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Expected and Unexpected Photochemical Reactions of Acyl Iodides

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Abstract—Photolysis of acyl iodides RCOI (R = Me, Me_2CH, Ph) under UV irradiation in toluene environment for 20–55 h proved to be a simple and efficient method of preparation of symmetrical α-diketones RCOCOR. In contrast, the photolysis under the same conditions of acyl iodides RCOI [R = $Me(CH_2)_3$, Me_3C] did not lead to the formation of the corresponding diacyls, and the reaction products were unexpected 1,1-bis(4-methylphenyl)pentane and a mixture of isomeric 3- and 4-methyl(*tert*-butyl)benzenes respectively. The most probable mechanism of their formation is the primary photochemical acylation of toluene in the aromatic ring followed by the photochemical reduction of the arising butyl 4-methylphenyl ketone in the case of the valeroyl iodide or the photochemical Norrish type I cleavage of isomeric 3- and 4-methylphenyl (*tert*-butyl) ketones in event of the pivaloyl iodide. In the photolysis of acetyl iodide (R = Me) in benzene or toluene alongside the diacetyl formation polyarylation process was observed of acylated and iodinated into the aromatic ring solvents with the formation of polymeric products with semiconductor and paramagnetic properties.

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It was formerly reported that on the photolysis of acetyl iodide the diacetyl MeCOCOMe did not form [1]. This fact was ascribed to the short lifetime of $MeCO^\bullet$ radical (10^{-11} s) decomposed further under the UV irradiation into $Me^\bullet$ radical and carbon monoxide CO.

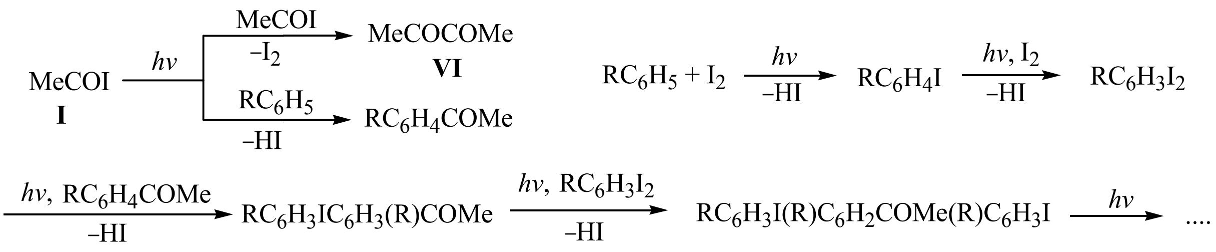
Yet in the course of the systematic research on acyl iodides application as reagents and synthons in organic and organoelemental synthesis [2] we established a possibility to obtain symmetric diacyls by photochemical dissociation of acyl iodides RCOI (R = Me, Me_2CH, Ph) [3].

We report here on the search for the optimum conditions of the photochemical conversion of acyl iodides RCOI [R = Me (**I**), Me_2CH (**II**), Me_3C (**III**), $Me(CH_2)_3$ (**IV**), Ph (**V**)] into α-diketones.

It was established that the photolysis of MeCOI (**I**) under the irradiation with a mercury-quartz lamp OKN-11 in the medium of benzene or toluene that were sensitizers of photochemical reactions [4] within 19–21 h led to the formation of diacetyl (**VI**) in amounts of 62 and 49% from the theoretical respectively. Alongside the diacyl black nonmelting polymers formed insoluble in organic solvents. The polymer formed at the photolysis of MeCOI in benzene has the elemental composition close to the formula $C_{14}H_8I_2O$ (**VII**), and in toluene, to $C_{16}H_{15}IO$ (**VIII**). The formation of these polymers shows the proceeding of concurrent processes of photochemical iodination and acylation with acetyl iodide of the aromatic ring of solvents with subsequent polyarylation, a characteristic photochemical reaction of such aromatic compounds substituted in the ring [5] (Scheme 1).

