rate distilled at 195–200° (2 mm.) as a colorless oil; yield 145 g. or 44%; $n^{25}D$ 1.4797; d^{25}_4 0.955; sapn. no., 167 (calcd. 169).

The 2-ethyl hexoate, benzoate and furoate (see Table I) were prepared in a manner similar to the laurate. The yields were between 50 and 65%.

Dihydro-*nor*-dicyclopentadienyl Isothiocyanate (E or F).—A mixture of 132 g. of dicyclopentadiene, 75 g. of water, and 76 g. of ammonium thiocyanate was rapidly stirred and heated at 90–95° under a reflux condenser. To the hot, stirred solution, 100 g. of concentrated hydrochloric acid (37% HCl) was added dropwise during the course of one hour while the reaction mixture was maintained at 90–95° and rapidly agitated. The mixture was then stirred for three hours longer at 90–95°, filtered hot by suction to remove traces of polythiocyanic acid, and the clear, filtered oil layer was separated, washed with water and distilled *in vacuo*. The product distilled at 127–132° (2 mm.) as a pale yellow oil, having a characteristic odor; yield 120 g. or 62%. The analytical sample boiled at 140–142° (6 mm.); $n^{25}D$ 1.5580; d^{25}_4 1.1318.

Anal. Calcd. for $C_{11}H_{13}NS$: N, 7.33; S, 16.75. Found: N, 6.96; S, 16.93.

Dihydro-*nor*-dicyclopentadienyl Thiourea.—A mixture of 19 g. of dihydro-*nor*-dicyclopentadienyl isothiocyanate and 100 g. of concentrated ammonium hydroxide was rapidly stirred and heated under a reflux condenser on a steam-bath for two hours during which time a semi-solid mass formed. One hundred grams additional ammonium hydroxide was then added and the mixture stirred for three hours longer at 90–95°. The solid mass obtained in almost quantitative yield was recrystallized from ethanol to give colorless plate-like crystals, m. p. 203–204° (uncor.).

Anal. Calcd. for $C_{11}H_{16}N_2S$: C, 63.46; H, 7.69; N, 13.46; S, 15.38. Found: C, 63.51; H, 7.56; N, 13.49; S, 15.00.

Acetylamino-dihydro-*nor*-dicyclopentadiene.—A mixture of 180 g. of glacial acetic acid and 145 g. of dihydro-*nor*-dicyclopentadienyl isothiocyanate was boiled under reflux for four hours and the product was then distilled *in vacuo*. The fraction boiling at 155–175° (4 mm.) was a viscous oil; yield 63 g. It was distilled to give a heart cut (28.5 g.) boiling at 170–175° (3 mm.) which crystallized on standing. After recrystallization from petroleum ether, m. p. 129–130° (uncor.).

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.39; H, 8.90; N, 7.33. Found: C, 75.14; H, 8.88; N, 7.22.

Dihydro-*nor*-dicyclopentadienyl Thioacetic Acid.—To 26.4 g. of dicyclopentadiene there was added 18.4 g. of thioglycolic acid. A vigorous reaction occurred during which the temperature rose rapidly to 90°. At this point cooling was applied and, after the reaction had subsided, the mixture was heated for one hour longer at 90° to complete the reaction. The product was then distilled *in vacuo* to give 30 g. of thick oil boiling at 190–200° (4 mm.).

Upon redistillation it boiled at 182° (2 mm.) and crystallized on standing; m. p. 53–54° (from petroleum ether).

Anal. Calcd. for $C_{12}H_{16}O_2S$: C, 64.29; H, 7.14; S, 14.28; acid no., 251. Found: C, 64.01; H, 6.88; S, 13.84; acid no., 252.

Acknowledgment.—The analyses of the above products were performed by Mr. Clyde W. Nash of these laboratories.

Summary

1. Dicyclopentadiene reacts with hydrochloric, hydrobromic, hydriodic and thiocyanic acids to yield unsaturated addition-rearrangement products. It also adds organic carboxylic acids to one of its double bonds to yield esters of hydroxy-dihydro-*nor*-dicyclopentadiene. These reactions are catalyzed by hydrogen ions or by acidic catalysts. Thioglycolic acid adds to dicyclopentadiene to yield an unsaturated thioether instead of an ester.

