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ELECTROCHEMICAL STUDIES OF ORGANOMETALLIC COMPOUNDS

II. THE POLAROGRAPHIC REDUCTION OF ORGANOMERCURY SALTS

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SUMMARY

The polarographic reduction of organomercury salts of the type RHgX has been investigated in different solvents (CH_3CN, DMF, ethanol/benzene). The influence of the solvent and of the nature of X and the structure of R upon the half-wave reduction potentials of RHgX are discussed.

INTRODUCTION

Organomercury salts which have been studied to date may be reduced at the dropping mercury electrode (DME) via two one-electron stages by a scheme first advanced by Benesch[1]:

$$\begin{array}{ll} RHgX + e \rightarrow RHg^{\bullet} + X^{-} & \text{1st wave} \\ RHg^{\bullet} + e \rightarrow RH + Hg & \text{2nd wave} \end{array} \qquad (1)$$

In order to establish the exact mechanism for the reduction of RHgX compounds at the DME it is necessary to establish the molecular form of RHgX reacting at the electrode, the behaviour of the RHg radical at potentials intermediate between those of the first and second waves and the product of the reduction process occurring at the potential of the second wave. On the other hand, it is also necessary to know how structural changes in the compound RHgX affect the reduction potentials and what further information may be extracted from the polarographic data for organomercury chemistry. All these problems are discussed in this paper on the basis of data reported here and elsewhere. The compounds which have been investigated are listed in Tables 1–4.

RESULTS AND DISCUSSION

1. *The effect of the nature of X on the reduction of RHgX compounds*

In previous studies it has been shown that in aqueous ethanol the half-wave potentials of the first polarographic wave obtained for various compounds of formula RHgX but with the same group R do not depend on the nature of X (where X = halogen or OH)[2–4], the wave being irreversible in all cases. The reasons for the value of $E_{\frac{1}{2}}$ being independent of X was not discussed, however, in these reports. Some authors have assumed the initial ionization of RHgX as an explanation of this observation[5,6],

$$\mathrm{RHgX} \leftrightarrow \mathrm{RHg}^+ + \mathrm{X}^- \qquad (2)$$

the first wave corresponding to a reversible one-electron reduction of the cation to the radical. Husch and Oldham[7] have pointed out, however, that the ionization constants of RHgX (see eqn. 2) in aqueous ethanol are small, and that the apparent independence of $E_{\frac{1}{2}}$ on X (where X = Cl, Br, I) when $(C_2H_5)_4NI$ is the supporting electrolyte, may be explained in terms of an exchange of Cl and Br for I from the electrolyte which occurs quantitatively in such solutions[8]. Husch and Oldham[7] have also noted that RHgX is reduced reversibly in $(C_2H_5)_4NX$ as the supporting medium while RHgI in the presence of KCl is reduced irreversibly. Butin *et al.* have derived the relation $E = \text{const.} - RT/nF \ln [i^{\frac{1}{2}}/(i_d - i)]$ for the reduction of RHgX when the anion of the supporting electrolyte differs from that of the organomercury salt and is not a stronger complexing agent with the mercury atom so that anion exchange may occur. Use of this equation to describe the polarographic wave observed gives a slope for E *versus* $\ln [i^{\frac{1}{2}}/(i_d - i)]$ close to that necessary for the reversible process.

Similarly, reduction of alkylmercury cations in the absence of complexing agents leads to an irreversible first step, while the presence of an excess of complexing agent, for example rodanide, thiourea etc.[10], produces a complex which reduces reversibly. The more stable the complex produced, the more negative are the potentials necessary for its reduction[11]. On this basis, complexation constants of RHgX with thiols and other Brönsted bases have been determined[8,10] and the possibility of the formation of complexes of the type $RHgX_2^-$ also demonstrated[9,12].

Dessy *et al.*[13] have studied the reduction of RHgX in the aprotic medium dimethoxyethane with $(C_4H_9)_4NClO_4$ as the supporting electrolyte. These authors (through the use of triangular voltametry) have found that the first step in this process is irreversible but the effect of the nature of the halogen on the value of $E_{\frac{1}{2}}$ was not discussed.

