## 7-LITHIO-NORBORNADIENE

### J. STAPERSMA and G. W. KLUMPP\*

Scheikundig Laboratorium der Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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Abstract -A synthesis of the title compound is described as well as its reactions with some electrophiles.

Notwithstanding their utility as starting materials for the elaboration of more complex cage compounds<sup>1</sup> and of specifically substituted cyclopentanoids,<sup>2</sup> bicyclo [2.2.1] hept-2-enes carrying a functionalized carbon chain at C-7<sup>3</sup> are still lacking an easy general route of synthesis. Thus, Diels-Alder reaction of cyclopentadienes properly substituted at C-5 is often thwarted by the notorious [1, 5] hydrogen shift,<sup>4</sup> a difficulty which is aggravated if less reactive acetylenic dienophiles (or appropriate synthons)<sup>5</sup> are to be used. Alternative routes utilizing fulvenes are afflicted with problems of stereospecificity in the tetragonalization step<sup>6</sup> as approaches are involving nucleophilic addition onto 7-norbornenone<sup>7</sup> and reactions of 7metallo-norbornenes with electrophiles.8 The seemingly easiest way to circumvent the latter problem, use of more "symmetrical" norbornadienes metalated at C-7, is confronted with the often discussed<sup>9</sup> difficulty of preparing 7-norbornadienyl anionoids as well as with the ease with which the retro Diels-Alder reaction may assert itself in certain systems of this kind.10 Reaction of quadricyclanone (as a norbornadienone synthone) with nucleophiles followed by isomerization of the product suffers from the laborious route to the ketone.<sup>11</sup>

We now wish to report an efficient preparation of 7lithio-norbornadiene  $(1a)^{12a}$  and of some 7substituted norbornadienes which can be derived from 1a.

In 1976 Freeman and Hutchinson described a method for the preparation of organolithium compounds from alkyl halides.<sup>13</sup> Their method parallels related work with the sodium-naphthalene system with two very important modifications: use of a sterically more crowded electron carrier to favour electron transfer over radical combination, and substitution of lithium for sodium as the metal in order



to lower the degree of carbanion character of the organometallic species formed.

We reacted 7-chloro-norbornadiene 1b14 with the Freeman and Hutchinson reagent lithium p,p'di-tbutylbiphenyl. Deuterium oxide quench of this mixture afforded norbornadiene, determined by mass spectrometry to contain  $96 \pm 1^{\circ}$ , d<sub>1</sub>, as the only product. <sup>1</sup>HNMR spectroscopy indicated that the D atom was located at the 7-position exclusively. Carbon dioxide quench afforded norbornadiene-7-carboxylic acid 1c<sup>12b</sup> in 64% yield. Reaction with N.Ndimethylformamide followed by acid work-up and purification by steam distillation gave norbornadiene-7-carbaldehyde  $1d^{15}$  (52%). 1d could also be prepared by reduction of the methyl ester 1e.<sup>12b</sup> derived from the acid 1c (97%), to the alcohol 1f (96%), followed by Pfitzner Moffatt oxidation<sup>16</sup> (51  $^{\circ}_{o}$ ). In this way the use of lithium aluminium deuteride allowed the introduction of deuterium into the aldehyde carbon. The tosylhydrazones lg and lh derived<sup>17</sup> from these aldehydes 1d and 1d-8-d, are the starting materials for the preparation of tetracyclo  $[3.3.0.0^{2.4}, 0^{3.6}]$  oct-7-ene. a new isomer of the (CH)<sub>8</sub> family.<sup>1</sup>

Thus, the preparation of 7-lithio-norbornadiene 1a leads to a series of interesting compounds, some of which are intermediates in the synthesis of strained molecules.

Answers to theoretical questions need the purification of **1a**, which implies mainly the separation from the biphenyl. Preliminary efforts to obtain 7norbornadienyl anionoids in a purer and less reactive state failed: attempted preparation of a mercury derivative led to unstable products as indicated by the formation of metallic mercury, while reaction with tetraphenyl phosphonium bromide, which worked well for cyclopropyl lithium,<sup>18</sup> yielded a very complex mixture (at least 18 components found by GC/MS after reaction with acetone). Although conclusions about the nature of the 7-norbornadienyl anion therefore still have to wait, the argument proferred in support of its anti-bicycloaromaticity "otherwise reasonable attempts to prepare (it) have failed"94 is no longer wholly valid.

