ISSN 1070-4280, Russian Journal of Organic Chemistry, 2008, Vol. 44, No. 10, pp. 1549–1550. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © L.G. Shagun, I.A. Dorofeev, L.V. Klyba, I.A. Tokareva, M.G. Voronkov, 2008, published in Zhurnal Organicheskoi Khimii, 2008, Vol. 44, No. 10, pp. 1570–1571.

SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
B.A. Trofimov on his 70th anniversary

Photochemical Disproportionation of 1-Iodoacetone. New Method of Synthesis 1,3-Diiodoacetone

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Received May 6, 2008

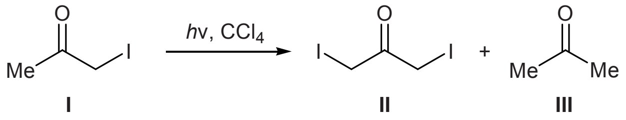
DOI: 10.1134/S1070428008100278

Photochemical transformations of α-halo ketones were studied in detail using α-halocyclohexanones as examples [1]. It was found that photochemical reactions of 1-chloro-, 1-bromo-, and 1-iodocyclohexanones involve homolytic dissociation of the carbon–halogen bond. Photolysis of 1-halocyclohexanones in alcoholic medium is often accompanied by cleavage of C–C bond with formation of ω,ω-dialkoxyalkanoic esters [2]. Irradiation of 3-chlorobicyclo[2.2.1]hept-5-en-2-one and α,α,α-trichloro- and α,α,α-tribromacetophenones in methanol was reported to produce the corresponding alcoholysis products [3–5].

The main products formed by photolysis of acetone in carbon tetrachloride (λ 313 nm) were chloroacetone and 1,1,1-trichlorobutan-3-one, which resulted from decomposition of CCl_4 into $Cl^{\cdot}$ and $Cl_3C^{\cdot}$ radicals [6]. According to the NMR data, the formation of chlorine-containing ketones was favored by photochemical excitation of a donor–acceptor complex derived from acetone and CCl_4 [7]. Irradiation of acetone in the absence of other solvent was characterized by low conversion (2% in 24 h), and the products were biacetyl, acetylacetone, and acetonylacetone [7]. Irradiation of acetone at λ 313 nm in the gas phase gave methyl and acetyl radiclas whose secondary reactions, including elimination and combination, produced carbon(II) oxide and ethane [8].

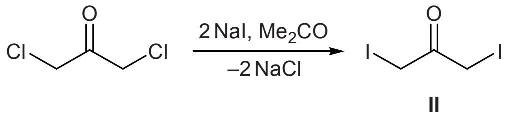
We examined photochemical transformations of iodoacetone (**I**) in carbon tetrachloride under argon upon irradiation at λ 254 nm and found that compound **I** undergoes disproportionation into 1,3-diiodoacetone (**II**) and acetone (**III**) with an overall yield of 90% (Scheme 1). The progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy which showed that 1,3-diiodoacetone (**II**) [^1H NMR spectrum: δ 3.9 ppm (4H, CH_2I); ^{13}C NMR spectrum, δ_C, ppm: 1.68 (CH_2I), 195.63 (C=O)] and acetone (**III**) [^1H NMR spectrum: δ 2.0 ppm (3H, CH_3); ^{13}C NMR spectrum, δ_C, ppm: 29.62 (CH_3), 202.40 (C=O)] are formed in the initial stage of the process. As the relative intensity of signals from acetone and 1,3-diiodoacetone increased (7 h), the intensity of signals from iodoacetone decreased [^1H NMR spectrum, δ, ppm: 2.26 (3H, CH_3), 3.63 (2H, CH_2); ^{13}C NMR spectrum, δ_C, ppm: 6.11 (CH_2I), 25.72 (CH_3), 197.70 (CO)], indicating accumulation of disproportionation products **II** and **III**. The minor products were chloro ketones. After 7 h, their fraction was 8–10% (according to the MS data).

Scheme 1.

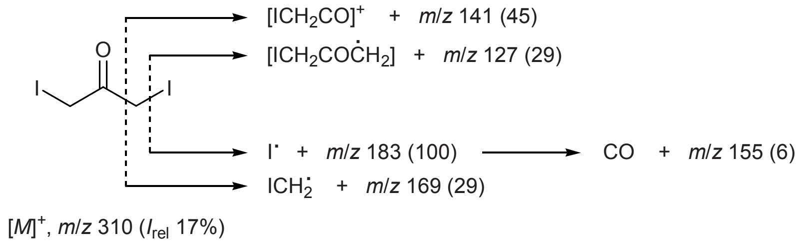


Study on the mechanism of the above reaction is now in progress. Analogous disproportionation of halo ketones was not reported previously. The structure of

Scheme 2.



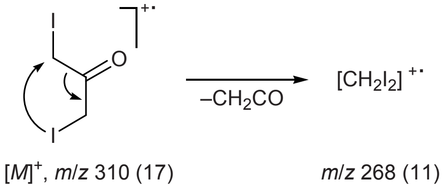
Scheme 3.



1,3-diiodoacetone (**II**) was proved by independent synthesis according to the procedure described in [9] (Scheme 2). The IR, ^1H and ^{13}C NMR, and mass spectra, analytical data, and melting points of samples of **II** obtained by photochemical transformation of iodoacetone and by halogen exchange in 1,3-dichloroacetone were identical.

Ionization of diiodoacetone **II** under electron impact gives its molecular ion $[M]^+$ with *m*/*z* 310 (Scheme 3). Its subsequent fragmentation involves mainly cleavage of the C–I bond to produce $[M - I]^+$ ion with *m*/*z* 183 as the most abundant, indicating very easy elimination of iodine from the molecular ion. The presence in the mass spectrum of a strong odd-electron $[CH_2I_2]^{+\cdot}$ ion peak, *m*/*z* 268 (22) is likely to result from migration of the halogen atom and elimination of ketene molecule (Scheme 4).

Scheme 4.



Thus we have described novel photochemical disproportionation of iodoacetone, which may be regarded as a simple and convenient method for the synthesis of 1,3-diiodoacetone.

1,3-Diiodopropan-2-one (II). A solution of 1.2 g (6.5 mmol) of iodoacetone in 10 ml of carbon tetrachloride was saturated with argon and irradiated with UV light at room temperature over a period of 7 h (until the main products no longer accumulated in the mixture). The mixture was cooled to –20°C, and the precipitate was filtered off and dried under reduced pressure. Yield 0.45 g (45%), colorless crystals, mp 61–62°C (from ethanol); published data [9]: mp 62–63°C. IR spectrum, ν, cm^{-1}: 2981, 2930, 1723, 1648, 1368, 1248, 1193, 1011, 845, 682, 575, 516, 414 (cf. [9]).

The IR spectra were recorded in KBr on a Bruker IFS-25 instrument. The ^1H and ^{13}C NMR spectra were measured on a Bruker DPX-400 spectrometer at 400 and 100 MHz, respectively. The mass spectra were obtained on a GCMS-QP5050A instrument (electron impact, 70 eV; quadrupole mass analyzer; direct sample admission into the ion source). Photolysis of iodoacetone **I** was performed in a quartz flask under irradiation with a DRT-230 mercury lamp (λ 254 nm). The purity of the products was checked by TLC on Silufol UV-254 plates using chloroform as eluent.

This study was performed under financial support by the President of the Russian Federation (program for support of leading scientific schools, project no. NSh-255.2008.3).

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