CONCLUSIONS

The reaction of cationic allyl complexes of manganese, rhodium, and iron with organometallic nucleophiles may proceed by three pathways: 1) addition of the nucleophile, 2) transallylation, and 3) reduction of the cationic complex.

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OXIDATIVE HALOGENATION OF AROMATIC COMPOUNDS IN

THE Pb₃O₄-Hal⁻-CF₃CO₂H SYSTEM

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Lead tetraacetate has been used for the oxidative chlorination [1], bromination [2], and iodination [3] of aromatic compounds in CF_3CO_2H .

In the present work, we studied the possibility of using a less expensive and more available Pb(IV) compound, namely red lead oxide (red lead), in these reactions.

 $\begin{array}{l} \mathrm{ArH} + \mathrm{Pb}(\mathrm{IV}) + \mathrm{Hlg}^{-} \xrightarrow{\mathrm{CF}_{3}\mathrm{COOH}} \mathrm{ArHlg} + \mathrm{H}^{+} + \mathrm{Pb}(\mathrm{II}) \\ \mathrm{ArH} = \mathrm{PhH}, \, \mathrm{PhF}, \, \mathrm{PhCl}, \, \mathrm{PhBr}, \, \mathrm{PhI}, \, \mathrm{PhMe}, \\ p - \mathrm{MeC}_{6}\mathrm{H}_{4}\mathrm{NO}_{2}, \, \, \mathrm{PhNO}_{2}, \, \, \mathrm{PhCF}_{3}, \, \, \mathrm{Hlg} = \mathrm{Cl}, \, \mathrm{Br}, \, \mathrm{I}. \end{array}$

In addition to the clear advantages of reactions in $Pb(OAc)_4$ -ArH-Hal⁻-CF₃CO₂H systems which permit the preparation of haloaromatic compounds under mild conditions using stoichiometric amounts of alkali metal halides, such methods have a number of drawbacks. As a consequence of the extremely high hygroscopicity of $Pb(OAc)_4$ obtained by dissolving Pb_3O_4 in CF₃CO₂H-(CF₃CO)₂O at 25°C over 5 days [4], this reagent is generated *in situ* by dissolving Pb_3O_4 in CF₃CO₂H. The participation of the acetoxy ligands of lead tetraacetate in the reaction and their oxidation lead both to nonproductive consumption of the oxidizing agent and the formation of side products such as the products of the methylation and acetoxymethylation

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TABLE 1. Oxidative Halogenation of Aromatic Compounds in 1:1:1 ArH-Pb₃O₄--KHal Systems in CF_3CO_2H at 20°C

ArH substrate	Yield of ArHal, % (p:o)		
	ArCl	ArBr	ArI
PhMe PhMe PhH PhF PhCI PhBr PhI PhNO ₂	$\begin{array}{c} 84 (45:55) *\\ 96 (35:65) **\\ 63\\ 86 **\\ 90 (91:9)\\ 90 (73:27)\\ 95 (68:32)\\ 80 (44:56)\\ 40 \end{array}$	$\begin{array}{c} 65 (52:48) \\ 100 (57:43) ** \\ 73 \\ 96 * \\ 100 (94:6) \\ 96 (78:22) \\ 96 (73:27) \\ 92 (85:15) \\ 90 *** \end{array}$	$\begin{array}{c} 62(61:39)\\ 98(70:30) **\\ 65\\ 94**\\ 100(95:5)\\ 100(94:6)\\ 98(88:12)\\ 98(88:12)\\ \end{array}$

*In the 4:1 CF₃CO₂H-H₂O system.

**In the 3:1:1 ArH-Pb₃O₄-KHal system (the yield was calculated relative to KHal introduced).

***1:2:2 PhNO₂-Pb₃O₄-KBr.

of the substrate and α -oxidation of alkylarenes [5]. In addition, the synthesis of lead tetraacetate by heating Pb₃O₄ in an acid—anhydride mixture in itself requires careful temperature maintenance and high purity of the reagents [6].

We have shown that the halogenation of aromatic compounds proceeds smoothly in ArH-Hal $-Pb_3O_4-CF_3CO_2H$ systems not only in the absence of trifluoroacetic anhydride but also in the presence of small amounts of water which provide for improved solubility of the alkali metal halides introduced (Table 1). The reaction usually requires several hours at about 20°C for completion. The haloarene yields upon the halogenation of halobenzenes are close to quantitative upon using stoichiometric (equimolar) amounts of the reagents. Halogenation of benzene and toluene under these conditions is accompanied by the formation of di- and polyhalogenation products. The reaction selectivity in this case may be readily increased by adding an excess of the aromatic substrate.

