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A Convenient Route to Aryl Substituted Chloro and Bromo Olefins

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Abstract: A wide range of aryl substituted chloro and bromo olefins has been prepared by treating α-chloro and α-bromophosphonates derived from 1-hydrido-5,5-dimethyl-1,3,2-dioxaphosphorinane with sodium hydride in THF at 0°C followed by an aldehyde.

One of the most preferred routes to prepare heavily substituted olefins is by reacting phosphonate carbanions with a carbonyl compound *via* the Horner-Wadsworth-Emmons reaction.[1] Synthesis of olefins of the type **I**, ArC(X)=CHR (X = Cl, Br) by this route[2] would require the corresponding α-halogenophosphonates $(RO)_2P(O)CH(X)Ar$ (X = Cl, Br). Recently, we have reported a convenient route to obtain such α-chloro and α-bromophosphonates from α-hydroxyphosphonates using $SOCl_2$ or $SOBr_2$.[3]

Herein, we report the synthesis of olefins of the type **I** from α-halogenophosphonates **1-5** [3](Scheme 1).

Typical experimental procedure (for 11): A solution of **3** (0.90g, 2.96 mmol) in THF was added rapidly to a slurry of sodium hydride (0.18g, 60% dispersion, 4.5 mmol) in THF at 0°C, followed immediately by 4-methyl benzaldehyde (0.36g, 3 mmol). After stirring at 0°C for 1h, the mixture was brought to room temperature and stirred for 6h. Then crushed ice was added, the product extracted with ether and chromatographed over silica gel using hexane followed by CH_2Cl_2 - hexane (1:5) to afford **11** (0.61g, 80%, *E*/*Z* mixture). One isomer (assumed to be *E*) crystallized out from the mixture after 3 days in 20% yield.
Mixture of isomers: ^{1}H NMR: 2.38, 2.39 (2s, 3H, 2 C-C$\underline{H}_3$), 3.83, 3.86 (2s, 3H, 2 OC$\underline{H}_3$), 6.80-7.70 (m, 9H, Ar($\underline{H}$) + C$\underline{H}$=CCl). ^{13}C NMR: 21.2, 21.3 (2 C-$\underline{C}$H$_3$), 55.3, 55.4 (2 O$\underline{C}$H$_3$), 113.8, 113.9, 124.5, 128.0, 128.6, 129.0, 129.3, 130.0, 130.2, 130.6, 131.1, 132.1, 132.7, 137.7, 160.0 (Ar($\underline{C}$) + $\underline{C}$H=$\underline{C}$Cl).
Solid isomer: m. p. 78°C. ^{1}H NMR: 2.38 (s, 3H, C-C$\underline{H}_3$), 3.86 (s, 3H, OC$\underline{H}_3$), 6.89-7.70 (m, 9H, Ar($\underline{H}$) + C$\underline{H}$=CCl). ^{13}C NMR: 21.4 (C-$\underline{C}$H$_3$), 55.5 (O$\underline{C}$H$_3$), 113.9, 124.6, 128.1, 129.1, 129.4, 137.5, 160.0 (Ar($\underline{C}$) + $\underline{C}$H=$\underline{C}$Cl). MS: 258 (M^+) & 260 (M^+), 223, 208, 179, 178, 165, 152, 135, 115, 89, 77, 63, 39.

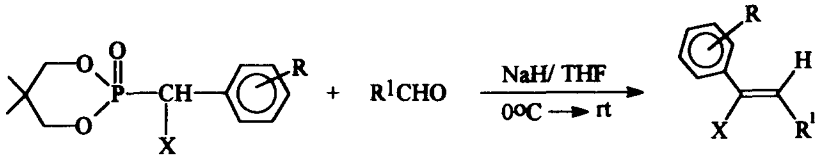
The following points are noteworthy:

(i) In contrast to earlier reports where the use of two equivalents of base gave the acetylene,[2,3] we did not observe the formation of acetylene even with a four-fold excess of sodium hydride in the reactions of the α-chlorophosphonates. In the case of α-bromophosphonates, reaction of **5** with 4-methoxy benzaldehyde gave the acetylene with 4 equiv. of NaH and the bromostilbene with 2 equiv. of NaH. Reaction of **17** with 4-methyl benzaldehyde gave only the acetylene (Scheme 2).

(ii) Use of *n*-BuLi or NaH in DMSO (compound **6**) did not offer any advantage.

iii) In general, the *E* and *Z* isomers were formed in approximately 3:2 ratio, except in the case of compound **10** where only a single isomer was observed.

(iv) This procedure affords easy access to a wide range of aryl substituted bromo olefins which are otherwise difficult to obtain.[4]



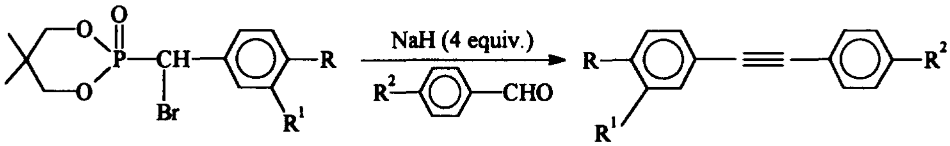
1: X = Cl; R = H
2: X = Cl; R = 4-Me
3: X = Cl; R = 4-OMe
4: X = Br; R = H
5: X = Br; R = 4-Me

6: R = H; R^1 = 4-Me-C_6H_4
7: R = H; R^1 = PhCH=CH
8: R = H; R^1 = Me_2CH
9: R = 4-Me; R^1 = 4-OMe-C_6H_4
10: R = 4-Me; R^1 = PhCH=CH
11: R = 4-OMe; R^1 = 4-Me-C_6H_4
12: R = 4-OMe; R^1 = Me-CH=CH

6-12: X = Cl, yield 60-90%
13-16: X = Br, yield 20-30%

13: R = H; R^1 = 4-Me-C_6H_4
14: R = H; R^1 = PhCH=CH
15: R = 4-Me; R^1 = 4-OMe-C_6H_4
16: R = 4-Me; R^1 = PhCH=CH

Scheme 1



5: R = Me; R^1 = H
17: R = OMe; R^1 = Br

18: R = Me; R^1 = H; R^2 = OMe
19: R = OMe; R^1 = Br; R^2 = Me

Scheme 2

In conclusion, our method offers a simple and convenient route to aryl substituted chloro and bromo olefins.

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