REACTION OF MERCURY ACYLATES WITH ALKYL HALIDES

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Previously we had shown that the alkylation of the Hg salt of difluoronitroacetic acid with alkyl halides in ether gives, together with the corresponding alkyl difluoronitroacetates also products that are formed via cleavage of the C—O bond of the solvent, namely ethyl difluoronitroacetate and the corresponding alkyl ethyl ethers [1]. The direction of the alkylation of mercury acylates as a function of the nature of the acylating moiety and the n-donor capacity of the solvent was studied in the present paper.

The reaction of Hg difluoronitroacetate with MeI in THF proceeds even at ∿20° C and is not accompanied by an exothermic effect. Together with methyl difluoronitroacetate, the THF cleavage product, namely 4-methoxybutyl difluoronitroacetate, was obtained in higher yield.

$$[O_2NCF_2CO_2]_2Hg + MeI \xrightarrow[-HgI_2]{THF} O_2NCF_2COOMe + O_2NCF_2CO_2(CH_2)_4OMe$$

In the case of ether, which has a lower n-donor capacity than THF, the formation of methyl difluoronitroacetate predominated [1].

In contrast to the difluoronitroacetate [1], Hg acetate does not react with MeI in ether at ∿20° or at reflux. In THF the reaction of Hg acetate with EtI proceeds at reflux and leads to obtaining ethyl acetate and 4-ethoxybutyl acetate in close yields.

$$[MeCO_2]_2Hg + EtI \xrightarrow[-HgI_2]{THF} MeCO_2Et + MeCO_2(CH_2)_4OEt$$

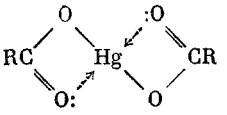
The found possibility of obtaining 1,4-butanediol derivatives was used to synthesize the corresponding esters of trifluoroacetic and 2,4,5-trichlorophenoxyacetic acids.

$$[RCO_2]_2Hg + R'I \xrightarrow[-HgI_2]{THF} RCO_2(CH_2)_4OR' + RCOOR'$$

$$R = CF_3,\ 2,4,5\text{-}Cl_3C_6H_2OCH_2,\ R' = Et,\ n\text{-}Bu$$

The reactivity of Hg trifluoroacetate in this reaction is close to that of Hg difluoronitroacetate, the 2,4,5-trichlorophenoxyacetate is less active, while Hg acetate is even less active. As a result, the reactivity of the Hg acylates when alkylated with alkyl halides, and also the ratio of the formed products, are determined mainly by the nature of the acyl moiety and the n-donor capacity of the solvent.

The data in [1] and the results of the present study, and also the known tendency of Hg salts to form complexes, make it possible to regard the Hg acylates as being intramolecular electron-donor-acceptor (EDA) complexes, in which the electron-deficient Hg atom is coordinated with the n-electrons of carbonyl oxygen.



This assumption makes it possible to explain the obtained results. Thus, the presence of electronegative substituents in the acid moiety, and consequently an increase in the acid strength, leads to a weakening of the EDA interaction due to a decrease in the n-electron

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density on the carbonyl O atom, and explains the higher reactivity of the Hg salts of strong acids. A decrease in the acid strength is the reason for enhancing the EDA interaction, which significantly stabilizes the Hg acylates and substantially lowers their reactivity. For this reason Hg acetate, in contrast to the difluoronitroacetate [1], does not react at ~20° even with MeI in THF, the same as in ether or MeCN.

The EDA character of the Hg acylates is also qualitatively confirmed by the fact that Hg trifluoroacetate and the difluoronitroacetate are readily soluble in THF and MeCN, in which connection solution in THF is accompanied by some exothermic heat, which testifies to the substantial competing EDA interaction of THF with the Hg atom. At the same time, Hg acetate is difficulty soluble in these solvents, which is apparently explained by its weak competing EDA interaction with the solvent due to the stronger EDA interaction of the carbonyl O atom and Hg atom in this compound. This competing EDA interaction of Hg acylates with n-donor solvents is specifically the reason for obtaining the cleavage products of the C—O bond of the solvent during alkylation. The EDA nature of the Hg acylates explains the predominant formation of 1,4-butanediol derivatives in the case of alkylating the Hg salts of strong carboxylic acids in THF, and also the increase in the yield of the cleavage products of the C—O bond of the solvent when ether [1] is replaced by the more n-donor THF, which was shown on the example of alkylating Hg difluoronitroacetate.

