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Synthesis of Trivalent Phosphorus Derivatives by Light-Induced Dibromophosphination of Akenes

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Abstract—Light-induced dibromophosphination of alkenes was studied. Dehydrobromination of the synthesized bromoalkylphosphonous dibromides gave the corresponding dibromophosphinoalkenes which were converted into alkenylphosphonous acids and their cyclic esters, benzo[1,3,2]dioxaphospholes.

Keywords: P(III) acid derivatives, phosphines, dibromophosphination of alkenes, dehydrobromination, benzo[1,3,2]-dioxaphospholes

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Light-induced reactions of unsaturated compounds are presently a well-studied practical synthetic approach to phosphonous acid dibromides [1, 2]. Along with the unusually facile P–C bond formation, the advantage of this approach consists in that P(III) acid bromides, unlike corresponding chlorides, are quite resistant to oxidation, and, at the same time, their bromine atoms exhibit a high reactivity in substitution reactions. Thus, alkylphosphonous dibromides obtained from alkynes undergo facile alcoholysis under the action of saturated and unsaturated alcohols and react with alkynyllithium [3]. The light-induced addition of phosphorus tribromide to alkenes is a reversible reaction, and the position of equilibrium depends on the temperature.

To gain a deeper insight into the preparative potential of this important reaction of organophosphorus compounds with alkenes and prepare novel P(III) and P(IV) derivatives, in the present work we studied the dibromophosphination of alkenes **1a–1v** under UV irradiation (Scheme 1).

It was found that the yield of adducts **2** depends on the steric factor. Thus, the yield of the adduct decreases in the series CH_2=CH_2, MeCH=CH_2, Me_2C=CH_2, Me_2C=CHMe, Me_2C=CMe_2, PhMeC=CH_2, Ph_2C=CH_2, PhCH=CHPh [4]. It can be suggested that the steric factor strongly affects the position of equilibrium.

As known [2], the light-induced addition of PBr_3 to styrene **1j** occurs in a regioselective manner: the bromine atom attaches to the least shielded carbon atom to form 1-(dibromophosphino)-1-phenyl-2-bromoethane **2j**. The reactions of haloalkylethenes **1b and 1c** occur in high yields but with a slightly lower selectivity than in the case of styrene. 3,3,3-(Trichloromethyl)propene **1d** and 1,1-dichloroethene **1k** could not be reacted. At the same time, (trichlorosilyl)ethene **1e** undergoes a fairly facile dibromophosphination to form regioisomeric dibromophosphines **2e** and **2e'** with a total yield of 40% (Scheme 2).

The regioisomer ratio determined from the integral intensity of their signals in the ^{31}P NMR spectrum is **2e** : **2e'** = 4 : 1. The ^1H NMR spectrum the **2e'** isomer contains two multiplets of the $CHPBr_2$ (3.31 ppm, $^2J_{HP}$ = 18.7, $^3J_{HH}$ = 7.5 Hz) and CH_2Br protons (3.65 ppm, $^3J_{HP}$ = 6.5 Hz). The spectral pattern is complicated by the exchange Cl_3Si chlorine for bromine exchange.

Scheme 1.

$$\underset{\textbf{1a–1v}}{R^1R^2C{=}CR^3R^4} + PBr_3 \xrightarrow{h\nu} \underset{\textbf{2a–2v}}{R^1R^2C(PBr_2)CBrR^3R^4}$$

R^2 = R^3 = R^4 = H, R^1 = Br (**1a**), CH_2Br (**1b**), CH_2Cl (**1c**), Cl_3C (**1d**), Cl_3Si (**1e**), Cl_2CH_3Si (**1f**), $(CH_3)_3Si$ (**1g**), Bu (**1h**), $PhOCH_2$ (**1i**), Ph (**1j**); R^3 = R^4 = H, R^1 = R^2 = Cl (**1k**), R^1 = Cl, R^2 = CH_2Cl (**1l**); R^1 = R^2 = CH_3 (**1m**), R^1 = R^2 = $BuOCH_2$ (**1n**), R^1 = CH_3, R^2 = Ph (**1o**), R^1 = R^2 = Ph (**1p**); R^1 = R^2 = CH_3, R^3 = Br, R^4 = H (**1q**); R^1 = R^2 = R^3 = CH_3, R^4 = H (**1r**); R^1 = R^3 = H, R^2 = R^4 = Ph (**1s**); R^1 = R^3 = H, R^2 = R^4 = CH_2Br (**1t**); R^1 = R^2 = R^3 = R^4 = CH_3 (**1u**); cyclohexene (**1v**).