Reaction of syn-7-bromo-norbornene with the Freeman and Hutchinson reagent followed by N,N-dimethylformamide quench and acid work-up afforded a 1:3,5 mixture of syn- and anti-7-norbornenyl carbaldehyde in 45 °, yield. This result parallels the problems encountered with 7-metallonorbornenes mentioned above.<sup>8</sup>

#### EXPERIMENTAL

General and analytical procedures. IR spectra were recorded as 10% solns in CCl<sub>4</sub> or CHCl<sub>3</sub> on a Perkin-Elmer 237 or 580B spectrophotometer. Only strong (s) and medium (m) absorptions are given  $(cm^{-1})$  with a precision of 5 cm<sup>-1</sup>. Mass spectra were obtained from a Varian Mat CH3-DF spectrometer (70 eV). For GC/MS a Varian Aerograph 1740 was coupled to the mass spectrometer. Peak heights of fragments are given in brackets relative to the base peak (100%). Gaschromatographic analyses were performed on a Varian Aerograph 90P or 920. H<sub>2</sub> was used as carrier gas. Columns (0.4 × 150 cm; stainless steel) used: 15 % SE 30 (A). 15% Apiezon M (B), 10% SE 30 (C), all on Chromosorb WAW-DMCS, 60-80 mesh and 20 % SE30 (D) on chromosorb W, 30-60 Prepgrade. All NMR spectra were recorded on a Bruker WH-90 spectrometer in CDCl<sub>3</sub> with CHCl<sub>3</sub> or CDCl<sub>3</sub> as internal standard. Chemical shifts ( $\delta_{1MS}$ ) are given in ppm with a precision of 0.01 ppm (<sup>1</sup>H) or 0.1 ppm  $(^{13}C)$ , coupling constants have an accuracy of 0.3 Hz (<sup>1</sup>H) or 1.5 Hz  $(^{13}C)^{19}$  Only  $^{1}J_{13C-1H}$  are given, although many of the signals showed further splittings: those which showed no further splittings are indicated by an asterisk. Abbreviations used: b = broad, p = pseudo, s = singulet, d = doublet, t = triplet, ga = guartet, gi = guintet, sx = sextet, m = multiplet. M.ps are uncorrected. All solvents were distilled shortly before use: ethereal solvents were distilled from LiAlH<sub>4</sub> and stored over Na-wire, DMSO was distilled from CaH, and stored over molecular sieves, DMF was dried according to ref. 20 and stored over molecular sieves, and benzene was dried by distillation, discarding the first distillate, and stored over molecular sieves. All reactions were carried out in previously dried glassware under N2, except radical anion reactions which were performed under argon. Some of the reaction mixtures were worked up by short path evaporative distillation (MDA); temperatures given are heating bath temps.

7-Chloro-norbornadiene (1b). The procedure given in ref. 14c could be improved by adding the amount of thionyl chloride required to bind the  $H_2O$  formed.

Norbornadiene-7-d<sub>1</sub>. To a stirred soln of 5.0 mmol (0.3 M) radical anion<sup>13</sup> kept at  $-78^{\circ}$  223.5 mg (1.8 mmol) 1b was added with a syringe. After 5 min the mixture was quenched with  $1 \text{ ml } D_2O$ . The mixture was allowed to warm to room temp and then transferred into a separatory funnel with the aid of 25 ml n-pentane. The organic layer was extracted 8 times with 25 ml H<sub>2</sub>O, washed once with 10 ml brine and dried over MgSO<sub>4</sub>. The mixture was concentrated carefully with a vacuum-jacketed 20 cm vigreux column at 760 torr. The residue was connected to a trap maintained at - 196° and volatile products were collected there under reduced pressure (caltorr). The contents of the cold trap were subjected to glc (A, 60<sup>°</sup>). Only one product was found, identical with authentic norbornadiene with regard to vpc-retention time and 'H NMR spectrum, except that in the latter the intensity of the H<sub>7</sub> absorption was halved relative to norbornadiene. Yield (after preparative glc): 63.5 mg (0.7 mmol, 39 ""). Mass spectrometry indicated the presence of  $96 \pm 1^{\circ}$ ,  $d_1$ . Calculated for C<sub>7</sub>H<sub>7</sub>D: 93.0689; found: 93.0682.

