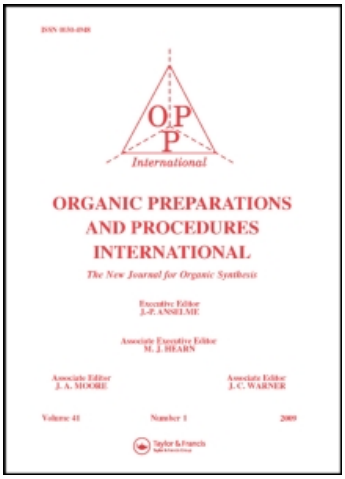


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

IMPROVED METHOD FOR BISALLYLATION OF *cis*-BICYCLO [3.3.0]OCTANE-3,7-DIONE via THE CLAISEN REARRANGEMENT

K. Sambasivarao[a]; J. M. Cook[a]
[a] Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, WI

To cite this Article Sambasivarao, K. and Cook, J. M.(1990) 'IMPROVED METHOD FOR BISALLYLATION OF *cis*-BICYCLO [3.3.0]OCTANE-3,7-DIONE via THE CLAISEN REARRANGEMENT', Organic Preparations and Procedures International, 22: 5, 630 — 632
To link to this Article: DOI: 10.1080/00304949009356336
URL: http://dx.doi.org/10.1080/00304949009356336

IMPROVED METHOD FOR BISALLYLATION OF cis-BICYCLO [3.3.0]OCTANE-3,7-DIONE via THE CLAISEN REARRANGEMENT

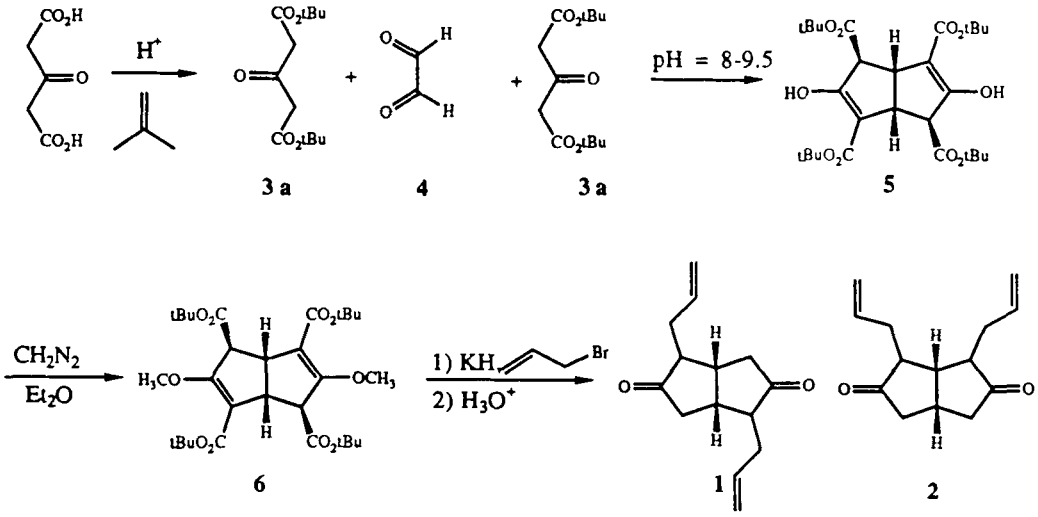
Submitted by (09/11/89)

K. Sambasivarao*† and J. M. Cook

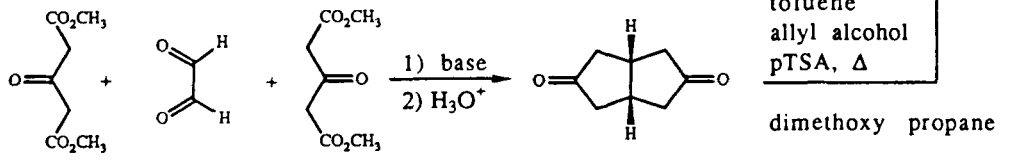
Department of Chemistry
University of Wisconsin-Milwaukee
Milwaukee, WI 53201

In connection with our research toward the preparation of polyquinanes,[1] the synthesis of 2,6- and 2,8-diallyl-cis-bicyclo [3.3.0] octane-3,7-diones (1 and 2) was of interest. Although the two diones (1 and 2) could be prepared via the Weiss reaction from di-t-butyl 3-oxoglutarate[2] (3a) and glyoxal (4) [route 1] as illustrated in Scheme 1, the necessary synthesis of 3a and the use of diazomethane (5→ 6) were disadvantages of the sequence on a large scale.

Route 1



Route 2



Since cis-bicyclo [3.0]octane-3,7-dione 7 is readily available in 500 g quantities from the inexpensive dimethyl 3-oxoglutarate,[3] direct access to 1 and 2 from 7 would greatly facilitate entry into tetracyclic polyquinanes.[1a]

In this regard, the report by Hund and Pollack[4] attracted our attention. Although Lorette and Howard[5] subsequently employed this simple method to allylate various acyclic and alicyclic ketones, the procedure has not found many applications in organic synthesis.[6] However, when dione 7 was heated with 2,2-dimethoxypropane, allyl alcohol (excess) in refluxing toluene in presence of p-toluenesulfonic acid [route 2], an 80% yield of diones 1 and 2 was realized and isolated in a ratio of 3:2.[7] The diones were accompanied by a small amount of monoalkylated material which was easily removed by chromatography and identified by comparison to an authentic sample.[1a] The spectra of 1 and 2 were identical to those prepared by the longer route.[1a] The two-step sequence has been repeated on a 5 g scale with ease to consistently provide 1 and 2

