

SHORT
COMMUNICATIONS

Synthesis of Symmetric α -Diketones

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Received February 14, 2008

DOI: 10.1134/S1070428008060250

The known procedure for the synthesis of aliphatic α -diketones is fairly complex: it is based on reaction of ketones of the RCOCH_2R series with isoamyl nitrite or *p*-nitroso-*N,N*-dimethylaniline [1], followed by hydrolysis of the resulting compounds with mineral acids. α -Diketones can also be prepared by oxidation of the corresponding hydroxy compounds or their derivatives [2, 3]. For example, the synthesis of symmetric α -diketones by oxidation of bis-trimethylsilyl ethers derived from enediols with bromine in aprotic solvents was reported [4].

We have developed a simple and effective procedure for the synthesis of symmetric α -diketones on the basis of photochemical dissociation of acyl iodides. It is known [5] that acyl iodides RCOI readily undergo homolytic dissociation of the C–I band; this process partially occurs even on exposure to daylight. However, the product expected to be formed via recombination of acetyl radical, biacetyl MeCOCOMe , was not detected previously in the photolysis of acetyl iodide; this was rationalized in term of a short lifetime of MeCO^\cdot ($\sim 10^{-11}$ s) [6].

On the other hand, we have found that photochemical dissociation of acyl iodides RCOI in toluene (which is known to act as triplet sensitizer) gives the corresponding symmetric α -diketones RCOCOR in 40–95% yield.

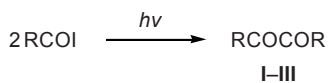
The importance of the proposed procedure for the synthesis of α -diketones from the preparative viewpoint follows from accessibility of initial acyl iodides which are readily obtained from the corresponding

acyl chlorides [7] or by exchange reaction of the simplest acyl iodide, i.e., acetyl iodide, with carboxylic acids [8].

A 50-ml quartz flask equipped with a reflux condenser and protected from atmospheric moisture was charged with a solution of 17.0 g of acetyl iodide in 10 ml of toluene, and the solution was irradiated with an OKN-11 mercury lamp over a period of 55 h. When the reaction was complete, the mixture was filtered from the precipitate of crystalline iodine, and the filtrate was distilled under reduced pressure. Yield of biacetyl (**I**) 4.0 g (93%), bp 88–90°C; published data [1]: bp 88°C. The IR spectrum of the product coincided with that of an authentic sample. Found, %: C 55.02; H 6.67. $\text{C}_4\text{H}_6\text{O}_2$. Calculated, %: C 55.81; H 7.02.

Likewise, a solution of 17.5 g of benzoyl iodide in 8 ml of toluene was irradiated with UV light over a period of 20 h. The solvent and a part of iodine were distilled off. The remaining iodine was removed from the crystalline product under reduced pressure. Yield of benzil (**II**) 7.1 g (88.4%), mp 95°C; published data [1]: mp 95–96°C. The IR spectrum of the product coincided with that of an authentic sample. Found, %: C 79.52; H 5.06. $\text{C}_{14}\text{H}_{10}\text{O}_2$. Calculated, %: C 79.98; H 4.79.

A solution of 9 g of isobutyryl iodide [8] in 8 ml of toluene was irradiated with UV light over a period of 20 h. The mixture was subjected to distillation under reduced pressure, and the product was treated with copper powder to remove elemental iodine. Yield of α -diketone **III** 1.3 g (40.6%), bp 140–145°C, $n_D^{20} = 1.5310$. IR spectrum: ν 1705 cm^{-1} (C=O). Found, %: C 67.00; H 9.88. $\text{C}_8\text{H}_{14}\text{O}_2$. Calculated, %: C 67.57; H 9.92.



I, R = Me; II, R = Ph; III, R = Me_2CH .

REFERENCES

1. *Weygand–Hilgetag Organisch-chemische Experimentierkunst*, Hilgetag, G. and Martini, A., Eds., Leipzig: Johann Ambrosius Barth, 1964, 3rd ed. Translated under the title *Metody eksperimenta v organicheskoi khimii*, Moscow: Khimiya, 1968, p. 294.
2. Blomquist, A.H., Liu, L.H., and Bohrer, J.C., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 3643.
3. Blomquist, A.H., Burge, R.E., and Sucusy, A.C., *J. Am. Chem. Soc.*, 1952, vol. 74, p. 3636.
4. Strating, J., Reiffers, S., and Wynberg, H., *Synthesis*, 1971, p. 209; *ibid.*, p. 211.
5. Voronkov, M.G., Vlasova, N.N., and Trukhina, A.A., *Atsiliodidy v organicheskom sinteze. Sovremennyi organicheskii sintez* (Acyl Iodides in Organic Synthesis. Modern Organic Synthesis), Moscow: Khimiya, 2003, p. 9.
6. Kroger, P. and Riley, S., *J. Chem. Phys.*, 1977, vol. 67, p. 4483.
7. Teobald, D.W. and Smith, J.C., *Chem. Ind.*, 1958, vol. 32, p. 1007.
8. Voronkov, M.G., Belousova, L.I., Trukhina, A.A., and Vlasova, N.N., *Russ. J. Org. Chem.*, 2003, vol. 39, p. 1702.