Scheme 2.

$$\underset{\textbf{1e}}{Cl_3SiCH{=}CH_2} + PBr_3$$

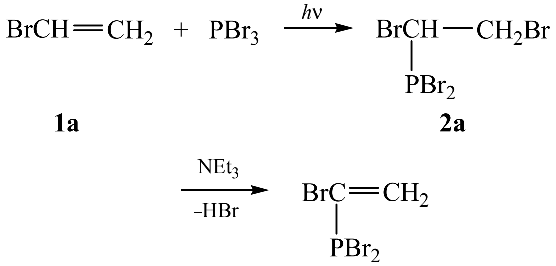
$$\xrightarrow{h\nu} \underset{\textbf{2e}}{Cl_3SiCH(PBr_2)CH_2Br} + \underset{\textbf{2e'}}{Cl_3SiCHBrCH_2PBr_2}$$

Scheme 3.

$$\underset{\textbf{1g}}{(CH_3)_3SiCH{=}CH_2} + PBr_3$$

$$\xrightarrow{h\nu} \underset{\textbf{2g}}{(CH_3)_3SiCH(PBr_2)CH_2Br} + \underset{\textbf{2g'}}{(CH_3)_3SiCHBrCH_2PBr_2}$$

Scheme 4.



$$\underset{\textbf{1a}}{BrCH{=}CH_2} + PBr_3 \xrightarrow{h\nu} \underset{\textbf{2a}}{\underset{PBr_2}{BrCH}{-}CH_2Br} \xrightarrow[-HBr]{NEt_3} \underset{\textbf{3}}{\underset{PBr_2}{BrC}{=}CH_2}$$

The reaction of (dichloromethylsilyl)ethene **1f** with PBr_3, leading to 2-bromo-1-(dichloromethylsilyl)-1-(dibromophosphino)ethane **2f** and its regioisomeric 1-bromo-1-(dichloromethylsilyl)-2-(dibromophosphino)ethane **2f'** in a 1 : 4 ratio, occurs in a similar way. The regionisomer ratio was determined from the intensities of the ^{31}P NMR signals at δ_P 180.5 and 172.2 ppm

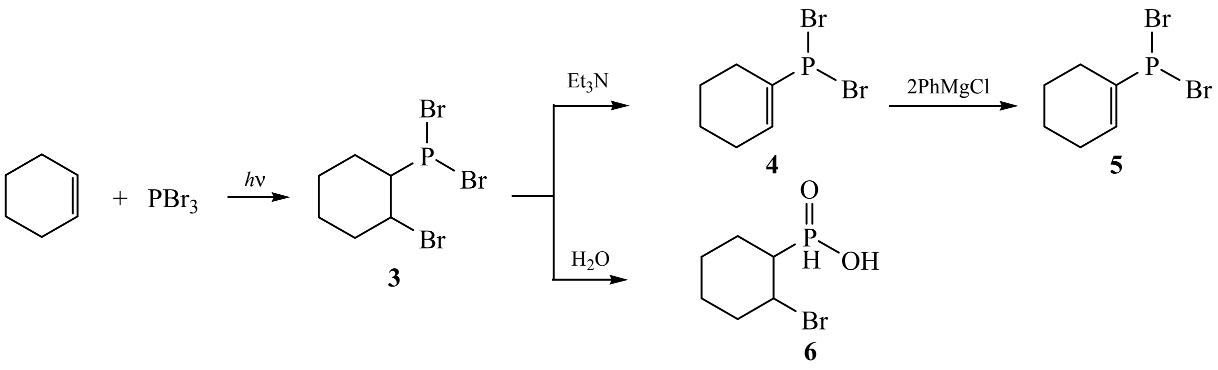
The highest yield in the series of the silicon-containing alkenes was obtained with (trimethylsilyl)ethene **1g** (Scheme 3). Therewith, the reaction proceeds with the highest regioselectivity: the ratio of 1-bromo-2-(trimethylsilyl)-2-(dibromophosphino)ethane **2g** and 2-bromo-2-(trimethylsilyl)-1-(dibromophosphino)ethane **2g'**, as determined from the intensity ratios of the corresponding signals in the ^1H and ^{31}P NMR spectra, is 10 : 3.

