boiling 57–60° (37 mm.) and having an infrared spectrum identical to that of pure methyl methanesulfinate (VII). The methyl chloride collected accounted for 67% of the chlorine in the sulfinyl chloride used and the sulfur dioxide, after oxidation to sulfate ion and precipitation as barium sulfate, corresponded to 87% of the sulfur present in the methyl sulfite.

Reaction of I *with methyl chlorosulfonate.* Methyl chlorosulfonate, $ClSO_3CH_3$ (26.1 g., 0.2 mole), was mixed with 16.5 g. (0.2 mole) of I at low temperature and the mixture was allowed to stand at ice temperature overnight. The next morning the entire reaction mixture had solidified. About 25 ml. of methylene chloride was added, but the solid did not dissolve. The mixture was heated until the solid melted (above 60°) and an attempt was made to distil it at reduced pressure. No recognizable product was obtained and the experiment was discontinued because the results indicated that methyl chlorosulfonate was not an intermediate product in the reaction under investigation.

Attempted reaction of I *with methyl chlorosulfinate.* To 33 g. (0.4 mole) of I, 46 g. (0.4 mole) of methyl chlorosulfinate, $ClSO_2CH_3$, was added at Dry-Ice temperature without evidence of reaction. The mixture was allowed to warm to room temperature and stand for several hours without any diminution of the red color of I and without the evolution of any volatile material into the cold trap. The experiment was discontinued as the failure to decolorize I seemed to indicate that methyl chlorosulfinate was not an intermediate in the reaction between I and methyl sulfite.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, AMOCO CHEMICALS CORP.]

Free-Radical Phosphonation of Aromatic Compounds

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Received September 25, 1961

Free phosphonyl radicals, generated from diethyl phosphite and *t*-butyl peroxide, react with polycyclic aromatic and heterocyclic compounds to give phosphonic acid derivatives in good yields. This novel reaction has been studied with naphthalene, anthracene, phenanthrene, dibenzofuran, and carbazole. Anthracene and phenanthrene give mainly the 9-isomer; the others give isomer mixtures. Ferrocene and pyridine are not phosphonated by this procedure. Diethyl isobutylphosphonate, a by-product of these reactions, is probably formed through an intermediate from diethyl phosphite and *t*-butoxy radical.

Although aromatic reactions of phenyl radicals have been known since 1895,[1] free-radical aromatic substitutions were not recognized until twenty-five years ago.[2] The substituting radical has usually been alkyl, aryl, or acyl.[3] Substitution in the aromatic ring by an inorganic radical, free phosphonyl, has only recently been announced.[4]

This novel reaction may prove useful for synthesis of surface-active agents, pesticides, and plasticizers. Its scope has been explored by treating diethyl phosphite and *t*-butyl peroxide with four aromatic and three heterocyclic compounds. In two cases, pure phosphonic acids were isolated by hydrolysis of their esters; in the others, mixtures of isomers were not separated. A by-product, diethyl isobutylphosphonate, has been noted in these reactions; to shed light on how it formed, diethyl phosphite was treated separately with *t*-butyl peroxide, *t*-butyl alcohol, and isobutylene; in the last two reactions, catalytic amounts of *t*-butyl peroxide were used.

EXPERIMENTAL

Diethyl phosphite was purchased from Virginia-Carolina; *t*-butyl peroxide, *t*-butyl alcohol, isobutylene, the three arenes, dibenzofuran, and carbazole were from Matheson Coleman & Bell or from Eastman. Ferrocene was from Ethyl. The dibenzofuran and ferrocene were recrystallized before use; the other materials were used as purchased.

In all experiments, a slight excess over 0.5 mole of *t*-butyl peroxide was used per mole of aromatic compound. Enough diethyl phosphite—at least equimolar with aromatic—was added to dissolve all the aromatic. To keep reaction temperatures at 130–150°, low-boiling products were allowed to escape by refluxing under a condenser containing stationary water.

Phosphonation of naphthalene. A mixture of 50 g. (0.4 mole) of naphthalene, 51.2 g. (0.4 mole) of diethyl phosphite, and 37.5 ml. (0.2 mole) of *t*-butyl peroxide was refluxed 8 hr. Volatile material was collected in two traps, one cooled with ice and water, one with Dry Ice and acetone. Uncondensed gas was passed into a bulb for analysis by mass spectrometry.

