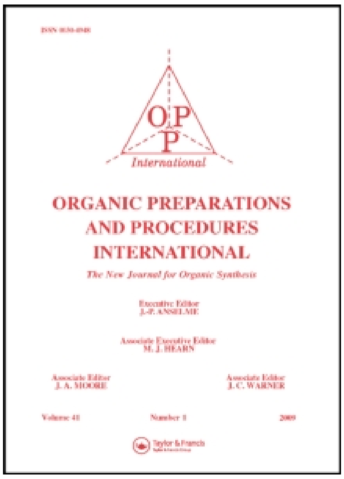

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A SHORT SYNTHESIS OF *cis*-1,7,7-TRIMETHYLBICYCLO[4.4.0]DEC-3-ENE

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OPPI BRIEFS

A SHORT SYNTHESIS OF cis-1,7,7-TRIMETHYLBICYCLO[4.4.0]DEC-3-ENE

Submitted by
(02/19/88)

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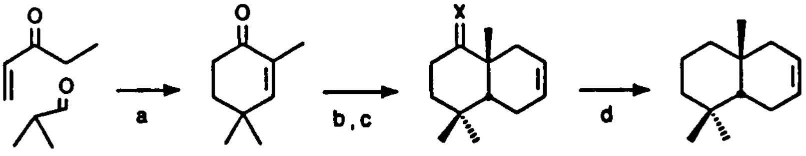
As part of our interest in the synthesis of terpenes and potential ambra odorants, we required a short, efficient route to cis-1,7,7-trimethylbicyclo-[4.4.0]dec-3-ene (1); the trans isomer (2) had previously been prepared by the pyrolysis of the acetate.[1] We herein report a four-step preparation of the title compound.

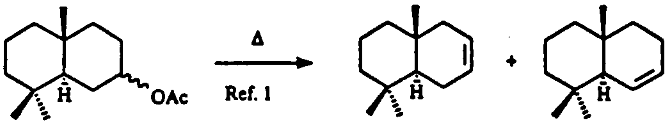


3

4, X = O
5, = SCH_2CH_2S
6, = NNHTos

1

a, C_6H_6, H_2SO_4; b, 1,3-butadiene, $AlCl_3$; c, $H_2NNHTos$, AcOH; d, $NaBH_4$, EtOH



2

Acid-catalysed Robinson annelation[2] of isobutyraldehyde with ethyl vinyl ketone affords the known 2,4,4-trimethyl-2-cyclohexenone (3) in 57% yield. The procedure for Diels-Alder cyclization of 3 with butadiene[3] in the presence of $AlCl_3$ (modified for large scale and inexpensive glassware) gave cis-1,5,5-trimethylbicyle[4.4.0]dec-8-en-2-one (4) in 47% yield.[4] Attempts to convert the carbonyl to methylene via Wolff-Kishner or Clemmensen reduction of 4 were unsuccessful and only starting material was recovered. Conversion of 4 to the dithioketal (50%) followed by treatment with Raney Nickel gave a mixture of four isomeric olefins (68%). The preparation of isomer 1 as the exclusive product was accomplished via formation of the tosylhydrazone 6 in acetic acid[5] (91%) followed by reduction with sodium borohydride (68%). Notably the methyl singlets of 1 appear well separated for the cis isomer (δ 0.93, 0.86, 0.81) while they appear overlapped for the trans isomer 2 (δ 0.87, 0.81).[1]

EXPERIMENTAL SECTION[6]

2,4,4-Trimethyl-2-cyclohexenone (3), prepared from the reaction of ethyl vinyl ketone[7] and isobutyraldehyde as described by Heathcock and McMurry,[2] was isolated by distillation under aspirator pressure (81-85°/19 mm Hg, 57%) and identified by comparison of its NMR spectral data with the literature values.[8]

