

PHOTOINDUCED REACTIONS OF ORGANIC COMPOUNDS
WITH TRANSITION-METAL COMPLEXES.

VII.* PHOTOCHEMICAL OXIDATIVE COUPLING OF ARENES
UNDER THE ACTION OF CHLORIDE COMPLEXES OF Os(IV),
Ir(IV), AND Rh(III)

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We showed earlier that under the action of light the $PtCl_6^{2-}$ ion reacts with arenes, olefins, acetone, alkyl derivatives of tin and germanium, and hexane with the formation of σ complexes of Pt(IV) or π -olefin complexes of Pt(II) [2-8]. The irradiation of a solution of $PtCl_6^{2-}$ and carbon monoxide leads to the formation of a carbonylchloro-Pt(II) complex [1]. In the present work we describe the first results of an investigation of photo-induced reactions of some aromatic compounds with the complexes $OsCl_6^{2-}$, $IrCl_6^{2-}$ and $RhCl_3$.

The irradiation of a solution of Na_2OsCl_6 and anisole in acetic acid with the total radiation of a high-pressure mercury lamp leads to the formation of a small amount (yield 7% calculated on Os) of a mixture of dimethoxybiphenyl isomers. According to the PMR spectra, in the mixture the isomers with the methoxy groups in the 4 and 4' positions of biphenyl predominates. Biphenyls substituted in 2 and 3 positions are formed in amounts that are smaller by factors of ~ 2 and ~ 4 . Unfortunately, the high extinction coefficient of the $IrCl_6^{2-}$ ion in the visible region of the spectrum did not permit the use of high concentrations of this complex in the analogous reaction. In this case the reaction was conducted with the use of a suspension of the sparingly soluble salt $(NH_4)_2IrCl_6$ in an acetic acid-water-anisole mixture, and the saturated solution of the iridium complex was subjected to irradiation. Unlike the reaction with $OsCl_6^{2-}$, the photochemical dimerization of anisole under the action of $IrCl_6^{2-}$ leads to a mixture of 2-, 3-, and 4-substituted biphenyls in approximately equal amounts (monitoring by means of PMR). Finally, the irradiation of a solution of anisole and $RhCl_3$ in acetic acid gave substituted biphenyls in 15% yield, and the proportions of isomers were the same as in the case of $OsCl_6^{2-}$ (i.e., 4,4'-dimethoxybiphenyl predominated). The photochemical reactions of the complexes $IrCl_6^{2-}$ and $OsCl_6^{2-}$ with arenes that are less strongly electron-donating than anisole and toluene (e.g., with benzene and nitrobenzene) do not lead to the formation of biaryls. The reactions of these complexes with toluene give low yields of isomeric bitolyls.

The irradiation of frozen solutions of Na_2OsCl_6 or $(NH_4)_2IrCl_6$ in CH_3COOH at 77 K in absence of an arene leads to the appearance of signals in the ESR spectrum. These signals form a quartet with relative intensities of 1:3:3:1 and with $a_H \approx 2.3$ mT (Fig. 1) and probably belong to the methyl radical. On the irradiation of such solutions containing also an arene (anisole, toluene, naphthalene), in the ESR spectrum, apart from the intense quartet arising from CH_3^{\cdot} , we observe a number of weaker additional lines (Fig. 1), which may belong to radical or radical-cation species formed from the arene. However, the rigorous identification of such radical products is impossible because of the superposition of their signals on the spectrum of the methyl radical.

In view of these experiments and of data in the literature on the thermal oxidative dimerization of arenes under the action of compounds of Tl(III), Hg(II), Pb(IV), Fe(III) or Co(III) [9] we may postulate a probable scheme of the photochemical oxidation of arenes and the decarboxylation of acetic acid by osmium or iridium complexes. At the first stage there occurs the photoexcitation of the complex of the metal M (regarding the photoexcitation of the $IrCl_6^{2-}$ ion see [10]) (1).

*For VI sec [1].

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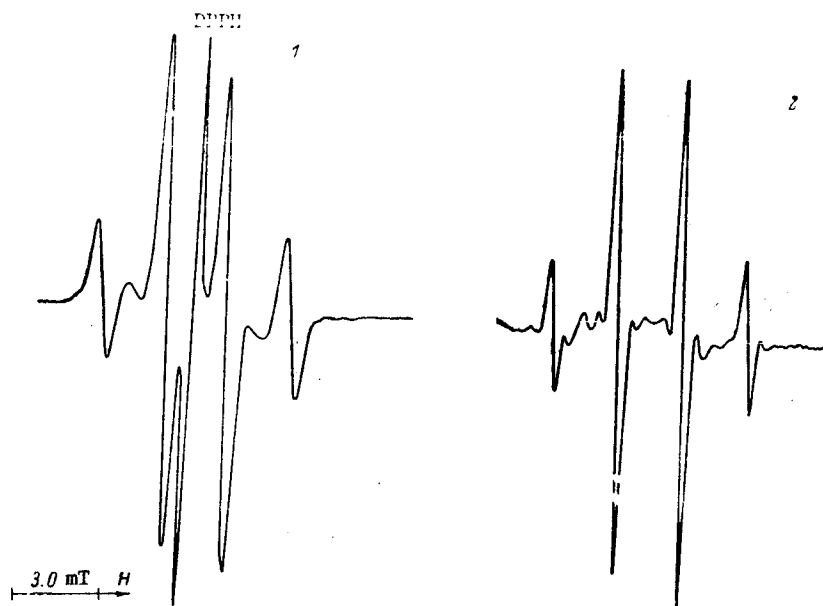
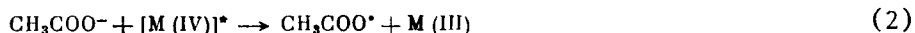


