Tetrahedron Letters No.1, pp. 7-9, 1964. Pergamon Press Ltd.
Printed in Great Britain.

REACTION OF YLIDES WITH HALOCARBENES

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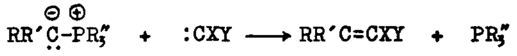
(Received 18 October 1963)

AS is the established fact in the Wittig reaction (1), all reactions of P-ylides with aldehydes, epoxides, ketene and isocyanate are believed to involve the nucleophilic attack of P-ylides. On the other hand, the electrophilic character of halocarbenes has also been confirmed from their reactivities toward some olefins (2).

Now we have studied the reaction between the two reagents and obtained olefins in good conversions according to the following equation.



$$RR'\overset{\ominus}{\underset{\cdot\cdot}{C}}-\overset{\oplus}{P}R''_3 \ + \ :CXY \longrightarrow RR'C=CXY \ + \ PR''_3$$

A less reactive S-ylide similarly reacted with halocarbenes, but the yields of the expected products were very low.

In connection with our reaction, a recent report (3) on the formation of olefins from diazoalkanes and halocarbenes is of very interest. Probably the latter reaction would proceed by the electrophilic attack of the carbene on the nucleophilic center of diazoalkane which is considered to be one kind of N-ylide.

Some combinations of dichloro-, dibromo- and phenylchlorocarbenes with triphenylphosphonium fluorenylide (PPF) (4), tri-n-butylphosphonium fluorenylide (BPF) (1) and dimethylsulfonium fluorenylide (MSF) (5) have been studied. Results are presented in Table I. The olefins obtained were identified by the appearance of new infrared absorptions near 1600 cm^{-1} arising from olefins conjugated with aromatic ring, the comparison of their melting points with those in the literature (3), and their elemental analyses.

TABLE I

Reaction of Ylides with Halocarbenes

Run No.	Ylide	Source of carbene	Reaction temp. and time	9-Sub. fluorene(F) (yield and m.p.)
1	PPF	$CHCl_3$	10-15° 4 hr.	Dichloromethylene-F (50% [a]; 129-130°)
2	PPF	$C_6H_5CHCl_2$	70° 12 hr.	α-Chlorobenzylidene-F (84% [a]; 119-120°)
3	BPF	$C_6H_5CHCl_2$	70° 12 hr.	α-Chlorobenzylidene-F (77% [a]; 119-120°)
4	MSF	$CHCl_3$	10-15° 4 hr.	Dichloromethylene-F (9%; 129-130°)
5	MSF	$CHBr_3$	10-15° 4 hr.	Dibromomethylene-F[b] (2%; 122-123°)

a. Based on consumed ylide.

b. New compound (Found: C, 50.32; H, 2.86; Br, 46.35. $C_{14}H_8Br_2$ requires C, 50.04; H, 2.40; Br, 47.56%).

A typical expample of the reaction is as follows. Chloroform (6.0 g.) was added dropwise at 10-15° to a stirred mixture of PPF (6.0 g.) and potassium t-butoxide (6.3 g.) in benzene (200 ml.). The mixture was stirred for a further 3 hr. at room temperature. After removal of inorganic material by filtration, the solvent was evaporated in a vacuum. The residue was treated with ethanol to separate the unchanged ylide (0.8 g.), and the dissolved portion was evaporated to dryness. The resulting solid was redissolved in benzene, and the solution was washed with 5% hydrochloric acid and water. Evaporation of benzene afforded the crude olefin (1.5 g.) which recrystallised from ethanol as light-yellow needles, m.p. 129-130° [lit. (3), 132°].

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