelis, *Ann.*, **315**, 43 (1901); m.p. 194°.

Five of the carboxynitrophenylphosphonic acids[2] were prepared from the corresponding nitrotolylphosphonic acids by means of the convenient pyridine-permanganate oxidation procedure described by Morgan and Herr.[3] The nitro-*m*-tolyl- and nitro-

(1) J. D. Thayer, H. J. Magnuson, and M. S. Gravatt, *Antibiotics and Chemotherapy*, **3**, 256 (1953); G. O. Doak, L. D. Freedman, J. W. Clark, Jr., and E. L. Petit, *Antibiotics and Chemotherapy*, **8**, 342 (1958).

(2) *Viz.*, 2-carboxy-4-nitro-, 2-carboxy-5-nitro-, 3-carboxy-4-nitro-, 5-carboxy-2-nitro-, and 4-carboxy-3-nitrophenylphosphonic acids.

(3) P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 5264 (1952).

TABLE II

CARBOXYNITROPHENYLPHOSPHONIC AND PHOSPHINIC ACIDS

Compound	Yield, %	M.P.	P		N		Neut. Equiv.	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
$2\text{-}HO_2C\text{-}3\text{-}O_2NC_6H_3PO_3H_2\cdot H_2O$[a]	24	204–215 dec.	11.68	11.30	5.28	5.25	88.4	[b]
$2\text{-}HO_2C\text{-}4\text{-}O_2NC_6H_3PO_3H_2$[c]	35	192–194	12.54	12.35	5.67	5.65	82.4	[b]
$2\text{-}HO_2C\text{-}5\text{-}O_2NC_6H_3PO_3H_2\cdot H_2O$[d]	55	192–194	11.68	11.39	5.28	5.20	88.4	[b]
$3\text{-}HO_2C\text{-}4\text{-}O_2NC_6H_3PO_3H_2$	51	190–206 dec.	12.54	12.17	5.67	5.58	82.4	82.3
$3\text{-}HO_2C\text{-}5\text{-}O_2NC_6H_3PO_3H_2$[e]	79	230.5–233	12.54	12.31	5.67	5.46	82.4	82.2
$5\text{-}HO_2C\text{-}2\text{-}O_2NC_6H_3PO_3H_2$[e]	14	208–218 dec.	12.54	12.35	5.67	5.62	82.4	82.9
$4\text{-}HO_2C\text{-}2\text{-}O_2NC_6H_3PO_3H_2\cdot H_2O$[e]	16[f]	228–238 dec.	11.68	11.64	5.28	5.19	88.4	88.0
$4\text{-}HO_2C\text{-}3\text{-}O_2NC_6H_3PO_3H_2$	67	213–217.5	12.54	12.42	5.67	5.60	82.4	83.5
$2\text{-}(HO_2C\text{-}5\text{-}O_2NC_6H_3)_2PO_2H$[e]	37	292–296	7.82	7.66	7.07	7.06	132.1	134.4

[a] Calcd.: H_2O, 6.80. Found: weight loss at 100°, 6.27. [b] When the neutral equivalent was determined with thymolphthalein in the usual manner, the results were higher than theoretical and not closely reproducible. This fact suggests that the third dissociation constant is abnormally low; *cf.* H. H. Jaffé, L. D. Freedman, and G. O. Doak, *J. Am. Chem. Soc.*, **76**, 1548 (1954). [c] Dried *in vacuo* at 100° before analysis. [d] Calcd.: H_2O, 6.80. Found: weight loss at 100°, 6.73. [e] Calcd.: H_2O, 6.80. Found: weight loss at 100°, 6.69. [f] Based on *p*-carboxyphenylphosphonic acid.