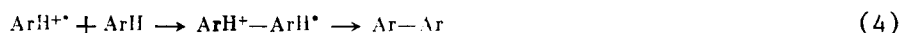
Fig. 1. ESR spectra of frozen solutions of $(\text{NH}_4)_2\text{IrCl}_6$ in acetic acid at 77 K in absence (1) and in presence (2) of toluene.



The second stage may consist in the transfer of an electron to the excited species from the acetate ion (2) or from the arene (3).



The radical formed in reaction (2) loses CO_2 and is converted into a methyl radical, which is recorded in the ESR spectrum. As is well known, the formation of alkyl radicals in the oxidation of carboxylic acid readily occurs under the action of metal compounds [11]. A stage of electron transfer from the arene is also proposed for processes of the oxidation of aromatic compounds by metal complexes [9, 12-25]. In some cases it was found to be possible to observe the ESR spectra of the intermediately formed arene radical cations [12, 13, 15, 19]. The radical cation may react with another arene molecule, as a result of which a biaryl is formed [9] (4).



In the irradiation of a solution of OsCl_6^{2-} and p-xylene in acetic acid p-tolualdehyde was formed as the main product, which can also be explained on the basis of a scheme including the transfer of an electron at the first stage. In fact, in this case the p-xylene radical cation can abstract a proton from the methyl groups. The p-methylbenzyl radical formed by reaction with oxygen dissolved in the acetic acid gives finally the aldehyde.

However, there are alternative possible schemes of the dimerization reaction of arenes. For example, it is not ruled out that the first stage of the reaction consists in the photolysis of the M-Cl [10] or M-OH (see [26]) bond with formation of chlorine or hydroxyl free radicals, which then react further with the aromatic substrate.

EXPERIMENTAL

The ESR spectra were determined on a 3-cm range ÉPR-2- spectrometer (designed at the Institute of Chemical Physics).

All the reactions were conducted in air in a cylindrical quartz vessel, diameter 2 cm, cooled with flowing water to a temperature of 15°C. Irradiation was with the full radiation of a DRSh-1000 high-pressure mercury lamp (1000 W), the solution being agitated vigorously with a magnetic stirrer.

A solution of 0.4 ml of anisole, 0.12 g of $\text{Na}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$, and 0.4 ml of H_2O in 7.2 ml of CH_3COOH was irradiated for 11 h. To the solution 3 ml of water was added, and the

material was extracted with chloroform. The extract was washed with water and dried with Na_2SO_4 , and chloroform was vacuum-evaporated. The residue was separated on Silufol plates (the eluent was hexane-benzene 3:1). We obtained 0.004 g (7%) of a mixture of dimethoxybiphenyls. The main component of the mixture was 4,4'-dimethoxybiphenyl. PMR spectrum (in CDCl_3 , δ , ppm): 3.83 s (CH_3); 6.92 and 7.46, two pseudodoublets (aromatic protons). According to the PMR spectrum (signals in the range 6.6-7.6 ppm, singlets at δ 3.80 and 3.77 ppm) the mixture also contains isomers of dimethoxybiphenyls with the methoxy group on the 2 and 3 position of the benzene ring.

A solution of 0.05 g of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 0.4 ml of anisole, and 0.6 ml of H_2O in 7 ml of CH_3COOH was irradiated for 2 h. We obtained 0.006 g (15%) of a mixture of dimethoxybiphenyls.

A solution of 0.12 g of $\text{Na}_2\text{OsCl}_6 \cdot 2\text{H}_2\text{O}$, 0.4 ml of p-xylene, and 0.4 ml of H_2O in 7.2 ml of CH_3COOH was irradiated for 5 h. From the reaction mixture by means of TLC on Silufol we isolated 0.006 g of p-tolualdehyde. PMR spectrum: 2.41 (CH_3), 7.23 and 7.70 two pseudodoublets (aromatic protons), 9.83 (CHO).

CONCLUSIONS

The irradiation of solutions of anisole and the complex OsCl_6^{2-} , IrCl_6^{2-} , or RhCl_3 in acetic acid leads to the formation of dimethoxybiphenyls. Reaction probably starts with the transfer of an electron from the arene to an excited species of the complex.

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