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Nucleophilic Substitution with Phosphide Anions Prepared by an Action of Sodium Dihydridobis(2-methoxyethanolato)aluminate on Phosphorus Compounds

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Phosphide anions, prepared by an action of sodium dihydridobis(2-methoxyethanolato)aluminate on derivatives of phosphine, phosphine oxide, or phosphorus esters, react with primary and secondary alkyl halides to produce phosphine derivatives having a newly formed phosphorus-carbon bond. The reactivity increases in the order of chloride<bromide<iodide and of secondary<primary in alkyl halide. Reaction of phosphide anion is also feasible with *p*-toluenesulfonate. Reaction of an anion of diphenylphosphine oxide seems to proceed mainly as an S_N2 type process.

As a chemical modification of sugar derivatives, we[1-3] synthesized compounds having a phosphorus atom instead of oxygen atom in the hemiacetal ring. Paulsen and Greve[4] reported a preparation of sugar derivatives bearing a phosphorus-carbon bond by addition of dialkylphosphonates to glyculoses. The addition of phosphonates to ketoses is a good method to prepare a phosphorus-carbon bond on sugar skeletons,[5] however a fundamental work[6] on the reactivity of α-hydroxyalkylphosphonates with some halogenating reagents failed to afford desired results, *i.e.*, some elimination reactions occurred instead of the substitution reaction.

The addition reaction of phosphorus compounds having a P–H bond to unsaturated double bonds such as C=C, C=N, and C=O always possesses a potential possibility to produce isomeric adducts. Addition of phenylphosphine to 3-*O*-acetyl-5,6-dideoxy-1,2-*O*-isopropylidene-6-*C*-nitro-α-D-*xylo*-hex-5-enofuranose actually gave both compounds of α-D-glucofuranose and β-L-idofuranose derivatives.[7,8]

Preparation and reaction of metal phosphides have widely been investigated.[9] Reactions of alkali phosphides with alkylating reagents are often used for the preparation of tertiary phosphines.[10] Phosphide anions could also be prepared by an action of hydrides on phosphorus compounds in a heterogeneous mixture[9,10] as well as by an action of sodium dihydridobis(2-methoxyethanolato)aluminate (SDMA) in a homogeneous mixture.[11,12] SDMA was sometimes used to prepare a P–H group from P–OR groups of phosphorus esters connected with sugar derivatives such as 5,6-dideoxy-1,2-*O*-isopropylidene-5-*C*-[(methoxy)phenylphosphinyl]-3-*O*-methyl-α-D-*xylo*-hexofuranose;[13] therefore, the reagent seems to be applicable toward sugar derivatives since it does not act on any functional groups other than phosphorus moiety.

To prevent the occurrence of isomeric products at the stage of phosphorus-carbon bond formation, we attempted to adopt a nucleophilic substitution with phosphide anion. This paper deals with a preparation of phosphide anions by an action of SDMA and their reaction with alkyl halides or *p*-toluenesulfonates to produce secondary and tertiary phosphine derivatives.

Results

Reaction with Alkyl Halides. Reaction of diphenylphosphine oxide (**1**) with some alkyl halides was carried out in the presence of SDMA in some solvents under reflux. The reaction proceeded according to

$$\underset{\mathbf{1}}{Ph_2P(O)H} + RX \xrightarrow{NaAlH_2(OCH_2CH_2OMe)_2} \underset{\mathbf{2}}{Ph_2P(O)R}, \quad (1)$$

giving the corresponding alkyldiphenylphosphine oxides in moderate to good yields, results being summarized in Table 1.

The reaction of **1** with SDMA proceeded very fast and predominantly gave the corresponding phosphide anion. The reactivity of the anion with alkyl halides seems to depend largely on the nature of alkyl halides employed. The isolated yield increased in the order of chloride<bromide<iodide in alkyl halides. The reaction with primary alkyl halides proceeded faster than that with secondary alkyl halides which required higher reaction temperature and/or prolonged reaction time. The reaction using SDMA is superior to those using sodium amide or lithium tetrahydridoaluminate, as judged from the product yield. Addition of sodium iodide to the reaction mixture remarkably improved the yield.