The ^1H NMR spectra of the reaction products contain signals of dibromophosphine **2g'** as a weakly coupled ABCX system: δ_{HA} = 4.12 ppm, $J_{H_AH_B}$ = 10, $J_{H_AH_C}$ = 3.5, J_{H_AP} = 8.5 Hz; δ_{HB} = 3.61 ppm, $J_{H_BH_C}$ = 9.0, J_{H_BP} = 3.0; δ_{HC} = 2.25 ppm, J_{H_CP} = 14.5 Hz. The value of the J_{H_BP} vicinal constant of 3.0 Hz is indicative of preferential realization of a partially eclipsed molecular conformation. The methyl groups on silicon appear as a doublet at 0.4 ppm

The synthesized dibromophosphines enter various reactions involving both the dibromophosphino and bromoalkyl groups: dehydrobromination, alcoholysis, reactions with Grignard reagents to form phosphines, and hydrolysis to form an alkylphosphonous acid (see table). Thus, the bromophosphination of bromoethene results in exclusive formation of 1,2-dibromo-1-(dibromophosphino)ethane **2a** whose dehydrobromination under the action of trimethylamine provides 1-bromo-1-(dibromophosphino)ethene **3a** (Scheme 4). The structure of compound **3a** was proved by ^1H, ^{31}P, and ^{13}C NMR spectroscopy. Similarly, the dehydrobromination of dibromophosphine **2b** leads to 3-bromo-2-(dibromophosphino)propene **3b**.

Cyclohexene **1v** actively reacts with PBr_3 under UV irradiation (cf. [4]) to form 2-bromo-1-(dibromophosphino)cyclohexane **2v.** The dehydrobromination of the latter gives rise to 1-(dibromophosphino)cyclohexene **4** (Scheme 5). The hydrolysis of compound **2v** with water in dioxane forms (2-bromocyclohexyl) phosphonous acid **6**. The reaction of compound **4** with phenylmagnesium bromide leads to 1-(diphenylphosphino)cyclohexene **5**. A similar diphenylphosphine **8**

Scheme 5.



Physicochemical characteristics, elemental analyses, and ^{31}P NMR data for dibromoalkyl(alkenyl)phosphonites and their derivatives

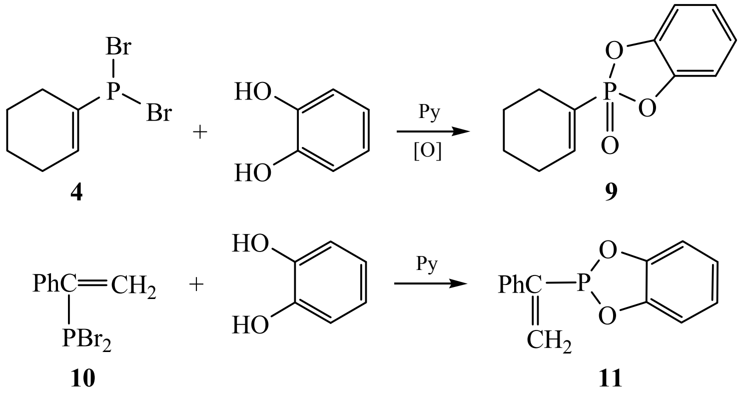
Comp. no.	Yield, %	bp, °C (mmHg) mp, °C	d_4^{20}, g/mL	n_D^{20}	Found, %		Formula	Calculated, %		δ_P, ppm
					P	Br		P	Br	
2a	30	107 (2)	2.6383	1.6745	8.20	84.64	$C_2H_3Br_4P$	8.01	84.78	150.4
2b	60	43	–	–	7.91	81.60	$C_3H_5Br_4P$	7.82	88.69	176.4
2c	58	110 (1) 28	–	–	8.93	69.04	$C_3H_5ClBr_3P$	8.92	69.04	179.5
2h	40	98 (2)	1.8767	1.5853	8.73	67.55	$C_6H_{12}Br_3P$	8.57	67.45	187.8
2i	65	165 (0.1)	–	–	7.82	60.55	$C_9H_{10}Br_3OP$	7.82	60.55	179.8
2j	60	90 (0.5) 45	–	–	8.26	63.95	$C_8H_8Br_3P$	8.18	64.08	179.9
2m	40	73 (1)	2.0950	1.6118	9.48	73.35	$C_4H_8Br_3P$	9.31	73.38	191.6
2n	60	106 (0.1)	–	–	6.58	50.89	$C_{12}H_{24}Br_3O_2P$	6.58	50.89	193.6
2v	50	125 (2)	2.0316	1.6283	8.78	67.94	$C_6H_{10}Br_3P$	8.81	67.85	198.0
3a	53	51 (2)	2.4711	1.6651	10.44	80.79	$C_2H_2Br_3P$	10.26	80.63	137.5
3b	50	65 (1)	2.3124	1.6496	9.97	77.14	$C_3H_4Br_3P$	9.85	77.22	150.0
4	60	97 (2)	1.8332	1.6166	11.39	58.77	$C_6H_9Br_2P$	11.32	58.84	157.5
5	90	155 (0.1)	–	–	11.63	–	$C_{18}H_{19}P$	11.49	–	–2.02
6	30	79	–	–	21.10	–	$C_6H_{12}O_2P$	21.05	–	32.06
7	50	63 (2)	1.6414	1.5668	11.31	58.33	$C_6H_{11}Br_2P$	11.20	58.40	158.9
8	70	70 (0.1)	1.0700	1.5786	11.54	–	$C_{18}H_{21}P$	11.58	–	–5.23

