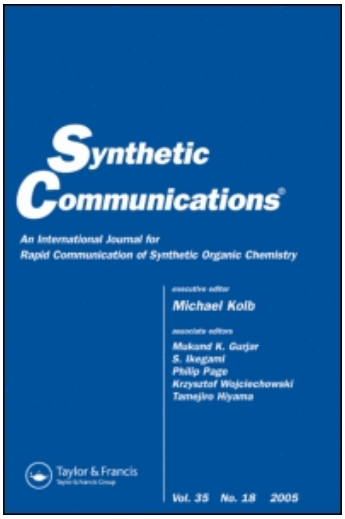



**Synthetic Communications**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597304

# A Convenient Synthesis of Cyclcheptane-1,3-Dione

Vidya Bhushan[a]; S. Chandrasekaran[a]
[a] Department of Chemistry, Indian Institute of Technology, Kanpur, India

**To cite this Article** Bhushan, Vidya and Chandrasekaran, S.(1984) 'A Convenient Synthesis of Cyclcheptane-1,3-Dione', Synthetic Communications, 14: 4, 339 — 345
**To link to this Article: DOI:** 10.1080/00397918408062832
**URL:** http://dx.doi.org/10.1080/00397918408062832

SYNTHETIC COMMUNICATIONS, 14(4), 339-345 (1984)

# A CONVENIENT SYNTHESIS OF CYCLOHEPTANE-1,3-DIONE

Vidya Bhushan and S. Chandrasekaran*

Department of Chemistry,
Indian Institute of Technology, Kanpur 208 016, India



1,3-Diketones are an important class of compounds in view of the distinct structural features and high synthetic utility. Inspite of the high potential of the 1,3-cycloalkadiones in organic synthesis, only a few methods are available for their synthesis. It has been shown that $\alpha,\beta$-epoxy ketones give 1,3-diketones in the presence of Pd(0).[1] Recently, 1,3-cycloalkadiones have been syntnesized by various transformations of bis(trimethylsilyloxy)cycloalkenes.[2,3] However, these methods have only limited applicability. Although there are several methods available for medium to large scale preparations of cyclopentane-1,3-dione[4-7] and cyclohexane-1,3-dione,[8] the only synthetic route to cycloheptane-1,3-dione is due to Eistert et al.,

* To whom correspondence should be addressed.

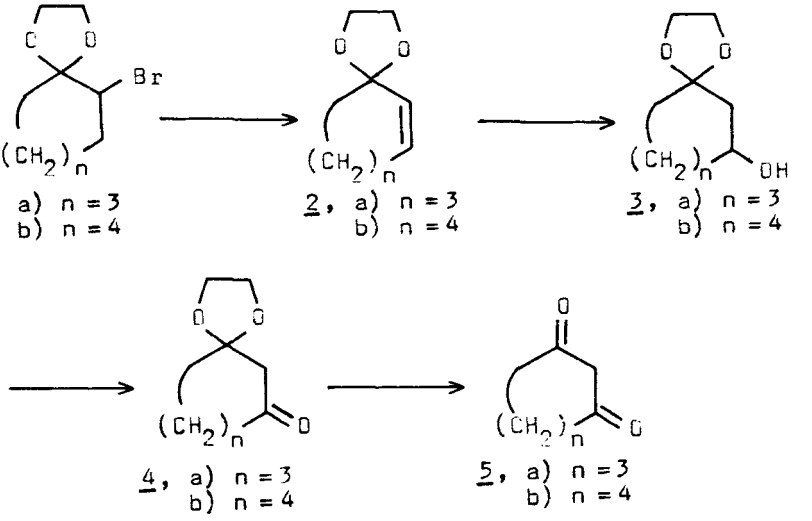


 0039-7911/84/1404-0339$3.50/0

involving the ring expansion of monoethylene acetal of cyclohexane-1,3-dione using diazoacetic ester.[9]

Recently, we reported a methodology for the one-pot α-bromoacetalization of carbonyl compounds using ethylene glycol and phenyltrimethylammonium tribromide (PTT) in dry tetrahydrofuran to give the corresponding α-bromoacetals in very good yield.[10] In our attempts to explore the potential usefulness of these easily synthesized α-bromoacetals as valuable synthons, we have come up with a facile synthesis of cycloheptane-1,3-dione.

