ml. of carbon disulfide was added slowly with stirring 15.3 g. (0.10 mole) of 2,5-dichlorothiophene. The mixture was stirred for 47 hours at room temperature and then slowly added to a mixture of ice and hydrochloric acid. The resulting precipitate was filtered and extracted with hot methanol. Evaporation of the methanol with the aid of an air jet yielded 4 g. of yellow crystals.

Meanwhile, the carbon disulfide layer was separated from the filtrate and evaporated to dryness. The solid residue was extracted with hot methanol and the extract was evaporated to dryness to yield an additional 5 g. of yellow crystals. The two crops of crystals were combined and dissolved in boiling glacial acetic acid. Treatment of the glacial acetic acid solution with Norit followed by partial evaporation and cooling, yielded 7 g. (24%) of phenyl 2,5-dichloro-3-thienyl sulfone, which melted at 126.5–128° after recrystallization from methanol; no depression resulted on admixture with an authentic sample prepared as described below.

Anal. Calcd. for $C_{10}H_{16}S_2O_2Cl_2$: C, 40.94; H, 2.07; Cl, 24.19; mol. wt., 293. Found: C, 41.18; H, 2.08; Cl, 24.10; mol. wt., 291.

Using the general procedure described by Hartough[6] for the preparation of 2-thiophenesulfonyl chloride, 15.3 g. (0.10 mole) of 2,5-dichlorothiophene was added slowly with stirring to 15.6 g. (0.134 mole) of chlorosulfonic acid cooled to 10°. The resulting solution was poured on ice, neutralized with 10% aqueous sodium hydroxide and evaporated to dryness. Extraction of the residue with boiling methanol yielded 17 g. (66%) of sodium 2,5-dichloro-3-thiophenesulfonate. A mixture of this sulfonate (17 g., 0.0664 mole) and 27.8 g. (0.134 mole) of phosphorus pentachloride was heated on the steam-bath for 8 hours, cooled and extracted with carbon tetrachloride. The carbon tetrachloride and phosphorus oxychloride were subsequently removed by reduced pressure distillation at 50°. A solution of this sulfonyl chloride in 50 ml. of dry benzene was added dropwise to a stirred mixture of 100 ml. of dry benzene and 10 g. (0.075 mole) of anhydrous aluminum chloride, and the reaction mixture was stirred for 15 hours at room temperature and 2 hours at 80°. The resulting solution was added to a mixture of ice and hydrochloric acid and the water layer was separated and extracted with benzene. The combined benzene extracts were evaporated to a solid residue. The residue was washed with cold methanol, dissolved in boiling methanol and treated with Norit. Partial evaporation of the methanol followed by cooling yielded 11 g. (56%) of phenyl 2,5-dichloro-3-thienyl sulfone, which melted at 126–128° after recrystallization from methanol and petroleum ether.

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(6) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 513.

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Disubstituted Phosphine Oxides and Disubstituted Phosphinic Acids. II. The Di-*n*-alkyl Series[1]

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In the first paper of this series,[4] three members of the new class of organophosphorus compounds, the di-*n*-alkylphosphine oxides, and the corresponding phosphinic acids were reported. Eight new di-*n*-alkylphosphine oxides and seven new di-*n*-alkylphosphinic acids have since been synthesized.

The di-*n*-alkylphosphine oxides reported here are all neutral, moderately stable, white solids. The di-*n*-amyl-, di-*n*-heptyl- and di-*n*-nonylphosphine oxides are less stable than the other members of the series. This conclusion is based upon the following tests: (a) the samples were stored at room temperature and changes in melting points over periods of time varying from one week to two years noted, (b) a capillary tube containing the sample was placed in a bath maintained about three degrees below the melting point and the time required for the sample to partly decompose and melt was observed. The compounds with five, seven and nine carbon atoms in their alkyl groups showed signs of instability in one or both of these tests. For instance, their melting points decreased measurably in one to two weeks and as much as five to ten degrees in eight months. In test b, only five to seven minutes were required. In comparison, the di-*n*-hexyl- and di-*n*-octylphosphine oxides have maintained their original melting points over a period of one to two years and do not melt prematurely if held at temperatures just below their melting points. Di-*n*-undecylphosphine oxide showed no signs of instability in either of these tests. The melting points of the di-*n*-decyl-, di-*n*-dodecyl-, di-*n*-tetradecyl-, di-*n*-hexadecyl- and di-*n*-octadecylphosphine oxides have not decreased with time although all of these were prepared before any of the members with odd numbers of carbon atoms in an alkyl group.

