The Reaction of Enamines with Inorganic Halides

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Summary Enamines react with Group IV halides to form organometallic immonium type salts and organometallic enamines.

ALTHOUGH reactions of enamines with alkyl and acyl halides have been widely studied little is known of their reactions with inorganic halides. We report a new reaction in which inorganic halides combine with enamines to produce organometallic immonium salts and organometallic enamines.

$$MCl_4 + CH_2{=}C(NMe_2)R \rightleftharpoons Cl_3MCH_2\overset{+}{C}(NMe_2)RCl^- \xrightarrow{\text{base}} Cl_3MCH{=}C(NMe_2)R$$

Silicon tetrachloride reacts rapidly at room temperature with vinylidenebisdimethylamine, $CH_2{=}C(NMe_2)_2$ (I) to produce [2,2-bis(dimethylamino)vinyl]trichlorosilane (II). In this system the intermediate immonium salt is not isolable nor is it detectable by n.m.r. The same is true of the reaction of $SiCl_4$ and $GeCl_4$ with *NN*-dimethyl-α-styrylamine, $CH_2{=}C(NMe_2)Ph$ (III) which yield respectively trichloro-[α-(dimethylamino)styryl]silane (IV) and trichloro-[α-dimethylamino)styryl]germane (V).

The immonium salt generated in the reaction of $GeCl_4$ with (I) is not only detectable in the n.m.r. but is isolable as the 1,1-bis(dimethylamino)-2-(trichlorogermyl)ethylium chloride (VI). Addition of more base appears to convert this salt into an enamine-type product similar to (II) although this compound has not been isolated. Finally, the reaction of $SnCl_4$ with (I) produces an immonium salt, 1,1-bis(dimethylamino)-2-(trichlorostannyl)ethylium chloride (VII), which additional base does not seem to convert into the organometallic enamine. This series, Si, Ge, Sn, in which silicon prefers an unsaturated substituent, germanium can exist with saturated or unsaturated substituents and tin prefers only a saturated substituent is consistent with the order of ($p \rightarrow d$) π-bonding to these elements.[1]

Physical properties

Compound	M.p. or b.p. (mm Hg)	M^+	N.m.r.
(II)	60° (0·1)	246	(C_6H_6) τ 6·9 (s, 1H), 7·3 (s, 6H), 7·7 (s, 6H)
(IV)	120° (0·1)	279	(C_6D_6) τ 2·88 (s, 5H), 5·88 (s, 1H), 7·82 (s, 6H)
(V)	123°(0·1)		(C_6D_6) τ 2·92 (s, 5H) 5·65 (s, 1H), 7·91 (s, 6H)
(VI)	118—119°		(CD_3CN) τ 6·30 (s, 1H), 6·80 (s, 6H)
(VII)	119·5° decomp.		(CD_3CN) τ 6·57 (s, 1H), 6·80 (s, 6H)

An interesting feature of these systems in solution is their apparent dynamic equilibria with carbon–metal bonds rapidly making and breaking. For example, (II) in the presence of additional (I) will produce species in which the silicon has more than one organic substituent and these species can rapidly be reconverted into (II) by addition of $SiCl_4$. Furthermore, broadening of the n.m.r. lines of (VII) in the presence of an excess of (I) suggests rapid exchange of the organic substituent with free (I).

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[1] E. A. V. Ebsworth, in "The Bond to Carbon," ed. A. G. MacDiarmid, Marcel Dekker, New York, 1968, vol. 1, part 1, p. 86.