In the present work the effect of the halogen on the first reduction step of RHgX has been investigated for allyl- and phenyl-mercury halides in the following solvent systems: ethanol–water (1/1), ethanol–benzene (1/1), CH_3CN and DMF. The effect of the supporting electrolyte has also been studied in aqueous ethanol. The results obtained are shown in Table 1. In all the solvents studied except CH_3CN and DMF, the wave observed for allylmercury halides exhibits characteristics similar to those of the reversible wave. This is evident from the fact that the slope of $\log [i/(i_d - i)]$ *versus* E is equal to 62 mV, and also from the coincidence of the peaks in the cathodic and anodic branches of the oscillopolarogram when the latter is plotted as dE/dt *versus* E. In addition, it was found that the value of E for the first wave is independent of the depolarizer concentration. Replacement of KNO_3 or $NaClO_4$ by KCl as the supporting electrolyte shifts the value of $E_{\frac{1}{2}}$ to more negative potentials. Under these circumstances the ionization of C_3H_5HgCl into $C_3H_5Hg^+$ and Cl^- may be suppressed, which would account for the change in the potential. Similarly, the addition of ethylenediamine, a typical chelating and complexing agent, also shifts the value of $E_{\frac{1}{2}}$ by approximately the same amount to the negative side.

The solvent mainly affects the reduction pattern of the allyl- and phenylmercury halides. The first polarographic wave for C_3H_5HgX and C_6H_5HgX in CH_3CN and DMF is irreversible and the slopes of the plots of $\log [i/(i_d - i)]$ *versus* E

and of log $[i^{\frac{4}{3}}/(i_d - i)]$ *versus* E are 92 and 71 mV respectively (for C_3H_5HgCl) thus exceeding the value observed for the corresponding reversible processes. In comparatively highly ionizing solvents such as aqueous ethanol, DMF and CH_3CN the reduction of allyl- and phenyl-mercury halides is apparently independent of the nature of the halogen and occurs at approximately the same potential. However, replacing these solvents by a less polar mixture (ethanol–benzene 1/1) leads to a reduction in the ionizing ability of the halides and under such circumstances it is possible to observe a quite regular change in the ability of the Hg–X bond for reduction (brought about either by a change in the value of the dissociation constants for RHgX or because of a variation in the polarity of the bond).

TABLE 1

THE EFFECT OF SOLVENTS AND SUPPORTING ELECTROLYTE ON THE $E_{\frac{1}{2}}$ VALUES OF THE FIRST WAVE OF ALLYL- AND PHENYL-MERCURY HALIDES (THE $E_{\frac{1}{2}}$ VALUES ARE GIVEN IN V, SCE)

Compound	*Ethanol–water 1/1*				*CH_3CN*	*DMF*	*Ethanol–benzene 1/1*
	0.25 *N* KNO_3	0.25 *N* KCl	0.1 *N* $NaClO_4$	0.1 *N* $C_2H_4(NH_2)_2$ 0.1 *N* $NaClO_4$	0.1 *N* $(C_2H_5)_4NClO_4$	0.1 *N* $NaClO_4$	0.1 *N* $NaClO_4$
C_3H_5HgCl	−0.10	−0.22	−0.07	−0.26	−0.33	−0.32	−0.16
C_3H_5HgBr	−0.10	−0.22	—	—	−0.33	−0.32	−0.26
C_3H_5HgI	—	—	—	—	−0.34	−0.32	−0.39
C_6H_5HgCl					−0.38		
C_6H_5HgBr					−0.39		
C_6H_5HgI					−0.37		

From an analysis of the data reported in the literature and those obtained in this study, it is possible to draw the following conclusions regarding the mechanism of the first reduction step for organomercury salts: cleavage of an Hg–X bond involves addition of an electron and depending upon the conditions the reduction may be reversible or irreversible; the behaviour observed is influenced by the degree of ionization of the organomercury compound in solution, complex formation with the anion of the supporting electrolyte (or with other complexing agents) and the nature of the solvent (its polarity and solvating ability). Where the effect of the first two factors is small, the ability of the Hg–halogen bond to undergo reduction is found to correspond to its polarity and to decrease from Hg–Cl to Hg–I.