To remove unchanged starting material and partially hydrolyzed products, the reaction mixture was diluted with 200 ml. of ether, washed twice with 500 ml. of cold water, and extracted once with 250 ml. of 5% potassium hydroxide. Evaporation and steam distillation of the ether solution recovered 26 g. of the original naphthalene.

As the residue was neutral, no hydrolysis had occurred during the steam distillation. It was extracted three times with 200-ml. portions of ether; the ether solution was dried over sodium sulfate and evaporated. Distilling the residue *in vacuo* gave an 8-g. viscous, colorless fraction; b.p. 163–172° (0.4 mm.); $n^{20}D$ 1.5671.

Anal. Calcd. for diethyl naphthalenephoshonate, $C_{14}H_{17}PO_3$: C, 63.6; H, 6.4; P, 11.7; mol. wt. 264. Found: C, 63.3; H, 6.1; P, 11.3; mol. wt. 264.

Molecular weight was determined by mass spectrometry. The spectrum showed that small amounts of materials

(1) O. Kühling, *Ber.*, **28**, 41 (1895); E. Bamberger, *ibid.*, **28**, 403 (1895).

(2) D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

(3) O. C. Dermer and M. T. Edmison, *ibid.*, **57**, 77 (1957); D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957).

(4) E. K. Fields and R. J. Rolih, *Chem. and Ind.*, 999 (1960).

with masses 278 and 292 were present. The distillation residue weighed 4 g.; C, 65.3; H, 6.9, P, 10.0; mol. wt. 499.

The potassium hydroxide extract was acidified. A gummy solid precipitated which was taken up in benzene, washed twice with water, and evaporated *in vacuo* at 90°. The product was 12 g. of brittle orange solid, melting over the range 68–90°.

Anal. Calcd. for $C_{12}H_{15}PO_3$: C, 61.0; H, 5.5; P, 13.1. Found: C, 61.9; H, 6.5; P, 11.6.

Although with excess hydrogen and too little phosphorus, this material is probably the monoethyl ester of naphthalenephosphonic acid.

A 3.5-g. portion was hydrolyzed by being refluxed with a mixture of 30 ml. of ethanol and 15 ml. of concd. hydrochloric acid for 12 hr. Evaporation of the clear solution to dryness on the steam bath gave 2.8 g. of a grey solid, which was decolorized by solution in excess sodium bicarbonate and treatment with charcoal. The filtered solution was acidified, and the precipitated acid was stirred at 65° with 50 ml. of concd. hydrochloric acid to remove sodium ion; it was filtered, washed with water, and dried *in vacuo* at 60° to give 3 g. of white solid that softened at 150° and melted at 162° to 187° dec.

Anal. Calcd. for naphthalenephosphonic acid, $C_{10}H_9PO_3$: C, 57.7; H, 4.3; P, 14.9. Found: C, 57.5; H, 5.0; P, 14.6.

Based on analysis by mass spectrometry, the weights, in grams, of the products in the cold traps were: acetone, 3.0; isobutylene, 10.6; ethane, 1.3; isobutane, 0.13; *t*-butyl peroxide, 0.06; unresolved oxygen compounds, 2.8. Of the condensed gas, 88% was methane and 12% was ethane.

Phosphonation of anthracene. A mixture of 53.5 g. (0.3 mole) of anthracene, 170 ml. (1.33 moles) of diethyl phosphite, and 30.1 ml. (0.168 mole) of *t*-butylperoxide was heated at 150° for 40 hr. The mixture was distilled *in vacuo* to remove 120 ml. of diethyl phosphite; b.p. 65–69° (3 mm.). The residue was treated with 200 ml. of water to dissolve excess phosphite and precipitate a mixture of reaction products and unchanged anthracene. The solid was collected on a filter, washed with water, and sucked dry. It weighed 59.4 g. It was hydrolyzed by being refluxed with 500 ml. of ethanol and 150 ml. of concd. hydrochloric acid for 72 hr., then evaporated to dryness on a steam bath Heating the residue with 500 ml. of 5% potassium hydroxide, filtrating, and acidifying the filtrate gave 38.6 g. of a yellow acid; it was collected on a filter, washed with water, and dried. It melted at 279–282°.

