Preparative Derivatization of *endo*-Dicyclopentadiene via Metallation

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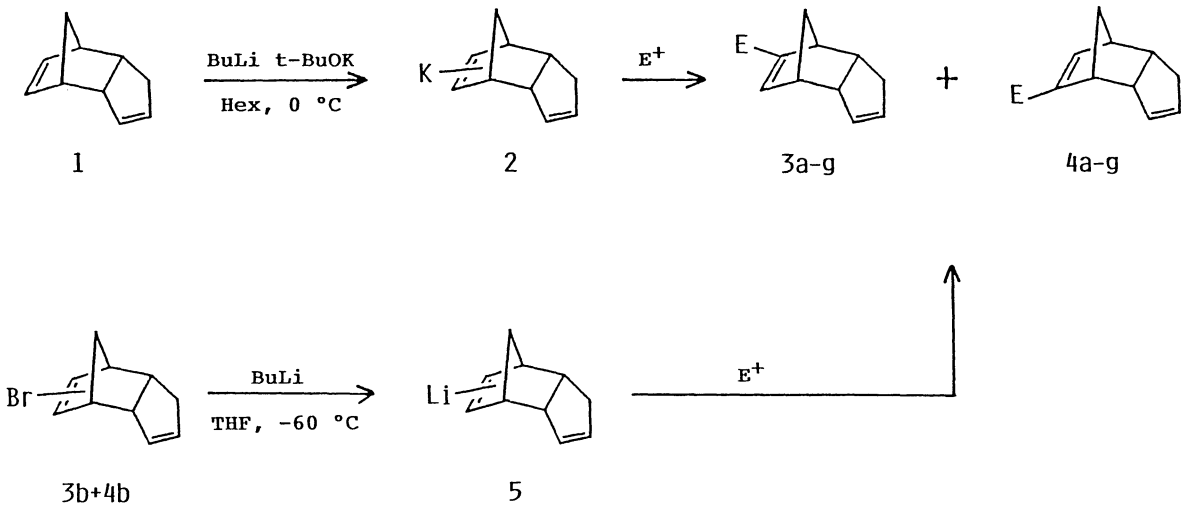
Synopsis. *endo*-Dicyclopentadiene has been selectively metallated with the base complex BuLi·*t*-BuOK in hexane at the olefinic positions in the norbornene moiety and a number of derivatives prepared by reaction of the metallated intermediate with electrophilic reagents. In particular, bromodicyclopentadiene thus obtained is a useful stock precursor for lithiodicyclopentadiene.

endo-Dicyclopentadiene (*endo*-tricyclo [5.2.1.$0^{2,6}$] deca-3,8-diene) (**1**) is an important compound as a direct precursor of synthetically useful cyclopentadiene. In view of ready thermal cycloreversion of dicyclopentadiene to cyclopentadiene, dicyclopentadienes can be regarded as stabilized as well as protected forms of usually labile cyclopentadienes. However, only a small number of substituted dicyclopentadienes have been obtained mostly by thermal dimerization of the corresponding monomers, and no practical way for derivatization of **1** itself has been described.[1] Here we report a metallation and functionalization of **1**.

Norbornene and norbornadiene have been metallated at the olefinic position with the base complex BuLi·*t*-BuOK.[2] There are essentially three possible sites for metallation with a strong base in the molecule of dicyclopentadiene (**1**) from the viewpoint of acidity of C-H bond; namely, the olefinic position of the norbornene part, the olefinc and allylic positions of the cyclopentene part. In fact, **1** was found to be metallated with the base complex selectively at the olefinic positions of the norbornene part (C-8 or -9). The metallated intermediate was assigned to be the potassium compound **2** in analogy with the metallation of norbornene.[2,3] Reactions of **2** with electrophilic reagents gave about 1 : 2.5 mixture of 8- and 9-substituted dicyclopentadienes, **3** and **4**, in moderate yields (Table 1, Method A). Hexane as solvent gave



Scheme 1.