2. *The effect of R on the first reduction step of RHgX*

According to the reaction scheme depicted in eqn. (1) a change in the value of $E_{\frac{1}{2}}$ should occur if the electronic effect of R changes while X remains the same. However, on the basis of the experimental evidence at present available it is difficult to reach this conclusion. It is in fact found that the range of potentials corresponding to the first reduction step of the compounds RHgX is rather narrow (0.10–0.70 V)*. Furthermore some of the data have been obtained under differing conditions which makes it virtually impossible to draw definite conclusions regarding the influence of R on the results. Studies of the polarographic reduction of RHg^+ cations in the absence of complexing agents have been discussed above and provide no conclusions regarding the effect of R in this case[9,10].

In the present work we have studied a series of compounds of the type RHgCl under the same conditions. The results obtained and the data available in the literature enable us to conclude that there is a definite tendency for the absolute value of the potential to increase in the series allyl < aryl < alkylmercury halides (Table 2).

TABLE 2

THE EFFECT OF R ON THE $E_{\frac{1}{2}}$ VALUE OF THE FIRST WAVE OF RHgCl

R	*Ethanol–water 1/1,* 0.1 *N KCl*[a]	*DMF,* 0.1 *N* $(C_2H_5)_4NClO_4$	90% *dioxane,* 0.1 *N* $(C_2H_5)_4NClO_4$
CH_3	0.418	0.68	0.64
C_2H_5	0.387	0.67	0.60
C_6H_5	0.152	—	0.35
α-$C_{10}H_7$	0.116	—	—
C_3H_5	—	0.32	0.28

[a] From the data of ref. 7.

3. *The RHg· radical and the second reduction step of RHgX*

The radical RHg·, a primary product of the first reduction step of RHgX, is active and highly unstable[15–18]. Isolation of R_2Hg as the single product of the electrolysis at the limiting current potential corresponding to the first wave could confirm the suggestion that at potentials intermediate between the first and second waves stabilization of RHg· occurs through disproportionation:

$$2RHg \rightarrow R_2Hg + Hg$$

instead of by dissociation

$$RHg\cdot \rightarrow R\cdot + Hg$$

Dessy *et al.*[13] have obtained convincing evidence that the C–Hg bond in RHg· adsorbed at a mercury surface[19,20] is somewhat weaker but this is insufficient to conclusively prove the existence of R· as a kinetically independent particle.

Upon attaining potentials sufficiently negative for the further reduction of RHg·, the rate of the electrochemical reaction exceeds that of dimerization and the resulting polarogram exhibits a one-electron reduction wave for RHg· corresponding to the cleavage of the C–Hg bond:

$$RHg\cdot + e \rightarrow Hg + R^- \xrightarrow{H^+} RH$$

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* An exception to this is provided by the reduction of organomercury compounds of the acetylene series[4] and of $(CH_3)_2CHHgX$ where $E_{\frac{1}{2}} = -1.307$ V[7].

TABLE 3

THE POLAROGRAPHIC PARAMETERS OF R_2Hg (DMF, 0.1 $N(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}) AND THE SECOND WAVE OF RHg· (90% DIOXANE, 0.1 $N(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1})

R	$-E_{\frac{1}{2}}$ *for* R_2Hg	$-E_{\frac{1}{2}}$ *for RHg·*	$\Delta E_{\frac{1}{2}}$
CH_3	2.88[a]	1.96	0.92
$C_5H_5FeC_5H_4$	2.68	1.84	0.84
$C_6H_4OCH_3$	2.69	1.81	0.88
$C_6H_4CH_3$	2.67	1.83	0.84
C_6H_5	2.58	1.78	0.80
C_6H_4F	2.51	1.75	0.76
$CH_2{=}CH{-}CH_2$	2.13	1.62	0.51
C_5H_5	0.72	0.75	−0.03
$CH_2{=}CH$ [b]	3.34	2.92	0.42
C_6H_5 [b]	3.32	2.92	0.40
C_6Cl_5 [b]	2.63	2.36	0.27

[a] From the data of ref. 22 (DMF, 0.1 $N(C_6H_{13})_4NClO_4$). [b] From the data of ref. 13 (dimethoxyethane, 0.1 $N(C_4H_9)_4NClO_4$).