A 6.5-g. portion was stirred with a solution of 10 g. of sodium acetate in 100 ml. of water at 70° for 0.5 hr., 1 g. of charcoal was added, the solution was filtered, and the filtrate was acidified. The white acid that precipitated was collected on a filter, washed, and dried in a vacuum oven at 120°. It weighed 6.2 g. and melted at 282–283° dec.

Anal. Calcd. for $C_{14}H_{11}PO_3$: C, 65.1; H, 4.3; P, 12.0. Found: C, 65.4; H, 4.7; P, 11.8.

To prove the structure of the phosphonic acid, a solution containing 1 g. in 50 ml. of 5% potassium hydroxide at 60° was treated with saturated potassium permanganate solution until the purple color persisted. Excess permanganate was destroyed with 2 ml. of ethanol; the solution was filtered, and the manganese dioxide on the filter was extracted with three 100-ml. portions of boiling ethanol. The combined ethanol extracts were concentrated to 20 ml., chilled, and filtered to give 0.62 g. (75%) of yellow anthraquinone melting at 286°; a mixed melting point with authentic anthraquinone was not depressed. The phosphonic acid was therefore anthracene-9-phosphonic acid.

Phosphonation of phenanthrene. A mixture of 35.6 g. (0.2 mole) of phenanthrene, 102.4 ml. (0.8 mole) of diethyl phosphite, and 21 ml. (0.112 mole) of *t*-butyl peroxide was heated at 133–138° for 24 hr. Work-up as for anthracene gave 23.6 g. of crude acid.

A 12.5-g. portion was dissolved in about 50 ml. of hot ethanol; the cooled solution deposited 0.6 g. of solid (m.p. 320–325°, P, 11.3) that was not further investigated.

The ethanol was removed by evaporation, and a viscous oil was obtained. Heating and agitation of the oil in a mixture of boiling benzene and cyclohexane caused it to solidify. Filtration gave 10.9 g. of phenanthrene-9-phosphonic acid; m.p. 227–230° (reported,[5] m.p. 228–230°).

Anal. Calcd. for $C_{14}H_{11}PO_3.H_2O$: P, 11.2. Found: P, 10.9.

Phosphonation of dibenzofuran. A mixture of 67.2 g. (0.4 mole) of dibenzofuran, 205 ml. (1.6 moles) of diethyl phosphite, and 42 ml. (0.24 moles) of *t*-butyl peroxide was heated for 24 hr. at 130–136°. The work-up was much the same as for anthracene. However, after the phosphonic acids were liberated from their salts, the water was decanted from the oily product; the decanted aqueous solution was evaporated, and the residue was extracted with hot absolute ethanol. On being filtered and evaporated, the ethanol solution gave 22 g. of crude diphosphonic acid. Calcd. value for phosphorus content is 18.9; found 20.4. The viscous oil was extracted with acetone, and the extract was evaporated to give 22.6 g. of crude dibenzofuran monophosphonic acid. The crude monophosphonic acid was dissolved in 5% sodium hydroxide, and the solution was acidified to *p*H 6, boiled with charcoal for 1.5 hr., filtered, and acidified. The viscous, oily precipitate was dissolved in acetone and filtered, and the acetone was evaporated. Drying the oil *in vacuo* at 45° overnight gave a solid that softened at 75° and melted at 90–95° dec.

Anal. Calcd. for dibenzofuran monophosphonic acid, $C_{12}H_9PO_4$: P, 12.5. Found: P, 11.7.