Table 1. Yields and Some NMR Data of Derivatives of Dicyclopentadiene

Entry	Electrophile	Product[a] (3+4)	Yield/%		^{1}H NMR[b]	
			Method A	Method B	δ(HC=)	δ(HC=CH)
a	$HCON(CH_3)_2$	E=CHO	42	57	6.9	5.4
b	$BrCH_2CH_2Br$	Br	61		5.95	5.6
c	C_6H_5CHO	$CH(OH)C_6H_5$	46	91	5.7	5.5
d	$(C_6H_5)_2CO$	$C(OH)(C_6H_5)_2$	63	91	5.2—5.7	
e	$(CH_3)_2CO$	$C(OH)(CH_3)_2$	13	45	5.7	5.45
f[c]	$ClCO_2Et$	CO_2Et	41	52	6.7	5.45
g	$(C_6H_5)_2S$	SC_6H_5	55	89	5.7	5.5

a) High-resolution mass spectroscopy gave the expected mol. weights. b) Data of mixture at 90 MHz. c) The anion solution was inversely added to an ethereal solution of excess reagent.

the best results for the metallation. Use of tetrahydrofuran (THF) resulted in very poor yields of products even at low temperatures. In hexane, the metallation was most conveniently and reproducibly conducted by stirring a 2 : 1 mixture of **1** and the base complex at 0 °C (ice bath) for 4—6 h.

Bromodicyclopentadiene (**3b**+**4b**), which can be prepared in fairly large quantity by Method A, is also a useful precursor for a metallated dicyclopentadiene; thus, treatment of the bromide mixture with BuLi in THF at −60 °C smoothly generated lithiodicyclopentadiene (**5**) which generally afforded quenching products in higher yields (Table 1, Method B).[4]

The product ratios were little affected by reaction conditions and the mixtures were usually difficult to separate, although **3a** and **4a**, and **3d** and **4d** were partially separated by chromatography on silica gel. The structures of products were mainly elucidated by ^{1}H NMR spectroscopy. The 400 MHz ^{1}H NMR spectrum of the bromide mixture (**3b**+**4b**) in $CDCl_3$ shows a set of two signals particularly for the three olefin protons (H-3,4, and H-8 or 9) and the bridgehead proton at C-1 (H-1) with 1 : 2.4 ratio. Appearance of two doublets (J=3.3 Hz) at δ=6.00 (0.7H) and 5.94 (0.3H), which are assignable to H-8 or -9, indicates introduction of the bromine atom at the norbornene double bond (C-8 or -9). H-1 is observed at δ=3.38 and 3.29 with the former predominant. Since H-1 of **4b** is expected to resonate at lower field than H-1 of **3b** owing to anisotropic effect of nearby bromine atom, the observation suggests the predominance of **4b** over **3b**. This is also supported from ^{1}H NMR analysis of other quenching products.

Although the present metallation and functionalization of **1** affords mixtures of two regioisomers, they can be used in mixtures for organic syntheses, because both isomers should lead to the same products through thermolytic cycloreversion.

Experimental

^{1}H NMR spectra were recorded on a JEOL FX-90Q or JEOL GSX-400 spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard. IR spectra were obtained from Hitachi EPI-G3 spectrometer, and mass spectra measured on a JEOL JMS-OlSG-2 or JEOL JMS-SX102 spectrometer. The microanalysis was performed at the Elemental Analysis Center, Faculty of Science, Osaka University.

Hexane was distilled from sodium metal and stored on sodium wire. Tetrahydrofuran (THF) was freshly distilled from sodium metal using diphenylketyl as indicator. BuLi and *t*-BuOK were purchased and used as such. Dicyclopentadiene was distilled in vacuo and middle fraction was used. For large scale preparation of bromodicyclopentadiene, commercial dicyclopentadiene was successfully used without further purification.

Metallation and Formylation of Dicyclopentadiene—A Standard Procedure for Method A. To a suspension of *t*-BuOK (1.12 g, 0.01 mol) in hexane (8 ml) was added dropwise hexane solution of BuLi (1.6 M, 6.6 ml) over a few min using a syringe with stirring in an ice bath under nitrogen atmosphere (1 M=1 mol dm^{-3}). After 15 min, dicyclopentadiene (**1**) (2.64 g, 0.02 mol) was added and the mixture stirred for 5 h. A solution of dimethylformamide (1.10 g, 0.015 mol) in dry ether (3 ml) was added in a few minutes. After 20 min, the reaction mixture was poured into ice-dil aq HCl, and extracted with ether (2×25 ml). The ether extract was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed on a short silica-gel column (hexane : AcOEt=9 : 1) to afford a mixture of **3a** and **4a** (0.67 g, 42% yield based on *t*-BuOK used) as a colorless oil. Found: m/z 160.0882. Calcd for $C_{11}H_{12}O$ 160.0888. ^{1}H NMR spectrum of this mixture showed two singlets of formyl proton at δ=9.52 (assigned for **4a**) and 9.63 (**3a**) in 2.5 : 1 integral ratio. The mixture was partially separated to **3a** and **4a** by careful chromatography.

