

THE REACTION OF 7-CHLORONORBORNADIENE WITH n-BUTYLLITHIUM
A NOVEL REARRANGEMENT OF NORBORNADIENYL ANION

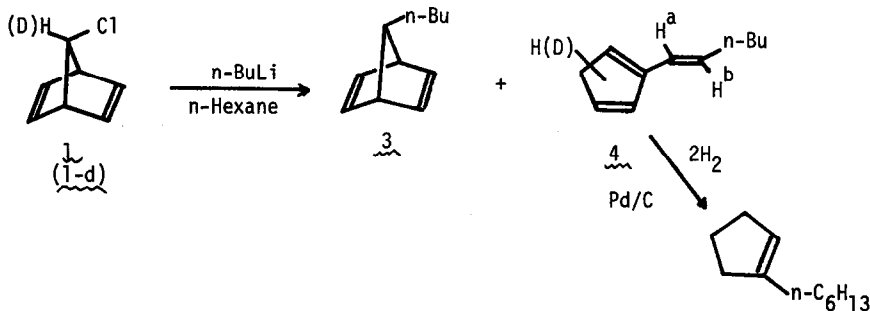
Shun-Ichi Murahashi, Ken-ichi Hino, Yusuke Maeda, Ichiro Moritani
Department of Chemistry, Faculty of Engineering Science,
Machikaneyama, Toyonaka, Osaka, Japan, 560

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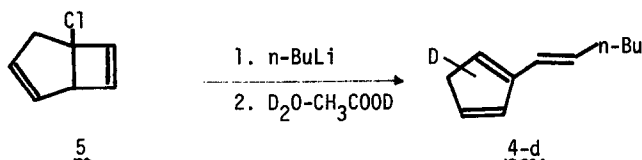
Norbornadienyliene is of interest since extended calculation predicted that norbornadienyliene would have the definitive probability of a singlet state stabilized nonclassical methylene (1). A possible α -elimination of 7-chloronorbornadiene (1) (2) to overcome the antiaromatic destabilization (3) of 7-norbornadienyl anion was examined. We now report that addition of n-butyllithium to the double bond of 1 favors over metalation at the 7-position of 1 giving 6-chloronorbornenyl anion (2) which undergoes subsequent new rearrangement resulting in 1,3-elimination. Recently, the structure of norbornenyl anion was focussed on in connection to a symmetrical nonclassical anion and a classical 3-norbornenyl anion (4).

Reaction of the chloride 1 with one-equivalent of n-BuLi in n-hexane at 0° produced C₁₁H₁₆ hydrocarbons in 60 % yield. Vpc analysis indicated the presence of two components in a 5 : 1 ratio. The minor product was assigned as 7-n-butylnorbornadiene (3) by comparison with the authentic sample derived from 7-t-butoxynorbornadiene and n-BuMgBr. The main highly unstable olefin (4) was purified by short-path distillation (90°/2 mm Hg). The nmr spectrum exhibited five vinyl protons at 6.50-5.50 (m), two allyl protons at 2.93 (s), two allyl protons at 2.08 (m), four methylene protons at 1.7-1.1 (m), and three methyl protons at 0.89. Double irradiation experiment indicated trans-configuration of 4 ($J_{H^aH^b} = 15$ Hz). This seems to be consistent with that expected to 2-(1-trans-n-hexenyl)cyclopentadiene (4). Confirmation of this structural assignment was achieved either by hydrogenation over Pd/C leading to 1-n-hexylcyclopentene or by treatment with TCNE leading to the cyclo-adduct, which showed satisfactory elemental analysis, mp 127-128°, m/e 276, nmr δ 6.4-6.25 (H, m), 6.05-5.78 (2H, m),

4.03 (H, m), 3.27 (H, m), 3.05 (2H, m), 2.3-1.7 (2H, m), 1.7-1.1 (4H, m), and 0.95 (3H, t).



A possible mechanism responsible for the formation of 4 via α -elimination was examined. Norbornadienylidene, if formed via α -elimination, would undergo, as seen in norbornenylidene (5), intramolecular rearrangement into bicyclo[3.2.0]heptatriene to which β -elimination of 5-chlorobicyclo[3.2.0]hept-2,6-diene (5) (6) would alternatively lead. Treatment of the chloride 5 with two equivalent of n-BuLi gave 4-d exclusively in 52 % yield. Therefore, α -elimination would be apparently involved in the reaction of 1 with n-BuLi. To clarify this point, reaction of 7-d-7-chloronorbornadiene (1-d) (8) with n-BuLi was carried out. If α -elimination is involved, the product 4 should not contain the deuterium. Actually, the product was the deuterated 4-d, and hence the α -elimination mechanism was completely eliminated.