Phosphonation of carbazole. A mixture of 66.9 g. (0.14 mole) of carbazole, 102.4 ml. (0.8 mole) of diethyl phosphite, and 37.5 ml. (0.2 mole) of *t*-butyl peroxide was refluxed for 18 hr. The colorless mixture turned black after 1 hr., light brown after 3 hr., and dark blue by 18 hr. It was poured on ice. The dark blue solid was collected on a filter and washed repeatedly to remove all water-soluble material. It was hydrolyzed by being refluxed for 16 hr. with a mixture of 200 ml. of ethanol and 200 ml. of concd. hydrochloric acid, then evaporated to dryness on a steam bath. To separate phosphonic acid from unchanged carbazole, the residue was stirred at 80° for 10 min. with 600 ml. of 5% aqueous potassium hydroxide and filtered. The insoluble solid, after being washed and dried, weighed 54 g. and melted at 242–244°; the mixed melting point with carbazole was 242–245°.

The alkaline filtrate was acidified with dilute hydrochloric acid, and the blue precipitate was collected on a filter, washed, and dried. It weighed 17.7 g. and melted at 155–185°. A portion was dissolved in potassium hydroxide, and the *p*H of the solution was adjusted to 8 with acetic acid. The solution was treated with charcoal, filtered, and acidified. The blue solid, after being washed and dried, melted at 155–210°.

Anal. Calcd. for the mono-potassium salt of carbazole-phosphonic acid, $C_{12}H_8PO_3NK$: N, 4.9; P, 10.9. Found: N, 4.7; P, 10.7.

Attempted phosphonation of ferrocene and pyridine. Ferrocene and pyridine were treated with equimolar amounts of diethyl phosphite and half-molar amounts of *t*-butyl peroxide at reflux for 20 hr. In both cases, diethyl isobutylphosphonate was the only phosphorus compound isolated. Ferrocene gave dark smeary products—apparently the same as obtained by treating ferrocene with *t*-butyl peroxide alone; they were not further investigated. Pyridine gave only water-soluble products and reacted as well with diethyl phosphite without peroxide as with it.

Reaction of diethyl phosphite with t-butyl peroxide. A mixture of 55 g. (0.4 mole) of diethyl phosphite and 29.2 g. (0.2 mole) of *t*-butyl peroxide was refluxed for 5.5 hr. Distillation at 13 mm. gave 43.7 g. (56%) of diethyl isobutylphosphonate boiling at 86–93°; this was identified by hy-

(5) B. M. Mikhailov and N. F. Kucherova, *Doklady Akad. Nauk S.S.S.R.*, **74**, 501–504 (1950).

drolysis with concd. hydrochloric acid to isobutylphosphonic acid, m.p. 120–123° after recrystallization from cyclohexane (reported 122–124° [4]; 125°[6]). The distillation residue was 12 g. of highly acidic, viscous material.

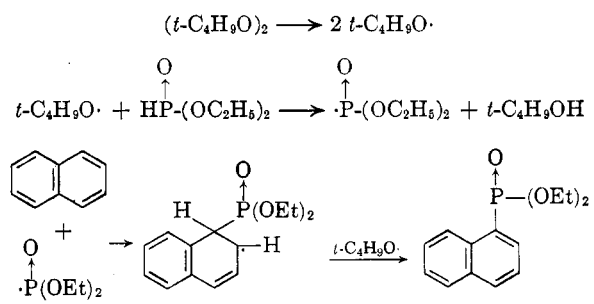
Reaction of diethyl phosphite with t-butyl alcohol. A mixture of 27.5 g. (0.2 mole) of diethyl phosphite, 37 g. (0.5 mole) of *t*-butyl alcohol, and 1.8 g. (0.025 mole) of *t*-butyl peroxide was heated in a stainless steel autoclave at 130° for 5.5 hr. The reaction mixture was distilled at atmospheric pressure, and products (33.1 g.) boiling between 44° and 88° were removed. On being strongly heated, 2 g. of a pale yellow, viscous oil slowly distilled at about 180° with considerable decomposition. The oil solidified on standing and melted at 105–110°. Recrystallization from a mixture of ethyl acetate and *n*-heptane gave isobutylphosphonic acid as a white solid melting at 120–123°. Evidently at the high temperature and in the closed system employed, the diethyl isobutylphosphonate was hydrolyzed to the free acid.

Reaction of diethyl phosphite with isobutylene. A mixture of 55.2 g. (0.4 mole) of diethyl phosphite, 1.8 g. (0.025 mole) of *t*-butyl peroxide, and 11.2 g. (0.2 mole of isobutylene was heated in a stainless steel autoclave for 23 hr. at 130°. During this time, pressure dropped slowly from an initial 150 p.s.i. to 25 p.s.i. The reactor contained 68.1 g. of a pale yellow-green liquid.

