A CONVENIENT SYNTHESIS OF 1-BROMOOLEFINS AND ACETYLENES BY A CHAIN EXTENSION OF ALDEHYDES

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Summary: Aldehydes are easily converted to 1-bromoolefins or terminal acetylenes by the use of Wittig reaction of bromomethylenetriphenylphosphorane which is prepared from bromomethyltriphenylphosphonium bromide with potassium tert-butoxide.

Transformation of aldehydes to acetylenes by chain extension is now of considerable value in organic synthesis. Recently, Corey and Fuchs reported "formyl-thynyl" conversion method which includes a Wittig reaction of dibromomethylenetriphenylphosphorane (prepared from  $CBr_4$  and  $Ph_3P$ ) yielding 1,1-dibromoolefins and their successive reduction.<sup>1</sup> Acetylenes are usually prepared by dehydrohalogenation of haloolefins. Thus, halomethylenation of aldehydes by Wittig reaction will lead to a more expeditious method to prepare acetylenes.

Ph<sub>3</sub>PCH<sub>2</sub>X·Y 
$$-HY$$
 Ph<sub>3</sub>P=CHX  
 $1$   $2$   
RCHO + 2  $-HX$  RCH=CHX  $-HX$  RC = CH  
 $3$   $4$ 

Treatment of chloromethyltriphenylphosphonium salts (<u>1</u>-a, X=Cl) with base is known to yield chloromethylenetriphenylphosphorane (<u>2</u>-a). However, the phosphonium salts <u>1</u>-a suffer from tedious preparation.<sup>2-5</sup> On the other hand, bromomethyltriphenylphosphonium salts such as bromide (<u>1</u>-b, X=Br) can easily be prepared from triphenylphosphine and dibromomethane,<sup>6</sup> but attempts to form

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bromomethylenetriphenylphosphorane (2-b) from the onium salt <u>1</u>-b using organolithium bases have yielded ambiguous results.<sup>6,7</sup> We have examined the reaction of the phosphonium salt <u>1</u>-b with several kind of bases and found that phosphorane <u>2</u>-b could be exclusively formed with potassium tert-butoxide.

When a suspension of the phosphonium salt <u>1</u>-b in dry tetrahydrofuran was treated with an equimolar amount of potassium tert-butoxide under an inert gas atmosphere at dry ice temperature, the yellow colored ylid <u>2</u>-b was formed. In the preparation of the ylid <u>2</u>-b, the reaction temperature is an important factor; at room temperature, the ylid seemed to be instantaneously quenched by tert-butanol produced from the base. The ylid was reacted with aldehydes to afford corresponding 1-bromoolefins <u>3</u> which are mainly composed of Z-isomers. Table 1 shows that aliphatic and  $\alpha,\beta$ -unsaturated as well as aromatic aldehydes qave the corresponding 1-bromoolefins, though the yields were favorable to aromatic ones. The stereoselectivity of the reaction was affected by the used solvent, as is well recognized in many Wittig reactions. For example, in the formation of 1-(2-bromoethenyl)naphthalene, the ratio Z-isomer/E-isomer changed from 6 in THF to 2.5 in toluene.

The 1-bromoolefins  $\underline{3}$  are usually converted into terminal acetylenes  $\underline{4}$ , whereas in the reaction system described here,  $\underline{4}$  can be directly obtained

Table 1.

(Ph <sub>3</sub> PCH <sub>2</sub> Br)Br	_1)	<sup>t</sup> BuOK	
	2)	R-CHO	R-Ch=Chb

the second se			
R-CHO	R-CH=CHBr	Yield %	ZE
©_сно	©~ <sup>Br</sup>	71	83 : 17
сно ФФ	© Br	81	86 : 14
О~сно	O~~Br	47	86 : 14
<i>Ц</i> Сно	Jan Jan Br	49	91 : 9
О~сно	O Br	72	77 : 23

without isolation of 3. When the Wittig reaction of 2-b with aldehydes was carried out in the presence of excess potassium tert-butoxide, the desired acetylenes were formed as shown in Table 2 (for aromatic acetylenes) and Table 3 (for aliphatic acetylenes). Similar to the case of formation of 1-bromoolefins, conjugated aldehydes afford more favorable results than aliphatic ones. The acetylenes thus obtained were contaminated with the corresponding bromoolefins which are entirely E-isomers, except for several aromatic acetylenes. This finding can be accounted for by a mechanism shown in the scheme. In dehydrohalogenation of haloolefins with base, Z-isomers are in general more rapidly consumed than E-isomers. By the use of these reactions, 1-bromo-3-(B-ionilidene)-1propene (5) and  $3-(\beta-ionilidene)-1$ propyne (6), key intermediates in the synthesis of retinal and vitamin A, were easily prepared from  $\beta$ -ionilideneacetaldehyde.

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1-b/2<sup>t</sup>BuOK

6 65(10)%

Table 2.  

$$(Ph_3PCH_2Br)Br = \frac{1}{2} \frac{2^{\dagger}BuOK}{2} Ar-C \equiv CH$$



+ ( ): Yield of Ar-CH=CHBr

Table 3.  
(Ph<sub>3</sub>PCH<sub>2</sub>Br)Br 
$$\xrightarrow{1}$$
 2 tBuOK  
2) R-CHO R-C=CH

R-CHO	R-C≋CH	Yield %
0~сно	0~=	40(7)
Land CHO	but "	35 (6)
Jan La CHO	hh#	62 (31)
О~СНО	0~=	45 (4)
		45 (4)

( ): Yield of R-CH=CHBr



Nap-CHO Nap-CH=CHBr	Ζ:Ε	
	in THF	6:1
	in Toluene	2.5:1

## References and Notes

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