Three of the nitrotolylphosphonic acids (*viz.*, 4-nitro-2-tolyl-, 5-nitro-2-tolyl-, and 4-nitro-3-tolylphosphonic acids) required for the syntheses described above were prepared from the corresponding diazonium fluoborates. The other two nitrotolylphosphonic acids were prepared by nitration of *m*-tolyl- and *p*-tolylphosphonic acids. The structure of the nitro-*m*-tolylphosphonic acid obtained was not established unequivocally, but it is probably 2-nitro-5-tolylphosphonic acid for the following reasons: (1) The compound does not form a water-insoluble magnesium salt either at room temperature or when heated. This behavior is characteristic of arylphosphonic acids containing bulky *o*-substituents such as the nitro group.[4] (2) The ultraviolet absorption spectrum (*cf.* Table III) resembles that of *o*-nitrophenylphosphonic acid and is much less intense than that of *m*- or *p*-nitrophenylphosphonic acid. Except for a slight bathochromic shift, a methyl group not adjacent to a nitro group produces little change in the first primary absorption band[5a] of an aromatic nitro compound; a methyl group *ortho* to a nitro group causes a decrease in intensity and a hypsochromic shift.[5b] The spectra given in Table III are consistent with these generalizations. (3) It has been shown[6] that chlorination of *m*-tolylphosphonic acid yields 2-chloro-5-tolylphosphonic acid and that bromination yields the corresponding bromo compound. It seems reasonable to assume that nitration, which is also an electrophilic substitution reaction, gives 2-nitro-5-tolylphosphonic acid.

The nitration of *p*-tolylphosphonic acid has been previously reported.[6] It has been generally assumed that the product is 3-nitro-4-tolylphosphonic acid. This assumption is, of course, very reasonable since the phosphono group is *meta*-directing.[7] Our observations are consistent with this formulation, for we have found that the nitrated material appears homogenous and, when heated with magnesia mixture, gives a 93% yield of insoluble magnesium salt.

TABLE III

ULTRAVIOLET ABSORPTION MAXIMA[a]

Compound	First Primary Band		Second Primary Band	
	λ_{max}, mμ	ϵ_{max}	λ_{max}, mμ	ϵ_{max}
$o\text{-}O_2NC_6H_4PO_3H_2$[b]	251	3,740	208	12,400
$5\text{-}CH_3\text{-}2\text{-}O_2NC_6H_3PO_3H_2$	264	3,390	208	13,100
$m\text{-}O_2NC_6H_4PO_3H_2$[c]	263	6,400	210	15,900
$2\text{-}CH_3\text{-}5\text{-}O_2NC_6H_3PO_3H_2$	278	9,700	210	16,200
$4\text{-}CH_3\text{-}3\text{-}O_2NC_6H_3PO_3H_2$	257	5,130	214	18,200
$p\text{-}O_2NC_6H_4PO_3H_2$[c]	270	10,400	213	5,950
$2\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3PO_3H_2$	271	10,900	207	13,880
$3\text{-}CH_3\text{-}4\text{-}O_2NC_6H_3PO_3H_2$	261	6,980	207	12,900

[a] All spectra were determined in 95% ethyl alcohol. [b] The spectrum of this compound is described in ref. 4, but the band at 208 mμ was not previously noted. [c] Taken from H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952). The band at 210 mμ for *m*-nitrophenylphosphonic acid was not previously noted.

Several attempts to prepare 2-nitro-4-tolylphosphonic acid (which we planned to oxidize to the carboxy compound) from the corresponding diazonium fluoborate were unsuccessful. Although a small amount of a phosphonic acid was isolated in each case, this material was devoid of nitrogen. The analytical data suggest that the unknown substance may be a dichlorotolylphosphonic acid. It appears that the behavior of 2-nitro-4-toluenediazonium fluoborate is similar to that previously observed with the *o*-nitrobenzenediazonium salt.[8]

(4) L. D. Freedman and G. O. Doak, *J. Am. Chem. Soc.*, **77**, 6221 (1955).

(5) (a) L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947); (b) W. G. Brown and H. Reagan, *J. Am. Chem. Soc.*, **69**, 1032 (1947).

(6) A. Michaelis, *Ann.*, **293**, 193 (1896).

(7) A. E. Goddard in J. N. Friend, *A Textbook of Inorganic Chemistry*, Vol. XI, Part III, Charles Griffin and Co., Ltd., London, 1936, p. 100.