2. The addition product of dicyclopentadiene and thiocyanic acid is a hydroisothiocyanate.

PHILADELPHIA, PENNSYLVANIA RECEIVED MARCH 30, 1945

[CONTRIBUTION FROM THE CENTRAL RESEARCH DEPARTMENT OF THE MONSANTO CHEMICAL COMPANY]

Isomerization of Alkylphosphites. III. The Synthesis of *n*-Alkylphosphonic Acids

BY GENNADY M. KOSOLAPOFF

Although the preparation of some members of the *n*-alkylphosphonic acid series has been reported occasionally since the middle of the last century, the amount of accurate scientific data on the properties and on the satisfactory synthetic methods remains meager.

This series of organo-phosphorus compounds is one of the basic series in the field of phosphorus derivatives, being comparable in position to the aliphatic monocarboxylic acids in the carbon realm. Yet, at the present time only the methyl-, ethyl-, propyl-, butyl- and *n*-heptyl-phosphonic acids appear to have been prepared in a state of sufficient purity to have been reported in the chemical literature.

It was felt that the information required to fill the gap should be obtained in order to study the properties of this important series. The review of the available synthetic methods showed that the preparation through the isomerization of alkyl phosphites under the influence of alkyl halides showed the best promise of synthesis of compounds of definite structure with satisfactory yields. Thus, in the modern times, Nylen[1] prepared methyl-, ethyl- and *n*-propyl-phosphonic acids through the reaction of sodium diethylphosphite with the corresponding alkyl halides, followed by hydrolysis of the resulting diethyl *n*-alkylphosphonates. Arbuzov and Arbuzova[2] prepared *n*-butylphosphonic acid through isomerization of tri-butylphosphite by *n*-butyl iodide, followed by hydrolysis of the dibutyl *n*-butylphosphonate. Finally, Fossek[3] reported the synthesis of a higher alkylphosphonic acid, *n*-heptylphosphonic acid, through reduction of 1-hydroxyheptylphosphonic acid.

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[1] P. Nylen, "Studien über org. Phosphorverbindungen," Upsala, 1930.

[2] Arbuzov and Arbuzova, *J. Russ. Phys.-Chem. Soc.*, **62**, 1533 (1930).

[3] Fossek, *Monatsh.*, **7**, 29 (1886).

The scope of the present work was set at the preparation of the complete series of *n*-alkylphosphonic acids with an even number of carbon atoms up to eighteen. A number of similar acids with odd number of carbon atoms were felt to be of sufficient interest to be included in the study; these were limited to the derivatives of readily obtainable *n*-alkyl halides.

It was found at an early stage of the investigation that, while the reaction of tri-ethylphosphite with alkyl halides gives satisfactory yields of the lower members of the diethyl *n*-alkylphosphonate series, difficulties are encountered when the higher alkyl halides are used; thus, excessively long reaction periods (up to forty-eight hours) are required, at 150–160°, to produce unsatisfactory yields (generally 50%, or less) of the phosphonic acid esters. At the same time, the necessary distillation of the product from the reaction mixture was found to lead to troublesome decomposition, even at oil-pump vacua. While the reaction time may be cut down by the use of pressure equipment and higher reaction temperatures, these expedients lead to an increase of the by-product, diethyl ethylphosphonate, and do not eliminate the decomposition difficulty mentioned above. Hence, although a number of diethyl alkylphosphonates were prepared by this method, it was not felt to be of satisfactory quality as a general synthetic method.

The di-alkylphosphites, in the form of the sodium derivatives, thus presented an alternate method of synthesis. The ethyl ester was used by many previous investigators. However, its sodium derivative presents several troublesome characteristics: its solubility in inert organic solvents is very limited, making it almost imperative to use warm anhydrous ether as the reaction medium, while the hygroscopicity of the product prohibits its ready handling except in suitably designed equipment. The higher dialkylphosphites were found to be eminently suitable, however, for the solution of the above difficulties. Among the available esters, the di-*n*-butyl compound appeared to be the most satisfactory one, being derived from a readily available and cheap alcohol. Its sodium derivative is readily soluble in inert organic solvents; of particular interest in this connection was its solubility in the lower petroleum fractions (hexane and heptane ranges) which have a number of favorable properties in the reaction under investigation: essential lack of solubility of sodium halides therein, ease of drying and relative lack of fire hazard over diethyl ether. The solutions of the sodium dibutylphosphite in hexane were found to be quite stable on ordinary exposures to atmospheric moisture, thus making it possible to use standard laboratory equipment with only the usual precaution against moisture (calcium chloride tubes). The reactions with the alkyl halides were found to proceed readily at reflux temperature of the solvent, being complete within three to six hours, thus showing a great advantage over the tri-ethylphosphite method mentioned above.