The highly basic carbanion R^- is stabilized via reaction with the protons of the medium to give a hydrocarbon. All the RHgX compounds investigated exhibited an irreversible second reduction step[1,7].

Normally the reduction of RHg· occurs at potentials which are more positive with respect to R_2Hg[13], thus confirming the reduction of RHg· rather than that of R_2Hg in the second stage*.

An analysis of the data obtained and those described elsewhere (Table 3) lead to the conclusion that the difference between the potentials for the second reduction step of the compound RHgX and of the respective symmetrical mercury compound (ΔE) gradually increases as the value of the potential increases. In other words, the more difficult it is to reduce the organomercury compound the greater the value of ΔE and, alternatively, the easier it is to reduce these compounds the smaller this difference. The plot shown in Fig. 1, which is based on the data of Table 3, illustrates this particular dependence. It should be noted that when RHgX is readily reduced the difference between $E_{\frac{1}{2}}$ for the first and second steps is sometimes so small that they join to give a single wave in the polarogram. Evidence for such behaviour has been found in the reduction of carboranyl-mercury halides. A one-step two-electron reduction of RHgX has also been reported elsewhere[14].

4. *The effect of structural changes in R on the second reduction step of RHgX*

Since the C–Hg bond in RHg· is somewhat weakened, it is not unreasonable to assume that during the reduction of RHg the electronic change is mainly localized in the half-filled orbital of R·. This is evident from the good linear relationship which is obtained between the electron affinity (E) of R· radicals and the values of $E_{\frac{1}{2}}$ for the

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* The reduction of $C_6H_5CHCOOC_2H_5HgBr$ provides an exception[21]. However, it is difficult to explain why CH_2COOCH_3HgI with a similar chemical structure should reduce by the Benesch mechanism. The reasons for such inconsistencies were not discussed in this particular paper.

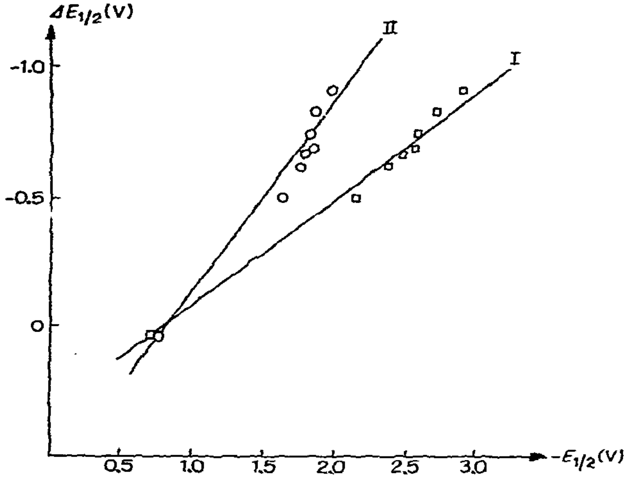
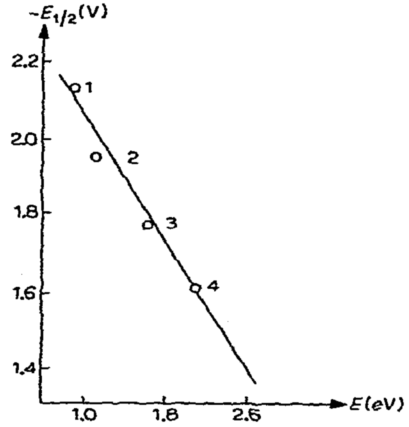


Fig. 1. A plot of $\Delta E_{\frac{1}{2}}$ *versus* $E_{\frac{1}{2}}$ for R_2Hg, (I) and $RHg^{\cdot}$, (II).