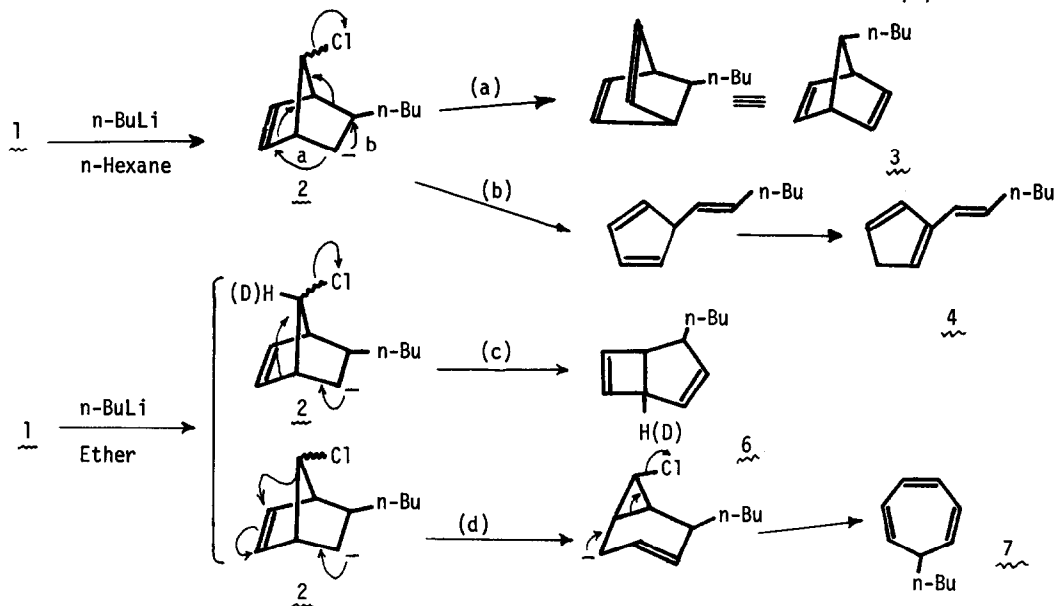


Interestingly, a solvent affects drastically on the products of this reaction.

Treatment of 1 with n-BuLi in ether at 0° afforded two C₁₁H₁₆ hydrocarbons in addition to 3 (4 %) and 4 (~1 %). The newly formed minor product was assigned as 7-n-butylcycloheptatriene (7) (5 %), bp 67-68°/7mmHg, nmr δ 6.54 (2H, t, J=2 Hz), 6.05 (2H, m), 5.05 (2H, q, J=5 Hz), 1.9-1.1 (6H, m) and 0.91 (3H, t, J=5 Hz). An authentic sample was prepared from tropylium perchlorate and n-BuMgBr. The nmr spectrum of the major component exhibited absorptions centered at δ 6.25 (H¹, d, J=3 Hz), 5.97 (H², d, J=3 Hz), 5.8-5.4 (H⁵, H⁶, m), 3.58 (H³, q) 2.87 (H⁷, m), 2.35 (H⁴, m), 1.31 (6H, m), and 0.93 (3H, t, J=6 Hz). This seems to be consistent with that expected to 4-n-butylbicyclo[3.2.0]hepta-2,6-diene (6) (40 %). Confirmation of this

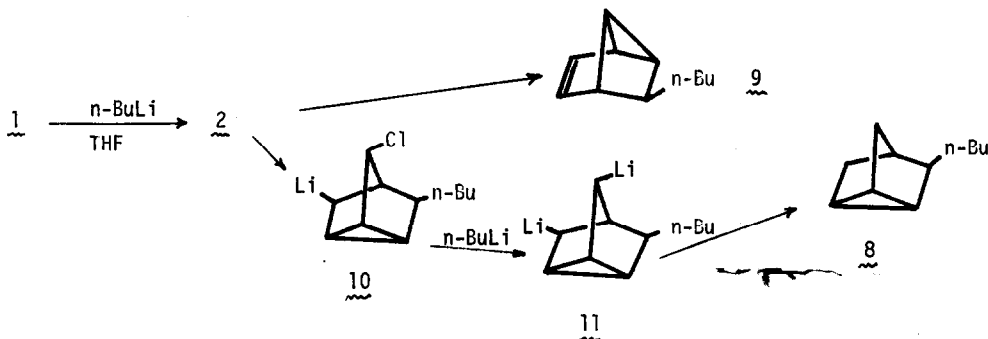
structural assignment was achieved by comparison of their spectral data with those of the authentic sample prepared by photochemical cyclization of 7 (8). Similar reaction of the d-labeled chloride (1-d) with n-BuLi afforded H¹-d-labeled 6.

Formation of 3-4 and 6-7 would be rationalized by addition of n-BuLi to the double bond of 1 giving a norbornenyl anion intermediate 2 which subsequently undergoes anionic rearrangement. Controlled experiments indicated no isomerization of these products occurred under the reaction conditions. The rearrangement of type (a), (b) and (d) have been demonstrated by reactions of 7-methoxynorbornadiene with t-BuLi (9), dehydronorbornyl chloride with sodium (10), and 7-acetoxynorbornadiene with LiAlH₄ in THF (11), respectively. Nevertheless, the interesting rearrangement giving 6, which may be elucidated by a course (c), finds no example in an anionic reaction, although this is a typical case of the degenerated carbonium ion of C₇H₇⁺ (12).



Furthermore, when the same reaction was performed in THF, the products consisted of two new C₁₁ hydrocarbons (25 %) in addition to 3 (10 %), 4 (10 %) and 7 (~1 %). 3-n-Butylnortricyclo[4.1.0.0^{3,7}]hept-4-ene (8) was assigned by comparison of an authentic sample (13). The structure of 2-n-butyltricyclo[4.1.0.0^{3,7}]hept-4-ene (9) was established by the nmr spectrum which exhibited similar pattern with that of tricyclo[4.1.0.0^{3,7}]hept-4-ene including the peculiar absorption of the endo-2 proton (14), nmr δ 5.78 (2H, m, vinyl), 2.85 (H, m, bridge head), 2.35-1.1 (9H, m,

cyclopropane and butyl), 0.90 (3H, t), and 0.90 (H, d-d, endo-2). Feasibly stabilized anion 2 in polar THF may have enough time to undergo either 8 directly or rearrangement into 10 followed by further halogen-metal interconversion leading to the dianion 11.



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