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	Phosphorus, % Calcd.	M.p., °C.	Phosphorus, % Found	Phosphorus, % Calcd.	Neut. equiv. Found	Neut. equiv. 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 phosphine oxides by warming with 1–2 moles of PCl_6 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.	Reaction 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

TABLE I

Compound	No.	Recrystallized[a] from	M.p., °C.	Analyses, %[b] Calcd. C	H	N	Found C	H	N
1-Methyl-1,2,3-triazole-4,5-dicarboxylic acid	1	W	179–180	...	..	24.56	...	..	24.30[c]
1-Butyl-1,2,3-triazole-4,5-dicarboxylic acid	2	W	136–136.5 d.	45.07	5.20	...	45.18	5.23	[d]
1-Benzyl-1,2,3-triazole-4-carboxaldehyde	3	E–W	89–90	...	..	22.45	...	..	22.33
1-Benzyl-4,5-bis-(1-hydroxy-1-methylethyl)-1,2,3-triazole	4	A	151–153	65.45	7.69	15.26	66.43	7.78	15.37
β-4-(1-Methyl-1,2,3-triazolyl)-acrylic acid	5	W	218–220	47.05	4.60	...	47.09	4.71	[e]
β-4-(1-Benzyl-1,2,3-triazolyl)-acrylic acid	6	E	216–219	62.87	4.84	...	62.72	4.93	[f]
1,2,3-Triazole-4-carboxaldehyde oxime	7	W	207–209	32.14	3.59	...	32.41	3.85	...
1,2,3-Triazole-4-carboxaldehyde 2,4-dinitrophenylhydrazone	8	E–A	270–271	38.99	2.54	...	39.28	2.60	...
1,2,3-Triazole-4-carboxaldehyde phenylhydrazone	9	E–W	160–162	...	..	37.39	...	..	37.25
1-Benzyl-1,2,3-triazole-4-carboxaldehyde 2,4-dinitrophenylhydrazone	10	E	228–230	...	..	26.70	...	..	26.70

[a] W, Water; E, ethanol; A, ethyl acetate. [b] C, H and N analyses by Micro Tech Laboratories, Skokie, Ill. [c] Neut. equiv.: calcd. 171, found 169. [d] Neut. equiv.: calcd. 106.6, found 107.4. [e] Neut. equiv.: calcd. 153.1, found 156.8. [f] Neut. equiv.: calcd. 229, found 226.

and 6, were prepared by the condensation of the triazolecarboxaldehydes with malonic acid. The aldehyde derivatives, compounds 7, 8, 9 and 10, were prepared by standard methods from the aldehydes. Attempts to prepare a pure thiosemicarbazone of 1,2,3-triazole-4-carboxaldehyde were unsuccessful.

The first compound listed has been reported recently[1] as an oxidation product of 1-methylbenzotriazole. The other compounds have not been described previously in the literature.

The benzyl azide,[2] methyl azide[3] and 1,2,3-triazole-4-carboxaldehyde[4] were made by literature methods; the butyl azide from butyl iodide and sodium azide. The 2,5-dimethyl-3-hexyne-2,5-diol was generously supplied by Air Reduction Chemical Company and the acetylenedicarboxylic acid was generously supplied by the National Aniline Division of Allied Chemical and Dye Corp. All other reactants were purchased from commercial sources.

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(1) W. E. Plaut, THIS JOURNAL, **76**, 5801 (1954).

(2) T. Curtius and G. Erhart, *Ber.*, **55**, 1565 (1922).

(3) O. Dimroth and W. Wislicenus, *ibid.*, **38**, 1573 (1905).

(4) R. Hüttel, *ibid.*, **74**, 1680 (1941).

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The Synthesis of the Six Isomeric 10-Dimethylphenyl-1,2-benzanthracenes[1,2]

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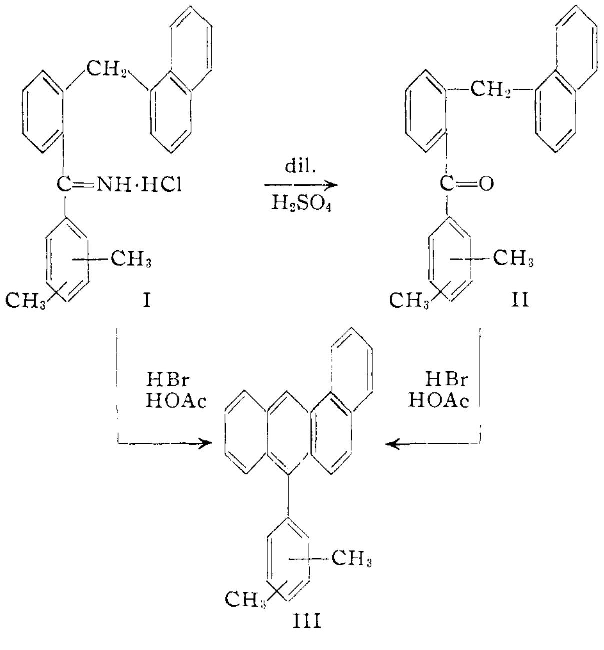
Bradsher's method of aromatic cyclodehydration[3] for the preparation of hydrocarbons was introduced in 1940. Later publications extended the usefulness of this synthesis. So for example Bradsher and Vingiello[4] prepared a series of 9-(*p*-monosubstituted phenyl)-anthracenes and Vingiello and Bořkovec[5] recently prepared 10-phenyl-1,2-benzanthracene and the three isomeric 10-monomethylphenyl-1,2-benzanthracenes. We now have extended Bradsher's aromatic cyclohydration reaction to the preparation of dimethyl substituted hydrocarbons.



Treatment of 1-(*o*-cyanobenzyl)-naphthalene with the appropriate Grignard reagents led to the corresponding ketimines, isolated as the hydrochlorides I, usually in high yield. The salts were hydrolyzed to the corresponding ketones II by refluxing with 25% sulfuric acid. In the case of the 2,6-dimethyl compound (II, 2,6-dimethyl), hydrolysis could not be effected under the specified conditions, but

(1) Presented before the Section of Organic Chemistry at the Sixth Southeastern Regional Meeting of the American Chemical Society, Birmingham, Alabama, October, 1954.

(2) This paper has been abstracted in part from the Masters thesis presented to the Virginia Polytechnic Institute by Alexej Bořkovec in 1953.

(3) C. K. Bradsher, THIS JOURNAL, **62**, 486 (1940).

(4) C. K. Bradsher and F. A. Vingiello, *ibid.*, **71**, 1434 (1949).

(5) F. A. Vingiello and A. Bořkovec, presented before the Division of Organic Chemistry at the 126th Meeting of the American Chemical Society, New York, N. Y., September 1954.