α-Bromoacetal of cycloheptanone 1b[10] was dehydrobrominated using potassium tert-butoxide in DMSO at room temperature within 6 hours in 75% yield. Alternatively, the olefinic acetal 2b could be prepared by refluxing the bromoacetal 1b in methanolic potassium hydroxide solution.[11] The olefinic acetal upon oxymercuration-demercuration yielded 93% of the hydroxyacetal 3b, which was oxidized by chromium trioxide-pyridine complex generated in situ in dichloromethane to give 95% yield of the ketoacetal 4b. The ketoacetal 4b underwent facile hydrolysis by 10% aqueous hydrochloric acid, resulting in the formation of cycloheptane-1,3-dione (5b) in 92% yield. We have thus achieved a simple synthesis of cycloheptane-1,3-dione starting from readily available cycloheptanone in an over-




all yield of 49%. An analogous sequence of reactions was followed in the case of cyclohexanone to get cyclohexane-1,3-dione (5a) in 43% overall yield. The hydrolysis of the ketoacetal 4a was effected by silica gel impregnated with 25% sulphuric acid.[12] This procedure overcame the difficulties encountered in the isolation of the dione 5a due to its high solubility in water.

## EXPERIMENTAL

Olefinic Acetal 2b: Potassium tert-butoxide (3.36 g, 30 mmol) was dissolved in dry DMSO (20 mL) at 40°C. To the resulting solution, the α-bromoacetal 1b[10] (4.7 g, 20 mmol) was added slowly dropwise at 30°C and stirred for 4 h. The reaction mixture was poured slowly into cold water and extracted with hexane (3 x 50 mL). The

hexane extract was washed several times with water, followed by brine and dried over $MgSO_4$; filtered and the solvent was removed under reduced pressure to yield 2.34 g of 2b (75%), bp 94-96°C (10 mm) [lit.[11] bp 67°C (2.4 mm)]. $^1H$ nmr ($CDCl_3$):δ1.4-2.5 (m, 8H), 3.8 (m, 4H), 5.66 (m, 2H).

Hydroxyacetal 3b: To a suspension of mercuric acetate (4.76 g, 15 mmol) in THF-water (1:1, 15 mL) was added 2b (2.31 g, 15 mmol) and stirred for 3 h at 30°C. To the resulting mixture kept at 0°C, was added 10% aq. sodium hydroxide solution (15 mL), followed by a solution of sodium borohydride (0.285 g, 7.5 mmol) in 10% aq. sodium hydroxide solution (15 mL). After stirring for 1 h, the reaction mixture was saturated with NaCl and stirred for 0.25 h with ethyl acetate. The organic layer was removed and the aq. layer was extracted with ethyl acetate (6 x30 mL). The combined organic layer was washed with brine and dried over $MgSO_4$. Removal of solvent afforded 2.4 g (93%) of an oil used in the next step without purification.

Ketoacetal 4b: To a solution of pyridine (13.22 g, 167.4 mmol) in dichloromethane (150 mL) was added chromium trioxide (8.37 g, 83.7 mmol) and celite (12 g) at 0°C. After stirring for 0.25 h, a solution of 2b (2.4 g, 13.95 mmol) in dichloromethane (5 mL) was added in one

portion and stirring was continued for 0.5 h at 25°C. Dry ether (150 mL) was added and filtered through a short pad of celite and $MgSO_4$. The filter pad was thoroughly washed with ether. The filtrate was evaporated and the excess pyridine was removed under reduced pressure at 60°C to afford 2.2 g (95%) of an oil. IR ($CHCl_3$): 1700 $cm^{-1}$. $^1H$ nmr ($CDCl_3$):δ1.66 (br, s, 6H); 2.23 (br, s, 2H); 2.56 (s, 2H); 3.76 (s, 4H).