3a: IR (CCl_4) 1675, 1590 cm^{-1}; ^{1}H NMR (90 MHz) δ=1.3—1.9 (m, 3H), 2.25 (m, 1H), 2.7—3.6 (m, 4H), 5.46 (s-like, 2H), 6.89 (d, J=3.0 Hz, 1H), 9.63 (s, 1H).

4a: IR (CCl_4) 1675, 1590 cm^{-1}; ^{1}H NMR (90 MHz) δ=1.3—1.9 (m, 3H), 2.25 (m, 1H), 2.7—3.6 (m, 4H), 5.52 (s-like, 2H), 6.96 (d, J=3.0 Hz, 1H), 9.52 (s, 1H).

Large Scale Preparation of Bromodicyclopentadiene (3b+4b): In a 1 L three necked flask equipped with a thermometer and two dropping funnels was placed dry hexane (350 ml) and then *t*-BuOK (44.88 g, 0.4 mol) under nitrogen atmosphere. The mixture was cooled below −50 °C in an ethanol-Dry Ice bath and added dropwise with BuLi in hexane (1.5 M, 280 ml, 0.42 mol) over 35 min under efficient magnetic stirring. After 15 min, **1** (100 ml, 98.6 g, 0.75 mol) was added over 10 min. The cold bath was replaced with an ice-bath and stirring continued for 6 h. The mixture was cooled again below −40 °C and 1,2-dibromoethane (42 ml, 91.6 g, 0.49 mol) in THF (60 ml) added at such rate that the inner temperature did not exceed −35 °C (ca. 40 min). The reaction mixture was allowed to warm up to about 0 °C over 1 h, and then added dropwise with water (100 ml). The organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was fractionally distilled in vacuo using a distilling column (1.5×25 cm) packed with glass helix: fraction 1, bp 40—49 °C/6 Torr (1 Torr=133.322 Pa), unreacted **1**, 54.8 g (0.415 mol); fraction 2, bp 52—83 °C/5 Torr, mixture of **1** and (**3b**+**4b**), 7.5 g; fraction 3, bp 85—87 °C/5 Torr (bp 76 °C/3 Torr), (**3b**+**4b**), 52.1 g (0.247 mol, 61.7%). ^{1}H NMR (400 MHz) δ=1.33 (d, J=8.0 Hz, 1H), 1.74—1.85 (m, 1.7H), 2.22—2.32 (m, 1.3H), 2.75 (m, 0.7H), 2.85—2.95 (m, 2.3H), 3.29 (m, 0.3H), 3.38 (m, 0.7H), 5.47 (m, 0.3H), 5.57 (m, 1H), 5.66 (m, 0.7H), 5.94 (d, J=3.3 Hz, 0.3H), 6.00 (d, J=3.3 Hz, 0.7H). Found: C, 57.15; H, 5.32; Br, 37.33%. Calcd for $C_{10}H_{11}Br$: C, 56.90; H, 5.25; Br, 37.85%.

Lithiation and Formylation of Bromodicyclopentadiene (3b+4b)—A Standard Procedure for Method B. To a solution of (**3b**+**4b**) (3.13 g, 0.015 mol) in THF (8 ml) was added dropwise BuLi (1.6 M in hexane, 8.3 ml, 0.013 mol) over a few minutes at −60 °C. The solution became cloudy in 20 min due to separation of LiBr. Dimethylformamide (1.16 g, 0.016 mol) was added dropwise, and the mixture allowed to warm up to room temperature over 30 min. The reaction mixture was worked up as described for Method A to afford (**3a**+**4a**) (1.21 g, 57%).

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4) Cyclohexanone gave adducts also in only moderate yield similar to acetone. Abstraction of active hydrogen may have competed with nucleophilic addition for these aliphatic ketones.