

SHORT
COMMUNICATIONS

Photochemical Reaction of Acyl Iodides with Alkenes and Thiophene

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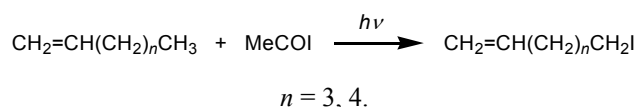
Received February 21, 2014

DOI: 10.1134/S1070428014080260

Acetyl iodide is known to add to the double bond of trimethylethylene at 25°C within 26 days forming first 2-acetyl-3-iodo-2-methylbutane which further eliminates HI giving 2-acetyl-2-methylbut-3-ene [1]. The process is accelerated at adding dimethylaniline to the reaction mixture. Yet also in this case the yield of the unsaturated ketone did not exceed 5%. The heating in the presence of dimethylaniline at 170–185°C for 3 h of a mixture of acetyl iodide with cyclohexene in 1 : 1 ratio provided tetrahydroacetophenone in 8.3% yield. Acetyl iodide added at –15°C to one as well as to both multiple bonds of thiophene followed by the decomposition of iodine-containing adducts with the liberation of elemental iodine. The final reaction products were acetothienone, diacetodihydrothiophene, and products of their polymerization.

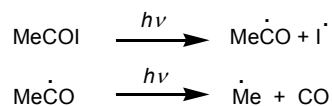
In the course of systematic research on the photochemistry of acyl iodides [2] we studied reactions of RCOI (R = Me, Ph) with alkenes (1-hexene, 1-heptene, cyclohexene), and also with thiophene under UV irradiation. As a source of UV light mercury-quartz lamp DRT-400, λ_{\max} 240–250 nm was used. The irradiation period was varied from 29 to 50 h.

Unlike the findings of [1] we revealed that acetyl iodide under the photochemical conditions did not add to the double bond either in 1-hexene or in 1-heptene. In both cases the replacement with iodine of hydrogen of the terminal methyl group of the initial olefin occurred affording the corresponding 6-iodohex-1-ene

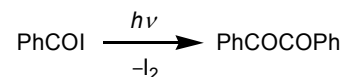


[†] Deceased.

and 7-iodohept-1-ene in 57–60% yields. Beside the unreacted initial olefins any other products, including also acetyl iodide, were not found. Under UV irradiation acetyl iodide decomposed [3], and the iodination occurred by arising iodine radicals.

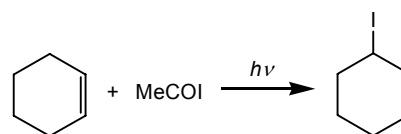


In the same conditions benzoyl iodide was converted into dibenzoyl with elemental iodine liberation. The initial olefins remain intact.

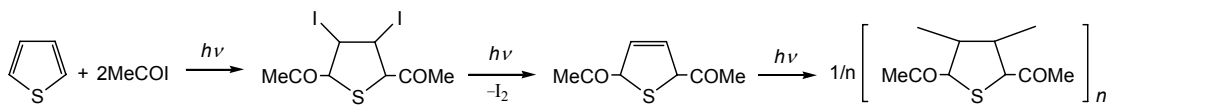


The photochemical behavior of benzoyl iodide in the environment of the studied olefins is analogous to its photolysis in arene medium (benzene, toluene) that we have observed before [4].

The reaction of cyclohexene with acetyl iodide under UV irradiation also proceeded as substitution of a hydrogen atom for iodine giving 3-iodocyclohexene in a 67% yield.



Acetyl iodide in this case also decomposed along the above mentioned process. Hence the photochemical reaction of acetyl iodide with cyclohexene and olefins proceeds unlike their reaction without UV irradiation.



The photochemical reaction of MeCOI with the studied olefins is the simplest method of preparation of the above mentioned iodine-containing unsaturated compounds. 6-Iodohept-1-ene and 7-iodohept-1-ene were previously synthesized by a more laborious procedure in the course of preparation of female sex pheromones [5, 6]. Their synthesis was underlain by the previous formation of tosylates of the corresponding 6- and 7-hydroxy-substituted alkenes followed by the cleavage of the obtained esters with sodium iodide.

Unlike the reactions with the alkenes under investigation the photochemical reaction of acetyl iodide with thiophene resulted in polymer formation. The process is accompanied with elemental iodine liberation. Analogous polymer was obtained at the low-temperature (-15°C) reaction of the same reagents but without UV irradiation [1]. This finding suggests that the reactions occur by identical mechanisms. This includes the MeCOI addition to both thiophene double bonds with subsequent iodine elimination and the polymerization of the formed diacetodihydrothiophene.

6-Iodohept-1-ene. *a.* A mixture of 8.5 g (0.05 mol) of acetyl iodide and 4.2 g (0.05 mol) of hex-1-ene was subjected to UV irradiation for 29 h. Then the mixture was distilled in a vacuum. Yield 6.01 g (57%) bp $78-79^{\circ}\text{C}$ (30 mm Hg), n_{D}^{20} 1.5100 (bp $84-85^{\circ}\text{C}$ (40 mm Hg), n_{D}^{20} 1.5121 [5]). ^1H NMR spectrum, δ , ppm: 1.31 m (4H, $\text{ICH}_2\text{CH}_2\text{CH}_2$), 1.85 q (2H, ICH_2CH_2 , 3J 7.0 Hz), 2.11 q (2H, $\text{CH}_2=\text{CHCH}_2$, 3J 6.3, 6.8 Hz), 3.21 t (2H, ICH_2 , 3J 7.0 Hz), 4.92 d.d (1H, $\text{HCH}=\text{CH}$, 3J 1.8, 10.3 Hz), 4.99 d.d (1H, $\text{HCH}=\text{CH}$, 3J 1.8, 17.0 Hz), 5.79 m (1H, $\text{CH}_2=\text{CH}$). ^{13}C NMR spectrum, δ , ppm: 7.15 (ICH_2), 29.93 (ICH_2CH_2), 29.61 ($\text{ICH}_2\text{CH}_2\text{CH}_2$), 31.82 ($\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 114.55 ($\text{H}_2\text{C}=\text{CH}$), 138.26 ($\text{H}_2\text{C}=\text{CH}$). Found, %: C 33.98; H 5.73; I 59.91. $\text{C}_6\text{H}_{11}\text{I}$. Calculated, %: C 34.3; H 5.27; I 60.41.

