Action of Methyl-lithium on 8,8-Dibromobicyclo[5,1,0]oct-3-ene. Preparation and Reactions of Some *endo*-Tricyclo[3,2,1,$0^{2,4}$]octane Derivatives

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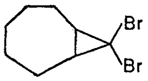
Summary Structure (**3**) has been assigned to a compound obtained, in 94% yield, by the action of ethereal methyl-lithium on 8,8-dibromobicyclo[5,1,0]oct-3-ene (**2**); some reactions of (**3**) and its dehydrobromination product (**4**) are described.

A very convenient general method for the synthesis of allenes[1,2] involves the treatment of 1,1-dibromocyclopropanes with lithium alkyls. Although larger ring cyclic allenes may be prepared in high yields by this procedure,[1] treatment of 8,8-dibromobicyclo[5,1,0]octane (**1**) with methyl-lithium in ether solution gave[3] other products in addition to the expected allene.

We now report that when 8,8-dibromobicyclo[5,1,0]oct-3-ene (**2**) was treated with methyl-lithium in ether solution under conditions such that a gentle rate of reflux was maintained, a sole product, which we believe to be *syn*-8-bromo-*anti*-8-methyl-*endo*-tricyclo[3,2,1,$0^{2,4}$]octane (**3**) was obtained as a colourless solid, m.p. 41—42°, in 94% yield. The structure assigned to (**3**) rests on its elemental composition, its mass [M^+ at m/e 200, 202(1:1)] and n.m.r. [(CCl_4) τ 7·91 (m, 2H), 8·27 (s, 3H), 8·4 (m, 4H), 8·7—9·3 (m, 4H)] spectra, and on its chemical reactions. Treatment of (**3**) with KOBu^t in Me$_2$SO solution for 16 h at 20° gave the olefin (**4**), which was isolated as a colourless liquid, b.p. 49—51°/14 mm in 67% yield [n.m.r. (CCl$_4$) τ 5·82 (s, 2H), 7·72 (m, 2H), 8·5—9·4 (m, other protons)]. When (**4**) was stirred with an aqueous solution of sodium periodate, sodium carbonate, and potassium permanganate for 18 h at 20°, *endo*-tricyclo[3,2,1,0^{2,4}]octan-8-one (**5**) was obtained; the latter compound, which was isolated as a colourless solid, m.p. 69—70° (lit.[4] 71—72°) in 59% yield had identical spectroscopic (n.m.r., i.r., m.s.) properties to those previously described[4,5] for (**5**).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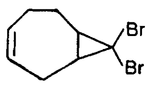
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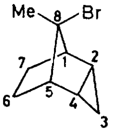

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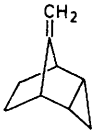

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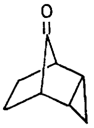
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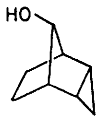

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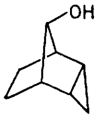

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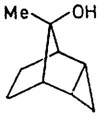


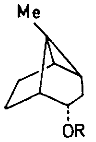
(8)

The structure of (**3**), except for the configuration at C-8, follows from the above data. As the rate of hydrolysis of the *p*-nitrobenzoate ester of (**6**) in 70% aqueous dioxan was found[5c] to be *ca.* 10^{11} times as fast as that estimated for the *p*-nitrobenzoate of the corresponding *syn*-alcohol (**7**), it seemed likely that solvolytic studies on (**3**) would provide evidence relating to its configuration at C-8. Indeed, convincing evidence that (**3**) was the *syn*-bromo-compound came from a comparison of its rate of hydrolysis with that of the mesylate ester of the *syn*-alcohol (**8**).†

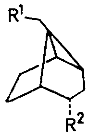
The hydrolysis product of both (**3**) and the mesylate ester of (**8**) was the rearranged alcohol, 5-methyl-*endo*-tricyclo-[3,3,0,0^{4,6}]octan-2-ol (**9a**). The latter compound was obtained rapidly and in virtually quantitative yield by treating (**3**) with silver perchlorate in aqueous acetone (5:95) solution at 20°; it was characterized as its *p*-nitrobenzoate ester (**9**; R = COC$_6$H$_4$NO$_2$), m.p. 100—101°. Similarly, treatment of (**3**) with silver perchlorate in methanol solution gave the corresponding rearranged methyl ether (**9b**). The n.m.r. spectra of (**9a**) and (**9b**) both display a double-triplet (*J* 6·5 and 9 Hz) which is characteristic of the methine proton resonance of an *endo*-2-substituted tricyclo[3,3,-0,0^{4,6}]octane derivative.[4,5,7]

Reaction of the olefin (**4**) with electrophilic reagents also gave rearranged products. Thus when (**4**) was treated with a stoicheiometric amount of bromine in dichloromethane solution at *ca.* −10°, *endo*-2-bromo-5-bromomethyltricyclo-[3,3,0,0^{4,6}]octane (**10**; R^1 = R^2 = Br) [n.m.r. (CCl$_4$) τ 5·64 (dt, *J ca.* 6 and 9 Hz, 1H), 6·23 (d, *J* 10·5 Hz, 1H), 6·45 (d, *J* 10·5 Hz, 1H), 7·1—9·3 (m, other protons)] was obtained in 96% yield. When (**4**) was treated with *m*-chloroperbenzoic acid in chloroform solution at 20°, (**10**; R^1 = OH, R^2 = OCOC$_6$H$_4$Cl) was obtained and not the expected epoxide.

The conversion of 8,8-dibromobicyclo[5,1,0]oct-3-ene (**2**) into (**3**), which appears to be mechanistically related to the methyl-lithium promoted conversion of 7,7-dibromobicyclo-[4,1,0]hept-2-ene (**11**) into (**12**),[8] possibly involves the bicyclic carbene (**13**). The latter species could rearrange *via* (**14**) to give the tricyclic carbene (**15**). However, whether or not (**15**) is an intermediate, it remains unclear why the formation of (**3**) is so stereoselective with respect to the configuration at C-8. In addition to its mechanistic interest, the conversion of (**2**) into (**3**) represents perhaps the most convenient synthetic entry into the *endo*-tricyclo-[3,2,1,0^{2,4}]octane and thence into the tricyclo[3,3,0,0^{4,6}]-octane ring system.



(9) a; R = H
b; R = Me



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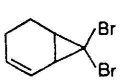

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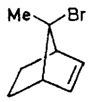

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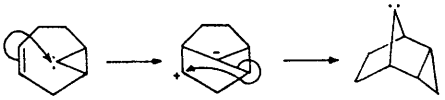
(13) (14) (15)

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† The *syn*-alcohol (**8**), m.p. 69—70°, was the sole product obtained when the ketone (**5**) was treated with methyl-lithium in ether solution. Spin-decoupling of the Eu(dpm)$_3$-shifted n.m.r. spectrum[6] of (**8**) indicated that its hydroxy-group was *syn* to the cyclopropane ring. Additional support for this assignment came from the observation that the *p*-nitrobenzoate ester of (**8**) was particularly resistant to hydrolysis.

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