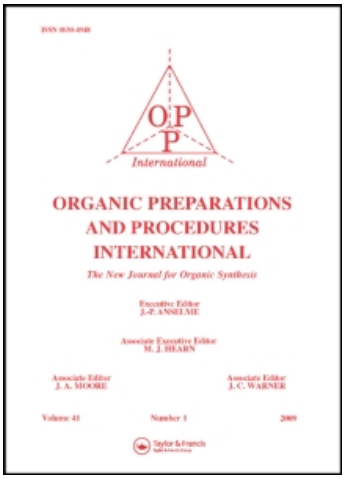

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FACILE PREPARATION OF *trans*-2,3-bis(-*tert*-BUTYLAMINOMETHYL) NORBORNENE

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11. The enantiomeric purity was determined by ^{1}H NMR with (+)-(*S*)-2,2,2-trifluoro-1-(9-anthryl)-ethanol as a chiral solvent. The corresponding (*R*)-enantiomer had $[\alpha]_D^{20}$ -113.8° (*c* 0.488, CH_2Cl_2).

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FACILE PREPARATION OF *trans*-2,3-bis(-*tert*-BUTYLAMINOMETHYL) NORBORNENE

Submitted by J. H. Wynne[†,††] and W. M. Stalick*[†]
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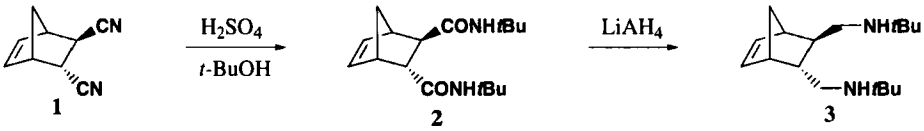
Norbornenes possessing sterically hindered amino pendant groups are a class of compounds used in the synthesis of novel advanced organic materials.[1] Polymers bearing amino and different heteroatom pendant groups are typically synthesized because they are able to chelate metals.[2] In addition, polymerization of compound **3**, where the bulky amino substituents are *t*-butyl groups, readily affords a material with a rigid backbone containing amine groups which have been shown to chelate to metals such as zinc and copper.[3] These molecules have also been employed in polymers for their non-linear optical properties.[3,4] The synthesis of diaminomethyl norbornene **3** has been reported in the literature albeit in only low to moderate yields.[5] This lengthy four-step procedure involves a Diels-Alder reaction between cyclopentadiene and fumaric acid, followed by reduction to the *trans*-diol, subsequent treatment of the diol with tosyl chloride in pyridine to give the ditosylate, which upon reaction with *t*-butylamine in DMF at 100° for prolonged periods, in a sealed reaction vessel, resulted in the desired product **3**. This typically used method requires the use of a specialized reaction vessel at elevated temperature and pressure. We now report that compound **3** can be easily synthesized in high yields by a very simple facile approach resulting in both high purity and yields.

Treatment of freshly cracked cyclopentadiene, with *trans*-fumaronitrile afforded the Diels-Alder adduct **1** in quantitative yields as previously reported.[6] Subsequent treatment under Ritter-type reaction conditions, employing *t*–butyl alcohol and conc. sulfuric in acid glacial acetic acid, transformed **1** to the di-*t*-butylamide **2**. This facile transformation can be performed in an Erlenmeyer flask and requires no inert atmosphere or special equipment. However, it is imperative that the temperature be maintained between 0 to 50° in order to prevent both ester and ether formation, which results if the temperature is not controlled.

Reduction of the diamide **2** with lithium aluminum hydride[7] results in the formation of the desired di-*t*-butylamine norbornene derivative **3**. The overall yield from cyclopentadiene is 81% compared to 47% by the reported procedure.[5]



EXPERIMENTAL SECTION

Melting points were determined on a Thomas Hoover melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were taken on a Bruker 300 MHz spectrometer. FTIR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer. The elemental analysis was performed by Desert Analytics, Tucson, AZ 85717. Diethyl ether and THF were both distilled from sodium/benzophenone under nitrogen before use.