The chemical properties of the di-*n*-alkylphosphine oxides were investigated only in connection with the preparation of the phosphinic acids. It was found that the lower members of the series were oxidized readily by 30% hydrogen peroxide. This reagent became less effective as an oxidizing agent with increasing molecular weight of the phosphine oxides, di-*n*-octadecylphosphine oxide being unaffected by it. This is probably due to mutual insolubility and lack of effective mixing. With chlorine or phosphorus pentachloride, a vigorous reaction took place, forming the di-*n*-alkylphosphinyl chlorides, $R_2P(O)Cl$. These were not isolated but were hydrolyzed *in situ* to the phosphinic acids.

A plot of the melting points of the di-*n*-alkylphosphine oxides against the number of carbon atoms in an alkyl group shows a gradual increase in melting point with increasing chain length. A smooth curve passes through all these points with the exception of that for di-*n*-undecylphosphine oxide.

The di-*n*-alkylphosphinic acids are white crystalline compounds of high stability. They are weak acids, the end-point in a potentiometric titration usually being taken at about *p*H 10.5. A plot of the melting points against the number of carbon atoms in an alkyl group reveals that, in contrast to the di-*n*-alkylphosphine oxides, the melting points alternate in a manner analogous to that characteristic of the normal fatty acids and the straight chain dicarboxylic acids. The effect decreases rapidly with increasing molecular weight. This is the first time that such an alternation has been observed in a series of organophosphorus compounds. The *n*-alkylphosphonic acids, $RP(O)(OH)_2$, are the only other fairly complete series, and the melting points of the members from *n*-butyl to *n*-octadecyl cluster around 100°.[5]

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(1) Submitted to the Temple University Graduate Council in partial fulfillment of the requirements for the Ph.D. degree.

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(4) Robert H. Williams and Lyle A. Hamilton, THIS JOURNAL, **74**, 5418 (1952).

(5) G. M. Kosolapoff, *ibid.*, **67**, 1180 (1945).

TABLE I

PREPARATION AND PROPERTIES OF DI-*n*-ALKYLPHOSPHINE OXIDES AND DI-*n*-ALKYLPHOSPHINIC ACIDS

	$R_2P(O)H$					$R_2P(O)OH$[a]				
n-RX	Mol. ratio RX:Mg DBP[b]	Yield, %	M.p., °C.	Phosphorus, % Found	Calcd.	M.p., °C.	Phosphorus, % Found	Calcd.	Neut. equiv. Found	Calcd.
$C_5H_{11}Br$	3.0:3.0:1.0	12.0	65–66 d.	16.59	16.28	68–69	14.98	15.02	217	206.3
$C_6H_{13}I$	3.3:3.0:1.0	38.5	76.5	14.17	14.19	78–79[e]	...	...	234	234.3
$C_7H_{15}Br$	3.0:3.0:1.0	33.7	80.6–81.6 d.	12.57	12.58	77–78	...	...	260	262.4
$C_8H_{17}I$	3.3:3.0:1.0	70.0	85	11.30	11.29	85	10.69	10.67	290	290.4
$C_9H_{19}Br$	3.0:3.0:1.0	50.0	88–89 d.	10.35	10.24	84–85	9.87	9.73	321	318.5
$C_{10}H_{21}Br$	3.0:3.0:1.0	31.0	91.5–92.5	9.44	9.37	87.7–88.3[f]	8.95	8.94	351	346.5
$C_{10}H_{21}Br$	3.0:3.0:0.5	66.5	91.5–92.5	...	...					
$C_{11}H_{23}I$	3.0:3.0:1.0	27.0	96–97	8.53	8.64	89–90	...	...	383	384.6
$C_{11}H_{23}I$	3.0:3.0:0.5	62.0	96–97	...	...					
$C_{12}H_{25}Br$	3.0:3.0:1.0	35.0	97.2–97.8	7.80	8.02	93.8–94.8	7.66	7.69	402	402.6
$C_{14}H_{29}Cl$	3.0:3.0:1.0	51.0	102–103	6.96	7.00	97–98	6.74	6.75	460	458.7
$C_{16}H_{33}I$	3.0:3.0:1.0	34.8	106–107	6.21	6.21	102.5–103.5	5.97	6.02	519	514.8
$C_{18}H_{37}Br$	3.0:3.0:1.0	26.0	109–109.5[c]	5.61	5.58	105.3–106	5.40	5.43	583	570.9

[a] Prepared from the phosphinic oxides by warming with 1–2 moles of PCl_5 in benzene, then hydrolyzing. [b] DBP = di-*n*-butyl phosphite. [c] Melting point erroneously reported as 105.5° in reference 3. [e] G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950), reported 78–79°. [f] W. C. Drinkard and G. M. Kosolapoff, THIS JOURNAL, **74**, 5520 (1952), report 87–88°.