The dibutyl *n*-alkylphosphonates, thus obtained, were handled with considerably less difficulty than were the corresponding ethyl esters. They show much better stability to hydrolysis, thus making it possible to separate the sodium halide by washing with water, while the corresponding diethyl esters necessitate centrifuging for the removal of the colloidally-dispersed sodium halide; in the latter case even prolonged centrifuging, at times, is ineffective for complete removal of the salt which is essential for good yields upon distillation. The isolation of the alkylphosphonates requires, after washing, only drying and distillation *in vacuo;* the yields obtained ranged generally at 80%, or better, with the limiting factor, in small runs, being the fact that these esters distill essentially without residue, thus making it difficult to recover, in pure state, the "tails" of a given run. In several cases the yields approached the theoretical. In view of these points of superiority over the diethyl esters, it is curious that the sodium dibutylphosphite had not been used previously for syntheses of this type.

The conversion of the dibutyl alkylphosphonates into the corresponding phosphonic acids was found to proceed readily when the esters were refluxed with concentrated hydrochloric acid for several hours. The workers cited above used for this purpose dilute hydrochloric acid, with the hydrolyses being conducted in sealed tubes at high temperatures. The use of sealed tubes was felt to be undesirable by the writer for operations on a moderate scale, while the use of autoclaves in the presence of hydrogen chloride fumes generally leads to bad corrosion difficulties. Hence, the finding that concentrated hydrochloric acid can be used for satisfactory hydrolyses in standard laboratory equipment was of considerable utility in these syntheses. Generally, essentially quantitative yields of crude alkylphosphonic acids were obtained, from which 75–85% of the products were obtained in pure state; however, the latter figure is quite conservative since the main aim of the study was the collection of physical constants of pure acids.

Experimental Part

Syntheses with Tri-ethylphosphite.—The equipment and the procedure were identical with those described in the first paper of this series.[4] *n*-Alkyl bromides were used as alkyl halides, with the reaction temperatures ranging from 150 to 160°. For the higher members reaction time ranged up to forty-eight hours, when the evolution of ethyl bromide became insignificant. The data may be found in Table I.

Syntheses with Sodium Dibutylphosphite.—Metallic sodium (1.15 g., 0.05 mole) was placed into a three-necked round bottom flask, provided with a dropping funnel, a sealed stirrer and a reflux condenser closed with a calcium chloride tube; 150 ml. of dry hexane, or heptane, was placed into the flask and, while the liquid was being gently re-

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[4] G. M. Kosolapoff, THIS JOURNAL, 66, 109 (1944).

TABLE I

R-	$RPO(OC_2H_5)_2$ B. p., °C.	$RPO(OC_2H_5)_2$ B. p., Mm.	$RPO(OC_4H_9)_2$ B. p., °C.	$RPO(OC_4H_9)_2$ B. p., Mm.	$RPO(OC_4H_9)_2$ n^{25}_D	$RPO(OC_4H_9)_2$ d^{25}_4	*MR* Obs.	*MR* Calcd.	$RPO(OH)_2$ M. p., °C.	$RPO(OH)_2$ Eq. wt. Obs.	$RPO(OH)_2$ Eq. wt. Calc.
CH_3—	90	10[a]							104-105[a]		
C_2H_5—	86-88	9[a]	137-139	17	1.4258	0.9623	59.09	59.13	61-62[b]	55.6	55
$CH_3(CH_2)_2$—	92-93	9[a]							72.5-74.5[a]		
$CH_3(CH_2)_3$—			160-162	20[c]	1.4302	.9462	68.28	68.4	103.4-104[c]	68.8	69
$CH_3(CH_2)_4$—			167-169	17	1.4318	.9428	72.60	72.98	120.5-121.5	75.9	76
$CH_3(CH_2)_5$—	140-144	17	182-184	20	1.4332	.9366	77.17	77.60	104.5-106	82.7	83
$CH_3(CH_2)_6$—			188-190	17	1.4355	.9313	82.20	82.22	103-103.5[d]	89.8	90
$CH_3(CH_2)_7$—			147-148	2	1.4370	.9262	86.56	86.84	99.5-100.5	97.2	97
$CH_3(CH_2)_8$—	177-186	17	159-161	2	1.4391	.9253	90.98	91.45	99-100	104.3	104
$CH_3(CH_2)_9$—	186-193	17	161	1	1.4402	.9232	95.37	96.05	102-102.5	110.8	111
$CH_3(CH_2)_{11}$—	165-175	3	196-199	3	1.4432	.9153	104.9	105.3	100.5-101.5	124.9	125
$CH_3(CH_2)_{13}$—	*ca.* 200	3	217-219	3	1.4460	.9114	114.1	114.55	97-98	139.1	139
$CH_3(CH_2)_{15}$—			226-228	2	1.4481	.9090	123.2	123.8	94.5-95.5	153	153
$CH_3(CH_2)_{17}$—			248-250	2	1.4499	.9037	132.6	133.02	98.5-99	167.2	167