The polymers obtained are paramagnetic semiconductors. In their ESR spectra singlet signals are observed with the characteristics inherent to the polymers with a well-developed conjugation system (see the table). Polymer **VII** is apparently built from the regularly alternating blocks IC_6H_2COMe and IC_6H_3, and polymer **VIII**, from fragments $IC_6H_2CH_3$ and $CH_3C_6H_2COMe$. The concentration of the paramagnetic centers in polymer **VIII** (2.1×10^{19} spin/g) is by an order of magnitude larger than in polymer **VII** (2.9×10^{18} spin/g), and the conductivity of the former is 2.6 times lower [7.7×10^{-8} (**VII**),

Scheme 1.



$$MeCOI\ (\mathbf{I}) \xrightarrow{h\nu} \begin{cases} \xrightarrow[-I_2]{MeCOI} MeCOCOMe\ (\mathbf{VI}) \\ \xrightarrow[-HI]{RC_6H_5} RC_6H_4COMe \end{cases} \qquad RC_6H_5 + I_2 \xrightarrow[-HI]{h\nu} RC_6H_4I \xrightarrow[-HI]{h\nu,\ I_2} RC_6H_3I_2$$

$$\xrightarrow[-HI]{h\nu,\ RC_6H_4COMe} RC_6H_3IC_6H_3(R)COMe \xrightarrow[-HI]{h\nu,\ RC_6H_3I_2} RC_6H_3I(R)C_6H_2COMe(R)C_6H_3I \xrightarrow{h\nu} ....$$

R = H, Me

1.2×10^{-10} (**VIII**) Ohm/cm]. These differences may be due to the higher iodine content in polymer **VII**. On additional doping of the polymers with iodine vapor for 24 h the conductivity of polymer **VIII** considerably increased (to 1.9×10^{-6} Ohm/cm), and the concentration of unpaired spins increased two-fold (to 3.8×10^{19} spin/g), whereas in polymer **VII** these parameters changed insignificantly (see the table). The sharp increase in the conductivity of polymer **VIII** at the relatively small increase in the concentration of the paramagnetic centers after its doping with iodine may be due to the formation of diamagnetic bipolarons governing the conductivity. The broadening of signals and increased g-factor in the doped polymers manifest the interaction between the unpaired electron and the orbitals of the heavy iodine atom.

The fact that the residual content of acyl iodide after the studied reaction in toluene was only 16% compared with 33% in benzene was the reason of the choice of toluene as the solvent for further investigation of the photochemical transformations of acyl iodides.

For instance, the increase of the duration of the acetyl iodide photolysis in toluene to 55 h resulted in nearly quantitative yield of diacetyl (**VI**) (93%). Similarly, in the photolysis in toluene environment of acyl iodides **II** and **V** for 20 h the symmetric diacyls RCOCOR **IX** and **X** formed in 49 and 89% yield respectively. The side polymeric products in these processes formed in insignificant amounts. The studied potochemical dissociation of acyl iodides **I, II**, and **V** is now the simplest and the most efficient preparation procedure of the corresponding α-diketones **VI, IX**, and **X** (Scheme 2).

Scheme 2.

$$\underset{\mathbf{I,\ II,\ V}}{2RCOI} \xrightarrow{h\nu} \underset{\mathbf{VI,\ IX,\ X}}{RCOCOR}$$

