

The Reaction of Ylides with Halocarbenes*

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A new method of haloölefin formation has been found which involves an electrophilic attack by halocarbenes on the nucleophilic carbon of P- and S-ylides.

The increasing interest has been shown in the chemistry of carbenes, especially on the electronic state of the divalent carbon species. As far as halocarbenes such as dichloro- and dibromocarbenes are concerned, it is apparent that they are in the singlet state at usual reaction conditions. Namely, the electrophilic nature of these carbenes is substantiated in their reactions with olefins, amines, alkoxides, triphenylphosphine, and sodiomalonates¹⁾.

The Wittig's discovery excited considerable attention to the chemistry of P- and S-ylides. Some similar reactions with epoxides, Schiff bases, α , β -unsaturated esters, and nitrosobenzene have also been reported²⁾. It seems that these reactions, including the Wittig reaction, involve an attack by electrophilic carbon or nitrogen of these reagents on the negatively-charged carbon of P- or S-ylides. Recently, this has been confirmed kinetically in the Wittig reaction of a carbomethoxy-P-ylide with a series of aromatic aldehydes³⁾.

Based on the fact that the electronic character of ylides is opposite to that of halocarbenes, the reaction of these two reagents was examined expecting the formation of haloölefins as illustrated:



where X and/or Y are halogen atoms.

The following P- and S-ylides as substrates were prepared by the literature procedure. This class of ylides belongs to the resonance-stabilized type. Triphenylphosphonium cyclopentadienylide (PPP), triphenylphosphonium fluorenylide (PPF), tri-*n*-butylphosphonium fluorenylide (BPF), dimethylsulfonium fluorenylide (MSF), carbethoxymethylenetriphenylphosphorane (PPCM), α -carbethoxyethylidenetriphenylphosphorane (PPCE), α -carbethoxybenzylidenetriphenylphosphorane (PPCB), dicarbethoxymethylenetriphenylphosphorane (PPDC), and dicyanomethylenetriphenylphosphorane (PPDN). Dichlorocarbene was generated *in situ* from chloroform and potassium *t*-butoxide, or by refluxing sodium trichloroacetate in aprotic solvents. Similarly, bromoform, dichlorofluoromethane, and benzal chloride were used as the precursor of dibromo-, chlorofluoro-, and phenylchloro-carbenes, respectively.

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Table 1 Formation of α -haloolefins from ylides and halocarbenes.

Run No.	Ylide	Source of carbene	Reaction temp. and time	Product M.p. or b.p., yield ^a
1	PPP	CHCl ₃	10-15°C, 4 hrs.	Unreacted
2	PPP	C ₆ H ₅ CHCl ₂	70-75°C, 12 hrs.	Unreacted
3	PPF	CHCl ₂ F	10-15°C, 4 hrs.	9-(Chlorofluoromethylene)fluorene m.p. 76-77°C ^b , 21% (43%)
4	PPF	CHCl ₃	10-15°C, 4 hrs.	9-(Dichloromethylene)fluorene m.p. 129-130°C ^c , 44% (50%)
5	PPF	CCl ₃ COONa	75-80°C, 12 hrs.	9-(Dichloromethylene)fluorene m.p. 129-130°C ^c , 41%
6	PPF	C ₆ H ₅ CHCl ₂	70-75°C, 12 hrs.	9-(α -Chlorobenzylidene)fluorene m.p. 119-120°C ^d , 59% (84%)
7	BPF	C ₆ H ₅ CHCl ₂	70-75°C, 12 hrs.	9-(α -Chlorobenzylidene)fluorene m.p. 119-120°C ^d , 77%
8	MSF	CHCl ₃	10-15°C, 4 hrs.	9-(Dichloromethylene)fluorene m.p. 129-130°C ^c , 9%
9	MSF	CHBr ₃	10-15°C, 4 hrs.	9-(Dibromomethylene)fluorene m.p. 122-123°C ^e , 2%
10	PPCM	CHCl ₃	10-15°C, 4 hrs.	Ethyl β,β -dichloroacrylate b.p. 78-82°C/43 mm. ^f , 10%
11	PPCM	CCl ₃ COONa	75-80°C, 12 hrs.	Ethyl β,β -dichloroacrylate b.p. 78-82°C/43 mm. ^f , 21%
12	PPCM	C ₆ H ₅ CHCl ₂	75-80°C, 15 hrs.	Ethyl trans- β -chlorocinnamate b.p. 95-115°C/3 mm. ^g , 25% ^h
13	PPCE	CCl ₃ COONa	75-80°C, 12 hrs.	Ethyl β,β -dichloromethacrylate b.p. 90-92°C/43 mm. ⁱ , 45%
14	PPCB	CCl ₃ COONa	75-80°C, 12 hrs.	Ethyl β,β -dichloro- α -phenylacrylate b.p. 112-114°C/2 mm. ^j , 38% (46%)
15	PPDC	CCl ₃ COONa	75-80°C, 12 hrs.	Ethyl dichloromethylenemalonate b.p. 95-100°C/8 mm. ^k , 7% (16%)
16	PPDN	CCl ₃ COONa	75-80°C, 12 hrs.	Dichlorovinylidene cyanide m.p. 65°C ^l , 5%