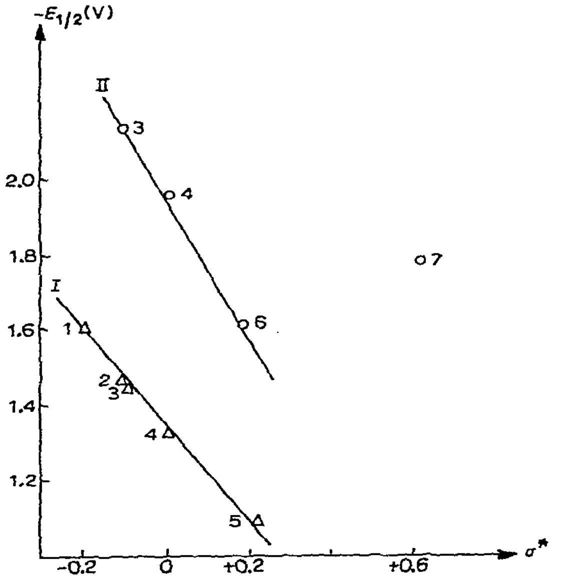


Fig. 2. A plot of $E_{\frac{1}{2}}$ for the second wave of RHgX *versus* the electron affinity E of $R^{\cdot}$. 1, $R=C_2H_5$; 2, $R=CH_3$; 3, $R=C_6H_5$; 4, $R=C_3H_5$.

Fig. 3. A plot of $E_{\frac{1}{2}}$ *for* $RHg^{\cdot}$ *versus the Taft* σ^* *constants:* I, from the data of ref. 7; II, from the data of Table 3. 1, $R=i\text{-}C_3H_7$; 2, $R=n\text{-}C_3H_7$; 3, $R=C_2H_5$; 4, $R=CH_3$; 5, $R=C_6H_5CH_2$; 6, $R=C_3H_5$; 7, $R=C_6H_5$.

second wave[23]. A good linear correlation between E and $E_{\frac{1}{2}}$ for the second wave has also been obtained for the hydrocarbon radicals investigated in this work (Fig. 2). From this plot it is possible to estimate graphically that the electron affinities of the ferrocenyl and $C_5H_4M(CO)_3$ radicals ($M=Mn$, Re) are $E_{C_5H_5FeC_5H_4} \approx 1.5$ eV, $E_{C_5H_4Mn(CO)_3} \approx 2.5$ eV and $E_{C_5H_4Re(CO)_3} \approx 2.4$ eV respectively.

It should be pointed out that the number of methods available at present for determining the electron affinities of organic radicals is rather small and that those available have somewhat low accuracies. Thus polarography may provide a valuable technique, and organomercury compounds a convenient source, for the determination of electron affinity values.

In the light of the ideas considered above, the $E_{\frac{1}{2}}$ value of the second wave should be less affected by those factors which affect the first wave *i.e.* the supporting electrolyte, nature of the solvent etc. Thus the half-wave potential should be to some extent dependent on the nature of R. In fact, literature data show that the $E_{\frac{1}{2}}$ values for the second wave of some RHgX compounds in which the carbon atom is joined to the mercury atom through sp^3 hybridization may be correlated with the Taft inductive σ^* constants for the respective radicals. A plot drawn on the basis of our data and of those of Husch and Olham[7] is given in Fig. 3. The point corresponding to the $E_{\frac{1}{2}}$ value of the second wave for C_6H_5HgCl does not, however, fit this linear dependence; this may be attributed to the fact that in addition to the inductive effect R is in this case also stabilized by a conjugation effect.

5. *The effect of substituents in the phenyl ring on the reduction of organomercury salts*

The reduction of ring substituted benzyl- and phenyl-mercury bromides and the respective mercury cations at the DME has been studied in aqueous organic media[24,25]. The $E_{\frac{1}{2}}$ values of the first and second waves of the mercury cations and the $E_{\frac{1}{2}}$ value of the second wave of RHgBr may be correlated with the Hammett σ constants. Such correlation was not observed for the $E_{\frac{1}{2}}$ value of the first wave of RHgBr. The study of the influence of substituent effects on $E_{\frac{1}{2}}$ values is of great importance in understanding the nature of the particles reacting at the DME during the reduction of RHgX. However, no systematic correlational analysis has been performed for the $E_{\frac{1}{2}}$ values of RHgX with different sets of substituent constants. For this reason we have studied the reduction of *p*-substituted phenylmercury chlorides at the dropping mercury electrode. In aqueous ethanol, CH_3CN and DMF, it has been found that the reduction waves of C_6H_5HgCl are distorted by maxima of a rather complicated and differing shape (Fig. 4), and for this reason the $E_{\frac{1}{2}}$ values of such waves are not suitable for accurate correlation with the structure of such compounds. In fact, well defined diffusion-controlled waves could only be obtained in 90% dioxane. The results are shown in Table 4.