Nitration of *m*-carboxyphenylphosphonic acid with anhydrous nitric acid gave a satisfactory yield of a mononitrated compound. The structure of this material was not proven, but it almost certainly is 3-carboxy-5-nitrophenylphosphonic acid since both the carboxy and phosphono groups are *meta*-directing. Nitration of *p*-carboxyphenylphosphonic acid under similar conditions yielded a mixture of 4-carboxy-2-nitro- and 4-carboxy-3-nitrophenylphosphonic acids. The mixture could not be separated into pure compounds by fractional recrystallization from 9*N* hydrochloric acid. Moreover, the magnesium salt technique[9] could not be employed in the usual way since neither isomer forms an insoluble magnesium salt. However, when the mixture was esterified to yield the carbethoxynitrophenylphosphonic acids, the 3,4- isomer could be precipitated by heating in the presence of magnesium ion. The 2,4- isomer left in solution was then isolated by a procedure similar to that used for *o*-nitrophenylphosphonic acid.[4]

2-Carboxy-3-nitrophenylphosphonic acid was prepared in moderate yield from the corresponding diazonium fluoborate. No convenient syntheses of 2-carboxy-6-nitro or 3-carboxy-2-nitrophenylphosphonic acid could be devised.

All of the carboxynitrophenylphosphonic acids were exceedingly soluble in water, and in general were difficult to isolate and purify. They were less soluble in hydrochloric acid, which was frequently used for recrystallization. The melting points were neither sharp nor closely reproducible, and in some cases melting was accompanied by obvious decomposition. Attempts to dephosphonate several of the compounds by heating at 240° yielded only black, insoluble solids. This is in sharp contrast to the behavior of many arylphosphonic acids which on heating are cleanly dephosphonated according to the equation[10]:

$$RPO_3H_2 \xrightarrow{240^\circ} RH + HPO_3$$

EXPERIMENTAL[11]

4-Nitro-2-tolylphosphonic acid and bis(4-nitro-2-tolyl)phosphinic acid. 2-Methyl-4-nitrobenzenediazonium fluoborate[12] was suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide in the usual manner.[8a] After steam distillation the residual liquid was cooled to 25° whereupon the phosphinic acid crystallized. It was washed several times with boiling water and purified by reprecipitation from sodium bicarbonate solution and subsequent recrystallization from 95% ethanol.

4-Nitro-2-tolylphosphonic acid was isolated and purified by procedure A as previously described.[8a]

5-Nitro-2-tolylphosphonic acid and bis(5-nitro-2-tolyl)phosphinic acid were prepared by the method described above. The phosphinic acid was isolated and purified by the procedure described for bis(*p*-bromophenyl)phosphinic acid.[13]

4-Nitro-3-tolylphosphonic acid and bis(4-nitro-3-tolyl)phosphinic acid were prepared from 3-methyl-4-nitroaniline[14] by the procedure described above. After the steam distillation, the residual liquid was filtered hot. The crude phosphinic acid, which remained on the filter paper, was purified by reprecipitation from sodium carbonate solution and subsequent recrystallization from 95% ethanol.

2-Nitro-5-tolylphosphonic and 3-nitro-4-tolylphosphonic acids. These compounds were prepared by nitrating the appropriate tolylphosphonic acid by the procedure previously used for the nitration of phenylphosphonic acid.[4] Both compounds were extremely soluble in water, aqueous acids, alcohol, ether, and dioxane. The wide melting point range of 2-nitro-5-tolylphosphonic acid indicates that it is slightly impure, but no suitable recrystallizing solvent could be found. By contrast, 3-nitro-4-tolylphosphonic acid melted rather sharply. This compound could be recrystallized from 6*N* hydrochloric acid, but this did not appreciably effect its melting point or ultraviolet absorption.

2-Carboxy-4-nitrophenylphosphonic acid. 4-Nitro-2-tolylphosphonic acid (21.7 g.), dissolved in a mixture of 120 ml. of pyridine and 70 ml. of water, was oxidized with potassium permanganate. After steam distillation to remove pyridine, the reaction mixture was filtered, stirred for 30 min. with 1.2 kg. of Dowex-50 (hydrogen ion form), and finally passed through a Dowex-50 column. The resulting solution was evaporated to dryness, and the residue recrystallized from 6*N* hydrochloric acid.