Reaction with Alkyl p-*Toluenesulfonates.* Reaction of **1** with alkyl *p*-toluenesulfonates was carried out in the presence of SDMA in tetrahydrofuran under reflux. Yields of products, obtained according to

$$\underset{\mathbf{1}}{Ph_2P(O)H} + R'OTs \xrightarrow{NaAlH_2(OCH_2CH_2OMe)_2} \underset{\mathbf{3}}{Ph_2P(O)R'}, \quad (2)$$

$$R' = i\text{-Pr},\ c\text{-}C_6H_{11},\ C_{10}H_{19}$$

were good and the results were shown in Table 2.

Reaction of Phenylphosphine or Methyl Phosphinates with Alkyl Halides or p-*Toluenesulfonates.* Reaction of methyl phenylphosphinate with isopropyl iodide in tetrahydrofuran in the presence of SDMA under reflux also gave the corresponding phosphine oxide in 46% yield. The reaction of phenylphosphine with alkyl halides or *p*-toluenesulfonates in tetrahydrofuran

Table 1. Reaction of diphenylphosphine oxide with alkyl halides (RX) in the presence of SDMA

RX	Solvent	Reaction temperature/°C	Reaction time/h	Product	Yield/%
EtBr	THF	65	4.5	$Ph_2P(O)Et$	Quant.
EtI	THF	65	8	$Ph_2P(O)Et$	41
$PhCH_2Cl$	THF	65	6	$Ph_2P(O)CH_2Ph$	12 (33)[a]
i-PrBr	THF	65	7	$Ph_2P(O)$*i*-Pr	12 (46)[a]
i-PrI	THF	65	6	$Ph_2P(O)$*i*-Pr	91 (98)[a]
i-PrI	THF	65	4.5	$Ph_2P(O)$*i*-Pr	19[b]
i-PrI	THF	R.T.	5	$Ph_2P(O)$*i*-Pr	0[c]
c-$C_6H_{11}Cl$	Toluene	111	11.5	$Ph_2P(O)$*c*-C_6H_{11}	6
c-$C_6H_{11}Cl$	Toluene	111	110.5	$Ph_2P(O)$*c*-C_6H_{11}	62
c-$C_6H_{11}Cl$	Toluene	111	11	$Ph_2P(O)$*c*-C_6H_{11}	31[d]
c-$C_6H_{11}Cl$	Dioxane	101	10	$Ph_2P(O)$*c*-C_6H_{11}	6
c-$C_6H_{11}Cl$	Diglyme	140	10	$Ph_2P(O)$*c*-C_6H_{11}	55
c-$C_6H_{11}Br$	THF	65	6	$Ph_2P(O)$*c*-C_6H_{11}	21
c-$C_6H_{11}I$	THF	65	6	$Ph_2P(O)$*c*-C_6H_{11}	38
2-$C_8H_{17}Cl$	THF	65	8	$Ph_2P(O)$2-C_8H_{17}	7
$C_{10}H_{19}Cl$[e]	Toluene	111	16	$Ph_2P(O)C_{10}H_{19}$[f]	11
$C_{10}H_{19}Br$[g]	THF	65	5.5	$Ph_2P(O)C_{10}H_{19}$[f]	8

a) Parentheses indicate that the yield was determined from ^1H NMR spectrum. b) Lithium tetrahydridoaluminate was used instead of SDMA. c) Sodium amide was used instead of SDMA. d) Sodium iodide (1 equiv.) was added to the reaction mixture. e) Menthyl chloride. f) Neomenthyl derivative was the major product. g) Menthyl bromide.

