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ON ASSISTANCE IN β-ELIMINATION REACTIONS

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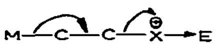
SUMMARY

It has been shown that organomercury compounds containing strongly electronegative groups in the β-position and which are not capable of inter- and intramolecular interaction with the mercury atom, undergo symmetrization and substitution reactions rather than β-elimination in the presence of nucleophiles.

INTRODUCTION

Organometallic compounds with strongly electronegative substituents in the β-position readily undergo β-elimination, a reaction that has been explained either in terms of σ,σ- and σ,π-conjugation at the moment of nucleophilic attack on the metal atom[1] or through the formation of a β-onium complex[2].

N: nucleophile



E electrophile

In an earlier study involving (*cis*-2-chlorovinyl)mercury chloride we found that with this compound β-elimination does not take place because of intramolecular coordination between the mercury atom and the electron-releasing chlorine[3], since in this case nucleophilic attack on the metal (including nucleophilic assistance[4]) is quite impossible. In other cases where the group X exerts a sufficiently strong attraction, a dynamic mesomeric effect should be produced, and thus it might be expected that in the presence of substituents such as trifluoromethyl and trinitromethyl β-elimination would occur in the presence of nucleophiles.

RESULTS AND DISCUSSION

To examine this suggestion, we have studied the effects of potassium iodide and cyanide and ammonia on (3,3,3-trifluoropropyl)- and (3,3,3-trinitropropyl)-mercury chlorides. Ammonia did not effect the reaction of these compounds whereas the use of potassium salts led to the formation of substitution and symmetrization products without the evolution of ethylene.

$$XCH_2CH_2HgCl + KCN \rightarrow (XCH_2CH_2)_2Hg$$

$$X = CF_3, C(NO_2)_3$$

$$CF_3CH_2CH_2HgCl + KI \rightarrow CF_3CH_2CH_2HgI$$

$$(O_2N)_3CCH_2CH_2HgCl + KI \rightarrow (O_2N)_3CCH_2CH_2HgI$$

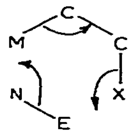
$$\downarrow \text{Simultaneous}$$

$$[(O_2N)_3CCH_2CH_2]_2Hg + HgI_2$$

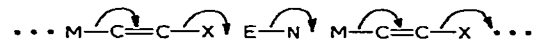
The structures of 3,3,3-trifluoropropyl derivatives were confirmed by NMR studies (data given in Tables 1 and 2). The ^{19}F NMR spectrum (Table 2) for (3,3,3-trifluoropropyl)mercury chloride, which gives a very low value for $J(CF_3Hg)$, indicates that no coordination occurs between the fluorine and mercury atoms in the molecule (at least in carbon tetrachloride solution). It is probable that in organometallic compounds of this type the γ-fluorine atom is incapable of producing a donor effect since it has been observed that (3,3,3-trifluoropropyl)magnesium chloride is stable in ether[5] and that (3,3,3-trifluoropropyl)boron difluoride remains virtually unaffected on heating to 160°[6].

From this it must be concluded that β-elimination only occurs when the β-substituent possesses a lone pair of electrons, thus allowing it to produce onium complexes with an electrophile or with the electrophilic component of a nucleophilic agent. This is impossible with (*cis*-2-chlorovinyl)mercury chloride owing to the intervention of intramolecular coordination, while in the cases already mentioned the absence of a β-substituent possessing lone-pair electrons also prevents β-elimination.

Since charge transfer along a σ,σ-conjugated chain is only possible through the intervention of a transition state:



or linear structures of the type ...M–C=C–X→E–N→M–C=C–X... (or alternatively)



the attack of a nucleophile on the metal atom must occur simultaneously with that of an electrophile on the β-substituent possessing lone-pair electrons before β-elimination will occur. Such a simultaneous attack is somewhat similar to an assistance in heterocyclic substitution since the net result is that a 1,3-conjugate system participates in the formation of a coordinative transition complex. For this reason the effect could be termed "conjugative assistance".

EXPERIMENTAL

NMR spectra were measured on a Hitachi–Perkin–Elmer R-20 instrument at 60 MHz.

TABLE 1

PMR SPECTRA OF 3,3,3-TRIFLUOROPROPYL DERIVATIVES (IN CCl_4 SOLUTION)[a]

Compound	δ(ppm)		J (Hz)			
	$CH_2(CF_3)$	$CH_2(Hg)$	CH_2–CH_2	CH_2–CF_3	CH_2–Hg	CH_2–C–Hg
$CF_3CH_2CH_2HgCl$	2.55	1.99	7.9	10.1	223.0	226.0
$CF_3CH_2CH_2HgI$	3.06	2.09	6.8	10.1	198.0	217.5
$(CF_3CH_2CH_2)_2Hg$	2.48	1.15	7.9	10.5	110.4	109.5

[a] With hexamethyldisiloxane as a standard.

