



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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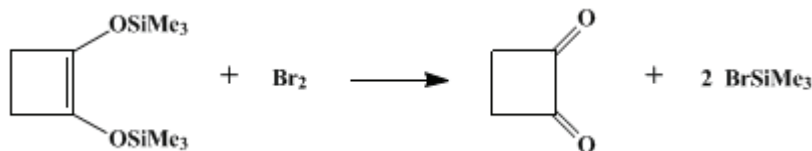
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,2-CYCLOBUTANEDIONE



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1. Procedure

Caution! This reaction should be carried out in a dark hood to prevent the photoinduced polymerization of the dione.

A 1-L, three-necked, round-bottomed flask equipped with a 500-mL dropping funnel, a nitrogen-inlet tube, a mechanical stirrer, a low-temperature thermometer, and a calcium chloride drying tube is charged with 172 g (0.75 mol) of 1,2-bis(trimethylsilyloxy)cyclobutene (Note 1) and 375 mL of anhydrous pentane (Note 2). A dry nitrogen atmosphere is maintained in the system (Note 3) and the solution is cooled to -60°C by means of a dry ice-methanol bath. Then a solution of 120 g (0.75 mol) of bromine and 375 mL of anhydrous pentane is added dropwise with stirring over a period of 2 hr. When the addition is complete, the mixture must be heated to 40°C for 2 hr (Note 4) and concentrated by removing ca. 550 mL of solvent under reduced pressure (15 mm) at room temperature. To isolate the dione the residue is cooled to -60°C by immersion of the flask in a dry ice-methanol bath. The crystallized product is quickly filtered through a hermetically sealed (Note 3), 250-mL sintered-glass funnel (porosity 3), a dry nitrogen pressure being used to push down solvent. The yellow solid is washed with stirring with eight 25-mL portions of anhydrous pentane cooled to -60°C and sucked as dry as possible on the filter. The pentane used in the washing is concentrated under reduced pressure (15 mm) at room temperature to ca. 15 mL, then the flask is again cooled to -60°C . The crystallized product is washed with four 15-mL portions of anhydrous pentane cooled to -60°C as before. The two batches of crystals are of approximately equal purity. The yield of 1,2-cyclobutanedione is 42–46 g (70–73%), mp 65°C (Note 5).

2. Notes

1. The 1,2-bis(trimethylsilyloxy)cyclobutene is prepared according to the procedure of Bloomfield.²
2. Pentane is distilled prior to use (bp $36^{\circ}\text{C}/760$ mm) and stored over sodium wire.
3. *Caution! Moisture must be avoided to prevent the ring contraction of the dione into 1-hydroxycyclopropanecarboxylic acid.*²
4. This heating is necessary to complete the reaction.²
5. The yellow product shows in the ^1H NMR (CCl_4) a single signal at 2.98 ppm indicating its high degree of purity. It can be sublimed under vacuum (15 mm) at room temperature, mp 65°C ; IR (CCl_4) cm^{-1} : 1778 and 1810; UV (hexane) nm max (ϵ): 407 (4), 423 (8), 436 (10.5), 453 (19), 463 (17), 489 (42), and 500.5 (28). The dione can be stored at 0°C in a hermetically sealed flask in the dark for months.

3. Discussion

This method of preparation of the 1,2-cyclobutanedione is an adaptation of that independently described by Denis and Conia³ and by Heine.⁴ Acyloins, 1,2-cyclobutanediols, imidazole, thioimidazole, and amino- and cyanofuran derivatives are readily available^{5,6} from bis(trimethylsilyloxy)alkenes.

The bis(trimethylsilyloxy)alkene bromination procedure is a large-scale preparation that gives excellent yields of cyclic and acyclic 1,2-diones; however, when enolizable 1,2-diketones are produced,

some complications can be encountered.^{7,8}

References and Notes

1. Laboratoire des Carbocycles, Universite de Paris-Sud, 91405 ORSAY, France.
 2. Bloomfield, J. J.; Nelke, J. M. *Org. Synth. Coll. Vol. VI*, **1988**, 167.
 3. Denis, J. M.; Conia, J. M. *Tetrahedron Lett.* **1971**, 2845–2846.
 4. Heine, H. G. *Chem. Ber.* **1971**, *104*, 2869–2872.
 5. Ruhlmann, K. *Synthesis* **1971**, 236–253.
 6. Conia, J. M.; Barnier, J. P. *Tetrahedron Lett.* **1971**, 4981–4984.
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Acyloins

1,2-cyclobutanediols

amino- and cyanofuran derivatives

bis(trimethylsiloxy)alkenes

bis(trimethylsiloxy)alkene

cyclic and acyclic 1,2-diones

1,2-diketones

bromine (7726-95-6)

sodium wire (13966-32-0)

Pentane (109-66-0)

Imidazole (288-32-4)

hexane (110-54-3)

1,2-bis(trimethylsiloxy) cyclobutene,
1,2-bis(trimethylsiloxy)cyclobutene (17082-61-0)

1,2-Cyclobutanedione (33689-28-0)

1-hydroxycyclopropanecarboxylic acid (17994-25-1)

thioimidazole

