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A Novel Reaction of Oxaphosphoranes Leading to 7-membered Cyclic Vinylidene Acetals

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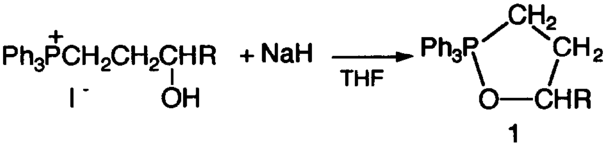
Abstract: **Reaction of oxaphosphoranes with paraformaldehyde yielded novel 7-membered cyclic vinylidene acetals in almost quantitative yield. Phosphonium betaines reacted with parformaldehyde to give new betaines, which further reacted with paraformaldehyde to afford olefins via Wittig reaction.**

Oxaphosphoranes are interesting compounds because of their unique structure and synthetic utility.[1)] In 1967, Hands and Mercer reported the first isolation of the parent 2,2,2-triphenyl-1,2-oxaphosphorane.[2)] Because their synthetic utility in the formation of homoallylic alcohols appeared promising, it was surprising to find that very few substituted derivatives of oxaphosphoranes had been prepared.[3)] Recently, we have reported the general synthesis of 3-hydroxyalkyltriphenylphosphonium salts.[4)] These results prompted us to investigate the reactivity of substituted oxaphosphoranes. In this communication, we report the synthesis of 7-membered cyclic vinylidene acetals by the reaction with paraformaldehyde.

Oxaphosphoranes **1** were prepared by the reaction of the corresponding 3-hydroxyalkyltriphenylphosphonium salts with sodium hydride.

Scheme 1



Treatment of oxaphosphoranes **1** with paraformaldehyde resulted in the formation of acetal **2** in nearly quantitative yield (Table1).

Scheme 2

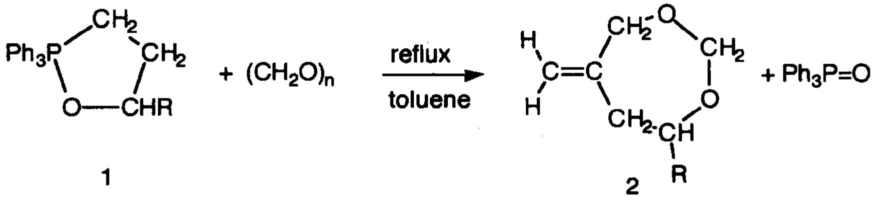


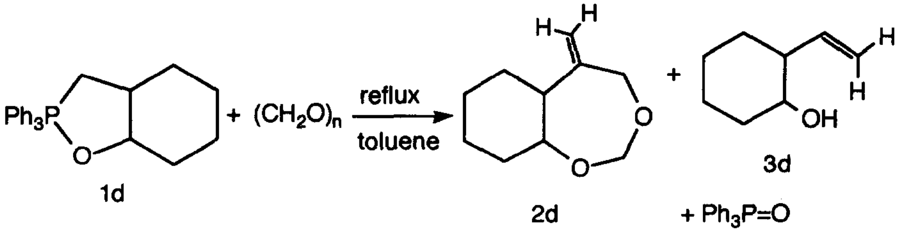
Table 1. Reaction of Oxaphosphoranes 1 with Paraformaldehyde

1		Conditions		Products (Yield/%)	
	R	Time/h	Solvent	2	Triphenylphosphine oxide
1a	H	0.1	Benzene reflux	**2a** 80	95
1b	Me	6	Benzene reflux	**2b** 70	75
1b	Me	1	Toluene reflux	**2b** 95	95
1c	Et	1	Toluene reflux	**2c** 95	95

In the case of oxaphosphorane **1a**, the reaction proceeds at relatively low temperature. Even in refluxing ether, the reaction was completed within 5 h. However, elevated temperature is required in the cases of **1b** and **1c**. Normal Wittig reaction products, homoallyl alcohols **3a-c**, were not observed in the reaction mixture by ^{1}H NMR analysis.

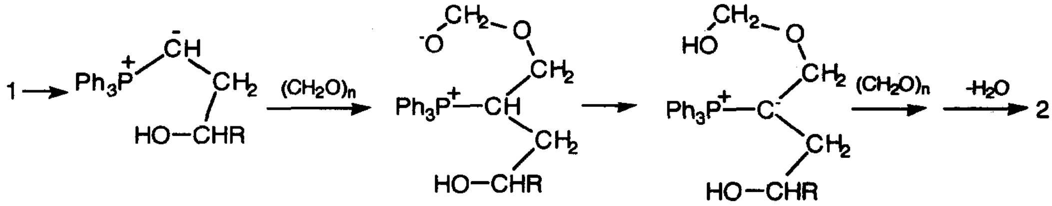
To confirm the possibility of the formation of bicyclic vinylidene acetals, the reaction of oxaphosphorane **1d** with paraformaldehyde was carried out. The desired product **2d** (24%) was obtained along with vinylidene cyclohexanol **3d** (35%).