To hydrolyze the ester to the free acid, a 4.0-g. sample of this solution was refluxed overnight in 25 ml. of concd. hydrochloric acid. The hot reaction mixture was evaporated to drive off hydrochloric acid. Upon dilution with water, an oil was precipitated. It was extracted with ether; evaporation gave 1.59 g. of a brown oil that solidified on cooling. Crystallization of this solid from cyclohexane gave colorless isobutylphosphonic acid; m.p. 121–123°.

DISCUSSION

The reaction of diethyl phosphite, *t*-butyl peroxide, and naphthalene—as an example of the general phosphonation reaction—probably involves the scission of peroxide to *t*-butoxy radicals, formation of phosphonyl radical from phosphite, and addition to naphthalene. Full aromaticity is restored by another butoxy radical:

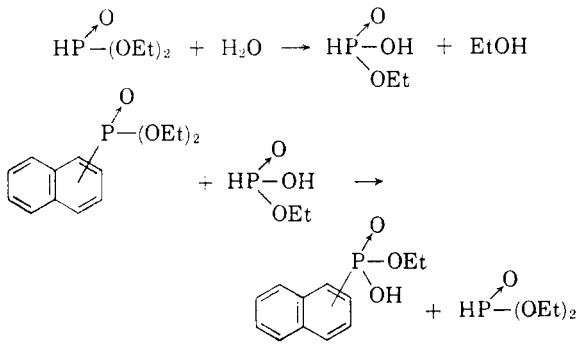


Although this sequence shows the formation of α-naphthalene phosphonic ester, a mixture of α- and β-isomers is obtained. The proportions have not been determined.

Such analytical procedures as infrared and mass spectrometry and gas chromatography have thus far helped only a little in analyzing higher-molecular weight aromatic phosphonic esters. They are too low in volatility, tend to decompose readily at elevated temperatures in the presence of acidic impurities, and give overlapping phosphorus and aromatic absorption bands in the infrared region. Purification is complicated because phosphonic acids often precipitate as their monosodium or potassium salts when solutions of them in sodium or potassium hydroxide are acidified.[7]

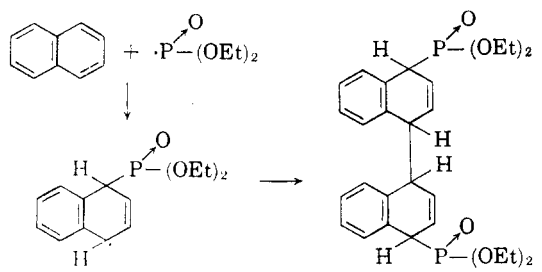
Production of methane in the reaction shows that some *t*-butoxy radicals decompose further to acetone and methyl radical, despite the presence of diethyl phosphite. Such decompositions may occur towards the end of the reaction, when phosphite concentration is low. Methyl radicals can react with naphthalene to give methylnaphthalenes which may also phosphonate. Such seems to be the case; although the main peak in the mass spectrum of diethyl naphthalenephosphonate showed mass 264, small amounts of the next higher homologues with one and two more methyl groups showed the presence of diethyl methylnaphthalenephosphonate and dimethylnaphthalenephosphonate.

Water is formed in the reaction mixture by the dehydration of *t*-butyl alcohol. Although diethyl phosphite is the most readily hydrolyzed of the reaction components, the prolonged reaction time allows some ester exchange, as proved by the isolation of the monoethyl naphthalenephosphonate:



Similar reactions may involve phosphorous acid as well as its monoethyl ester.

The residue left after distillation of the diethyl naphthalenephosphonate had an elemental composition almost the same as the distilled ester, but about twice the molecular weight. Coupling of an intermediate is indicated:



(6) I. Arbuzov, *J. Russ. Phys. Chem., Soc.*, **45**, 690 (1913).