From this Table, it may be seen that the $E_{\frac{1}{2}}$ value of the first wave is hardly affected by the replacement of one substituent by another. The $E_{\frac{1}{2}}$ value for the second wave of *p*-substituted phenylmercury chlorides is apparently dependent to a certain extent upon the nature of the substituent; introduction of electron-releasing substituents shifts the $E_{\frac{1}{2}}$ values to positive potentials, while the introduction of electron-attracting groups leads to negative potentials.

A systematic correlational analysis of the $E_{\frac{1}{2}}$ values obtained with the different sets of σ available (σ_p, σ_p^+, σ_p^0) indicated that the best correlation for $E_{\frac{1}{2}}$ is observed with the σ_p^0 constants. The substituent effect may be expressed by the relation $E_{\frac{1}{2}} = (0.205\,\sigma_p^0 - 1.78)$ V, the correlation coefficient r being equal to 0.971 (Fig. 5). The data obtained indicate that the dependence on the polar substituent effect is quite small in the reduction of RHg· at the DME as is usually the case when homolytic fission of the bond in the *para* position of the phenyl ring with respect to a substituent occurs in the

TABLE 4

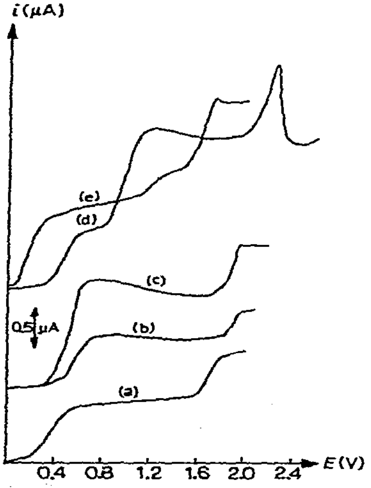
THE DEPENDENCE OF THE $E_{\frac{1}{2}}$ VALUES ON THE SUBSTITUENTS IN p-XC_6H_4HgCl (90% DIOXANE, 0.1 N $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}, SCE)

X	$-E_{\frac{1}{2}}(p\text{-}XC_6H_4HgCl)(V)$	
	1	2
CH_3	0.33	1.83
CH_3O	0.31	1.81
H	0.35	1.78
F	0.36	1.75
Cl	0.35	1.75
Br	0.34	1.69
C_2H_5OOC	0.34	1.69
$\Delta E_{\frac{1}{2}}$	0.05	0.14

transition state[26]. These results are in good agreement with the suggestion that reduction of an adsorbed RHg· radical containing a weakened C–Hg bond occurs at the mercury surface in the second step.

EXPERIMENTAL

The polarographic technique employed was as described in the previous



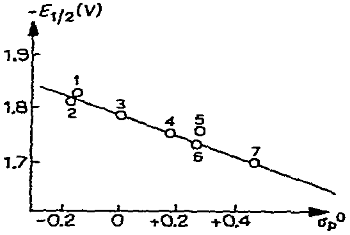


Fig. 4. Polarograms of C_6H_5HgCl: (a) in 90% dioxane/H_2O, 0.1 N $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}; (b) in absolute DMF, 0.1 N $(C_2H_5)_4NClO_4$, $c=2\times10^{-3}$ mol·l^{-1}; (c) in absolute DMF, 0.1 N $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}; (d) in absolute CH_3CN, 0.1 N $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}; (e) in 70% C_2H_5OH/H_2O, 0.1 N $(C_2H_5)_4NClO_4$, $c=1\times10^{-3}$ mol·l^{-1}.

Fig. 5. A plot of $E_{\frac{1}{2}}$ for the second wave of p-XC_6H_4HgC *versus* the σ_p^0 values; 1, $X=CH_3$; 2, $X=CH_3O$; 3, $X=H$; 4, $X=F$; 5, $X=Cl$; 6, $X=Br$; 7, $X=COOC_2H_5$.

communication. The compounds studied were prepared by procedures described in the literature and had satisfactory analyses and melting points.

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