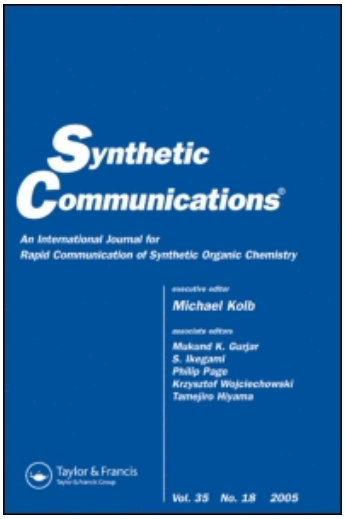

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Short, Convenient Preparative Procedures for 7-Isopropylidenenorbornane, 7-Isopropylidenenorbornene, and 7-Isopropylidenenorbornadiene

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SHORT, CONVENIENT PREPARATIVE PROCEDURES FOR 7-ISOPROPYLIDENENORBORNANE, 7-ISOPROPYLIDENENORBORNENE AND 7-ISOPROPYLIDENENORBORNADIENE

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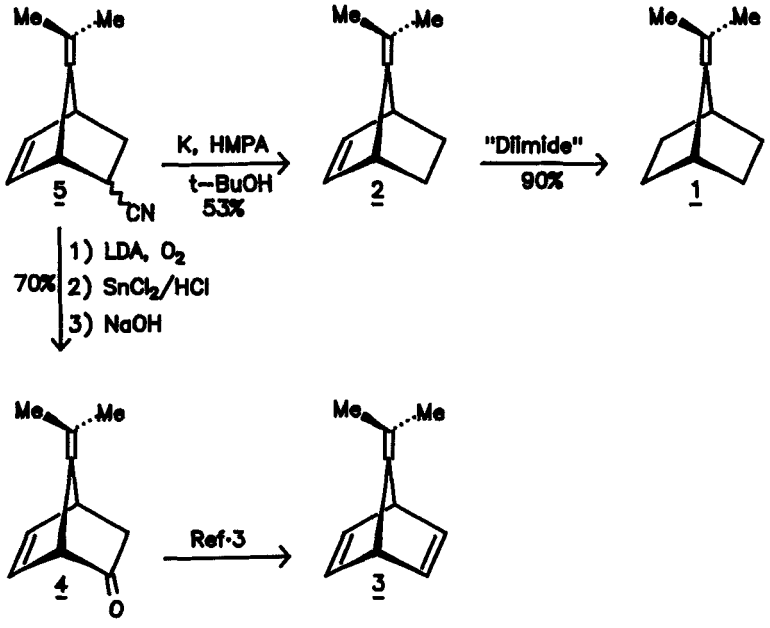
Abstract: Short synthetic routes to the title compounds 1-3 from readily available Diels-Alder adduct 5 of 6,6-dimethylfulvene and acrylonitrile are described.

The norbornane derivatives, 7-isopropylidenenorbornane 1, 7-isopropylidenenorbornene 2 and 7-isopropylidenenorbornadiene 3 with ascending degree of unsaturation, and of pedagogic importance, have evoked a great deal of interest as excellent mechanistic probes for the study of stereoelectronic effects in electrophilic addition reactions.[1] Also, 2 and 3 are celebrated examples in which homoconjugation is readily palpable through PES & NMR studies.[2] In connection with

an ongoing effort,[1e,f] we needed ready access to 1-3 and their substituted derivatives. These olefins have been earlier prepared[3] through the bicyclic enone 4[1a,4] in multistep sequences. The bicyclic enone 4 in turn was obtained from further manipulation on the Diels-Alder adduct of 6,6-dimethylfulvene with either acrylic acid[1a] or α-acetoxyacrylonitrile.[4] Herein we describe short and convenient preparative routes to 1-3 from the readily available[5] Diels-Alder adduct 5 of 6,6-dimethylfulvene and acrylonitrile.

The Diels-Alder adduct 5,[5] obtained as a mixture of exo- and endo-isomers from 6,6-dimethylfulvene and acrylonitrile was directly subjected to reductive



decyanation with K in HMPA following a procedure described by Normant's group[6] to furnish 2 (55%) in one step (cf.4-5 steps used earlier).[1a,3] Diimide reduction on 2 proceeded smoothly and regioselectivity with reduction of the norbornene double bond to furnish 1 (90%).