***trans*-2,3-Dicyanonorborn-5-ene (1).**- This compound was prepared according to a modified literature report.[6] Into a 250 mL round bottomed flask under a positive flow of nitrogen was added fumaronitrile (9.37 g, 120 mmol). Methanol (100 mL) was distilled into the reaction vessel and the solution was stirred for 15 min and then cooled to 0° in an ice bath. An aliquot of dicyclopentadiene (15.86 g, 240 mmol), was cracked and cyclopentadiene distilled directly into the chilled, stirred fumaronitrile solution. The reaction mixture was allowed to warm to RT and stirred overnight before it was concentrated on the rotary evaporator. Final traces of solvent and unreacted cyclopentadiene were removed under high vacuum (14 h), to afford the desired product in a quantative yield as a white powder, mp. 94-95°, *lit.*[6] 92-94°.

***trans*-2,3-bis(*tert*-Butylamido)norborn-5-ene (2).**- Into a 125 mL Erlenmeyer flask covered with a watch glass, were placed conc. sulfuric acid (5.01 g) and glacial acetic acid (25 mL). The acid solution was chilled in an ice bath for 15 min until the temperature was 5°. Then compound **1** (1.75 g, 25 mmol) was added in one portion and the solution was stirred for 5 min before the addition of *t*-butyl alcohol (3.70 g, 50 mmol). The mixture was allowed to warm to RT and was stirred overnight. It was then diluted with H_2O (50 mL) and neutralized to litmus paper using solid Na_2CO_3. The insoluble solid that formed was collected and washed with cold H_2O (3 x 15 mL). The desired amide was obtained quantatively and in sufficient purity (after drying) to be used in subsequent reactions; a sample for analysis was obtained as a colorless solid by crystallization from methanol, mp 254-256° (dec.). IR (neat): 3303, 3199, 3079, 2960, 2864, 2756, 1624, 1539, 1447, 1358, 1262, 1358, 1262, 1208, 1046, 1008, 900, 792 cm^{-1}. ^1H NMR (THF-*d8*): δ 6.13 (bs, 1H), 5.78 (bs, 1H), 5.46 (dd, 1H), 5.27 (dd, 1H), 2.94 (d, 2H), 2.36 (d, 2H), 2.14 (d, 1H), 1.73 (d, 1H), 0.64 (s, 9H), 0.62 (s, 9H). ^{13}C NMR (THF-*d8*): δ 174.5, 172.9, 138.1, 135.3, 51.2, 50.2, 49.3, 48.8, 48.4, 47.1, 29.2.

Anal. Calcd for $C_{17}H_{28}N_2O_2$; C, 69.83; H, 9.65; N, 9.58. Found C, 69.91; H, 9.88; N, 9.45

***trans*-2,3-bis(-*tert*-Butylaminomethyl)norborn-5-ene (3).**- Into a 50 mL round bottomed flask

equipped with a condenser and an addition funnel was placed a suspension of $LiAlH_4$ (0.52g, 13.68 mmol) in anhydrous ether (15 mL). The solution was chilled in an ice bath and compound **2**, (2.00 g, 6.84 mmol) in 20 mL of THF, was added dropwise over one hour. After the addition was complete, the ice bath was replaced with a heating mantle and the solution was refluxed for 15 h. The solution was then cooled to 0° and H_2O (10 mL) was added cautiously with vigorous stirring for 30 min, followed by the addition of NaOH (3.20 g, in 8 mL of H_2O). The resulting solution was stirred for 1 h, before it was neutralized with 5 M HCl. The solution was extracted with CH_2Cl_2, and washed with H_2O (2 x 15 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting oil was dissolved in 20 mL of ether and precipitated by addition of conc. HCl until no more solid formed. The solid hydrochloride salt was collected and neutralized to pH 7 with 1M aqueous NaOH. The yellow oil which separated as the top layer was extracted into 20 mL of ether. After drying, the solution was evaporated to dryness to afford 1.47 g. (81%) of the desired product as a yellow oil whose spectroscopic properties matched those previously reported.[5] IR (neat): 3263, 3061, 2961, 2902, 2862, 2810, 1479, 1384, 1359, 1332, 1229, 1717, 1095 and 1019 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.18 (dd, 1H), 5.99 (dd, 1H), 5.65 (bs, 1H), 2.98 (bs, 1H), 2.91 (dd, 4H), 2.29 (dd, 2H), 1.76 (d, 2H), 1.45 (dt, 2H), 1.12 (s, 9H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 137.71, 133.37, 65.79, 50.09, 48.07, 47.15, 46.73, 45.48, 45.13, 28.95 and 15.20.

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