Table 2. Reaction of phosphorus compounds with alkyl halides or alkyl *p*-toluenesulfonates (RX) in the presence of SDMA

RX	Phosphorus compound	Solvent	Reaction temperature/°C	Reaction time/h	Product	Yield/%
i-PrOTs[a]	$Ph_2P(O)H$	THF	65	10	$Ph_2P(O)$*i*-Pr	94
$C_{10}H_{19}OTs$[b]	$Ph_2P(O)H$	THF	65	10	$Ph_2P(O)C_{10}H_{19}$[c]	55
c-$C_6H_{11}OTs$[d]	$PhPH_2$	Toluene	75—80	9	PhP(H)*c*-C_6H_{11}	75
i-PrBr	PhP(O)(OMe)Me	THF	65	7	PhP(O)(Me)*i*-Pr	— (6)[e]
i-PrI	PhP(O)(OMe)Me	THF	65	11	PhP(O)(Me)*i*-Pr	15 (46)[e]
$C_{10}H_{19}Cl$[f]	PhP(O)(OMe)H	Diglyme	110	10	PhP(O)(H)$C_{10}H_{19}$[g]	86
i-PrBr	$PhPH_2$	THF	65	6	PhP(H)*i*-Pr	Quant.
c-$C_6H_{11}Cl$	$PhPH_2$	THF	65	12	PhP(H)*c*-C_6H_{11}	77
2-$C_8H_{17}Cl$	$PhPH_2$	THF	65	11	PhP(H)2-C_8H_{17}	95
$C_{10}H_{19}Cl$[f]	$PhPH_2$	THF	65	32.5	PhP(H)$C_{10}H_{19}$[g]	82

a) Isopropyl *p*-toluenesulfonate. b) Menthyl *p*-toluenesulfonate. c) Neomenthyl derivative was the major product. d) Cyclohexyl *p*-toluenesulfonate. e) Parentheses indicate that the yield was determined from ^1H NMR spectrum. f) Menthyl chloride. g) The product was a mixture of neomenthyl and menthyl derivatives.

proceeded according to

$$\underset{\mathbf{4}}{PhPH_2} + R''X \xrightarrow{NaAlH_2(OCH_2CH_2OMe)_2} \underset{\mathbf{5}}{PhP(H)R''}, \quad (3)$$

R″=Secondary alkyl
X=Halogen or *p*-toluenesulfonyloxy

giving the corresponding secondary phosphines in excellent yields. These results are summarized in Table 2.

Discussion

The improvement of the yield of cyclohexyldiphenylphosphine oxide by addition of sodium iodide to the reaction mixture may be attributed to the first attack of iodine on cyclohexyl chloride followed by its replacement with phosphorus. The additivity effect will make valuable the present phosphorus-carbon bond forming reaction.

Ratios of neomenthyldiphenylphosphine oxide to menthyldiphenylphosphine oxide, as determined by optical rotation or HPLC, are 86:14 for the reaction of diphenylphosphine oxide with menthyl chloride, 63:37 for that with menthyl bromide, and 99:1 for that with menthyl *p*-toluenesulfonate. The ratio of neomenthylphenylphosphine to menthylphenylphosphine is 51:49 for the reaction of phenylphosphine with menthyl chloride in the presence of SDMA. The predominant production of the inverted product in the reaction of diphenylphosphine oxide with menthyl derivatives may indicate that the reaction proceeds mainly *via* an S_N2 process.

A comparison of yields of diphenylphosphine oxide

derivatives such as isopropyldiphenylphosphine oxide (48% yield from diphenylphosphinous chloride with propylene oxide)[14] and cyclohexyldiphenylphosphine oxide (30% yield from diphenylphosphine oxide with cyclohexane)[15] with those obtained in the present reaction may suggest that the reaction using SDMA is a good method to prepare a phosphorus-carbon bond. The homogeneous reaction mixture and simple operation and work-up as well as various types of phosphorus compounds being available as the precursor of phosphorus anion will also make the method useful for preparation of various types of derivatives of phosphines and phosphine oxides. The observed good yield for alkyl *p*-toluenesulfonates will make the present method hopeful in the field of carbohydrates.

