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SYNTHESIS OF NORBORNENE ENDO-EPOXIDE (3-OXATRICYCLO $[3.2.1.0^{2,4}]$ OCTANE).

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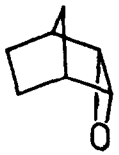
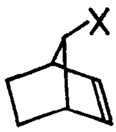
Epoxidation of norbornene derivatives usually proceeds according to the "exo-addition rule", so that the exo-isomers are the predominant products of the reaction. Endo-epoxy derivatives are thus very rare and have been little studied.[1]

In the present paper we describe the synthesis of 3-oxatricyclo $[3.2.1.0^{2,4}]$ octane (1), the parent of an endo-epoxy series. The key idea of the synthesis was to use as starting material a compound of type 2 with a syn substituent in position 7, such as would a)provide steric hindrance to exo-attack on the double bond and b)be easily removed without rupture of the epoxy ring. We chose as such a starting compound 7-syn-bromonorbornene (3). Although the bromine atom has effectively small steric requirements in ordinary cyclohexane systems, its steric effect can become quite considerable in many cases[2] and it acts as a sufficiently "large" substituent in the position 7 of norbornene.

Compound 3 was synthesized by a modification of the procedure described by H.Kwart and L.Kaplan[3]. Epoxidation of 3 gave a 1:1.8 mixture of the epoxides 4 (m.p 68.5-69.6°, from hexane) and 5 (b.p.103-104° /17mm/, n_D^{20} 1.5367) in 80% yield which were isolated and purified by chromatography on silica gel (ether-hexane 1:1).



1



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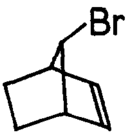

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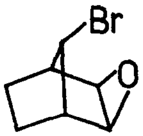

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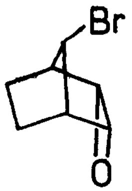

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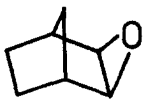

6

Reduction of **5** with tributyltin hydride at 140° and simultaneous sublimation of the resultant crystalline solid gave the endo-epoxide **1** (yield 65%): m.p.109.5-111.5°C; ^{1}H-NMR spectrum (δ,ppm): 3.5(broad s.,H-C_2,H-C_4), 2.24(s., H-C_1,H-C_5), 1.98(d.of quintets,syn H-C_8), 1.2-1.7(m.,anti H-C_7 and 4H of CH_2 groups); $J_{1,2}=J_{4,5}=2.2$ Hz, $J_{1,4}=J_{2,5}=1.0$ Hz, $J_{8s,8a}=9.2$ Hz, $J_{C^6H_2}=J_{C^7H_2}=9.0$ Hz, $J_{8s,1}=J_{8s,5}=J_{8s,6endo}=J_{8s,7endo}\sim 2$ Hz.

The spectral data of **1** differ remarkably from those of the corresponding exo-epoxide **6**.

Noteworthy are (a), the 0.5 ppm upfield shift of the H_2,H_4 signal in the PMR spectrum of exo-6 relative to endo-1, (b), an upfield shift of 0.65 ppm in the C^8H_2 signal of **6** (anti-H-C_8 0.67 ppm and syn-H-C_8 1.33 ppm). A similar shift difference is displayed in the spectra of **4** and **5**.

The configuration of the epoxide ring affects still more dramatically the ^{13}C-NMR spectra. The ^{13}C chemical shifts of **1**,**6**,**5** and **4** are as follows (15.08 MHz, $CDCl_3$, internal HMDS /1.95 ppm/, 20°C, δ ppm): C_1,C_5-37.8(**1**), 36.8(**6**), 44.4(**5**), 42.3(**4**); C_2,C_4-62.0(**1**),51.2(**6**),61.7(**5**),51.4(**4**); C_6,C_7-25.6(**1**),25,2(**6**),24.5(**5**), 24.3(**4**); C_8-50.6(**1**),26.3(**6**),69.0(**5**),43.0(**4**). Signal assignment was carried out by means of selective ^{13}C-$\{^1H\}$ double resonance experiments. The assignments for **1** and **6** agree with those given by Davies and Whithem[4].

Comparison of the ^{13}C-NMR chemical shifts of the exo and endo compounds reveals remarkable differences. First, the epoxy ring carbon signals of the exo-compounds are shifted distinctly upfield from the respective signals of the endo-compounds. Secondly, and of considerable interest is the drastic upfield shift of C_8-exo relative to C_8-endo, equal to 24-26 ppm, which is very large even on the ^{13}C-NMR scale.

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