(7) H. Z. Lecher, R. A. Greenwood, K. C. Whitehouse, and T. H. Chao, *J. Am. Chem. Soc.*, **78**, 5018 (1956); K. C. Whitehouse and H. Z. Lecher, U. S. Patent **2,799,701**, July 16, 1957.

Such coupled products have been isolated from the attack of phenyl and *t*-butoxy radicals on aromatic systems.[8,9] The coupled radical could become fully aromatic upon oxidation, either by the *t*-butoxy radicals or by air during subsequent manipulations.

Anthracene and phenanthrene gave high yields of apparently only one phosphonic acid; alkaline permanganate oxidation of the products gave anthraquinone and 2,2′-diphenic acid, respectively. The phosphonyl radical evidently attacked the 9-position in these two arenes. Anthracene-9-phosphonic acid has not previously been prepared; attempted phosphonation of anthracene with phosphorus trichloride or pentachloride in the presence of aluminum chloride was unsuccessful, and the reaction of 9-anthryllithium with phosphorus trichloride gave a low yield of tri-9-anthrylphosphine.[5] The high yield (96%) of anthracenephosphonic acid by free-radical phosphonation is in marked contrast to the low yields of other free-radical reactions of anthracene: benzoyl peroxide gave 15.2% of 9-benzoyloxyanthracene,[10] and *t*-butyl peroxide gave 7.5% of 9-methylanthracene, 7% of 9,9′,10,10′-tetrahydro-10,10′-dimethyl-9,9′-bianthryl, and 3% of anthraquinone.[8]

The position of the phosphonic acid group in the products from phosphonation of dibenzofuran has not been determined. Carboxymethyl radicals react with anthracene and phenanthrene at the 9-position,[11] as do phosphonyl radicals. By analogy, dibenzofuran may have given about 55% 1-, 30% 4-, and 15% 3-phosphonic acids—the isomer ratio obtained on carboxymethylation.

Carbazole did not react with the carboxymethyl radical; it phosphonated readily. The only other reported free-radical reaction with carbazole is bromination with *N*-bromosuccinimide and benzoyl peroxide to yield 55% 3-bromocarbazole.[12] The wide melting point range of our product indicated that it was a mixture of isomeric phosphonic acids.

The phosphonation of naphthalene, anthracene, phenanthrene, and dibenzofuran is consistent with the high reactivity toward free radicals of such fused-ring systems[13] and approximately parallels their affinities for methyl radicals.[14]

Attempts to phosphonate two additional heterocyclic systems were unsuccessful. *t*-Butyl peroxide converted ferrocene to dark, intractable products that indicated extensive degradation had occurred. In the presence or absence of peroxide, pyridine was converted by diethyl phosphite to a water-soluble product, probably ethylpyridinium monoethyl phosphonate. It may have phosphonated further in the pyridine ring, but its solubility in water prevented isolation.

An interesting side reaction occurring in the aromatic phosphonations was the formation of diethyl isobutylphosphonate in varying amounts. This product was obtained when diethyl phosphite and *t*-butyl peroxide reacted with isobutylene. Isobutylene formed in the phosphonations could arise by dehydration of *t*-butyl alcohol, which in turn was derived from *t*-butyl peroxide. However, all phosphonations were run open to the atmosphere and under conditions that allowed the escape of reactants boiling under 100°. Isobutylene reacted slowly with diethyl phosphite and peroxide in a closed system; it should have escaped as formed in an open system, before it could react with the phosphite. That so much isobutylphosphonate formed must mean the reaction, which goes so slowly in the presence of catalytic amounts of peroxide,[15] proceeds rapidly and efficiently when large amounts of free radicals are present.

CONCLUSION

Phosphonation by dialkyl phosphites and *t*-butyl peroxides provides a new, convenient synthesis for phosphonic acids. It appears particularly suited to the preparation of polynuclear phosphonic acids in high yields. Percentage yields and conversions, respectively, were: naphthalene, 51, 25; anthracene, 96, 50; phenanthrene, 60, 85; dibenzofuran, 69, 58; carbazole, 80, 15. However, as in attack by free organic radicals, mixtures of isomers are often obtained. Anthracene and phenanthrene give mainly single isomers, presumably because of greater charge localization at their 9- and 10- positions.

WHITING, IND.

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