For the preparation of 3, an improved access to the enone 4 was sought. When the mixture of exo- and endo-adducts 5 was subjected to oxidative decyanation following the procedure of Watt et.al,[7] 4 was obtained in 70% yield (cf.21% yield from the acrylic acid adduct of 6,6-dimethylfulvene).[1a] The enone 4 could be conveniently transformed to 3 following the procedure of Martin and Forster.[3]

In short, starting from 5, we have described short routes to 1-3 that are simple to execute, amenable to scale-up and require minimal purification maneuver.

Experimental

For a general write-up, see ref.8.

7-Isopropylidenenorborn-2-ene 2:

A suspension of finely cut potassium (1.15g, 29.5mg atom) in 35ml of dry ether was cooled to -5°C and a mixture of exo- and endo-5-cyano-7-7-isopropylidenenorborn-2-ene (5, 1.1g, 6.92 mmol),[5] dry t-BuOH (553mg, 7.46 mmol) and HMPA (2.9ml) in 10ml dry ether was slowly injected with stirring. The reaction mixture

was allowed to warm up to room temp. (20°C) over a period of 30min. and further stirred for 3.5h at room temp., after which it was cooled in an ice bath and quenched by careful addition of dry MeOH (5ml) followed by ice water (10ml). The organic layer was separated and the aqueous layer was extracted twice with ether (2 x 50 ml). The combined ether extract was washed with water, brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and column purification on silica gel (20g, elution with hexane) furnished 495mg (53%) of 7-isopropylidenenorborn-2-ene 2 (93% pure by GLC on Capillary Column); ^1H NMR ($CDCl_3$, 200 MHz): δ6.19 (2H, dd, $J_1=J_2=2Hz$, -CH=CH-), 3.27 (2H, m, bridgehead CH), 1.68-1.58 (2H, m, exo-$H_{5,6}$), 1.55 (6H, s, $\diagdown\!\diagup$ C=CMe_2), 1.07-0.99 (2H, m, endo-$H_{5,6}$); ^{13}C NMR ($CDCl_3$, 25 MHz): δ148.65, 136.12, 107.06, 41.59, 24.70, 19.41.

7-isopropylidenenorbornane 1:

Oxygen was bubbled at a moderate flow rate into a mixture of 2 (100mg, 0.75mmol), 99% hydrazine hydrate (0.7ml, 15mmol) and $CuSO_4.5H_2O$ (20mg) in ethanol (2ml) for 20min. at room temp. The mixture was diluted with crushed ice and extracted with ether. The ethereal layer was washed with 20% aq.HCl, water and dried. Removal of solvent furnished 3 (91mg, 90%);[3] ^1H NMR ($CDCl_3$, 100 MHz): δ2.52 (2H, m), 1.80-1.04 (8H, m),

1.61 (6H, s); ^{13}C NMR ($CDCl_3$, 25 MHz): δ143.30, 113.00, 35.76, 29.29, 20.58.

7-isopropylidenenorborn-5-ene-2-one 4:

To a magnetically stirred solution of lithium diisopropylamide (5.66mmol, prepared by the addition of 4.7ml of 1.6M n-BuLi in hexane to a stirring solution of diisopropylamine, 573mg) at -78°C under N_2 in 5ml of dry THF was added the adduct 5 (300mg, 1.89 mmol) in 3ml of THF and dry oxygen was bubbled into the lithio-nitrile solution for 45min. The reaction was quenched by the addition of 15ml of 1M $SnCl_2$ in 20% HCl and the mixture was stirred at room temp. for 1.5h. The mixture was cooled (ice-bath) and 3M NaOH solution (20ml) was added. The stirring was continued further for 1h at room temp. and the reaction mixture was extracted several times with ether. The combined ether extract was washed with water and dried. Removal of solvent and filtration through a silica gel column (20g) with 2% ethyl acetate-hexane furnished ketone 4 (197mg, 70%);[1a] ^1H NMR ($CDCl_3$, 100 MHz): δ6.70-6.54 (1H, m), 6.28-6.10 (1H, m), 3.70-3.42 (2H, m), 2.01 (2H, m), 1.64 (3H, s), 1.56 (3H, s); ^{13}C NMR ($CDCl_3$, 25 MHz): δ211.00, 146.30, 143.18, 131.00, 115.24, 57.88, 42.00, 40.35, 19.70, 19.29.

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