Experimental

Instruments and Materials. IR spectra were measured on Hitachi-Perkin-Elmer 337 and JASCO (Japan Spectroscopic Co.) A-3 spectrophotometers. ^{1}H NMR spectra were recorded on Hitachi-Perkin-Elmer R-20 (60 MHz) and Hitachi R-24 (60 MHz) spectrometers using tetramethylsilane as the internal standard. Mass spectra were obtained on a Hitachi RMU DMG GC-MS spectrometer. Optical rotations were determined with JASCO DIP-4 digital and Atago Polax photometers.

Isolation of products was performed by high pressure liquid chromatography using JASCO Uniflow-211 and Uvidec-100-II, by liquid chromatography using a UVICON-540 detector and a SF-100G fraction collector from Toyo Scientific Industry, or by thin layer chromatography. Melting and boiling points were uncorrected.

Phenylphosphine (bp 118 °C), methyl phenylphosphinate (bp 94—95 °C/0.5—1.0 mmHg[16]), and methyl methylphenylphosphinate (bp 100 °C/0.5 mmHg) from phenylphosphonous dichloride,[17-20] and diphenylphosphine oxide (mp 49 °C)[21] were used as the phosphide precursors. Commercially available SDMA (benzene or toluene solution) was used. Cyclohexyl chloride (bp 27.2 °C/8 mmHg) and bromide (bp 54 °C/17.5 mmHg) were prepared from cyclohexanol,[22,23] cyclohexyl iodide from cyclohexene,[24] and 2-chlorooctane from 2-octanol.[25] Menthyl chloride (bp 98 °C/18 mmHg) was prepared from L-menthol; $[\alpha]_D^{15}$ −47.7° (*c* 2.4, EtOH).[26] *p*-Toluenesulfonates of 2-propanol (bp 114 °C/3 mmHg), cyclohexanol, and L-menthol were prepared from corresponding alcohols and *p*-toluenesulfonyl chloride.

Synthesis of Menthyl Bromide. To a mixture of L-menthol (3.0 g) and hydrobromic acid (5.0 g) was added 2.5 ml of concentrated sulfuric acid under ice cooling, and then the solution was heated for 5 h at 105 °C. Filtration of the reaction mixture, extraction of the product by petroleum ether, and successive work-up and distillation gave the bromide in 71% yield: bp 113 °C/22 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.73 (d, J=7.1 Hz, 3H, Me), 0.91 (d, J=7.1 Hz, 6H, $CH(C\underline{H}_3)_2$), 0.58—3.00 (m, 9H, $C\underline{H}(CH_3)_2$ and ring protons other than CHBr), and 3.41—4.38 (m, 1H, CHBr); IR ν_{max}^{neat} 692 cm^{-1} (C–Br); $[\alpha]_D^{27.9}$ −29.0° (*c* 1.22, EtOH).

Found: C, 55.20; H, 8.88%. Calcd for $C_{10}H_{19}Br$; C, 54.79; H, 8.75%.

