Journal of Organometallic Chemistry, 154 (1978) C45—C48

Preliminary communication

TRIMETHYL(TRIHALOMETHYL)SILANES AS DIHALOMETHYLENE TRANSFER AGENTS

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(Received March 21st, 1978)

Summary

Trimethyl(trichloromethyl)silane and trimethyl(tribromomethyl)silane react with anhydrous potassium fluoride in diglyme to give good yields of CX_2 transfer products (dihalocyclopropanes) with olefins. Catalysis by 18-crown-6 ether is observed.

A variety of methods are available for the generation of dihalocarbene species [1], but particular efforts have been made to develop reagents which will transfer dihalomethylene under mild conditions. Among the most successful of these approaches are the phase-transfer reactions of haloforms with aqueous base [2], and in anhydrous systems, the thermolysis or iodide-ion induced decomposition of phenyl(trihalomethyl)mercury reagents [3] (eq. 1)*.

$$\mathrm{PhHgCX_3} \xrightarrow[\mathrm{NaI/30^\circ C}]{80^\circ\mathrm{C\ or}} \mathrm{PhHgX} + :\mathrm{CX_2} \qquad (1)$$

$$\mathrm{X_3SiCCl_3} \xrightarrow[\mathrm{X = F,\ 140^\circ C}]{\mathrm{X = Cl,\ 250^\circ C}} \mathrm{X_3SiCl} + :\mathrm{CCl_2} \qquad (2)$$

Certain organosilicon compounds have also been found to effectively transfer dichloromethylene upon thermolysis (eq. 2), but their utility is limited by the temperatures required [7,8]. We wish to report a method whereby trimethyl(trihalomethyl)silanes can be made to undergo α-dehalosilylation under ambient conditions to afford good yields of dihalomethylene transfer products with olefinic substrates**.

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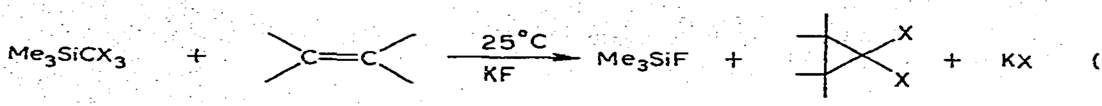
*Moderate yields of dichlorocarbene-olefin adducts have also been obtained from the reaction of Me_3SnCCl_3 with NaI (80°C) [4] and $(EtO)_2P(O)CCl_3$ with KF (110°C) [5]. Difluorocarbene has been generated from $[Ph_3PCF_2Br]Br$ and KF at room temperature [6].

**We have previously reported the fluoride-ion induced α-dehalosilylation of an α-chlorovinylsilane to give isopropylidene carbene insertion products with carbenophiles [9].

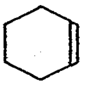
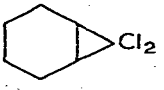
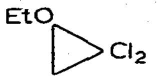
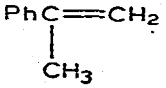
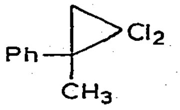
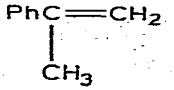
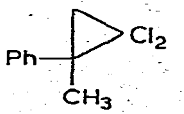
The overall transformation is illustrated by eq. 3 and the results for trimethyl(trichloromethyl)silane [10] are summarised in Table 1. In diglyme solvent, all olefins examined afforded good yields of dichlorocyclopropanes within 4—7 days at room temperature. The addition of catalytic amounts of 18-crown-6 ether [11], known to enhance the nucleophilicity of fluoride ion [12], strongly accelerated the rate of dichloromethylene transfer, typically

 (3)

(X = Cl, Br)

TABLE 1

REACTION OF TRIMETHYL(TRICHLOROMETHYL)SILANE WITH OLEFINS[a]

Olefin	0.1 Equiv. 18-Crown-6	Reaction time	Product	(% yield)[b]
	No	6.5 days[c]		(80)
	Yes	1 day		(71)
	Yes	15 h		(62)[d]
	Yes	26 h		(71)[e]
	Yes	3.5 days		(76)[f]
$EtOCH{=}CH_2$	No	4 days		(77)
$EtOCH{=}CH_2$	Yes	9 h		(71)
 $PhC(CH_3){=}CH_2$	No	5 days		(55)
 $PhC(CH_3){=}CH_2$	Yes	1 day		(56)

