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WITTIG REACTION IN BENZENE-AQUEOUS ALKALINE SOLUTION

Waichiro Tagaki, Isao Inoue, Yumihiko Yano, and Tsuneo Okonogi
Department of Chemistry, Faculty of Technology, Gunma University,
Kiryu, Gunma, Japan

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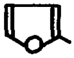
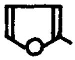
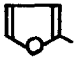
An enhanced rate or specificity has been observed in a number of micellar reactions[1] or under phase-transfer-catalysis.[2] For example, we have reported that sulfonium ylide generated in a benzene-aqueous alkaline solution is reactive enough in the reactions of aldehydes and ketones to give corresponding oxiranes in high yields.[3] Similar ylide reactivity can be expected in the reactions of phosphonium salt. This communication describes that Wittig's olefin synthesis can be performed in a benzene-aqueous alkaline solution by using aldehydes and alkylphosphonium halides.

The reaction was caried out by stirring a heterogeneous mixture of alkyltriphenylphosphonium halide (3 mmol), aldehyde (1.5 mmol), benzene (3 ml), and aqueous sodium hydroxide (9 ml) for one or few days at room temperature. The benzene extract of the reaction mixture afforded olefin and triphenylphosphine oxide as the main products. The results are shown in Table 1 and Figure 1.

The Table indicates that the methyl (R^1=H) and benzyl (R^1=C_6H_5) substituted salts give olefins ($R^1CH=CHR^2$) in more than 60% yield from both aliphatic and aromatic aldehydes. Olefins can also be obtained from the other salts having alkyl groups of ethyl (R^1=CH_3), hexyl (R^1=C_5H_{11}), allyl (R^1=CH_2=CH), and phenacyl (R^1=C_6H_5CO), although the yields are somewhat lower for these salts. Such a lower yield is mainly due to the decomposition of salt, and the yield can be raised by using more excess of salt since, in such a case, the starting aldehyde itself remains intact and can be recovered almost quantitatively. This may be illustrated by the data in Figure 1. Initially, increasing of base concentration raises the yield up to a maximum depending on the types of salt

Table 1. $$\underset{(3\ \text{mmol})}{(C_6H_5)_3\overset{+}{P}CH_2R^1X^-} + \underset{(1.5\ \text{mmol})}{R^2CHO} \xrightarrow{\text{benzene/NaOH}} R^2CH{=}CHR^1 + (C_6H_5)_3PO$$

R^1	R^2	X	NaOH (N)	reaction time (hr)	temp.	$R^2CH{=}CHR^1$ a,b,c,d yield (%)
H	C_6H_5	I	5	24	15°	80
H	C_6H_5	I	5	24	40°	99
H	C_6H_5	I	5	24	65°	24
H	p-Cl-C_6H_4	I	5	24	r.t.[e]	95
H	p-CH_3-C_6H_4	I	5	44	r.t.	55
H	p-CH_3O-C_6H_4	I	5	44	r.t.	38
C_6H_5CO	C_6H_5	Cl	5	24	r.t.	36
H	n-C_7H_{15}	I	5	48	r.t.	73
H		I	5	90	r.t.	63
H	$C_6H_5CH{=}CH$	I	5	90	r.t.	68
C_6H_5	C_6H_5	Cl	5	24	r.t.	81
C_6H_5	n-C_7H_{15}	Cl	5	24	r.t.	82
C_6H_5		Cl	5	44	r.t.	60
C_6H_5	$C_6H_5CH{=}CH$	Cl	5	44	r.t.	71
$CH_2{=}CH$	C_6H_5	Cl	0.5	24	r.t.	60
$CH_2{=}CH$	n-C_7H_{15}	Cl	0.5	64	r.t.	40
$CH_2{=}CH$		Cl	0.5	72	r.t.	15
$CH_2{=}CH$	$C_6H_5CH{=}CH$	Cl	0.5	72	r.t.	30
H	C_6H_5	Cl	0.5	24	r.t.	72
CH_3	C_6H_5	Br	15	24	r.t.	46
n-C_5H_{11}	C_6H_5	Br	15	24	r.t.	46

a) Yields, based on glc analysis.

b) Structures, based on nmr and mass analyses.

c) Starting aldehydes were recovered for the runs of lower yields.