Scheme 3



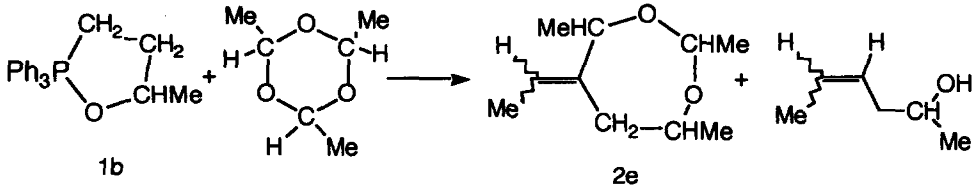
The reaction might proceed as follows. Oxaphosphorane **1** reacts with paraformaldehyde to give the corresponding betaine, which further reacts with another molecule of paraformaldehyde to afford **2**.

Mechanism



The reaction of **1b** with benzaldehyde afforded only the corresponding Wittig product (5-phenyl-4-penten-2-ol), suggesting that polymeric aldehydes are required in this reaction. Another commercially available polymeric aldehyde is only paraldehyde. Paraldehyde also reacted with **1b** to afford the corresponding **2e** as a mixture of *cis* and *trans* isomers along with the usual Wittig reaction products. Since the yield of **2e** was quite low (less than 5%), **2e** could not be isolated (Shceme 4).

Scheme 4



The present reaction is quite different from others. The reaction of oxaphosphoranes includes the preparation of homoallyl alcohols by the reaction with aldehydes. For example, Hands and Mercer reported that the reaction of oxaphosphoranes with aldehydes afforded the corresponding homoallyl alcohols.3) Corey and Kang reported that the reaction of α-lithiomethylenetriphenylphosphorane with epoxides afforded the corresponding homoallyl alcohols.5) Other types of the reactions were also reported. Le Corre and Hercouet prepared 2,3-dihydrofuranes by the intramolecular reaction of ω-acyloxy-n-propylidenephosphorane.6) Denny *et al.* reported that ethyl 2-phenylcyclopropanecarboxylate is produced in the reaction of carbethoxymethylenetriphenylphosphorane with styrene oxide at 200 °C.7) Schweizer and Creasy reported that thermolysis of 5-benzoyl-2,2,2,5-tetraphenyloxa-2-phosphorane afforded benzil, triphenylphosphine, and an olefin.8) However, there is no report on the reaction with paraformaldehyde to give cyclic vinylidene acetals.

The present reaction is interesting in that it can introduce three oxymethyl groups to phosphonium salts in one operation. This is the first example of the synthesis of 7-membered cyclic acetals from oxaphosphoranes, representing a new type of reaction for oxaphosphoranes. We are now currently continuing further investigation on the reaction and synthetic application of these compounds.

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8. Schweizer, E. E.; Creasy, W. S. *J. Org. Chem.* **1971**, *36*, 2244-2249.
9. Satisfactory mass spectra were obtained for all the new compounds. Spectral data of **2a**: ^{1}H NMR ($CDCl_3$) δ=2.53 (t, *J*=5.1 Hz, 2H, CH_2), 3.76 (t, *J*=5.1 Hz, CH_2O), 4.32 (s, 2H, OCH_2O), 4.80 (s, 2H, olefinic), 4.93 (s, 2H, CCH_2O). ^{13}C NMR ($CDCl_3$) δ=37.96 (CH_2), 68.86 (CH_2O), 73.42 (OCH_2O), 95.87 (CH_2=), 113.39 (CCH_2O), 146.40 (=C). **2b**: ^{1}H NMR ($CDCl_3$) δ=1.91 (d, *J*=6.4 Hz, 3H, CH_3), 2.39-2.48 (m, 2H, CH_2), 3.67-3.74 (m, 1H, CH), 4.32 (d, *J*=13.4 Hz, 1H, $OC\underline{H}HO$), 4.41 (d, *J*=13.4 Hz, 1H, $OCH\underline{H}O$), 4.66 (d, *J*=7.0 Hz, 1H, $C\underline{H}H$=), 4.93 (br s, 2H, $C\underline{H_2}O$), 4.98 (d, *J*=7.0 Hz, 1H, $CH\underline{H}$=). ^{13}C NMR ($CDCl_3$) δ=21.88 (CH_3), 44.89 (CH_2), 73.42 (OCH_2O), 75.50 (CH), 94.21 (CH_2=), 113.98 ($C\underline{C}H_2O$), 145.56 (=C). **2c**: ^{1}H NMR ($CDCl_3$) δ=0.96 (t, *J*=7.6 Hz, 3H, CH_3), 1.48-1.66 (m, 2H, $C\underline{H_2}CH_3$), 2.37-2.49 (m, 2H, CH_2), 3.41-3.47 (m, 1H, CH), 4.24 (d, *J*=13.4 Hz, 1H, $OC\underline{H}HO$), 4.39 (d, *J*=13.4 Hz, 1H, $OCH\underline{H}O$), 4.65 (d, *J*=6.7 Hz, 1H, $C\underline{H}H$=), 4.92 (br s, 2H, $CC\underline{H_2}O$), 5.01 (d, *J*=6.7 Hz, 1H, $CH\underline{H}$=). ^{13}C NMR ($CDCl_3$) δ=10.21 (CH_3), 28.92 ($\underline{C}H_2CH_3$), 42.86 (CH_2), 73.19 (OCH_2O), 80.51 (CH), 94.65 (CH_2=), 113.91 ($C\underline{C}H_2O$), 145.69 (=C).

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