Norbornadiene-7-carboxylic acid (1c). Two 3-necked flasks of suitable size were connected by an Y-piece in such a way that the whole apparatus could be turned around one point. In the smallest vessel a soln of 99 mmol (0.45 M) radical anion<sup>13</sup> was prepared and cooled to  $-78^{\circ}$ . At this temp 4.8 g (38 mmol) 1b was added all at once with a syringe. The largest vessel was filled with dry ice and after 5 minutes the mixture was poured on the CO<sub>2</sub>. The mixture was warmed to room temp and made basic with 2N NaOH. Neutral organic impurities were removed by twice extracting the aqueous layer with ether. Then the aqueous layer was acidified with 2NHCl and 5 times extracted with ether. The combined ethereal extracts were dried over MgSO<sub>4</sub> and after filtration concentrated with a rotary evaporator (760 torr, 50°). The residue was sublimed (1 torr, 80-100°), yield: 3.2 g (24 mmol, 64",) small white needles, mp 84.5 86°. Calculated for

 $C_{k}H_{k}O_{2}$ : 136.0524; found: 136.0525; *m/e*: 136 (28), 111 (100), 91 (95). 1R (CCl<sub>4</sub>): 3600-2200 (b, s), 1706 (s), 1304 (m 1260 (m), 721 (s), 656 (m). <sup>1</sup>H NMR: 3.14 (bt, 1.8 Hz, H<sub>7</sub>), 3.8 (psx, H<sub>1.4</sub>), 6.75 (pqa, H<sub>2.35.6</sub>), 11.78 (variable, bs, COOH <sup>13</sup>C NMR: 176.8 (C<sup>\*</sup><sub>8</sub>), 142.7 (CH, 175.0 Hz, C<sub>2.3</sub> or C<sub>5.6</sub>; 141.2 (CH, 177.2 Hz, C<sub>2.3</sub> or C<sub>5.6</sub>), 84.2 (CH, 135.3 Hz, C<sub>7</sub>; 51.0 (CH, 150 Hz<sup>21</sup>, C<sub>1.4</sub>).

Norhornadiene-7-carboxylic acid methyl ester (1e). 4.01 (30 mmol) Ic was added in small portions to a 5-fold exces ethereal CH<sub>2</sub>N<sub>2</sub>-soln kept at 0°. After the gas evolution had ceased the mixture was stirred for an additional 30 min. Thei the mixture was concentrated at 0° under reduced pressure (ca 10 torr) and the residue was MDA-distilled (10 torr 80-100°), yield: 4.4 g (29 mmol, 97 %) colourless liquid. Gle (B, 130') revealed the presence of a single component Calculated for  $C_{9}H_{10}O_{2}$ : 150.0681; found: 150.0678; m/ 150 (8), 119 (25), 118 (100), 91 (69). IR (CCl<sub>4</sub>): 3072 (m), 300. (s), 2948 (m), 1732 (s), 1432 (m), 1330 (m), 1304 (m), 1215 (s) 1197 (s), 1023 (s), 658 (m). <sup>1</sup>H NMR : 3.11 (bt, 1.8 Hz, H<sub>7</sub>), 3.60 (s, CH<sub>3</sub>), 3.85 (psx, H<sub>1,4</sub>), 6.74 (pqi, H<sub>2,3,5,6</sub>). <sup>13</sup>C NMR: 169.( (C8), 142.1 (CH, 175.0 Hz, C2.3 or C5.6), 140.4 (CH, 176.5 Hz C2.3 or C5.6), 84.0 (CH, 138.3 Hz, C7), 50.6 (CH, 150 Hz<sup>21</sup> C1.4), 50.4 (CH3, 147.1 Hz, OCH3).

