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REACTION OF ALKYLMERCURY AND ALKYLTIN COMPOUNDS WITH DIPHENYLMETHYL SALTS

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Alkyl derivatives of mercury and Group IVB elements containing β hydrogen atoms react with the ionic salts of triarylmethyl to form triarylmethane, an olefin, and the dealkylation product of the organometallic compound (OMC) [1-3]. These reactions are classified as β elimination [4, 5], and it has been shown that they are bimolecular and proceed in a single step, with simultaneous breaking of the β-C−H and C−M bonds (E_E2 elimination). For the reaction of (9-methyl-9-fluorenyl)trimethyltin with triphenylmethyl fluoborate, which also forms triphenylmethane and the corresponding olefin, an oxidation-reduction mechanism that includes a one-electron transfer has been demonstrated [6].

In a continuation of our investigation in a number of transition metal OMC, we have studied the reaction of dialkylmercury and tetraalkyltin compounds with diphenylmethyl salts. Such reactions of tetraalkyltins have not previously been investigated. The reaction of organo-Hg compounds with diphenylbromomethane was studied in [7]. The reaction of the latter with dibutylmercury was carried out under severe conditions, so that the products were butyldiphenylmethane in 35% yield, 1,1,2,2-tetraphenylethane, and the decomposition products of the starting materials.

In the present work, in the reactions with dialkylmercury and tetraalkyltin we used the anionized diphenylmethyl salt, viz., diphenylmethyl fluoborate (DPMF), since it has been shown [4] that in β elimination the reactive molecule is the triarylmethyl cation (or ion pair). DPMF was produced directly in the reaction mixture from Ph_2CHCl and $AgBF_4$. The solvents were MeCN and nitromethane.

The compounds that we chose: R_2Hg and R_4Sn, Ia-e and IIa-e, (where R = CH_3 (a), C_2H_5 (b), i-C_3H_7 (c), i-C_4H_9 (d), sec-C_4H_9 (e) and n-C_3H_7 (f)) made it possible to study the effect of the OMC radical on the reaction, in particular the presence of a β hydrogen atom.

I and II were reacted with DPMF at ~20°C in an Ar atmosphere in the absence of light and moisture (from 20 h to 4 days). The reactions with Ia, b are the slowest. IIa-e react substantially more slowly than do Ia-f. Therefore reaction with II was stopped after a week and the reaction mixture was decomposed by pouring into aqueous KCl. In all cases the starting IIa-e were isolated.

The composition and distribution of the reaction products of I and II depends on the structure of the OMC radical. When there is no β hydrogen in OMC (e.g., in Ia and IIa), the reaction is the slowest and the substitution (metal dealkylation) product, 1,1-diphenylethane, is formed:

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$$\begin{array}{r}(CH_3)_nM + (C_6H_5)_2CH^+BF_4^- \xrightarrow{MeCN} (C_6H_5)_2CHCH_3 + [(CH_3)_{n-1}MBF_4] \\ \big\downarrow KX \quad \\ (CH_3)_{n-1}MX \quad\end{array}$$

$$M = Sn,\ Hg;\ X = Cl,\ Br.$$

When OMC contains a β hydrogen, the reaction is predominantly β elimination to form an olefin and Ph_2CH_2. But in a number of cases, along with β elimination, substitution products, the respective alkyldiphenylmethanes, are formed. The main steps of these reactions can be presented in the scheme:

$$\begin{array}{r}R_nM + (C_6H_5)_2CH^+BF_4^- \xrightarrow{MeCN} (C_6H_5)_2CH_2 + (C_6H_5)_2CH{-}R + R_{-H} + [R_{n-1}MBF_4] \\ \big\downarrow KX \quad \\ R_{n-1}MX \quad\end{array}$$

$$M = Sn,\ Hg;\ R = C_2H_5,\ C_3H_7,\ i\text{-}C_3H_7,\ C_4H_9,\ i\text{-}C_4H_9,\ \text{sec-}C_4H_9;\ X = Cl,\ Br.$$

For isolation and identification, the alkylmercury fluoborates formed in the reactions with Ia-f were converted to the respective bromides with KBr. The organotin fluoborates were converted to the trialkyltin chlorides with KCl. Table 1 presents the yields of the isolated products of the reactions of Ia-f, and the composition of the hydrocarbon fractions as determined by PMR. Table 2 gives the main products of $Ph_2CH^+BF_4^-$ conversion when it reacts with IIa-e. In the reactions of R_2Hg and R_4Sn containing β hydrogens, olefin formation was recorded by GLC.

It must be noted that under our reaction conditions, I and II do not react with Ph_2CHCl, which contains a covalent C–X bond.