a. The figures in parentheses indicate conversions based on consumed ylides.

b. Reported m.p. 75-80°C (Ref. 11).

c. Reported m.p. 132°C (Ref. 12).

d. Reported m.p. 120-121°C (Ref. 12).

e. Reported m.p. 131-132°C (Ref. 11).

f. Reported b.p. 173-175°C (Ref. 13).

g. Reported b.p. 265°C (Ref. 14).

h. This value was determined by v.p.c. analysis.

i. A new compound. *Anal.* Calcd. for C₆H₈O₂Cl₂; C, 39.37; H, 4.41; Found; C, 39.75; H, 4.53.

j. A new compound. *Anal.* Calcd. for C₁₁H₁₀O₂Cl₂; C, 53.90; H, 4.11. Found; C, 54.32; H, 4.28.

k. A new compound. *Anal.* Calcd. for C₈H₁₀O₄Cl₂; C, 39.86; H, 4.18. Found; C, 39.49; H, 4.44.

l. Reported m.p. 63-64°C (Ref. 15).

Generally, a mixture of ylides and potassium *t*-butoxide was treated with halforms in benzene for 4 hrs. at 10-15°C. The reaction with benzal chloride, however, was conducted for 12 hrs. at 70-75°C. When sodium trichloroacetate was used as a source of dichlorocarbene, the reaction was carried out in diglyme or dioxane for 12 hrs. at 70-80°C. All results are summarized in Table 1. No attempt was made to optimize the yields by variation in reaction conditions, so that it is highly probable that the

yields can be somewhat improved.

The identifications of haloölefins obtained were made by appearance of conjugated C=C bands (near 1600 cm^{-1}), by comparison of their melting or boiling points with those in literatures, and by their elementary analyses.

The reaction was accompanied, more or less, with tar formation, as in cases of other reactions which proceed through the intermediate formation of carbenes. The yields were generally not so high, and the unreacted ylides could not be recovered except for a few cases.

When PPP was allowed to react with halocarbenes, no reaction was observed and good recoveries of the ylide were made. However, the fluorene analogue, PPF, afforded the expected haloölefins with no difficulty. Such difference in reactivity is also recognized in the Wittig reaction⁴⁾. The reactive BPF showed a higher yield. In the reaction of PPCM with halocarbenes, the yields were lower than expected, especially in basic media. This may be ascribed to in part subsequent side-reactions of the obtained product (α, β -unsaturated carbonyl compounds) with some nucleophilic species. In the case of MSF, the results were disappointing owing to its unusual instability.

The reaction with benzal chloride showed generally better results than that with chloroform or sodium trichloroacetate. Since phenylchlorocarbene seems to be less reactive than dichlorocarbene in electrophilic character, this would imply that the concentration of intermediate phenylchlorocarbene is larger than that of dichlorocarbene and/or that, in the former reaction, the stabilization of the transition state for the step leading haloölefin by overlap of the π -orbitals of the phenyl group with those of the incipient double bond results in the rate acceleration. More quantitative experiments would be necessary before the problem is thoroughly discussed.

