

SHORT
COMMUNICATIONS

Synthesis of Symmetric α -Diketones

M. G. Voronkov, L. I. Belousova, A. V. Vlasov, and N. N. Vlasova

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: Andreiwlasov@rambler.ru

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.

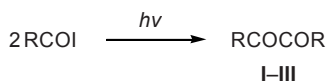
The importance of the proposed procedure for the synthesis of α -diketones from the preparative viewpoint follows from accessibility of initial acyl iodides which are readily obtained from the corresponding

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 Sucsy, 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.