Product Criteria. The following were identified on the basis of spectra for each product purified by liquid or thin layer chromatography: ethyldiphenylphosphine oxide (^{1}H NMR ($CDCl_3$) δ=1.16 (dt, J_{PCCH}=17.4 Hz, J_{HH}=7.5 Hz, 3H, Me), 2.26 (dq, J_{PCH}=11.7 Hz, J_{HH}=7.5 Hz, 2H, CH_2), and 7.10—8.26 (m, 10H, Ph)], benzyldiphenylphosphine oxide [^{1}H NMR ($CDCl_3$) δ=3.64 (d, J_{PCH}=14.0 Hz, 2H, CH_2) and 7.08—8.06 (m, 15H, Ph)], isopropyldiphenylphosphine oxide [^{1}H NMR ($CDCl_3$) δ=1.16 (dd, J_{PCCH}=16.4 Hz, J_{HH}=7.1 Hz, 6H, Me), 1.63—2.04 (m, 1H, P-CH), and 7.05—8.04 (m, 10H, Ph)], cyclohexyldiphenylphosphine oxide [^{1}H NMR ($CDCl_3$) δ=0.74—2.64 (m, 11H, C_6H_{11}) and 7.14—8.18 (m, 10H, Ph); MS m/e=284 (M^+)], neomenthyldiphenylphosphine oxide [^{1}H NMR ($CDCl_3$) δ= 0.25—3.05 (m, 19H, Me, $C\underline{H}(C\underline{H}_3)_2$, and ring protons) and 7.01—8.02 (m, 10H, Ph); MS m/e=340 (M^+)], (1-methylheptyl)diphenylphosphine oxide,[27] isopropylphenylphosphine [^{1}H NMR (CD_3OD) δ=1.01 (pair of dd, J_{PCCH} =18.3 Hz, J_{HH}=6.8 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.8—2.4 (m, 1H, CH), and 6.7—7.9 (m, 5H, Ph)], (1-methylheptyl)phenylphosphine [^{1}H NMR (CD_3OD) δ=0.41—2.63 (m, 17H, C_8H_{17}), and 7.08—8.02 (m, 5H, Ph)], cyclohexylphenylphosphine [^{1}H NMR (CD_3OD) δ=0.7—2.3 (m, 11H, C_6H_{11}) and 7.2—8.1 (m, 5H, Ph)], menthylphenylphosphine [^{1}H NMR (CD_3OD) δ=0.18—2.63 (m, 19H, $C_{10}H_{19}$) and 6.97—8.14 (m, 5H, Ph)], and isopropylmethylphenylphosphine oxide [^{1}H NMR ($CDCl_3$) δ=1.11 (pair of dd, J_{PCCH}=15.8 Hz, J_{HH}=7.5 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.72 (d, J_{PCH}=12.5 Hz, 3H, P-Me), 1.42—1.93 (m, 1H, CH), and 7.21—8.17 (m, 5H, Ph)].

The structure of the produced secondary phosphines was further confirmed by converting them into methyl esters of the phosphinic acids, *e.g.*, methyl isopropylphenylphosphinate [^{1}H NMR ($CDCl_3$) δ=1.11 (pair of dd, J_{PCCH}=17.3 Hz, J_{HH}=7.2 Hz, 6H, $CH(C\underline{H}_3)_2$), 2.01 (dq, J_{PCH}=14.2 Hz, J_{HH}=7.2 Hz, 1H, CH), 3.63 (d, J_{POCH}=10.8 Hz, POMe), and 7.1—8.0 (m, 5H, Ph); IR ν_{max}^{neat} 1203 (P=O) and 1032 cm^{-1} (P–O–Me); MS m/e=198 (M^+)] and methyl cyclohexylphenylphosphinate [^{1}H NMR ($CDCl_3$) δ=0.72—2.42 (m, 11H, C_6H_{11}), 3.65 (d, J_{POCH}=10.8 Hz, 3H, POMe), and 7.29—8.08 (m, 5H, Ph); IR ν_{max}^{neat} 1215 (P=O) and 1033 cm^{-1} (P–O–Me); MS m/e=238 (M^+)] after oxidation by hydrogen peroxide followed by methylation with diazomethane, and/or by converting them into phosphonium salts with methyl iodide, *e.g.*, isopropylmethylphenylphosphonium iodide [^{1}H NMR (CD_3OD) δ=1.06 (pair of dd, J_{PCCH}=14.4 Hz, J_{HH}=7.2 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.06 (d, J_{PCCH}=16.4 Hz, 3H, P-Me), 1.9—2.7 (m, 1H, CH), and 7.2—7.9 (m, 5H, Ph)].

*Reaction of Diphenylphosphine Oxide (**1**) with Isopropyl Iodide in the Presence of SDMA.* To a stirred tetrahydrofuran solution of diphenylphosphine oxide (2.0 g, 10 mmol) was added SDMA (3.0 g, 15 mmol) dropwise under nitrogen flow and then a solution of isopropyl iodide (3.0 g, 18 mmol) in tetrahydrofuran (8 ml) was added. The reaction mixture was refluxed for 6 h. Addition of 1.5 ml of water to the cooled and stirred reaction mixture at room temperature followed by extraction by chloroform and successive evaporation of the solvent gave crude isopropyldiphenylphosphine oxide in 98% yield. Separation by thin layer chromatography gave the pure product in 91% yield: ^{1}H NMR ($CDCl_3$) δ=1.16 (dd, J_{PCCH}=16.4 Hz, J_{HH}=7.1 Hz, 6H, $CH(C\underline{H}_3)_2$), 1.63—2.04 (m, 1H, $C\underline{H}(CH_3)_2$), and 7.05—8.04 (m, 10H, Ph).