[a] In diglyme with 2—4 equivalents KF vs. Me_3SiCCl_3 and excess olefin at 25°C. [b] GLPC yields. Dichloronorcarane [14], 1,1-dichloro-2-ethoxycyclopropane [15,16] and 1,1-dichloro-2-methyl-2-phenylcyclopropane [17] were GLPC-collected and identified by IR and NMR data. [c] Three equivalents KF/6 days + 1 equivalent KF/0.5 day for total consumption of Me_3SiCCl_3. [d] Isolated yield; 0.04 equivalents 18-crown-6. [e] 1/1 Me_3SiCCl_3/cyclohexene. [f] No diglyme; cyclohexene as solvent.

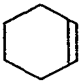
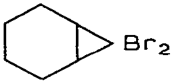
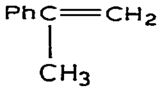
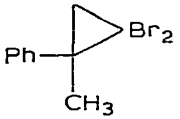
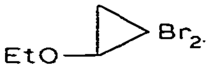
reducing the required reaction time to one day or less. Of significant interest is the observation that, at least with cyclohexene, the same yields of adduct dichlorocyclopropanes are obtained with either excess or equivalent amounts of olefin. Thus, the method may be applicable to situations where only limited quantities of an olefinic substrate are available. On the other hand, the reaction can be carried out in excess cyclohexene alone (no diglyme), provided that 18-crown-6 is employed as catalyst. Although 3.5 days were required for complete reaction under these conditions, the yield of dichlorocyclopropane product was in the same range afforded by other conditions examined.

In like fashion, the reaction of trimethyl(tribromomethyl)silane [13] with olefins in diglyme (eq. 3, X = Br) afforded good yields of dibromocyclopropane products (Table 2). All runs were carried out in the presence of catalytic amounts of 18-crown-6, and silane consumption was complete in less than one day under ambient conditions.

An experimental procedure, applicable to both the trimethyl(trichloromethyl)silane and trimethyl(tribromomethyl)silane systems is as follows. A flask equipped with magnetic stirring bar and septum-sealed side arm was sequentially charged with anhydrous 18-crown-6 (0.52 g, 2.0 mmol) and finely powdered dry potassium fluoride (6.0 g, 103 mmol) in a dry box. The flask was stoppered, removed from the dry box, and placed under positive nitrogen pressure. Cyclohexene (11 ml, 9.0 g, 110 mmol) and 14 ml diglyme were then added by syringe. The mixture was allowed to stir for several minutes and then 10.2 g (53 mmol) of trimethyl(trichloromethyl)silane was added.

TABLE 2

REACTION OF TRIMETHYL(TRIBROMOMETHYL)SILANE WITH OLEFINS[a]

Olefin	Reaction time	Product	(% yield)[b]
	11 h		(74)
 $PhC(CH_3)=CH_2$	18 h		(73)
$EtOCH=CH_2$	19 h		(60)[c]

[a] In diglyme/0.1 equivalent 18-crown-6 vs. Me_3SiCBr_3/2—3 equivalents KF and excess olefin at 25°C.
[b] GLPC yields. Dibromonorcarane [14], 1,1-dibromo-2-methyl-2-phenylcyclopropane [17] and 1,1-dibromo-2-ethoxycyclopropane [18] were identified by IR and NMR data. [c] Isolated, b.p. 51—54°C/6 mmHg (lit. [18], b.p. 62—63°C/8 mmHg).

The flask was stoppered, sealed with wax, and stirred for 15 h at 25° C, after which time no Me_3SiCCl_3 remained. Salts were removed by filtration, the filtrate (pentane added) washed several times with water and dried over anhydrous $MgSO_4$. The material remaining after solvent removal was distilled to give 5.4 g (62%) of 7,7-dichloronorcarane, b.p. 57—58° C/6 mmHg (lit. [14], b.p. 78—79° C/15 mmHg).

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