TABLE 2

^{19}F NMR SPECTRA OF 3,3,3-TRIFLUOROPROPYL DERIVATIVES (IN CCl_4 SOLUTION)[a]

Compound	$\delta(CF_3)$ (ppm)	J(Hz)	
		CH_2–CF_3	CF_3–Hg
$CF_3CH_2CH_2HgCl$	10.65	10.0	6.4
$CF_3CH_2CH_2HgI$	10.98	10.0	
$(CF_3CH_2CH_2)_2Hg$	10.14	10.6	21.2

[a] With trifluoroacetic acid as a standard.

(3,3,3-*Trinitropropyl*)*mercury chloride*

This was prepared from 1,1,1-trinitro-3-(trinitromethyl)mercurio propane by treatment with 6 *N* hydrochloric acid according to the procedure previously described[7], yield 90%, m.p. 145–146° (chloroform). Lit. m.p. 142°.

Bis(3,3,3-*trinitropropyl*)*mercury*

(3,3,3-Trinitropropyl)mercury chloride (0.33 g, 0.8 mmole) was added to 0.2 g (3 mmole) of potassium cyanide in ethanol (25 ml). After $1\frac{1}{2}$ h the alcohol was removed in vacuo and the residual solid extracted with hot chloroform to yield 0.20 g (90%) bis(3,3,3-trinitropropyl)mercury, m.p. 159–160° (chloroform). Lit. m.p. 155° [7].

(3,3,3-*Trifluorpropyl*)*mercury chloride*

Mercuric chloride (53.4 g, 0.20 mole) was added to a Grignard reagent produced from 4.8 g (0.20 g-atom) of magnesium and 29 g (0.22 mole) of 3,3,3-trifluoropropyl chloride in 125 ml of ether (the reaction having been initiated with bromine). After refluxing for $1\frac{1}{2}$ h, the mixture was decomposed with 2–3% hydrochloric acid and the ether evaporated. The product was filtered, refluxed with 2–3% hydrochloric acid for 2 h, re-filtered, dissolved in benzene and refluxed with charcoal for $1\frac{1}{2}$h. After evaporation of the benzene 57.6 g (86.5%) of (3,3,3-trifluoropropyl)mercury chloride was obtained, m.p. 73.2–73.6° (after recrystallization twice from benzene/hexane, 1/8). This could be distilled in vacuo without decomposition at 160°/2.5 mm. (Found: C, 10.82; H, 1.28. $C_3H_4ClF_3Hg$ calcd.: C, 10.82; H, 1.21%.)

Bis(3,3,3-*trifluoropropyl*)*mercury*

Potassium cyanide (10.4 g, 0.16 mole) in water (20 ml) was added to 13.3 g (0.04 mole) of (3,3,3-trifluoropropyl)mercury chloride in ethanol (25 ml) and the mixture stirred for 1½h. Benzene was added and the mixture filtered and dried over magnesium sulphate. Bis(3,3,3-trifluoropropyl)mercury (3.0 g, 50% yield in terms of the initial reactant concentration) was obtained, b.p. 83°/18 mm, n_D^{20} 1.4093 (Found: C, 18.52; H, 2.12. $C_6H_8F_6Hg$ calcd.: C, 18.26; H, 2.04%).

A fraction was also isolated with b.p. 160°/2.5 mm, which rapidly crystallized to give a solid of m.p. 72°. This was found to be the initial reactant.

(3,3,3-*Trifluoropropyl*)*mercury iodide*

Potassium iodide (16.6 g, 0.1 mole) in alcohol (90 ml) was added to 10 g (0.03 mole) of (3,3,3-trifluoropropyl)mercury chloride. The mixture was stirred for 2½ h and allowed to stand overnight. The resulting precipitate was dissolved in water and benzene added. The organometallic component of the resulting extract was dried over magnesium sulphate and after evaporation of benzene 7.10 g (56%) (3,3,3-trifluoropropyl)mercury iodide was obtained, m.p. 49.5–50.5°. After sublimation at 60°/2mm the product melted at 51–51.3°. Lit. subl. p. 60°[8]. (Found: C, 8.47; H, 0.84. $C_3H_4F_3HgI$ calcd.: C, 8.49; H, 0.95%.)

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