Cycloheptane-1,3-dione (5b): The compound 4b (2.2 g, 12.94 mmol) was stirred with 20% hydrochloric acid (15 mL) for 4 h at 30°C. The reaction mixture was poured into water and extracted with chloroform (5x30 mL). The organic extract was washed with saturated $NaHCO_3$ solution (2 x20 mL), followed by water and then with brine. The extract was dried ($MgSO_4$) and evaporated to yield an oil which was passed through a short pad of neutral alumina (elution with 1:1 ether-petroleum ether) to give cycloheptane-1,3-dione (1.5 g, 92%) as a liquid (bp 119-120°C (15 mm)).[9] $^1H$ nmr ($CDCl_3$):δ1.33-2.1 (m, 4H); 2.46 (m, 4H); 3.53 (s, 2H). Disemicarbazone, mp 204-206°C [lit.[9] mp 205-206°C (dec.)].

Olefinic Acetal 2a: Dehydrobromination of 1a with potassium tert-butoxide in DMSO yielded 80% of 2a, bp 74-76°C (17 mm) [lit.[11] bp 86.5-88.5°C (23 mm)].

$^1$H nmr ($CDCl_3$):δ1.06-2.4 (m, 6H); 3.83 (s, 4H); 5.28-5.88 (m, 2H).

Hydroxyacetal 3a: Oxy-mercuration-demercuration reaction as in the earlier case, yielded 76% of 3a which was purified by flash chromatography on silica gel (elution with 1:1 ether-petroleum ether).

Ketoacetal 4a: Oxidation of 3a with pyridine-chromium trioxide reagent afforded 86% of ketoacetal 4a as an oil. $^1$H nmr ($CDCl_3$):δ1.66 (br, s, 4H); 2.06 (br, s, 2H); 2.26 (s, 2H); 3.76 (s, 4H).

Cyclohexane-1,3-dione (5a): To a suspension of silica gel (100-200 mesh, 4.2 g) in dichloromethane was added 25% sulphuric acid (0.42 mL) with stirring. When the turbidity in the dichloromethane vanished, the ketoacetal 4a (0.75 g, 4.8 mmol) was added in a small amount of dichloromethane in one portion and stirred for 6 h at room temperature. Solid sodium bicarbonate was added until the effervescence ceased. The reaction mixture was filtered and the silica gel residue was thoroughly washed with a mixture of methanol-dichloromethane (1:19). The filtrate was evaporated to yield 0.5 g (93%) of the dione 5a, mp 105-106°C [lit.[8] mp 105-107°C].

## REFERENCES


1. M. Suzuki, A. Watanabe and R. Noyori, J. Am. Chem. Soc., 102, 2095 (1980).
2. Y. Ito, S. Fujii and T. Saegusa, J. Org. Chem., 41, 2073 (1976).
3. I. Nishiguchi, T. Hirashima, T. Shono and M. Sasaki, Chem. Lett., 551 (1981).
4. J. Sraga and P. Hrnciar, Z. Chem., 15, 189 (1975); Chem. Abstr., 83, 58201w (1975).
5. J.P. John, S. Swaminathan and P.S. Venkatramani, Org. Syn., 47, 83 (1967).
6. U. Hengartner and V. Chu, Org. Syn., 58, 83 (1978).
7. C. Lick and K. Schank, Chem. Ber., 111, 2461 (1978).
8. R.B. Thomson, Org. Syn. Coll. Vol. III, p. 278, Wiley and Sons, New York, 1962.
9. B. Eistert, F. Haupter and K. Shank, Justus Liebig. Ann. Chem., 665, 55 (1963).
10. S. Visweswariah, G. Prakash, Vidya Bhushan and S. Chandrasekaran, Synthesis, 309 (1982).
11. E.W. Garbisch Jr., J. Org. Chem., 30, 2109 (1965).
12. F. Huet, A. Lechevallier, M. Pellet and J.M. Conia, Synthesis, 63 (1978).