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were taken on a Hitachi R-20 instrument (60 and 56.45 MHz), using HMDS and CF_3COOH as the standards. The GLC analysis was run on an LKhM-8 MD chromatograph, using a 3 m × 3 mm column packed with 5% SE-30 deposited on Chromaton N-AW-DMCS, particle size 0.200-0.250 mm, and a 1 m × 3 mm column packed with 5% XE-60 deposited on Chezasorb AW-HMDS, particle size 0.200-0.360 mm, helium as the carrier gas, and a flow rate of 18.7 ml/min.

Reaction of Hg Difluoronitroacetate with MeI. With stirring, to a solution of 15 g (31.2 mmoles) of Hg difluoronitroacetate in 25 ml of abs. THF was added 8.9 g (62.7 mmoles) of MeI. Then the mixture was stirred for 10 h at ~ 20° and for 1 h at 70°. The precipitate was separated, the solvent was evaporated, and the residue was fractionally distilled in vacuo to give 5.1 g (36.1%) of 4-methoxybutyl difluoronitroacetate, bp 46° (1 mm), d_4^{20} 1.221; n_D^{20} 1.3976. Found: C 37.23; H 5.08; F 16.84; N 6.15%. $C_7H_{11}F_2NO_5$. Calculated: C 37.00; H 4.85; F 16.74; N 6.17%. ^{19}F NMR spectrum (δ, ppm): 14.87 br. s (CF_2NO_2). PMR spectrum (δ, ppm): 4.40 m (CH_2OCO) 3.32 m (CH_2O), 3.23 s (MeO), 1.52-1.85 m (CH_2CH_2). Infrared spectrum (ν, cm^{-1}): 1792 (C=O), 1600, 1270 (NO_2).

Fractional distillation of the trap contents gave 0.9 g (9.3%) of methyl difluoronitroacetate, bp 53° (100 mm), d_4^{20} 1.401, n_D^{20} 1.3562, cf. [1].

Reaction of Hg Acetate with EtI. To a suspension of 30 g (94 mmoles) of Hg acetate in 25 ml of abs. THF was added 25 g (160 mmoles) of EtI. The stirred reaction mixture was refluxed for 4 h. The precipitate was separated, the volatile products were distilled off at 110°, and the residue was fractionally distilled to give 7.8 g (30.5%) of 4-ethoxybutyl acetate, bp 36-38° (1 mm); d_4^{20} 0.945, n_D^{20} 1.4132. Found: C 59.61; H 10.41%. $C_8H_{16}O_3$. Calculated: C 60.00; H 10.00%. PMR spectrum (δ, ppm): 3.96 m (CH_2OCO), 3.35 q (CH_2O), 3.32 m (CH_2O), 1.95 s (MeCO), 1.56 m (CH_2CH_2), 1.10 t (Me).

The amount of formed ethyl acetate was determined chromatographically: ~ 3.5 g (24.9%).

4-Ethoxybutyl 2,4,5-Trichlorophenoxyacetate. Under the conditions of the preceding experiment, from 15 g (21.1 mmoles) of Hg trichlorophenoxyacetate [obtained from yellow mercury oxide and 2,4,5-trichlorophenoxyacetic acid in MeCN, mp 215-217° (decompn.)] and 6.7 g (43 mmoles) of EtI in 30 ml of abs. THF we obtained 5 g (33.4%) of 4'-ethoxybutyl 2,4,5-trichlorophenoxyacetate, bp 120° ($9 \cdot 10^{-3}$ mm), d_4^{20} 1.321, n_D^{20} 1.4250; the compound crystallizes on long standing, mp 46°. Found: C 47.43; H 4.81; Cl 29.79%. $C_{14}H_{17}Cl_3O_4$. Calculated: C 47.26; H 4.78; Cl 29.96%. PMR spectrum (δ, ppm): 7.28 s and 6.80 s (CH), 4.57 s (OCH_2CO), 4.08 m (CH_2OCO), 3.32 q (CH_2O), 3.25 m (CH_2O), 1.46-1.65 m (CH_2CH_2), 1.08 (Me).