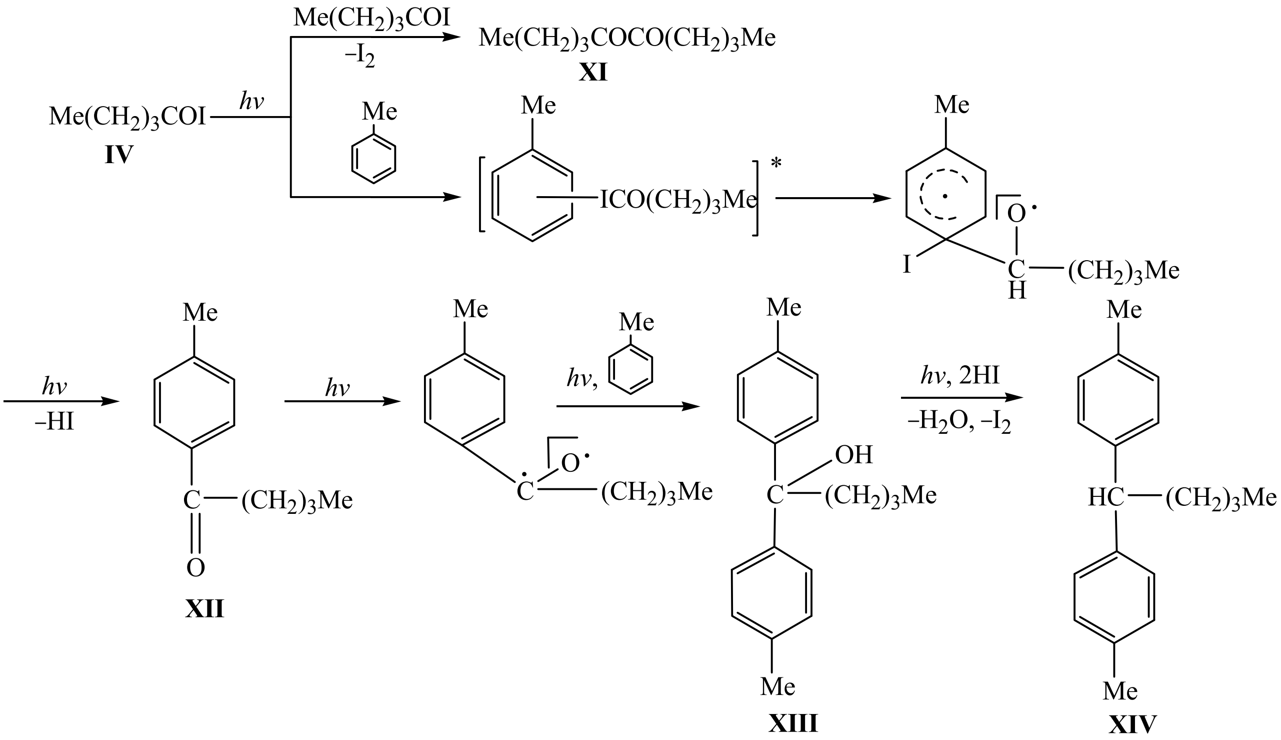
R = Me (**I, VI**), Me_2CH (**II, IX**), Ph (**V, X**).

Unexpectedly the photolysis under analogous conditions of acyl iodides **III** and **IV** did not yield the corresponding diacyls. After UV irradiation of the solution of acyl iodide **IV** in toluene for 26 h only trace amounts of decane-5,6-dione (**XI**) were identified. The main product of this reaction proved to be 1,1-bis(4-methylphenyl)pentane (**XIV**). It formed along the following most probable mechanism. In the first stage toluene is acylated into the *para*-position of the benzene ring analogously to the reaction with H-donors (to which belongs also the toluene [6]) of acyl chlorides [7]. The obtained in this stage 4-butyl methylphenyl ketone (**XII**) further adds