EXPERIMENTAL

Synthesis of ylides. All ylides were prepared by procedures previously described in literatures. The following constants were observed. PPP,⁵⁾ m.p. 229-230°C; PPF⁶⁾, m.p. 253°C; BPF,⁷⁾ m.p. 123 - 124°C; MSF⁸⁾, m.p. 75°C (decomp.); PPCM⁹⁾, m.p. 123 - 124°C*; PPCE,⁹⁾ m.p. 156 - 157°C; PPCB,^{**} m.p. 134.5 - 135.5°C; PPDC¹⁰⁾, m.p. 106 - 107°C; PPDN,¹⁰⁾ m.p. 187-188°C.

Reaction of ylides with halocarbenes. Typical examples are given below.

(a) 9-(Dichloromethylene)fluorene. (i) From PPF and sodium trichloroacetate. —Under nitrogen atmosphere, a mixture of 5.5 g. (0.013 mole) of PPF, 10.0 g. (0.054 mole) of sodium trichloroacetate in 120 ml. of diglyme was heated at 75 - 80°C for 12 hrs. with stirring. The reaction mixture became brown accompanying the evolution of carbon dioxide. After removal of inorganic material by filtration, diglyme was evaporated *in vacuo*. A benzene solution of the residue was washed with 5% hydrochloric acid and water, successively, and then dried. Distillation of benzene gave 1.3 g. (41%) of crude 9-(dichloromethylen)fluorene, and recrystallisation from ethanol gave the pure product as light yellow needles, m.p. 130 - 131°C. (ii) From MSF and

* The reported value is 7 degrees lower than this.

** A new ylide. *Anal.* Calcd. for $\text{C}_{28}\text{H}_{25}\text{O}_2\text{P}$; C, 79.23; H, 5.94. Found; C, 79.34; H, 6.02.

chloroform.—Into a stirred mixture of 5.0 g. (0.022 mole) of MSF, 11.2 g. (0.10 mole) of potassium *t*-butoxide and 70 ml. of benzene, 8.0 g. (0.07 mole) of chloroform was added dropwise at 10 - 15°C over a period of ca. 40 mins. under stream of nitrogen. Stirring was continued for additional 3 hrs. at room temperature. The reaction mixture was washed with water, dried, and the solvent was evaporated *in vacuo*. The tar-like residue was extracted with three 50 ml. portions of hot ethanol. The combined extracts were treated with Norit, and the alcohol was evaporated to dryness. Recrystallisation of the resulting solid (0.5 g., 9%) from ethanol afforded the pure olefin, m.p. 129 - 130°C.

(b) 9-(α -Chlorobenzylidene) fluorene. From BPF and benzal chloride.—A mixture of 9.0 g. (0.025 mole) of BPF, 14.0 g. (0.087 mole) of benzal chloride, 11.2 g. (0.10 mole) of potassium *t*-butoxide and 200 ml. of benzene was stirred at 75 - 80°C for 12 hrs. under nitrogen atmosphere. After removal of inorganic substance by filtration, the organic layer was concentrated *in vacuo*. The residue thus obtained was extracted with ethanol. Evaporation of ethanol yielded 5.5 g. (77 %) of crude 9-(α -chlorobenzylidene)fluorene. The pure product, m.p. 119 - 120°C, was obtained as yellow plates after a recrystallization from ethanol.

(c) Ethyl β, β -dichloro- α -phenylacrylate. From PPCB and sodium trichloroacetate.

—A mixture of 11.0 g. (0.026 mole) of PPCB, 21.0 g. (0.105 mole) of sodium trichloroacetate and 300 ml. of dioxane was stirred at 75 - 80°C for 12 hrs. under stream of nitrogen. After evaporation of dioxane, a benzene solution of the residue was washed with water, 5% hydrobromic acid, and water, successively, and then dried. When the combined aqueous layer was made basic with aqueous sodium hydroxide, 2.0 g. of the unchanged ylide was recovered. On the other hand, the organic layer was concentrated, and the residue was reextracted with ca. 100 ml. of petroleum ether to remove a tarry by-product. Then the solvent was distilled off, and the resulting liquid was fractionated under reduced pressure to give 2.4 g. (38%) of the expected ester, b.p. 112 - 114°C (2 mm.).

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