Norbornadiene-7-methanol (1f). To a stirred suspension o 1.2 g LAH in 140 ml anhyd diethyl ether 4.2 g (28 mmol 1e ii 40 ml anhyd diethyl ether was added dropwise. The resulting mixture was stirred for 16 hrs. The excess LAH was carefully destroyed with H<sub>2</sub>O. The ethereal layer was filtered and driec over MgSO<sub>4</sub>. The mixture was concentrated on a rotary evaporator (760 torr, 50°) and the residue MDA-distillec (10 torr, 80-100°), yield: 3.3 g (27 mmol, 96 %) colourles liquid. Glc (C, 120) showed the presence of a single component. Calculated for  $C_8H_{10}O$ : 122.0732; found 122.0735; m/e: 122 (8), 104 (14), 103 (9), 91 (100), 79 (19), 78 (54), 77 (34). 1R (CCl<sub>4</sub>): 3636 (m), 3320 (b, s), 3069 (m), 2980 (s), 2935 (m), 1543 (m), 1302 (m), 1018 (s), 650 (s). <sup>1</sup>H NMR 1.51 (variable, bs, OH), 2.72 (bt, 7.0 Hz, H7), 3.46 (psx, H1.4) 3.51 (d, 7.0 Hz, H<sub>8</sub>), 6.61 (bt, 1.8 Hz, H<sub>2.3</sub>), 6.86 (t, 2.0 Hz H<sub>5.6</sub>). <sup>13</sup>C NMR: 144.6 (CH, 171.3 Hz, C<sub>2.3</sub> or C<sub>5.6</sub>), 140.1 (CH, 172.8 Hz,  $C_{2,3}$  or  $C_{5,6}$ ), 87.0 (CH, 133.8 Hz,  $C_7$ ), 62. (CH<sub>2</sub>, 141.2 Hz,  $C_8$ ), 51.2 (CH. 148 Hz<sup>21</sup>,  $C_{1,4}$ ). The use c LAD instead of LAH afforded 1/-8-d, indicated b <sup>1</sup>HNMR to contain  $100 \pm 5\%$  8-d,

Norbornadiene-7-carbaldehyde (1d). Method A. To stirred soln of 70 mmol (0.3 M) radical anion<sup>13</sup> kept at -782.50 g (19.8 mmol) 1b in 2 ml anhyd THF was added with syringe. After 10 min 7.5 g anhyd DMF in 72 ml anhy ether was added. The resulting mixture was stirred for 1 hr a  $-78^\circ$ , then allowed to warm to room temp for 75 min. 50 n 2NHCl was added and the mixture was stirred for a additional hr. With the aid of 500 ml ether it was a transferred into a separatory funnel and the aqueous lay was separated. The ethereal layer was extracted with 100 r. H<sub>2</sub>O, 100 ml brine and dried over MgSO<sub>4</sub>. As 1d is ai sensitive these and further treatments of Id were as much possible performed in an inert atmosphere. The soln wfiltered and concentrated to cu 40 m at 760 torr. 160 ml H<sub>2</sub> was added and the mixture was steam distilled until the her temp reached 99.5° and crystals appeared in the cooler. Wi 50 ml ether the colourless distillate was transferred into separatory funnel. The aqueous layer was separated ai extracted twice with 50 ml ether. The combined ethere layers were washed with 15 ml brine and dried over MgSC After filtration the mixture was concentrated with a 10¢ vigreux column at 760 torr, and the residue MDA-distill (11 torr, 40-62), yield: 1.24g (10.4 mmol, 52 ") colourle liquid. Glc (A, 106<sup>°</sup>) indicated the presence of a sin<sub>i</sub> component. Calculated for C<sub>8</sub>H<sub>8</sub>O: 120.0575; four 120.0573; m/e: 120 (8), 119 (9), 105 (2), 92 (17), 91 (100), 78 ( IR (CCl<sub>4</sub>). 3075 (m), 2995 (m), 2812 (m), 2715 (m), 1720 1546 (m), 1303 (m), 651 (m).  $^1\rm H\,NMR$ : 3.04 (btd, 1.7 a 1.7 Hz, H<sub>2</sub>, 3.92 (ps, H<sub>1,4</sub>), 6.79 (t, 2.0 Hz, H<sub>2,3</sub> or H<sub>5,6</sub>), 6 (t, 2.0 Hz, H<sub>2,3</sub> or H<sub>5,6</sub>), 9.43 (d, 1.7 Hz, H<sub>8</sub>). <sup>13</sup>C NMR : 20 (CH, 172.1 Hz, C<sup>\*</sup><sub>8</sub>), 143.0 (CH, 170.6 Hz, C<sub>2.3</sub> or C<sub>5.6</sub>), 14

(CH, 175.0 Hz, C<sub>2.3</sub> or C<sub>5.6</sub>), 92.0 (CH, 135 Hz<sup>21</sup>, C<sub>7</sub>), 50.1 (CH, 150 Hz<sup>21</sup>, C<sub>1.4</sub>).