2-Carboxy-5-nitrophenylphosphonic acid. 5-Nitro-2-tolylphosphonic acid (108.6 g.) was oxidized by the procedure described above. After the steam distillation, the reaction mixture was filtered and adjusted to *p*H 0.8 to precipitate the *hemi*-potassium salt of 5-nitro-2-carboxyphenylphosphonic acid. The salt was dissolved in about 7 l. of water, and the potassium ion removed by passing the solution through a Dowex-50 column. The free acid was recovered by evaporating the resulting solution to dryness and was then recrystallized from 3*N* hydrochloric acid.

3-Carboxy-4-nitrophenylphosphonic acid was prepared from 4-nitro-3-tolylphosphonic acid by a procedure similar to that described above for 2-carboxy-4-nitrophenylphosphonic acid. Since less potassium permanganate was used, only 600 g. of Dowex-50 were required per 0.1 mole of starting material. Purification was effected by recrystallization from concentrated hydrochloric acid.

5-Carboxy-2-nitrophenylphosphonic acid. This compound was prepared and isolated by the procedure used for 3-carboxy-4-nitrophenylphosphonic acid. It was purified by recrystallization from 9*N* hydrochloric acid.

4-Carboxy-3-nitrophenylphosphonic acid was obtained by the oxidation of 3-nitro-4-tolylphosphonic acid. The solution obtained after stirring with Dowex-50 was evaporated to incipient crystallization. The crystals obtained on cooling were dissolved in water and passed through a Dowex-50 column. Evaporation of the resulting solution gave 4-car-

(8) (a) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951); (b) L. D. Freedman, H. Tauber, G. O. Doak, and H. J. Magnuson, *J. Am. Chem. Soc.*, **75**, 1379 (1953).

(9) This procedure (described in ref. 4) depends on the fact that most *meta*- and *para*-substituted arylphosphonic acids yield copious precipitates when heated with magnesia mixture but most *ortho*-substituted acids fail to give insoluble magnesium salts. However, a few carboxy-substituted phenylphosphonic acids do not form insoluble salts even in the absence of *ortho* groups, *e.g.*, *m*-carboxy-, 3-carboxy-4-nitro-, 3-carboxy-5-nitro-, and 4-carboxy-3-nitrophenylphosphonic acids.

(10) L. D. Freedman, G. O. Doak, and E. L. Petit, *J. Org. Chem.*, **25**, 140 (1960).

(11) Melting point determinations and analyses were performed as previously described: *cf.* ref. 8.

(12) Prepared by method II A of A. Roe, *Org. Reactions*, 204 (1949).

(13) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **75**, 683 (1953).

(14) A. McGookin and S. R. Swift, *J. Soc. Chem. Ind.*, **58**, 152 (1939).

boxy-3-nitrophenylphosphonic acid, which was purified by dissolution in ether, treatment of this solution with charcoal, and evaporation of the clarified solution.

3-Carboxy-5-nitrophenylphosphonic acid. A solution of 50 g. of *m*-carboxyphenylphosphonic acid in 270 ml. of anhydrous nitric acid (Baker and Adamson) was gently heated for about 3 hr. until approximately two thirds of the nitric acid was distilled. On cooling the reaction mixture to −25°, crystals were obtained which were washed with 8 ml. of cold water and then dried *in vacuo* at 100°.

4-Carboxy-2-nitrophenylphosphonic acid. p-Carboxyphenylphosphonic acid (40.4 g.) was nitrated with 200 ml. of anhydrous nitric acid by the procedure described above for the *meta* isomer. On cooling the reaction mixture, 39.6 g. (80%) of nitrated material, m.p. 191–200°, was obtained.

Anal. Calcd. for $C_7H_6NO_7P$: Neut. equiv., 82.4. Found: Neut. equiv., 83.5.