b. A mixture of 8.5 g (0.05 mol) of acetyl iodide and 4.2 g (0.05 mol) of 1-hexene was subjected to UV irradiation for 50 h, and then distilled in a vacuum. Yield 5.89 g (56%), bp $78-79^{\circ}\text{C}$ (30 mm Hg), n_{D}^{20} 1.5100 [5].

6-Iodohept-1-ene. A mixture of 8.5 g (0.05 mol) of acetyl iodide and 4.9 g (0.05 mol) of 1-heptene was subjected to UV irradiation for 29 h. Then the mixture

was distilled in a vacuum. Yield 6.7 g (60%), bp 82°C (20 mm Hg), n_{D}^{20} 1.4900 (bp $90-100^{\circ}\text{C}$ (40 mm Hg), n_{D}^{20} 1.4902 [6]). ^1H NMR spectrum, δ , ppm: 1.38–1.45 m (4H), 1.75–1.90 m (2H), 2.11 m (2H), 2.02–2.10 m (2H), 3.19 t (2H, 3J 6.8 Hz), 4.92–5.05 m (2H, $\text{CH}=\text{CH}_2$), 5.74–5.8 m (1H, $\text{CH}_2=\text{CH}$). ^{13}C NMR spectrum, δ , ppm: 7.40 (ICH_2), 29.32 (ICH_2CH_2), 29.34 ($\text{ICH}_2\text{CH}_2\text{CH}_2$), 28.90 ($\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 33.69 ($\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 114.80 ($\text{H}_2\text{C}=\text{CH}$), 138.30 ($\text{H}_2\text{C}=\text{CH}$).

Dibenzoyl. *a.* A mixture of 7 g (0.03 mol) of benzoyl iodide and 2.52 g (0.03 mol) of 1-hexene was subjected to UV irradiation for 29 h. The liberated iodine was sublimated in a vacuum. Yield 7.1 g (89%), mp $95-97^{\circ}\text{C}$ [7]. IR spectrum, ν , cm^{-1} : 3413, 3378, 1679, 1595, 1449, 1068, 755, 701.

b. A mixture of 11.6 g (0.05 mol) of benzoyl iodide and 4.9 g (0.05 mol) of 1-heptene was subjected to UV irradiation for 29 h and worked up as in procedure *a.* Yield 6.8 g (65%).

3-Iodocyclohexene. A mixture of 8.5 g (0.05 mol) of acetyl iodide and 4.1 g (0.05 mol) of cyclohexene was subjected to UV irradiation for 29 h and then distilled in a vacuum. Yield 7.06 g (67%), bp $78-79^{\circ}\text{C}$ (30 mm Hg), (bp 80°C (30 mm Hg), [8]). ^1H NMR spectrum, δ , ppm: 1.23, 1.43 d (4H, 3J 7.2, 6.75 Hz), 1.72, 2.16 d (4H, 3J 6.7, 7.8 Hz), 1.90, 2.37 d (4H, 3J 1.7, 7.8 Hz), 3.7 s (1H, 3J 4.1, 7.2 Hz), 5.58 s (1H, 3J 1.6 Hz), 5.72 s (1H, 3J 4.03 Hz). ^{13}C NMR spectrum, δ , ppm: 24.2 (ICH), 25.6 ($\text{ICHCH}_2\text{CH}_2$), 26.7 ($\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 40.8 (ICHCH_2), 126.9 ($\text{HC}=\text{CH}$), 129.2 ($\text{HC}=\text{CH}$).

Dibenzoyl. A mixture of 11.6 g (0.05 mol) of benzoyl iodide and 4.1 g (0.05 mol) of cyclohexene was subjected to UV irradiation for 29 h. After sublimation of iodine from the reaction mixture in a vacuum 8.1 g (77% of dibenzoyl was isolated [7].

Reaction of acetyl iodide with thiophene. A mixture of 3.4 g (0.02 mol) of acetyl iodide and 1.68 g (0.02 mol) of thiophene was subjected to UV irradiation for several minutes. Vigorous reaction was observed with the formation of a polymer product. Polymer was washed with chloroform and dried in a vacuum. IR spectrum, ν , cm^{-1} : 3095, 2922, 1707,

1430, 848, 693. Found, %: C 56.45; H 5.29; S 18.94. C₈H₁₀O₂S. Calculated, %: C 56.44; H 5.92; S 18.84.

IR spectra were recorded on a spectrophotometer UR-20 from thin film, ¹H, ¹³C NMR spectra were registered on a spectrometer Bruker DPX-400 (400 MHz) in CDCl₃ (internal references TMS and HMDS).

The study was carried out under a financial support of the Council on grants of the President of the Russian Federation (grant NSh-3649.2014.3)

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