4'-Butoxybutyl 2,4,5-Trichlorophenoxyacetate. In a similar manner, from 15 g (21.1 mmoles) of Hg 2,4,5-trichlorophenoxyacetate and 8 g (43.5 mmoles) of n-BuI in 30 ml of abs. THF we obtained 6.8 g (42%) of 4'-butoxybutyl 2,4,5-trichlorophenoxyacetate, bp 118° ($9 \cdot 10^{-4}$ mm); d_4^{20} 1.285; n_D^{20} 1.3905. Found: C 50.33; H 5.35; Cl 28.05%. $C_{16}H_{21}Cl_3O_4$. Calculated: C 50.07; H 5.48; Cl 27.77%. PMR spectrum (δ, ppm): 7.28 s and 6.80 s (CH), 4.55 s (OCH_2CO), 4.09 m (CH_2OCO), 3.24 m (CH_2OCH_2), 1.34-1.67 m (CH_2CH_2), 0.84 (Me).

4-Ethoxybutyl Trifluoroacetate. Under the conditions of the first experiment, from 15 g (35 mmoles) of Hg trifluoroacetate and 10.9 g (69.9 mmoles) of EtI in 20 ml of abs. THF we obtained 6 g (40.1%) of 4-ethoxybutyl trifluoroacetate, bp 55-57° (10 mm); d_4^{20} 1.103; n_D^{20} 1.3711. Found: C 44.63; H 6.07; F 26.97%. $C_8H_{13}F_3O_3$. Calculated: C 44.86; H 6.08; F 26.64%. ^{19}NMR spectrum (δ, ppm): −3.80 s (CF_3). PMR spectrum (δ, ppm): 4.30 m (CH_2OCO), 3.33 q (CH_2O), 3.30 m (CH_2O), 1.50-1.76 m (CH_2CH_2), 1.09 t (Me).

4-Butoxybutyl trifluoroacetate. Under the conditions of the first experiment, from 50 g (117 mmoles) of Hg trifluoroacetate and 42.9 g (233 mmoles) of n-BuI in 50 ml of THF we obtained 23.6 g (41.9%) of 4-butoxybutyl trifluoroacetate, bp 65-67° (2 mm); d_4^{20} 1.086; n_D^{20} 1.3787. Found: C 50.01; H 7.07; F 23.39%. $C_{10}H_{17}F_3O_3$. Calculated: C 49.59; H 7.02; F 23.55%. ^{19}F NMR spectrum (δ, ppm): −2.55 s (CF_3). PMR spectrum (δ, ppm): 4.30 m (CH_2OCO), 3.36 m (CH_2OCH_2), 1.35-1.82 m (CH_2CH_2), 0.88 t (Me).

The yield of the ethyl and butyl 2,4,5-trichlorophenoxyacetates and trifluoroacetates in the last four experiments was not estimated.

CONCLUSIONS

1. The alkylation of some mercury acylates with alkyl halides in THF was studied.

2. The mercury acylates can be regarded as being intramolecular electron-donor—acceptor (EDA) complexes, in which the carbonyl oxygen atom plays the role of donor, while the mercury atom plays the role of acceptor. The EDA interaction is determined by the electron density on the carbonyl oxygen, i.e., by the strength of the acid.

LITERATURE CITED

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STUDY OF REACTION OF ACETYLENE WITH ANILIDES BY THE MATHEMATICAL PLANNING METHOD

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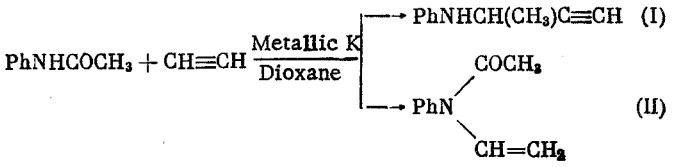
N-Vinylanilides [1, 2], and also 3-arylamino-1-butynes [3], are formed when acetylene is reacted with anilides in the presence of strong bases.



It seemed of interest to determine the yield of 3-anilino-1-butyne (I) and N-vinylanilide (II) as a function of the reaction conditions and find the optimum coupling parameters for the synthesis of each product, especially for (I), since compounds of this series have been difficulty acessible up to now, despite their biological activity [4-6] and broad synthetic possibilities [7].

The yields of (I) and (II) (respectively Y_1 and Y_2) were taken as the parameters to be optimized. From the preliminary experimental data we selected those experiments in which the reaction temperature (X_1), time (X_2), and catalyst concentration* (X_3) were varied, while the remaining conditions were kept constant.

*Metallic K, in % of weight of acetanilide.

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