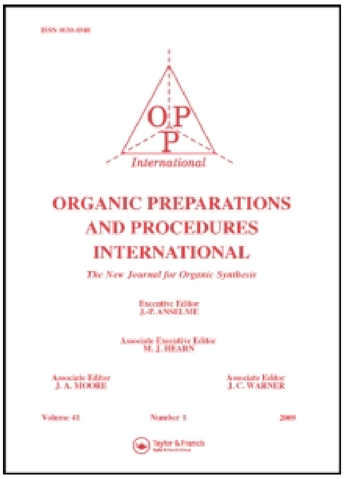

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A CONVENIENT, TWO-STEP SYNTHESIS OF BICYCLO[3,3,0]OCT-1(5)-ENE

Paul J. Okarma[a]; Joseph J. Caringi[a]
[a] Department of Chemistry, Yale University, New Haven, Connecticut

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Anal. Calcd for $C_{14}H_8F_5N_3O_4$: C, 44.58; H, 2.14; F, 25.18; N, 11.14

Found: C, 44.67; H, 2.22; F, 25.26; N, 11.06

NMR (DMSO-d_6): δ 3.26 (s, 3, N-CH_3), 7.2 (m, 3, ArH), 8.65, 9.0 (d, 2 meta coupled ArH). Mass spectrum: M+• 377.

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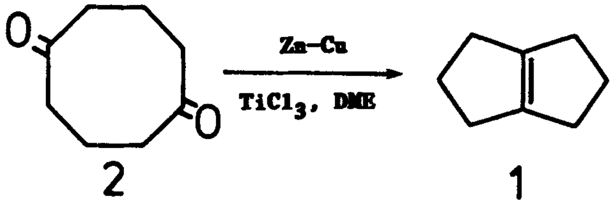
A CONVENIENT, TWO-STEP SYNTHESIS OF BICYCLO[3.3.0]OCT-1(5)-ENE

Submitted by Paul J. Okarma* and Joseph J. Caringi
(2/1/85)

Department of Chemistry
Yale University
New Haven, Connecticut 06511

During the course of a collaborative effort on the study of the solid state NMR spectra of alkenes, a sample of bicyclo[3.3.0]oct-1(5)-ene (1) was desired.[1] Although 1 had been prepared by a variety of routes,[2] none of them were convenient. It appeared possible to obtain 1 via a reductive coupling of carbonyl groups.[3] The use of the high dilution procedure of McMurry might allow the conversion of 1,5-cyclooctanedione (2) to 1.[4]



The oxidation of commercially available 1,5-cyclooctanediol produced **2** in excellent yield.[5] The conversion of **2** to **1** using $TiCl_3$ and Zn-Cu couple in dimethoxyethane under high dilution conditions produced **1** in 32% yield. The main difficulty lies in the volatility of **1** and the need for a careful distillation in its isolation.

EXPERIMENTAL SECTION

Bicyclo[3.3.0]oct-1(5)-ene **1**.- The general procedure of McMurry was followed. In an oven dried, three-necked flask fitted with a condenser were placed 3.0 g (45 mmol) of Zn-Cu couple,[6] 3.15 g (21 mmol) $TiCl_3$ and 50 ml of dry dimethoxyethane (dried by refluxing over sodium followed by distillation). The reaction was maintained under a positive pressure of argon and the other joints were sealed with rubber septa. The slurry was heated to reflux for one hour giving a black mixture. At continued reflux with stirring, 125 mg (0.89 mmol) of **2** in 30 ml of dry DME was added dropwise *via* a syringe pump over a 9 hr period followed by 12 hrs of reflux. An additional 125 mg (0.89 mmol) of **2** in 30 ml of dry DME was added dropwise over a 9 hr period and the reaction was heated to a gentle reflux for 12 hrs after the completion of the second addition. The reaction mixture was then cooled to room temperature and 25 ml of pentane was added. The mixture was filtered through a pad of Florisil and the flask was rinsed with an additional portion of pentane. The major portion of the solvents were removed by slow distillation through a 10 cm glass bead packed column. The solution then was transferred to a smaller flask with a minimum of pentane and the solution was further concentrated by distillation.

Examination of the pot residue by ^1H NMR showed it to be primarily DME and **1**. Pure **1** (62 mg, 32%) was isolated by preparative gas chromatography using a 12' x 1/4" 20 % SE-30 column at 80°.

Bicyclo[3.3.0]oct-1(5)-ene 1: ^{1}H NMR (90 MHz, $CDCl_3$): δ 2.18 (br s), lit.[2d] 2.18 (br s). Mass Spectrum (m/e, relative intensity): 109 (4,M+1), 108 (47, M+), 107 (7), 93 (43), 91 (28), 81 (7), 80 (100, P+), 79 (94), 78 (12), 77 (34), 67 (19), 66 (10), 65 (12).

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