The absence of diphenylmethane from the reaction products of Ia and IIa (see Tables 1 and 2) is an indication that in the other reactions this hydrocarbon is formed predominantly because of the β hydrogen in OMC. If the hydrogens are attached to a primary carbon, β elimination is slow, and alkyldiphenylmethane is formed (by substitution) simultaneously. When the OMC contains β hydrogens that are attached to secondary or tertiary C atoms, β elimination predominates (see Tables 1 and 2). An analogous relation of product composition in the reactions of Ia-f to the nature of the β hydrogen atoms in OMC was obtained when the reactions were carried out in nitromethane.

Hitherto in the reactions of alkyl derivatives of mercury and Group IVB elements with triarylmethyl salts, the formation of substitution products (trityl demercuration) has not been observed [1-3]. Such a difference in the reactions of R_2Hg and R_4Sn with DPMF may be related to the lesser steric hindrance in diarylmethyl salts than in triarylmethyl salts, and to the decreased stability [8] and corresponding increased reactivity of the diphenylmethyl cation.

The composition of the hydrocarbon fraction in the reaction of Id was somewhat unexpected. Along with the Ph_2CH_2 signals (δ, ppm) of 7.0 s and 3.9 s, PMR signals were detected at 1.6 d, 4.65 d, 5.4 d, and 6.8 s. The unknown compound is presumably 1,1-diphenyl-3-methylbutene-2 (III), the product of the reaction of diphenylmethyl cation with isobutylene that is released during the reaction:

$$\begin{array}{c}(C_6H_5)_2CH^+ + (CH_3)_2C{=}CH_2 \xrightarrow{MeCN} [(CH_3)_2\overset{+}{C}{-}CH_2CH(C_6H_5)_2] \xrightarrow{-H^+} \\ \to (CH_3)_2C = CHCH(C_6H_5)_2 \\ \text{(III)}\end{array}$$

TABLE 1. Yields of Main Products and Composition of Hydrocarbon Fractions of Reaction of R_2Hg with $Ph_2CH^+BF_4^-$

R	Yield, %				Composition of hydrocarbon fraction, %	
	hydrocarbon fraction	Ph_2CHOH	$Ph_2CHNHC(=O)Me$	RHgBr	Ph_2CH_2	Ph_2CHR
CH_3	35	47	*	30	–	100
C_2H_5	65	–	17	77	54	46
C_3H_7	90	2	6	88	100	0
i-C_3H_7	72	–	*	70	87	17
i-C_4H_9	89	–	6	85	56–70†	–
sec-C_4H_9	64	2	28	74	95	to 5

* Yield of N-(diphenylmethyl)acetamide not determined.

†Besides Ph_2CH_2, 1,1-diphenyl-3-methylbutene-2 was formed in 30-44% yield.

TABLE 2. Yields of DPMF Conversion Products and Composition of Hydrocarbon Fractions in Reaction of R_4Sn with $Ph_2CH^+BF_4^-$

R	Yield, %			Composition of hydrocarbon fraction, %	
	hydrocarbon fraction	Ph_2CHOH	$\underset{\mathrm{MeC{=}O}}{\mathrm{Ph_2CHNH}}$	Ph_2CH_2	Ph_2CHR
CH_3	17	10	56 *	–	100
C_2H_5	58	2	40	52	48
C_3H_7	68	2	22	100	–
i-C_4H_9	63	10	20	100	–
sec-C_4H_9	48	5	28	95	3–5

* Dibenzhydryl ether was also isolated in 3% yield.

To prove the structure of III, DPMF was reacted with isobutylene in MeCN and III was obtained; its PMR spectrum was entirely identical with that described above.

From Tables 1 and 2 it follows that in all the reactions with DPMF, N-(diphenylmethyl)acetamide is formed. This is related to the presence in MeCN solution of an equilibrium between diphenylmethyl cation and cation A [9]:

$$(C_6H_5)_2CH^+ + CH_3CN \rightleftarrows \underset{(A)}{(C_6H_5)_2CH - \overset{+}{N}\equiv C-CH} \tag{1}$$

PMR spectroscopic investigation of solutions of Ph_2CHCl in MeCN after addition of 1.5-fold excess of $AgBF_4$ showed that DPMF forms slowly. After some days a solution with a starting Ph_2CHCl concentration of $6.4 \cdot 10^{-2}$ M showed significant amounts of chloride. PMR (δ, ppm): 7.2 s (C_6H_5), 6.1 s (HCCl). Diphenylmethyl cation as it is formed is converted practically completely to cation A; the PMR signals corresponding to Ph_2CH^+ [8] were not detected. The slow formation of DPMF and the existence of equilibrium (1) can explain the fact that I and II react more slowly with DPMF than with triarylmethyl salts. Careful analysis by PMR, thin-layer chromatography, and chromato-mass spectroscopy of the isolated reaction products and the reaction mixtures showed that 1,1,2,2-tetraphenylethane – the usual dimerization product of the diphenylmethyl radical – was absent [10].