[a] P. Nylen, "Studien über org. Phosphorverbind.," Upsala, 1930. [b] Nylen (see above) reports m. p. 61.5-62.5°. [c] Arbuzov and Arbuzova[2]; they report m. p. 101-103°. [d] Fossek[3] reported m. p. 106°.

fluxed with agitation, dibutylphosphite (9.7 g., 0.05 mole) was added dropwise over twenty to thirty minutes, after which the refluxing and stirring were continued until the sodium was completely dissolved; this generally required three to five hours. The alkyl bromide (0.05 mole) was then added over thirty to forty-five minutes and the mixture stirred with gentle reflux for five to six hours. The separation of sodium bromide generally began after fifteen to twenty minutes and was essentially complete in two to three hours. After cooling, the mixture was washed thoroughly with water, the organic layer separated, dried by the distillation of the solvent under reduced pressure at essentially room temperature, and distilled *in vacuo* in a fractionating apparatus. The dibutyl *n*-alkylphosphonate was refluxed with 50-75 ml. of concentrated hydrochloric acid overnight, after which the reflux condenser was set for downward distillation and the mixture was distilled from an oil-bath, with consequent removal of butyl chloride and most of the residual butanol, as well as approximately one-half of the volume of the hydrochloric acid. On cooling, at this point, the alkylphosphonic acids, higher than decyl, crystallized readily into a crust which was separated. The lower acids, due to their greater solubility in aqueous media, generally did not give a solid crust; hence, these mixtures were carefully evaporated to dryness. The crude alkylphosphonic acid so obtained was then repeatedly recrystallized from hexane, or heptane, to a constant melting point, followed by drying *in vacuo* over solid potassium hydroxide. The ethylphosphonic acid was recrystallized from water, due to its poor solubility in petroleum solvents. All acids so obtained crystallized very readily frequently forming crystals 1-2 cm. long. These were generally clusters of flat needles, which were quite fragile, and upon drying greatly resembled naphthalene in their appearance.

The data obtained may be found in Table I.

It is interesting to note that the melting points of the acids studied do not present a regular "sawtooth" pattern *vs.* the number of carbons in the alkyl chain. There appears to be, instead, a grouping of melting points in the proximity of 100°.

Summary

A series of dibutyl alkylphosphonates has been prepared, with an even number of carbon atoms in the alkyl group, up to eighteen carbon atoms; similar esters of amyl-, heptyl- and nonylphosphonic acids were also prepared. The esters were converted into the corresponding alkylphosphonic acids, which were characterized.

A procedure giving good yields of the dibutyl esters and of the phosphonic acids has been evolved through the use of sodium dibutylphosphite.

DAYTON, OHIO

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DAVIDSON COLLEGE]

The Aqueous Solubility of Acetanilide

BY THOMAS S. LOGAN

Data for the aqueous solubility of acetanilide have been compiled by Seidell.[1] The data are not at all concordant. For instance, values at 25° vary from 0.54[2] to 0.61% acetanilide,[3] an over-all difference of about 12%. Data for the solubility of solid acetanilide in water are not listed in the "International Critical Tables." This paper reports determinations of this solubility from 0 to 70°. Such measurements have been reported by Schoorl and de Weerd.[4]

Experimental

Determination of Solubility.—The determinations were run in 50-ml. flasks. The flasks were closed by two-hole rubber stoppers having inlet and outlet tubes for withdrawing the solutions. The outlet tube had a plug of cotton in its upper part. Water and acetanilide were put in a flask and alternately heated and cooled until cooling produced a cloud of crystals. The flask and contents were then heated to several degrees above the temperature

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(1) Seidell, "Solubilities of Organic Compounds," third edition, Vol. II, pp. 600-604.

(2) Holleman and Antusch, *Rec. trav. chim.*, **13**, 293 (1894).

(3) J. Mahieu, *Bull. soc. chim. Belg.*, **45**, 667 (1936).

(4) Schoorl and de Weerd, *Rec. trav. chim.*, **41**, 15 (1922).