Experimental

Di-*n*-alkylphosphine Oxides.—The procedures used were similar to those reported in the first paper of this series.[4] Di-*n*-amyl-, di-*n*-heptyl-, di-*n*-nonyl- and di-*n*-decylphosphine oxides were prepared essentially as described previously for the di-*n*-hexylphosphine oxide. The preparation of di-*n*-undecyl-, di-*n*-dodecyl-, di-*n*-tetradecyl- and di-*n*-hexadecylphosphine oxides followed closely the method reported for di-*n*-octadecylphosphine oxide. Di-*n*-dodecyl-, di-*n*-tetradecyl- and di-*n*-hexadecylphosphine oxides were recrystallized from benzene or benzene–*n*-hexane mixtures. The lower members were all recrystallized from *n*-hexane.

All products were neutral by either a potentiometric titration or by a titration using phenolphthalein as an indicator. The important data for each preparation are summarized in Table I.

The percentage yields of the recrystallized phosphine oxides, based on dibutyl phosphite, varied from 12 to 70%, the average being 37%. The theoretical amount of phosphite was used since it was assumed during most of this work that the Grignard reagents were obtained in high yield. That this was not the case was indicated by observations that the vigorous exothermic reaction between di-*n*-butyl phosphite and the Grignard reagent usually ceased when 50 to 80% of the phosphite had been added. Repetition of preparations of the di-*n*-decyl- and di-*n*-undecylphosphine oxides, using half the amount of di-*n*-butyl phosphite, resulted in percentage yields approximately double those originally obtained. Thus the basic cause of the poor conversion of di-*n*-butyl phosphite to di-*n*-alkylphosphine oxides in this work appears to be low yields in the formation of the Grignard reagents. The very low yield of di-*n*-amylphosphine oxide was due to the precipitation of an intermediate complex as a hard unstirrable mass.

The members of the series from C-1 to C-4 are too unstable to be isolated by ordinary laboratory techniques. The reaction appears to take place readily, but in attempting to purify the crude liquid products by distillation, the corresponding phosphinic acids generally were formed. These acids have been reported previously.[6,7] No identifiable products were isolated from the reaction of methylmagnesium iodide and di-*n*-butyl phosphite.

Di-*n*-alkylphosphinic Acids. Method A.—All of the di-*n*-alkylphosphinic acids were prepared by treatment of the corresponding phosphine oxide in benzene solution, with PCl_5, followed by hydrolysis as described for di-*n*-octadecylphosphinic acid.[4] Di-*n*-dodecylphosphinic acid and higher members of the series were recrystallized from benzene or mixtures of benzene and alcohol. The lower members were recrystallized from *n*-hexane or *n*-hexane mixtures with alcohol or acetone. The melting points and analyses of these acids are listed in Table I.

Method B.—The acids with an even number of carbon atoms in an alkyl group were also obtained by the peroxide-catalyzed addition of *n*-1-olefins to hypophosphorous acid, using a modification of the procedure described in the literature.[8] The ratios of the reactants, the reaction conditions, and yields of recrystallized acids are summarized in Table II. The main product in each case was the mono-*n*-alkylphosphinic acid. Recrystallization from *n*-hexane readily separated the higher melting, less soluble di-*n*-alkylphosphinic acids.

TABLE II

PREPARATION OF DI-*n*-ALKYLPHOSPHINIC ACIDS FROM HYPOPHOSPHOROUS ACID

n-1-Olefin	Mole ratio reactants Olefin:H_3PO_2[c]:peroxide	Reaction Temp., °C.	Time hr.	$R_2P(O)$-OH % Yield
Hexene	2.0:1.0:0.15[a]	67–85	18	9.0
Octene	2.0:1.0: .08[a]	80–85	24	32.0
Decene	2.0:1.0: .11[b]	125–175	11	19.0
Dodecene	1.0:1.0: .08[a]	84	22	22.0
Tetradecene	2.0:1.0: .22[b]	135	17	16.6
Hexadecene	2.0:1.0: .17[b]	135	20	24.7
Octadecene	3.0:1.0: .19[b]	135	19	40.0

[a] Dibenzoyl peroxide with 1,4-dioxane solvent. [b] Di-*t*-butyl peroxide without solvent. [c] The hypophosphorous acid was a 50% aqueous solution.

Comparison of properties and mixed melting point determinations established that the samples prepared either by method A or method B were identical.

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(6) P. C. Crofts and G. M. Kosolapoff, THIS JOURNAL, **75**, 3379 (1953).

(7) G. M. Kosolapoff and R. M. Watson, *ibid.*, **73**, 4101 (1951).

(8) British Patent 660,918.

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Some New 1,2,3-Triazoles

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In the course of other work in these laboratories we had occasion to prepare a number of simple 1,2,3-triazoles. Since no further work with these compounds is planned in the immediate future it seems appropriate to report their properties now. The compounds prepared are described in Table I.

The first four compounds in Table I were made by the reaction of alkyl azides with acetylenic compounds. The triazolylacrylic acids, compounds 5