*Reaction of Diphenylphosphine Oxide (**1**) with Menthyl Chloride in the Presence of SDMA.* To a toluene (80 ml) solution of **1** (2.0 g, 9.9 mmol) was added SDMA (2 equivalents) in toluene (10 ml), and then menthyl chloride (1.7 g, 9.9 mmol) was successively added under nitrogen atmosphere. Refluxing the mixture for 16 h at 111 °C followed by work-up, separation of the products from the starting materials by liquid chromatography, and crystallization from petroleum ether gave 0.29 g of a mixture of neomenthyldiphenylphosphine oxide (86%) and menthyldiphenylphosphine oxide

(14%) in 11% yield, $[\alpha]_D^{12.4}$ +34.2° (*c* 0.75, EtOH).[28] The structure was confirmed by ^{1}H NMR and mass spectra.

The following product ratios and optical rotation values were obtained: neomenthyldiphenylphosphine oxide: menthyldiphenylphosphine oxide 63:37 from menthyl bromide, $[\alpha]_D^{24}$ +2.1° (*c* 1.6, MeOH); 99:1 from menthyl *p*-toluenesulfonate with diphenylphosphine oxide; neomenthylphenylphosphine: menthylphenylphosphine 51:49 from menthyl chloride with phenylphosphine, $[\alpha]_D^{27}$ −16° (*c* 1.6, EtOH).[26,28]

Reaction of ***1*** *with Isopropyl* p-*Toluenesulfonate in the Presence of SDMA.* To a stirred tetrahydrofuran (20 ml) solution of **1** (0.43 g, 2.1 mmol) and SDMA (2 equivalents) was added isopropyl *p*-toluenesulfonate (0.46 g, 2.1 mmol), and then the reaction mixture was heated for 10 h under reflux in nitrogen flow. Work-up (addition of 1 ml of water and evaporation of volatile materials) of the reaction mixture and separation of the product by liquid chromatography gave isopropyldiphenylphosphine oxide (0.48 g) in 94% yield, whose structure was confirmed by ^{1}H NMR spectrum.

Reaction of ***1*** *with Isopropyl Iodide in the Presence of Lithium Tetrahydridoaluminate.* To a stirred tetrahydrofuran solution of **1** (0.26 g, 2.1 mmol) was added lithium tetrahydridoaluminate (0.11 g, 2.9 mmol), and then isopropyl iodide (0.45 g, 2.6 mmol) was added. The mixture was heated for 4.5 h under reflux in nitrogen flow. Work-up and purification of the product gave isopropyldiphenylphosphine oxide (0.10 g) in 19% yield: mp 143—144 °C;[29] IR $\nu_{max}^{CHCl_3}$ 1165 cm^{-1} (P=O).

*Reaction of Phenylphosphine (****4****) with Isopropyl Bromide.* To a stirred tetrahydrofuran (50 ml) solution of phenylphosphine (1.02 g, 9.3 mmol) was added SDMA (2 equivalents) in 20 ml of tetrahydrofuran dropwise under nitrogen atmosphere, then isopropyl bromide (1.14 g, 9.3 mmol) was added to the solution, and the mixture was heated for 6 h under reflux. Addition of 2 ml of water followed by filtration and evaporation of the solvent under nitrogen atmosphere and removal of volatile material gave isopropylphenylphosphine (1.73 g) in quantitative yield. The ^{1}H NMR spectrum of the product in CD_3OD confirmed the structure. The structure was further reconfirmed by converting the phosphine to methyl isopropylphenylphosphinate.

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