EXPERIMENTAL SECTION

Bisallylation of *cis*-Bicyclo[3.3.0]octane-3,7-dione (7).- To a three-necked flask equipped with a Vigreux column, a Dean-Stark apparatus, and a reflux condenser was added cis-bicyclo[3.3.0]octane-3,7-dione (2.76 g, 20 mmoles), allyl alcohol (15 mL, excess), 2,2-dimethoxypropane (7.5 mL, excess) and p-toluenesulfonic acid (100 mg) in 100 mL of dry toluene. The reaction mixture was stirred at 110° (oil bath temperature) for 5 hrs. Afterwards, the Vigreux column was removed and the reaction mixture held at reflux for 36 hrs. During the first few hours of heating, it was necessary to remove the toluene, acetone and allyl alcohol which had been collected (30 mL) in the Dean-Stark apparatus, after which additional toluene (30 mL) was added to the reaction mixture. After completion of the reaction (TLC), the solution was allowed to cool and was washed ($NaHCO_3$, 2 x 100 mL; brine, 100 mL) and dried ($MgSO_4$). Removal of the solvent under reduced pressure furnished an oily residue (3.7 g), which was charged onto a silica gel (100 g) column. Elution with EtOAc-hexane (1:3) furnished 2.5 g (50%) of dione 1, bp. 150°/0.5 mm Hg. Further elution of the column with the same solvent gave 1.35 g (32%) of the dione 2 as a colorless liquid, 150°/0.5 mmHg. Continued elution with EtOAc-hexane (3:7) gave 0.3 g (8%) of 2-allyl cis-bicyclo[3.3.0]octane-3,7-dione as a colorless liquid, bp. 130°/0.5 mmHg. The spectra (^1H and ^{13}C NMR) and R_f values of 1 and 2 and of the monoallyl derivative were identical to those previously reported [route 1].[1]

Acknowledgements.- The authors wish to thank the NSF (Grant CHE- 8604443) and the Graduate School (UWM) for generous support of this work.

REFERENCES

† Present address: Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.

1. a) G. Lannoye, K. Sambasivarao, S, Wehrli and J. M. Cook, J. Org. Chem., 53, 2327 (1988); b) K. Sambasivarao, G. Kubiak, G. Lannoye and J. M. Cook, ibid., 53, 5173 (1988); c) A. K.

Gupta, G. S. Lannoye, G. Kubiak, J. Schkeryantz, S. Wehrli and J. M. Cook, J. Am. Chem. Soc., 111, 2169 (1989).

2. Dimethyl 1,3-acetonedicarboxylate (3b) is substantially less expensive than di-t-butyl 3-oxoglutarate (3a).

3. S. H. Bertz, J. M. Cook, A. Gawish and U. Weiss, Org. Syn., 64, 27 (1986).

4. C. D. Hurd and M. A. Pollack, J. Am. Chem. Soc., 60, 1905 (1938).

5. N. B. Lorette and W. L. Howard, J. Org. Chem., 26, 3112 (1961).

6. a) F. E. Ziegler, Chem. Rev., 88, 1423 (1988); b) J. K. Crandall and H. S. Magaha, J. Org. Chem., 47, 5638 (1982); c) A. Horeau, E. Lorthiou, J. P. Guette, C. R. Acad. Sci. Ser. C., 269, 558 (1969); d) P. F. Schuda, J. L. Philips and M. Morgan, J. Org. Chem., 51, 2742 (1986); e) N. Fukada, M. L. Trudell, B. Johnson and J. M. Cook, Tetrahedron Lett., 26, 2139 (1985).

7. Compounds 1 and 2 were isolated as a mixture of regioisomers (see ref. 1a for details).

****

BIOMIMETIC MODELING OF ASYMMETRIC SYNTHESIS OF ARYLALKYL SULFOXIDES USING β -CYCLODEXTRIN COMPLEXES†

Submitted by (08/11/89)

K. Rama Rao*, H. M. Sumpath Kumar, N. Bhanumathi and P. B. Sattur

Organic Chemistry-I, Indian Institute of Chemical Technology
Hyderbad 500 007, INDIA

Chiral sulfoxides are becoming increasingly important as chiral auxiliaries in asymmetric synthesis for the transfer of chirality from sulfur to carbon.[1] So far chiral sulfoxides have been obtained mainly through menthyl sulfinate esters.[2] To date, no general and easily accessible method has been reported for the asymmetric oxidation of prochiral sulfides.[3] A more sophisticated and practical approach for asymmetric induction would be through "host-guest" complexation involving water as the reaction medium as observed in physiological processes. In continuation of our studies on biomimetric asymmetric synthesis,[4] we now report a simple method for the asymmetric oxidation of prochiral sulfides (1) in water employing β-cyclodextrin (β-CD) as a chiral template and sodium hypochlorite as an oxidizing agent.

The inclusion complexes were prepared by adding the pure sulfide in ethanol to an aqueous solution of β-cyclodextrin in equimolar ratio at 60° to yield crystalline complexes, as shown by the upfield shift of H-3 and H-5 protons of cyclodextrin.[5] All the sulfides (1) formed inclusioncompounds on an equimolar basis with cyclodextrin as determined from the amount of