forms from 2-(dibromophosphino)hex-1-ene **7** obtained by dehydrobromination of 1-bromo-2-(dibromophosphino)hexane **2h** (see table).

For structural assessment compound **5** was oxidized with air oxygen into the corresponding phosphine oxide.

Dibromophosphine **4** readily reacts with pyrocatechol in the presence of pyridine as a base to form the corresponding cyclic phosphonate **9** because of the fast oxidation with air oxygen (Scheme 6). An analogous reaction of styryldibromophosphine **10** gives 2-(1-phenylvinyl)benzo[1,3,2]dioxaphosphole **11**.

Scheme 6.



The structures of all the products were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Their principal physicochemical characteristics and elemental analyses are listed in the table.

Thus, the light-induced bromophosphination of alkenes, while being a reversible reaction, allows preparation of bromoalkylphosphonous dibromides. Making use of the ability of the bromine atoms in the dibromophosphino group, as well as the ability of the bromoalkyl group to undergo dehydrobromination one can prepare a wide range of organophosphorus compounds.

EXPERIMENTAL

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained on a Bruker Avance III spectrometer (400 MHz) in $CDCl_3$.

Synthesis of dibromophosphines *(general procedure).* A tubular quartz reactor equipped with a magnetic stirred was charged with 0.32 mol of PBr_3 and 0.11 mol of alkene at a constant temperature (with low-boiling alkenes, a reverse trap cooled with an acetone–dry ice mixture was used). The mixture was irradiated at 10°C with UV light by means of a DRSh-1000 lamp (λ 253.7 nm). The reaction progress was monitored by ^{1}H NMR. The irradiation time was 0.5–3 h. After completion of the reaction, PBr_3 was distilled off at 1 mmHg, and the residue was fractionated in high vacuum.

Esterification of dibromophosphines *(general procedure).* Pyrocatechol, o.1 mol, was slowly added dropwise to a stirred and cooled solution of 0.107 mol of pyridine and 0.05 mol of dibromophosphine in 150 mL of dry ether. The reaction mixture was stirred for 1 h, and the precipitate of pyridine hydrobromide was then filtered off. The solvent was distilled off, and the residue was fractionated in a vacuum.

Dehydrobromination of dibromophosphines *(general procedure).* A solution of 0.15 mol of dibromophosphine in 0.4 mol of dry benzene was treated under stirring with a solution of 0.16 mol of pyridine in benzene, and the reaction mixture was then heated under reflux for 2 h. The precipitate of pyridine hydrobromide was then filtered off, the solvent was distilled off, and the residue was fractionated in a vacuum.

Reactions of dibromophosphines with Grignard reagents. A solution of 0.15 mol of dibromophosphine in ether was added dropwise to a stirred and cooled solution of 0.305 mol of Grignard reagent in dry ether. The reaction mixture was stirred for 0.5 h and excess Grignard reagent was decomposed with saturated aqueous NH_4Cl. The ether layer was dried with $MgSO_4$. The solvent was then distilled off, and the residue was fractionated in a vacuum. All operations were performed under argon.

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