Method B. To a soln of 3.28 g (26.9 mmol) If and 17.0 g dicyclohexyl carbodiimide in 50 ml anhyd benzene and 11.4 ml anhyd DMSO 1.3 g H<sub>3</sub>PO<sub>4</sub> was added all at once. The resulting mixture was stirred at room temp for 18 hr, then diluted with 40 ml ether and 10.2 g oxalic acid dihydrate was carefully added. After the gas evolution had ceased the mixture was filtered off and the filtrate extracted 3 times with 80 ml H<sub>2</sub>O, washed once with brine and dried over MgSO<sub>4</sub>. For further work-up: see method A. The use of 11-8-d<sub>2</sub> afforded 14-8-d<sub>1</sub> indicated by <sup>1</sup>H NMR to contain 100  $\pm$  5% 8-d<sub>1</sub>.

Tosythydrazones (1g and 1h). 1g and 1h were prepared according to ref. 17, yield: 92% small white needles, m.p. 140–141" (dec). Calculated for  $C_8H_9N_2$ :† 133.0766; found; 133.0761; m/e: 133 (100), 91 (30). 1R (1g, CHCl<sub>3</sub>): 3205 (m), 3070 (m), 3023 (m), 1599 (m), 1547 (m), 1496 (m), 1417 (m), 1363 (m), 1327 (m), 1307 (m), 1188 (m), 1168 (s), 1093 (m), 1045 (m), 945 (m), 923 (m), 813 (m), 705 (m), 622 (m), 'H NMR (1g): 2.42 (s, CH<sub>3</sub>), 3.16 (bdt, 65 and 1.5 Hz, H<sub>7</sub>), 3.49 (psx, H<sub>1,4</sub>), 6.58 (bt, 2.0 Hz, H<sub>2,3</sub>), 6.81 (t, 2.1 Hz, H<sub>5,6</sub>), 7.05 (d, 6.5 Hz, H<sub>8</sub>), 7.32 (bd, 2H, 8.2 Hz, Ar-H), 7.51 (variable, bs, N-H), 7.79 (md, 2H, 8.2 Hz, Ar-H). The use of 1d-8-d<sub>1</sub> afforded 1h which was shown by 'H NMR to contain 100  $\pm$  5", 8-d<sub>1</sub>.

Syn- and anti-7-Norbornenyl carbaldehyde. Procedure A given for 1d was used with 801.0 mg (4.6 mmol) syn-7-bromonorbornene except that the mixture was MDA-distilled (9 torr, ca 80) immediately after concentration, yield: 281.0 mg colourless distillate. Preparative glc (D, 103) afforded 188 mg (1.5 mmol; 35%) anti-7-norbornenyl carbaldehyde (rel. ret. vol.: 0.64; m/e: 122 (17), 94 (33), 91 (26), 77 (31), 66 (100), IR (CCl<sub>4</sub>): 3073 (m), 2985 (s), 2879 (m), 2802 (m), 2700 (m), 1721 (s), 1570 (m), 1321 (m), 1124 (m), 874 (m), 679 (m). <sup>1</sup>H NMR: 1.09 (m, H<sub>5.6.endu</sub>), 1.67 (m, H<sub>5.6exu</sub>), 2.32 (psx, H<sub>7</sub>), 3.13 (psx, H<sub>1.4</sub>), 6.10 (t, 2.0 Hz, H<sub>2.3</sub>), 9.53 (d, 1.5 Hz, H<sub>8</sub>)), 50 mg (0.4 mmol, 10<sup>1</sup>/<sub>2</sub>) syn-7-norbornenyl carbaldehyde (rel. ret. vol.: 0.78; m/e: 122 (5), 91 (17), 86 (35), 84 (55), 78 (35), 66 (100). IR (CCl<sub>4</sub>): 2983 (s), 2948 (s), 2876 (m), 1720 (s), 1331 (m), 872 (m), 719 (m). <sup>1</sup>H NMR: 1.10 (m, H<sub>5.9</sub>, enda). 1.77 (m, H<sub>5.6,exa</sub>), 2.20 (m, H<sub>7</sub>), 3.17 (psx, H<sub>1.4</sub>), 6.06 (bt, 1.8 Hz,  $H_{2,3}$ ), 9.66 (d, 3.4 Hz,  $H_8$ )) and 43 mg starting material (rel. ret. vol.: 1.00). The syn aldehyde was synthesized independently.<sup>22</sup> To prove that the other aldehyde was a stereoisomer both aldehydes were reduced to the corresponding alcohols according to ref. 22 and catalytically hydrogenated to the same alcohol, bicyclo-[2.2.1]heptane-7methanol.23

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# $\dagger$ These compounds do not yield a molecular ion corresponding to the formula $C_8H_9N_2SO_2C_7H_7$ .