This material was dissolved in a mixture of 65 ml. of absolute ethanol and 65 ml. of carbon tetrachloride, and the solvents slowly removed by distillation. The residue, which consisted of crude isomeric carbethoxynitrophenylphosphonic acids, was dissolved in 200 ml. of 10% aqueous ammonia and mixed with 640 ml. of 0.27*M* magnesium chloride solution. The resulting solution was boiled for at least 30 min. in order to precipitate the magnesium salt of the 3,4 isomer. The precipitate, after being washed with hot water and dried *in vacuo*, weighed 10.7 g. The filtrate from the magnesium salt was made alkaline (*p*H > 10) with 30 ml. of 20% sodium hydroxide solution, filtered and then aerated to remove ammonia. The resulting solution was stirred for 30 min. with 350 g. of Dowex-50 (which changed the *p*H of the solution to 0.6) and then passed through a Dowex-50 column. The residue obtained by evaporating this solution to dryness was recrystallized from 9*N* hydrochloric acid to yield pure 4-carboxy-2-nitrophenylphosphonic acid. Obviously, the ester was cleaved to the free carboxy group during the course of the separation procedure. Mixed melting point of the pure acid with authentic 4-carboxy-3-nitrophenylphosphonic acid (the preparation of which is described above) was 191–198° with decomposition.

2-Carboxy-3-nitrophenylphosphonic acid. 6-Nitroanthranilic acid[15] (35 g.) was converted to the corresponding diazonium fluoborate in 73% yield. The dried salt was suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide in the usual manner.[8a] After the steam distillation, the residual liquid in the distilling flask was filtered from tarry material, all of which was alkali-insoluble, and the filtrate was evaporated to 125 ml. The crystalline solid obtained on cooling was dissolved in aqueous potassium hydroxide (30%), and the *p*H adjusted to 7.6. The resulting solution was treated with charcoal and then acidified to Congo Red. The precipitate obtained was dried and extracted with ether in a Soxhlet apparatus in order to remove unphosphonated organic acids. The ether insoluble residue was dissolved in warm water and passed through a Dowex-50 column in the hydrogen ion form. The effluent was taken to dryness, and the solid recrystallized from 6*N* hydrochloric acid to yield pure 2-carboxy-3-nitrophenylphosphonic acid. A second crop was obtained by evaporating the original filtrate from 125 ml. to 15 ml. The solid thus obtained was purified in the same manner as the main crop.

Bis(2-carboxy-5-nitrophenyl)phosphinic acid. Bis(5-nitro-2-tolyl)phosphinic acid (16.8 g.), dissolved in a mixture of 75 ml. of pyridine and 75 ml. of water, was oxidized with 125 g. of potassium permanganate. After steam distillation, the reaction mixture was filtered, decolorized with charcoal, and then added slowly, with good stirring, to 150 ml. of 6*N* hydrochloric acid. The phosphinic acid, which separated on cooling, was removed by filtration and recrystallized from 90% aqueous acetone.

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(15) R. Kahn, *Ber.*, **35**, 3857 (1902); see also M. T. Bogert and V. J. Chambers, *J. Am. Chem. Soc.*, **27**, 649 (1905).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF COLORADO]

Stepwise Chlorination of 1,1,2-Trifluoro-2-chloroethyl *n*-Propyl Ether[1]

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The stepwise photochemical chlorination of 1,1,2-trifluoro-2-chloroethyl *n*-propyl ether was carried out and the products were isolated and identified.

Previous papers,[2-4] described the methods for the preparation of several fluoroalkyl ethers and of their chlorinated derivatives.

The present paper reports a study of the stepwise photochemical chlorination of 1,1,2-trifluoro-2-chloroethyl *n*-propyl ether in the liquid phase.

The determination of the ratios of the monochlorinated product shows the following weight ratios of the isomers.

$$\text{II:III:IV} = 1.6:1.0:1.5$$

It is interesting to note that the chlorination[5] of I or of II, III, and IV individually did not yield a separable entity of the α,α-dichloro isomer (X)

(1) This paper represents parts of a thesis submitted by G. Pavlov to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, June 1958, and parts from the Master's thesis of F. M. Hammock, submitted to the Graduate School, University of Colorado, August 1959, whose current address is U. S. Air Force Academy, Colorado Springs, Colo.

(2) J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *J. Am. Chem. Soc.*, **70**, 1550–52 (1948).

(3) J. D. Park, D. M. Griffin, and J. R. Lacher, *J. Am. Chem. Soc.*, **74**, 2292 (1952).

(4) J. D. Park, Buck Stricklin, and J. R. Lacher, *J. Am. Chem. Soc.*, **76**, 1387 (1954).

(5) J. D. Park, D. R. Wolf, M. Shahab, and J. R. Lacher, *J. Org. Chem.*, **23**, 1474 (1958).