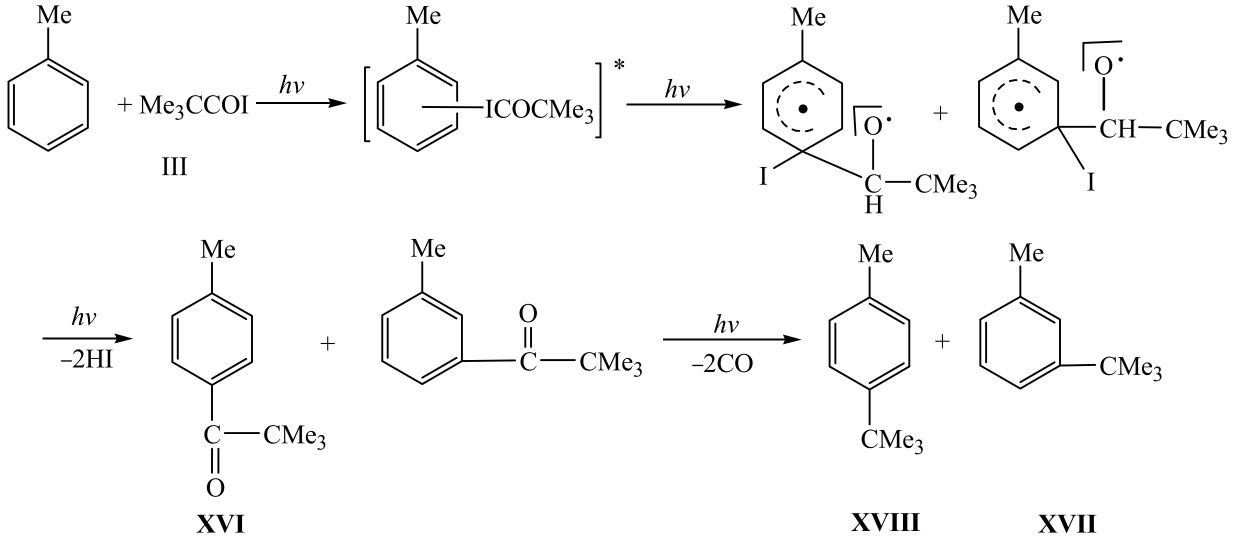
Parameters of electroconductivity and ESR spectra of polymers **VII** and **VIII**

Polymer (solvent)	Before (after) doping with I_2	σ, Ohm/cm	ESR signal			Asymmetry parameter
			N, spin/g	Δ*H*, Oe	g-factor	*A*/*B*
VII (benzene)	before	7.7×10^{-8}	2.9×10^{18}	10.6	2.0039	0.81
	after	4.8×10^{-7}	2.3×10^{18}	11.8	2.0050	0.78
VIII (toluene)	before	1.2×10^{-10}	2.1×10^{19}	6.9	2.0032	0.83
	after	1.9×10^{-6}	3.8×10^{19}	8.6	2.0042	0.62

Scheme 3.



Scheme 4.



a toluene molecule to the carbonyl group followed by the reduction of the formed 1,1-bis(4-methylphenyl) pentan-1-ol (**XIII**) with the liberated hydrogen iodide (Scheme 3).

A similar mechanism of benzophenones reduction was formerly described [8].

After the photolysis of acyl iodide **III** a mixture was isolated of isomeric 3- and 4-methyl(*tert*-butyl)benzenes **XVII** and **XVIII** in a ratio 1.5:1 (overall yield 45%). Alongside these products trace amount of *tert*-butyl methylphenyl ketone was identified. The formation of the latter indicates that in this case also the toluene is acylated into *meta*- and *para*-positions followed by the photochemical Norrish type **I** cleavage of the obtained isomeric ketones [9] (Scheme 4).

After the photolysis of acyl iodides **III** and **IV** in benzene or in its absence but in the presence of elemental copper or ittrium chloride whose photolytic activity has been discovered before [10] no the corresponding α-diketones or other products were found, the initial reagents were recovered intact.

The differences in the photolysis directions of acyl iodides **I, II, V**, on the one hand, and **III, IV**, on the other hand, are due to the sharp distinctions in their dissociative ability, and also to the difficulties arising in further recombination of bulky acyl radicals $RCO^\cdot$ with substituents R = Me_3C (**III**) and $Me(CH_2)_3$ (**IV**) (Scheme 2).

EXPERIMENTAL

As a source of UV radiation a mercury-quartz lamp of low pressure OKN-11 was applied. IR spectra were recorded on a spectrophotometer UR-20 from thin films. ^1H and ^{13}C NMR spectra were registered on a spectrometer Bruker DPX-400 at operating frequency 400 MHz from solutions in $CDCl_3$ (internal references TMS or HMDS). ESR spectra were measured at room temperature on a radiospectrometer SE/X-2547 (Radiopan) of sensitivity 5×10^{10} spin/g equipped with a magnetometer and the high frequency meter. The concentration of the paramagnetic centers was calculated by procedure [11] using calibrated standards of diphenylpicrylhydrazyl and a nomogram of the double integration of the derivative of the absorption line [12]. The electroconductivity of polymers **VII** and **VIII** was measured on a standard teraohmmeter E6-13A. The studied samples were prepared as pellets pressurized at 700 kg/cm^2. Iodine doping of polymers was performed by diffusion method in the gas phase.