d) Cis/trans isomer ratio was approximately 1 : 1 for each cases of $R^1 \neq H$

e) Room temperature: 15-25°

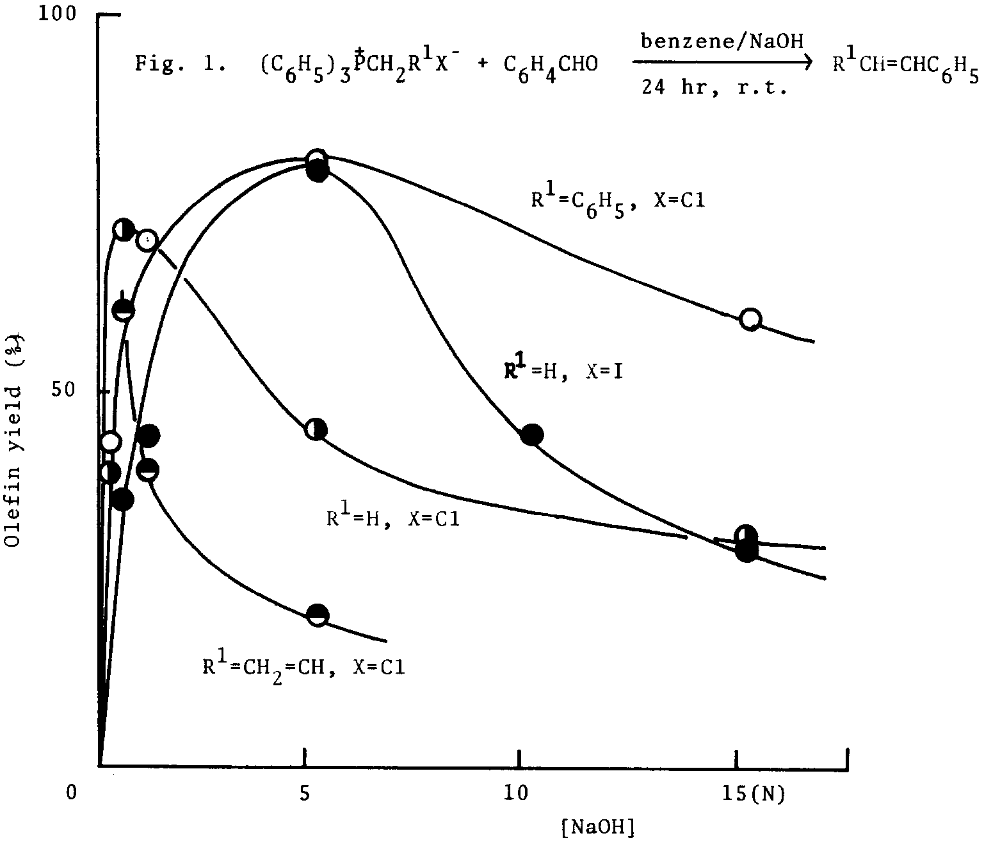


Fig. 1. $(C_6H_5)_3\overset{+}{P}CH_2R^1X^- + C_6H_4CHO \xrightarrow[\text{24 hr, r.t.}]{\text{benzene/NaOH}} R^1CH=CHC_6H_5$

and counter anion. Further increase of base concentration, however, reduces the yield. Before the maxima, a part of salt can be recovered, while after the maxima salt disappears on decomposition. Thus the yield appears to be determined by a competetion between the rate of olefin formation and the rate of salt decomposition which are the function of base concentration. An exception is the phenacyl substituted salt which is stable and less reactive, and the remaining unreacted salt is recovered almost quantitatively.

The above reaction was found to be specific to aldehydes. Ketones are unreactive: no olefin from acetophenone, and only a trace of olefin was detected for cyclohexanone and n-butylmethylketone, respectively. Nevertheless, the present method may be useful since a wide varieties of olefins, $R^1CH=CHR^2$, can be prepared by choosing an appropriate combination of salt and aldehyde under very mild conditions.

References

1. (a) E. H. Cordes and R. B. Dunlap, Accounts Chem. Res., **2**, 329 (1969).

   (b) E. J. Fendler and J. H. Fendler, Adv. Phys. Org. Chem., **8**, 271 (1970).

   (c) E. H. Cordes and C. Gitler, Progr. Bioorg. Chem., **2**, 1 (1973).

   (d) E. H. Cordes (Ed.), " Reaction Kinetics in Micelles," Plenum Press, New York, 1973.

2. (a) C. M. Starks, J. Amer. Chem. Soc., **93**, 195 (1971).

   (b) C. M. Starks and R. M. Owens, J. Amer. Chem. Soc., **95**, 3613 (1973).

3. (a) Y. Yano, T. Okonogi, M. Sunaga, and W. Tagaki, J.C.S. Chem. Comm., 527 (1973).

   (b) Y. Yano, T. Okonogi, and W. Tagaki, J. Org. Chem., **38**, 3912 (1973).