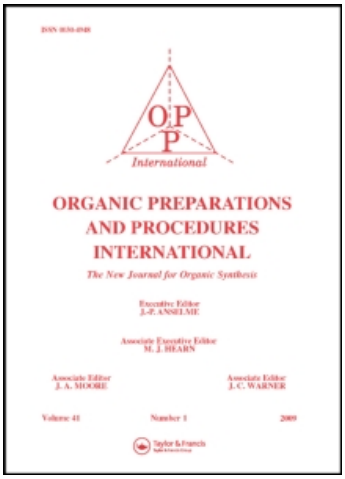


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

A CONVENIENT LARGE-SCALE PREPARATION OF *endo*-2-METHYLBICYCLO[2.2.1]HEPT-5-ENE-*exo*-2-CARBOXYLIC ACID

Alan R. Katritzky[a]; Qingmei Hong[a]; Zhijun Yang[a]; Darren J. Cundy[a]; Katherine Brown-Wensley[b]
[a] Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, FL, USA [b] Corporate Research Laboratories, 3M Company, St Paul, MN, USA

To cite this Article Katritzky, Alan R. , Hong, Qingmei , Yang, Zhijun , Cundy, Darren J. and Brown-Wensley, Katherine(1995) 'A CONVENIENT LARGE-SCALE PREPARATION OF *endo*-2-METHYLBICYCLO[2.2.1]HEPT-5-ENE-*exo*-2-CARBOXYLIC ACID', Organic Preparations and Procedures International, 27: 5, 574 — 575
To link to this Article: DOI: 10.1080/00304949509458507
URL: http://dx.doi.org/10.1080/00304949509458507

5. Trimethylsilylmethanol is available from Aldrich Chemical Co. (30,529-4).

6. S. Ambasht, S. K. Chiu, P. E. Peterson and J. Queen, *Synth. Commun.*, 318 (**1980**).

7. A. G. Schultz, F. P. Lavieri, M. Macielag and M. Plummer, *J. Am. Chem. Soc.*, **109**, 3991 (1987).

8. For a study of photoinduced SET reactions of 2,5-cyclohexadienones derived from **1**, see A. G. Schultz, J. E. Reilly and Y. Wang, *Tetrahedron Lett.*, In press.

****

A CONVENIENT LARGE-SCALE PREPARATION OF *endo*-2-METHYLBICYCLO[2.2.1]HEPT-5-ENE-*exo*-2-CARBOXYLIC ACID

Submitted by (01/26/95)

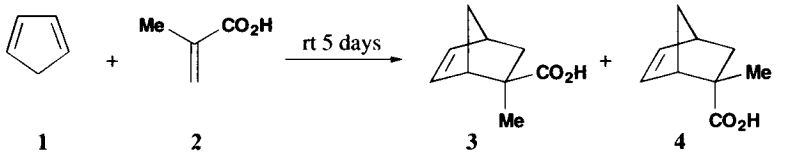
Alan R. Katritzky*, Qingmei Hong, Zhijun Yang, Darren J. Cundy

Center for Heterocyclic Compounds, Department of Chemistry
University of Florida, Gainesville, FL 32611-7200, USA

and Katherine Brown-Wensley

Corporate Research Laboratories
3M Company, St. Paul, MN 55144, USA

The Diels-Alder condensation of cyclopentadiene (**1**) with methacrylic acid (**2**) has been reported on several occasions.[1-3] In each case, the reaction gave mixtures of the *exo* (**3**) and *endo* isomers (**4**) which were separated either by repeated fractional recrystallization[3] or *via* a multistep lactonization method.[1] However, there are substantial discrepancies in the *exo/endo* isomer ratios reported by these groups. For example, Meek and Trapp[1] have reported that heating methacrylic acid and cyclopentadiene in toluene at 150° (sealed tube) gave a mixture of *exo* and *endo* isomers in a ratio of 65 to 35, while Moriarty *et al.*[3] obtained a ratio of 90 to 10 when methacrylic acid and cyclopentadiene were heated at reflux for 4 hrs. In connection with other work, we needed to prepare the pure *exo* isomer in quantity. Accordingly, this reaction has been reinvestigated and optimized.



1 2 3 4

Thus, when equimolar amounts of methacrylic acid and cyclopentadiene were stirred at room temperature, NMR investigations indicated that the reaction reached completion after 5 days and that the product mixture possessed an *exo/endo* ratio of 65 to 35. These measurements also indicated that approximately 15% of methyacrylic acid was left unreacted due to redimerization of cyclopentadiene monomer. More importantly, we have found that the desired *exo* isomer **3** precipitated directly from the reaction mixture. Simple filtration followed by washing with pentane afforded the pure **3** in 33% yield. This procedure obviates the necessity for the isolation of the *exo* isomer **3** by either repeated fractional recrystallization or by the tedious lactonization method. The procedure is expected to be of potential industrial importance due to its simplicity, low cost, mild conditions and suitability for large-scale operation.

EXPERIMENTAL SECTION

Melting points were determined on a Bristoline hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer with TMS as an internal reference. ^{13}C NMR spectra were recorded at 75 MHz on the same instrument using the solvent peak ($CDCl_3$, δ 77.0 ppm; DMSO-d_6, δ 39.50 ppm) as reference. Microanalyses were carried out using a Carlo Erba 1106 elemental analyser. Cracking dicyclopentadiene was carried out at 190° and the cyclopentadiene monomer which formed was freshly distilled (bp. 42°) and used immediately in the next step.

***endo*-2-Methylbicyclo[2.2.1]hept-5-ene-*exo*-2-carboxylic Acid (3).**- A mixture of cyclopentadiene (133g, 2.01mol) and methacrylic acid (173g, 2.01mol) was stirred at room temperature for 5 days. The reaction mixture was allowed to stand at -5° to 0° for an additional 24 hrs. The white precipitate which formed was collected and washed with pentane (2 x 30mL) to afford 100g (33%) of the pure *exo*-product as a colorless solid, mp. 78-80°, lit.[3] mp. 81-82°. ^{1}H NMR ($CDCl_3$): δ 12.18 (s, br, 1H), 6.24 (dd, 1H, J_1 = 5.4 and J_2 = 2.7Hz), 6.10 (dd, 1H, J_1 = 5.4 and J_2 = 3.3Hz), 3.06 (s, 1H), 2.84 (s, 1H), 2.44 (dd, 1H, J_1 = 12.1 and J_2 = 3.7Hz), 1.47 (s, 3H), 1.16 (s, 3H), and 0.87 (d, 1H, J = 12.1Hz). ^{13}C NMR ($CDCl_3$): δ 186.0, 138.7, 133.5, 50.4, 49.5, 49.0, 42.8, 37.3 and 24.2.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.01; H, 7.95. Found: C, 70.93; H, 8.01

REFERENCES

1. J. S. Meek and W. B. Trapp, *J. Am. Chem. Soc.*, **79**, 3909 (1957).

2. R. V. Moen and H. S. Makowski, *Anal. Chem.*, **43**, 1629 (1971).

3. R. M. Moriarty, C. C. Chien and T. B. Adams, *J. Org. Chem.*, **44**, 2206 (1979).

****