Initial acyl iodides **I, III–V** were obtained by treating the corresponding acyl chlorides with anhydrous sodium iodide [13], isobutyryl iodide (**II**) was prepared by the reaction of isobutyric acid with acetyl iodide [14].

Photolysis of acetyl iodide (I) in benzene solution. A solution of 8.5 g (50 mmol) of acetyl iodide in 6 ml of benzene charged into a quartz flask of 50 ml capacity equipped with a reflux condenser was kept under UV irradiation for 21 h. On completion of the reaction the liquid phase of the reaction mixture was filtered off and distilled at the atmospheric pressure. We isolated 2.0 g of the fraction boiling at 70–80°C and containing 33% of the initial acetyl iodide and 67% of diacetyl (**VI**), yield on initial acetyl iodid 62%. IR spectrum, ν, cm^{-1}: 1795 (CO in MeCOI), 1700 (CO in MeCOCOMe). Found, %: I 24.65. C_2H_3OI. Calculated, %: I 74.07.

The filtered off solid precipitate was washed with ethanol, ether, and it was kept for 24 h in a vacuum-desiccator. We isolated 6.5 g of black polymer, nonmelting, insoluble in ethanol, ether, aliphatic and aromatic hydrocarbons, acetone, chloroform, and tetrachloromethane. IR spectrum, ν, cm^{-1}: 1695 (CO), 1600, 1545 (C–C of benzene ring), 1010, 860, 760 (C–H of ring), 420 (C–I). Found, %: C 33.02; H 2.38; I 59.92. $C_{14}H_8I_2O$. Calculated, %: C 37.66; H 1.79; I 56.95.

Photolysis of acetyl iodide (I) in toluene. *a.* A solution of 17.0 g (100 mmol) of acetyl iodide in 10 ml of toluene was kept under UV irradiation for 19 h. On completion of the reaction the reaction mixture was filtered and distilled to separate 2.5 g of a fraction with bp 80–100°C containing diacetyl (**VI**) with an impurity of 16% of acetyl iodide (yield of diacetyl on initial acetyl iodid 48%). IR spectrum, ν, cm^{-1}: 1795 (CO in MeCOI), 1700 (CO in MeCOCOMe). Found, %: I 12.15. C_2H_3OI. Calculated, %: I 74.67.

The filtered off solid precipitate was washed with methanol and ether. We isolated 7.8 g (46%) of black polymer, nonmelting, insoluble in water, methanol, ether, acetone, toluene, deuterochloroform, and tetrachloromethane. IR spectrum, ν, cm^{-1}: 1700 (CO), 1610, 1550 (C–C of benzene ring), 1000, 850, 780 (C–H of ring), 450 (C–I). Found, %: C 54.31; H 4.20; I 36.22. $C_{16}H_{15}IO$. Calculated, %: C 54.87; H 4.32; I 36.24.

b. A solution of 17.0 g (100 mmol) of acetyl iodide in 10 ml of toluene in a quartz flask of 50 ml capacity equipped with a reflux condenser and isolated from the access of moisture was kept under UV irradiation for 55 h. On completion of the reaction the reaction mixture was filtered and distilled under the atmospheric pressure. Yield of diacetyl (**VI**) 4.0 g (93%), bp 88–90°C (88°C [15]). IR spectrum coincided with the standard. Found, %: C 55.02; H 6.67. $C_4H_6O_2$. Calculated, %: C 55.81; H 7.02.

Photolysis of isobutyryl iodide (II). A solution of 9.0 g (45 mmol) of isobutyryl iodide in 8 ml of toluene was kept under UV irradiation for 20 h. The reaction mixture was distilled and treated with copper powder. Yield of α-diketone **IX** 1.6 g (49%), bp 140–145°C, n_D^{20} 1.5310. IR spectrum, ν, cm^{-1}: 1705 (CO). Found, %:

C 67.00; H 9.88. $C_8H_{14}O_2$. Calculated, %: C 67.57; H 9.92.

