

Photochemical Reactions of Acyl Iodides with Haloarenes

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We found previously that the photolysis of acyl iodides in arenes leads to the photochemical Friedel–Crafts reaction [1]. In particular, *ortho*- and *meta*-xylenes showing enhanced polarity of the aromatic ring undergo smooth acylation by acetyl iodide under photochemical conditions. The acylation of the aromatic ring is also the sole reaction route upon photolysis of trimethylacetyl and valeroyl iodides in toluene. A similar process was expected to occur on UV irradiation of a mixture of acyl iodides RCOI (R = Me, Ph) with haloarenes (fluoro-, chloro-, bromobenzene and dibromobenzenes).

However, the photolysis of acetyl iodide in chlorobenzene failed to give the expected acylation product, chloroacetophenone $\text{CH}_3\text{COC}_6\text{H}_4\text{Cl}$. UV irradiation (using an OKN-11 mercury lamp as the UV source) of an equimolar mixture of acetyl iodide and chlorobenzene for 29 h afforded acetyl chloride (yield 25%) with bp 50–51°C, n_D^{20} 1.389 (lit.: bp 52°C, n_D^{20} 1.389 [2]); diacetyl (14%) with bp 88–89°C, n_D^{20} 1.3950 (lit.: bp 88°C, n_D^{20} 1.3950 [2]); and iodobenzene (8%) with bp 186–187°C, n_D^{20} 1.6200 (lit.: bp 188°C, n_D^{20} 1.6200 [2]).

For $\text{C}_6\text{H}_5\text{I}$ anal. calcd. (wt %): I, 62.20.

Found (wt %): I, 63.17.

In addition, a powdered infusible black polymer **1** insoluble in water and common organic solvents was obtained, and its composition corresponded to the molecular formula $\sim\text{C}_{78}\text{H}_{53}\text{I}$ (C/H = 1.5).

For $\text{C}_{78}\text{H}_{53}\text{I}$ anal. calcd. (wt %): C, 83.8; H, 4.7; I, 11.4.

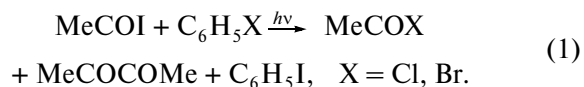
Found (wt %): C, 81.4; H, 5.1; I, 11.3.

The photochemical reaction of acetyl chloride with bromobenzene proceeds in a similar way. The UV irradiation of an equimolar mixture of MeCOI with $\text{C}_6\text{H}_5\text{Br}$ for 50 h leads to acetyl bromide (yield 20%) bp 78–79°C, n_D^{20} 1.4520 (lit.: bp 75–77°C, n_D^{20} 1.450 [2]), iodobenzene (9%), and diacetyl (16%). Polymeric product **2** corresponding to composition $\sim\text{C}_{16}\text{H}_{13}\text{I}$ also forms.

For $\text{C}_{16}\text{H}_{13}\text{I}$ anal. calcd. (wt %): C, 57.8; H, 3.9; I, 38.2.

Found (wt %): C, 58.8; H, 3.1; I, 37.8.

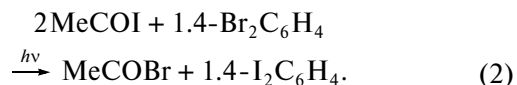
The reactions of acetyl iodide with monohalobenzenes can be represented by the following general equation:



Polymers **1** and **2** are the products of photochemical polyphenylation of iodobenzene formed at the first stage of the process. The lack of oxygen in the mixture of isolated polymeric products provides an additional confirmation for the absence of the acylation of the aromatic ring in this reaction.

The reactions of acetyl iodide with chloro- and bromobenzene can be assigned with good reason to the radical reactions of photosubstitution in aromatic ring where MeCOI behaves as the source of primary radicals. This is indicated by the presence in the reaction mixture of diacetyl MeCOCOMe resulting from the recombination of acetyl radical.

The photochemical reaction of acetyl iodide with 1,4-dibromobenzene, as distinct from the reaction with monobromobenzene, leads solely to diiodobenzene and acetyl bromide:



In particular, the UV irradiation of an equimolar mixture of acetyl iodide and 1,4-dibromobenzene for 50 h produces acetyl bromide (yield 95%) with bp 76°C, n_D^{20} 1.4530 (lit.: bp 75–77°C, n_D^{20} 1.45 [2]) and 1,4-diiodobenzene (yield 74%) with mp 130–131°C (lit.: mp 131–133°C [3]).

For C₆H₄I₂ anal. calcd. (wt %): C, 21.8; H, 1.2; I, 76.9.

Found (wt %): C, 20.9; H, 1.8; I, 76.1.

No fluorine exchange was observed on the UV irradiation of a mixture of acetyl iodide and fluorobenzene. Neither halogen exchange nor other photochemical transformations of MeCOI were also detected when fluorobenzene was replaced by hexafluorobenzene.

We also failed to obtain iodobenzene by the photolysis of benzoyl iodide in chlorobenzene or bromobenzene. The halobenzene was recovered, while polymeric compounds were isolated instead of benzoyl iodide.

In particular, after UV irradiation of an equimolar mixture of benzoyl iodide and chlorobenzene for 50 h, a powdered infusible black polymer **3** insoluble in water and common organic solvents and having the molecular formula C₂₀H₁₁O₂I was isolated from the reaction mixture.