We investigated the reaction of Ib with DPMF in deuteroacetone by PMR spectroscopy. The signals of the aromatic protons of Ph_2CHCl, the $Ph_2CH\overset{+}{N}\equiv CCD_3$ cation, and the product hydrocarbons overlap, so that it is impossible to measure the integrated intensity ratios precisely. The sum of the integrated intensities of the aromatic protons remains constant during the reaction, while with time there is a gradual decrease of the intensity of the methyne protons of cation A, and an increase in the intensity of the total protons of Ph_2CH_2 and 1,1-diphenylpropane. No anomalous changes appeared in the spectra of the reaction mixtures; in particular there was no chemically induced dynamic nuclear polarization effect.

These data, together with those on the composition of the reaction products of Ia-f and IIa-e, speak in favor of the heterolytic mechanism for β elimination.

EXPERIMENTAL

PMR spectra were obtained in CCl_4 and $CDCl_3$ solutions with Varian T-60 and Jeol FX-100 spectrometers. ^{13}C NMR spectra were recorded with a Jeol FX-100 spectrometer. Chemical shifts (δ, ppm) are given relative to HMDS internal standard. Gaseous reaction products were analyzed on a Tsvet chromatograph, model I-54, with flame ionization detector, column 2.3 m × 4 mm with 15% Apiezon L on silanized N-AW-DMCS chromaton, N_2 carrier gas. Reaction mixtures and products were analyzed by TLC on Al_2O_3 or UV-254 Silufol; materials were separated on Al_2O_3; the mobile phases were 5 : 1 hexane : benzene and benzene.

MeCN and nitromethane were purified by boiling and distillation over P_2O_5, then over CaH_2. Compounds Ia-f [11] and IIa-e [12] were synthesized by known procedures; their constants agreed with published data. $AgBF_4$ was obtained according to [13].

Reaction of Dialkylmercury (Ia-f) with DPMF. Reactions with I and II were carried out in a dry box in an Ar atmosphere in the absence of light. To a solution of 3.2 mmole of Ia-f in 20 ml of MeCN was added a solution of 4.6 mmole of $AgBF_4$ in 20 ml MeCN, and then portionwise 3.2 mmole of Ph_2CHCl in 10 ml of MeCN. The same quantities and concentrations of reagents were used for the reactions in nitromethane. The end of the reaction was determined by TLC, by the absence of the R_2Hg spot (R_f 0.9). If the solvent was MeCN, the reaction mixture was poured into 10% KBr solution and the desired material was extracted with CH_2Cl_2 (3 × 50 ml). If the solvent was nitromethane the reaction mixture was washed with KBr solution. Materials were separated by TLC.

Reaction of Tetraalkyltin with DPMF. To a solution of 3.2 mmole of IIa-e in 40 ml of MeCN were added 4.6 mmole of $AgBF_4$, and then portionwise 3.2 mmole of Ph_2CHCl in 10 ml of MeCN. After a week the reaction was stopped by pouring the reaction mixture into KCl solution. Reaction products were separated as in the experiments with I. Besides the materials listed in Table 2, the starting IIa-e (in 15-48% yield) and trialkyltin chlorides were separated. The latter were identified by TLC, ^1H NMR, and ^{13}C NMR.

1,1-Diphenyl-3-methylbutene-2, III. To a solution of 4.4 mmole of isobutylene in 50 ml of MeCN were added 3.2 mmole of Ph_2CHCl and 4.6 mmole $AgBF_4$. After 68 h the reaction mixture was poured into KBr solution. The desired material was separated by TLC as described above. There was obtained 41% of a viscous oil, III, R_f 0.65. PMR (CCl_4, δ, ppm): 1.63 d (6H, CH_3), 4.72 d (1H, H^2), 5.48 d (1H, H^1); 7.69 s (10H, C_6H_5). Found: C 91.91; H 8.24%. $C_{17}H_{18}$. Calculated: C 91.88; H 8.11%.

CONCLUSION

The composition of the products of the reaction of peralkylmercury and perlalkyltin compounds with diphenylmethyl fluoborate depends on the presence and nature of a β hydrogen in the alkyl radical. In the absence of a β hydrogen, substitution (dealkylation) occurs to form alkyldiphenylmethane; in its presence, β elimination and substitution take place.

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