Photolysis of pivaloyl iodide (III). A solution of 9.6 g (94 mmol) of pivaloyl iodide (**III**) in 10 ml of toluene was kept under UV irradiation for 22 h. We isolated from the reaction mixture 5.0 g (52%) of a fraction with bp 75–80°C containing mainly a mixture of **3- and 4-methyl-(*tert*-butyl)benzenes (XVII, XVIII)** in a ratio 1.5:1. IR spectrum, ν, cm^{-1}: 3960–2860 (C–H), 1600, 1480, 1460 (C–C of ring), 800, 760, 700 (C–H of ring). ^1H NMR spectrum, δ, ppm: 1.35 s [9H, *p*-$(CH_3)_3C$], 1.353 s [9H, *m*-$(CH_3)_3C$], 2.35 s (3H, *p*-Me), 2.39 s (3H, *m*-Me), 7.14, 7.32 d (2H, Ar, ^3J 8.32 Hz), 7.02, 7.23 m (4H, Ar). ^{13}C NMR spectrum, δ, ppm, isomer **XVIII**: 21.61 (CH_3), 31.38 [$(CH_3)_3C$], 34.25 (CH_3C), 125.09 (C^2), 128.70 (C^3), 134.73 (C^4), 148.11 (C^1); isomer **XVII**: 20.76 (CH_3), 31.35 [$(CH_3)_3C$], 34.48 (CH_3C), 122.23 (C^6), 126.02 (C^2), 126.11 (C^4), 127.92 (C^5), 137.36 (C^3), 151.03 (C^1).

Photolysis of valeroyl iodidea (IV). A solution of 10.0 g (47 mmol) of acyl iodide **IV** in 5 ml of toluene was kept under UV irradiation for 26 h. On completion of the reaction we isolated from the reaction mixture 5.0 g (45%) of **1,1-bis(4-methylphenyl)pentane (XIV)**, bp 165°C, n_D^{20} 1.5445.

IR spectrum, ν, cm^{-1}: CO is absent, 3020–2820 (C–H), 1600, 1500 (C–C of ring), 720, 690 (C–H of ring). ^1H NMR spectrum, δ, ppm: 0.89 t (3H CH_3CH_2, ^3J 6.91 Hz), 1.39 m (2H CH_3CH_2), 1.47 quintet (2H, $CH_3CH_2CH_2$, ^3J 6.91 Hz), 2.15 d.t (2H, CH_2CH, ^3J 7.55, ^3J 7.68 Hz), 2.42 s (6H, CH_3), 3.96 t (1H, $CHCH_2$, J 7.68 Hz), 7.20, 7.26 d (4H, Ar, ^3J 7.94 Hz). ^{13}C NMR spectrum, δ, ppm: 14.08 (CH_3CH_2), 21.04 (CH_3Ar), 22.82 (CH_3CH_2), 30.40 ($CH_3CH_2CH_2$), 35.65 ($CH_3CH_2CH_2CH_2$), 50.65 (CH), 127.76 ($C^{2,6}_{arom}$), 129.13 ($C^{3,5}_{arom}$), 135.39 (C^1CH), 142.76 (C^4Me). Found, %: C 88.99; H 9.96. $C_{19}H_{24}$. Calculated, %: C 90.47; H 9.52.

Photolysis of benzoyl iodide (V). A solution of 17.5 g (75 mmol) of benzoyl iodide in 8 ml of toluene was kept under UV irradiation for 20 h. From the reaction mixture toluene and partially iodine were distilled off. The remaining iodine was sublimed in a vacuum from the crystalline residue of dibenzoyl. We isolated 7.1 g (89%) of dibenzoyl **X**, mp 95°C (95–96°C [15]). IR spectrum coincided with the standard. Found, %: C 79.52; H 5.06. $C_{14}H_{10}O_2$. Calculated, %: C 79.98; H 4.79.

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