IR (cm⁻¹): 3070, 3016 (ν_{C-H} of ring), 1686 ($\nu_{C=O}$), 1601, 1452, 1418 (ν_{C-C} of ring), 932, 707, 682 (δ_{C-H} of ring), 545 (ν_{C-I}), 430 (δ_{C-C} of ring). The IR spectra were recorded as thin films on a UR-20 spectrophotometer.

For C₂₀H₁₁O₂I anal. calcd. (wt %): C, 58.5; H, 2.7; I, 30.9.

Found (wt %): C, 56.7; H, 2.7; I, 31.1.

The UV irradiation of an equimolar mixture of benzoyl iodide and bromobenzene under similar conditions led to polymer **4** with composition C₁₄H₇O₂I similar in properties to polymer **3**.

IR (cm⁻¹): 3070, 3023 (ν_{C-H} of ring), 1688 ($\nu_{C=O}$), 1602, 1453, 1423 (ν_{C-C} of ring), 934, 707, 683 (δ_{C-H} of ring), 551 (ν_{C-I}), 430 (δ_{C-C} of ring).

For C₁₄H₇O₂I anal. calcd. (wt %): C, 50.3; H, 2.1; I, 38.2.

Found (wt %): C, 49.1; H, 2.6; I, 37.3.

In this case, the polymers contain oxygen, as distinct from polymeric compounds **1** and **2** resulting from the photolysis of acetyl iodide in chlorobenzene or bromobenzene, and their IR spectra show absorption bands at 1688 and 1686 cm⁻¹ indicating the presence of the C=O group conjugated with the phenyl group. Therefore, we can conclude that polymers **3**

Electrical conductivity, ESR spectral parameters, and relaxation times for polymers **3** and **4**

Parametr		Polymer 3	Polymer 4
σ , S/cm		2.8×10^{-9}	1.3×10^{-8}
N , spin/g		1.8×10^{19}	1.9×10^{19}
ΔH , G		7.4	7.3
g		2.00497	2.00542
A/B		0.80	0.77
T_1 , ns	T_1'	2940.0	858.8
	T_1''	8913.0	3720.2
T_2 , ns	T_2'	—	2.61
	T_2''	132.5	126.4

Note: The values of T_1 and T_2 characterize the lifetime of electron spin in the excited state.

and **4** are the products of photochemical polycondensation of benzoyl iodide on account of its self-acylation accompanied by a competitive photochemical iodination of the benzene ring. The polymers are supposed to consist of alternating units $-[C_6H_4COC_6H_4COC_6H_3I-]$ (**3**) and $-[C_6H_4COC_6H_3ICO-]$ (**4**).

The properties of polymers **3** and **4** revealed by continuous-wave (CW) ESR are very close to those of polymers isolated earlier upon photolysis of acetyl iodide in benzene or toluene [3]. Both polymers show a pronounced paramagnetism and give rise narrow asymmetrical ESR signals in the range of g values typical of free radicals. The upper portion of the ESR lines is described by the Lorentzian curve, while the lower portion is expressed by the Gaussian curve, which can indicate their irregular structure. The concentration of paramagnetic centers corresponds to 10^{19} spin/g (table). However, the g factors of the signals differ markedly from spin-only values, which indicates a substantial contribution of spin-orbit interactions, and differ considerably from each other ($\Delta g = 0.00045$) (table).

The electrical conductivity of polymers **3** and **4** is typical of organic semiconductors in spite of high iodine content, but it is lower by an order of magnitude than the conductivity of polymers described in [3]. It seems to be due to the fact that the iodine atom is covalently bound to macromolecules in contrast to the polymers described earlier [3] doped with iodine and therefore showing higher electrical conductivity. The concentration of unpaired electrons and the ESR line widths, which characterize the environment of paramagnetic centers and amount to less than 10 G, allow one to detect spin echo in a pulsed mode at ambient temperature and to obtain relaxation times T_1 and T_2 for polymers **3** and **4**. According to ESR, T_2 (spin-

spin relaxation time) is much shorter than T_1 (spin–lattice relaxation time). This is typical of magnetically diluted paramagnets [4]. The relaxation time for polymers **3** and **4** is determined by two contributions, which is evidence of a complex character of interaction of unpaired electrons with the environment and requires a special study.

The ESR spectra were recorded at ambient temperature on a Radiopan SE/X-2547 spectrometer (Russia) with sensitivity of 5×10^{10} spin/g equipped with a magnetometer and high-frequency meter and on a Bruker ELEXSYS E-580 spectrometer (Germany) in CW and FT modes. The concentration of paramagnetic centers was calculated by the known procedure [5] using calibrated DPPH standards and a nomogram of double integration of the absorption line derivative [6]. Relaxation times T_1 and T_2 were determined with the use of the following pulse sequences: π - T - $\pi/2$ - τ - π for T_1 and $\pi/2$ - τ - π for T_2 , where $\pi/2 = 20$ ns, $\tau = 200$ ns, and $T = 1000$ ns [7].

Thus, this study has revealed the possibility to use acyl iodides as reagents in the photochemical exchange of chlorine or bromine atoms for iodine in haloarenes and for the photochemical preparation of α,ω -diiodopolyarylenes, polymers showing paramagnetic and semiconducting properties. The data given in the paper confirm the previously established large synthetic potential of acyl iodides as reagents and synthons in organic synthesis [8–11].

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