In contrast to the reactions of benzene and toluene in $Pb_3O_4-Cl^--CF_3CO_2H$ systems which proceed through the formation of mixed-ligand arylplumbates (IV) and leading to the formation of mixtures of aryl chlorides, biaryls, and arylacyloxylates [1], chlorination in the heterogeneous $Pb_3O_4-Cl^-$ system (i.e., in the presence of constant excess of chloride ions) proceeds only by the action of molecular chlorine formed under these conditions. This enhances the reaction selectivity although strongly deactivated substrates are chlorinated in these systems extremely slowly. Thus, for example, the total oxidation of nitrobenzene at 25°C (homogenization of the reaction mixture) proceeds over 48 h but the yield of nitrochlorobenzene after maintenance of the reaction mixture for 2 months is less than 40%. Under the same conditions, the chlorination of p-nitrotoluene proceeds quantitatively over 24 h.

Bromination and iodination under these conditions probably proceed by analogous reactions involving $Pb(OAc)_4$ [2, 3] and entail the intermediate formation of CF_3CO_2Hal (Hal = Br, I). However, the effective concentration of the halogenating reagent under these conditions is significantly lower, which leads to a decrease in the reaction rate and, for example in the bromination of nitrobenzene, the need to use excess oxidizing agent and bromide (see Table 1).

EXPERIMENTAL

The reaction mixtures were analyzed on an LKhM-8 chromatograph with a heat conductance detector and an LKhM-8M chromatograph with a flame ionization detector from 60 to 220°C using a 3000 × 3 mm column packed with 3% XE-60 on Chezasorb. The identification was carried out by comparing the retention times of the products and standard compounds. Analytical-grade Pb_3O_4 , pure-grade CF_3CO_2H , pure-grade KBr, pure-grade NaCl, and pure-grade KI were used without further purification. The aromatic substrates were purified by standard procedures.

<u>Oxidative Halogenation of Aromatic Compounds.</u> A sample of 5-10 ml CF_3CO_2H is added to weighed samples of Pb_3O_4 , an aromatic substrate, and alkali metal halide usually taken in equimolar ratio in amounts of 10^{-3} - 10^{-4} mole (see Table 1). The heterogeneous mixture is stirred with a magnetic stirrer until Pb₃O₄ dissolves completely. The mixture is then diluted with 50 ml water and extracted with four 15-ml CHCl₃ portions. The extract was dried over Na₂SO₄ and analyzed by gas-liquid chromatography.

CONCLUSIONS

Chlorination, bromination, and iodination of aromatic compounds may be carried out in the Pb_3O_4 -Hal -CF₃CO₂H system at room temperature. Halogenation under these conditions is not complicated by side reactions which are usual when lead tetraacetate is taken as the oxidizing agent.

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EFFECT OF A MAGNETIC FIELD ON THE KINETICS OF THE ANNIHILATION OF TRIPLET EXCIPLEXES

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UDC 541.12.038:538.12:541.127:541.141.7

Triplet exciplexes (TE) are intermediates in many photochemical oxidation-reduction reactions [1]. The annihilation of TE occurs by radiationless deactivation to the ground state and not due to a spin-orbital interaction, dissociation to radical-ions, or chemical reactions such as proton transfer. A magnetic field may affect the kinetics of the transition of TE to the ground state by a triplet mechanism due to anisotropy of the spin-orbital interaction in a heavy atom [2]. In the case of dissociation of TE to radical-ions in media with rather high dielectric constants (ε), we would expect an effect of a magnetic field due to a switchoff of singlet-triplet (T-S) transitions to radical pairs (RP) due to a hyperfine interaction (HFI) as observed for singlet exciplexes [3, 4].

In the present work, we studied the effect of an external magnetic field on the kinetics of the annihilation of TE arising upon the reaction of 9,10-anthraquinone (AQ) in the triplet state with triphenylamine (TPA) in solution.

EXPERIMENTAL

The absorption spectra and kinetics of the annihilation of the short-lived species were recorded using a laser photolysis apparatus using a dye laser with emission at 400 nm and a signal accumulation system and computer [5]. The kinetic curves were averaged over 128 flashes. The rate constant values were calculated, using a computer, by the method of least squares. Each value is the average of the results of at least ten experiments. The reagents were purified by recrystalization from ethanol. The solvents were distilled. Oxygen was removed by prolonged flushing with argon. An external magnetic field up to 3.4 kOe was pro-

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