cis-1,5,5,-Trimethylbicyclo[4.4.0]dec-8-en-2-one (4).- This compound was prepared by a modification of the procedure of Fringuelli and Wenkert.[3] To a flame dried 8 oz. clear glass bottle with metal twist-off cap (Miller Brewing Co., Milwaukee, WI) containing 3 (2.16 g, 15.6 mmol) in benzene (25 mL) under N_2 was added aluminum trichloride (2.02 g, 15.1 mmol) in benzene (25 mL). The mixture was allowed to stand for 40 min and then a solution of 1,3-butadiene (4.37 g, 80.9 mmol) in benzene (100 mL) was added using a syringe. The bottle was capped and heated in a sand bath to 70° for 52 hrs. After cooling, the reaction vessel was opened and water (50 mL) was cautiously added. The reaction mixture was extracted with methylene chloride (4 x 50 mL), the combined extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. The residue was chromatographed over silica gel (60-200 mesh) using hexane:ether (4:1) as eluent. The product fraction was distilled under high vacuum to afford 1.41 g (47%) of a clear oil, bp. 59-62°/0.08 mm Hg (kugelrohr). The NMR spectral data was identical to that reported in the literature.[3]

cis-1,5,5-Trimethylbicyclo[4.4.0]dec-8-ene p-Toluenesulfonylhydrazone (6).- To a solution of 4 (7.40 g, 38.5 mmol) in glacial acetic acid (50 mL) was added p-toluenesulfonhydrazide (14.34 g, 77.0 mmol). The reaction was stirred at 23° for 28 hrs, and then diluted with water (240 mL). The resultant white precipitate was collected by vacuum filtration and washed with water. The product was recrystallized from methanol: water (1:1) and dried in vacuo to afford a white crystalline solid, 12.59 g (91%), mp. 139-142°. ^1H NMR ($CDCl_3$): δ 7.9,7.3 (AA'BB', J_{ab} = 8, 4H), 5.58 (br s, 2H), 2.43 (s, 3H), 2.3-2.0 (m, 4H), 1.7-1.0 (m, 6H), 1.17 (s, 3H), 0.93 (s, 6H).

Anal. Calcd. for $C_{20}H_{28}N_2O_2S. H_2O$: C, 65.01; H, 7.91. Found : C, 65.33; H, 7.94

cis-1,7,7-Trimethylbicyclo[4.4.0]dec-3-ene (1).- To a stirred solution of 6 (13.42 g, 37.2 mmol) in absolute ethanol (250 mL) in a 500 mL 3-neck flask equipped with a condenser and thermometer under N_2 was added sodium borohydride (14.00 g, 0.37 mol) in ~ 0.5 g portions. The gas evolution which occurred with each addition was allowed to subside before adding a subsequent portion. The reaction mixture was heated to reflux for 25 hrs. The reaction mixture was cooled and cautiously treated with water (250 mL) and the resultant mixture was extracted with petroleum ether (4 x 100 mL). The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated under reduced pressure. The oily residue was distilled under high vacuum to afford the product as a colorless oil, 4.46 g (67%), bp. 42-43°/0.07 mm Hg (kugelrohr). ^1H NMR($CDCl_3$): δ 5.55 (m, 2H), 2.3-2.1 (m, 4H), 1.7-1.0 (m, 9H), 0.93 (s, 3H) 0.86 (s, 3H), 0.81 (s, 3H); $^{13}C(^1H)$NMR ($CDCl_3$): δ 125.9, 125.6, 47.7, 42.8, 41.1, 34.2, 33.8, 33.5, 32.1 31.9, 23.6, 21.4, 19.0;

GC/MS: M^+ = 178(8); m/e: 163(6), 124(53), 109(100), 93(22), 81(20), 69(11).

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A FACILE SYNTHESIS OF 3,4-DIHYDRO-1,5-BENZODIOXEPIN-2-ONES

Submitted by
(01/11/88)

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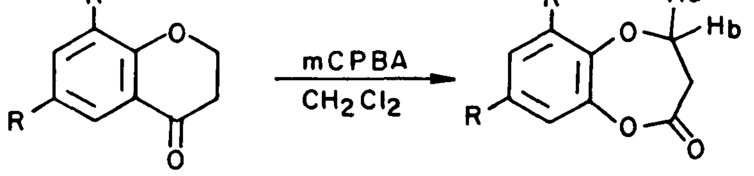
The oxidation of chromones and 3-formylchromones with m-chloroperbenzoic acid was previously reported[1,2] to afford 3-hydroxychromones. We now report the facile one-step synthesis of 3,4-dihydro-1,5-benzodioxepin-2-ones (IIa-e) in 60% yield by the Baeyer-Villiger



I II

a) $R = R^1 = H$; b) $R = CH_3$, $R^1 = H$; c) $R = H$, $R^1 = CH_3$; d) $R = Cl$, $R^1 = H$; e) $R = Br$, $R^1 = H$