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1-BENZOXEPIN AND ITS VALENCE ISOMERS, 4,5-BENZ-3-OXATRICYCLO[4.1.0.0^{2,7}]HEPTENE AND 3,4BENZ-2-OXABICYCLO[3.2.0]HEPTA-3,6-DIENE

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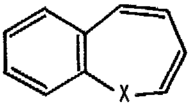
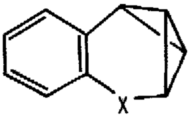
We have reported recently the synthesis of the valence isomers, (*2a*)[1] (*3a*)[1], (*2b*)[2,3], and (*3b*)[3], of the benzannelated cyclic conjugated systems such as (*1a*) and (*1b*)[4]. In order to clarify the chemical and physical properties of the bicyclo[1.1.0]butane incorporated in the cyclic conjugated framework, our attention was turned to a study of the synthesis of (*2*) in which the group X was substituted by an oxygen atom (*2c*).


(*1*)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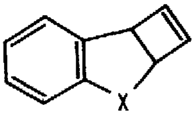
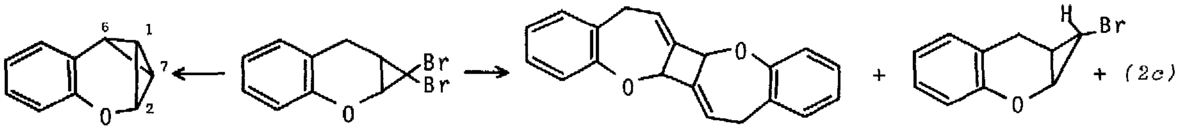

(*3*)

a: X=CH_2
b: X=S
c: X=O

The transformation of 7,7-dibromo-3,4-benz-2-oxabicyclo[4.1.0]heptene (*4*)[5] into 4,5-benz-3-oxatricyclo[4.1.0.0^{2,7}]heptene (*2c*) by the procedure developed by Moore[6] gave some initial difficulty. Treatment of *4* with excess *n*-butyllithium in refluxing hexane for 30 min gave as the major product, colorless plates of mp. 67-68.5°C (~33% yield), a compound whose mass spectrum (*m/e* 288, 144) suggests a dimeric product bearing a cyclobutane moiety, tentatively assigned structure (*5*)[7,8], corresponding to the initial formation of the cyclic allene, along with *exo*-7-bromo-3,4-benz-2-oxabicyclo[4.1.0]heptene (*6*)[5] and a minor amount of the desired *2c*. Methyllithium also failed to give appreciable amounts of the desired product. Successfull preparation of *2c* was achieved *by use less than an equivalent of n-butyllithium in stirred boiling cyclohexane* *under nitrogen atmosphere for a short period*; this gave yields of 20-25% *2c* along with 22% recovery of *4*.



(*2c*) (*4*) (*5*) (*6*)

In a typical experiment, a 500 ml three necked flask containing a magnetic stir bar and equipped with a condenser, a nitrogen inlet, and a dropping funnel was flushed with nitrogen and charged with 0.9 g (2.9 mmol) of *4* and 100 ml of cyclohexane (freshly distilled over $LiAlH_4$). While stirring and refluxing, 0.83 equivalent of *n*-butyllithium in hexane was added at once. After refluxing for ~1 min the reaction mixture was quenched with water and the aqueous layer was extracted with cyclohexane. The combined organic layer was dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was chromatographed on a short column of basic alumina (with 5% of ammonia water). Elution with cyclohexane gave a mixture of *4* and *2c*. After separation of crystallized *4* (200 mg, 22%) by trituration with hexane, the residue was distilled through a short-path distillation at 60-65°C (bath)/3 torr afforded 65-70 mg (20-25% yield based on the consumed *4*) of *2c*.

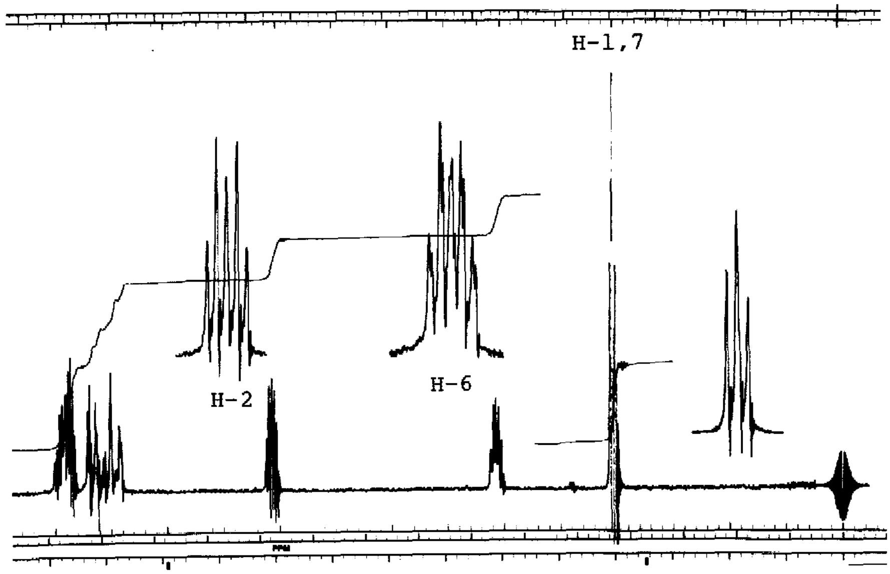
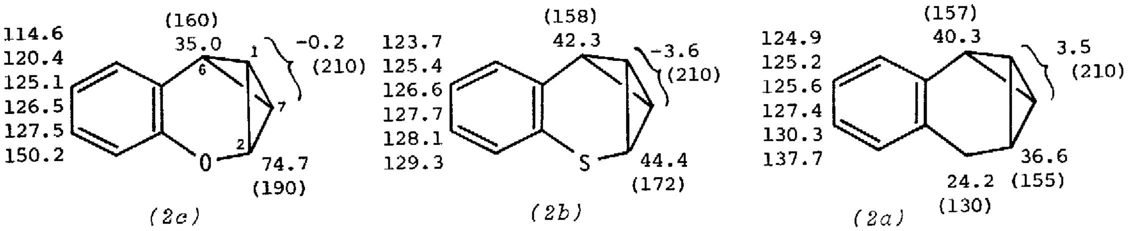


Fig. 1. 100 MHz Nmr spectrum of *2c*.

The structure of the bicyclobutane (*2c*) was based on its spectral characteristics [UV, λ_{max}(cyclohexane):233 nm(log ε 3.51), 237(s, 3.49), 246(s, 3.22), 279(3.29), 285.5(3.55); ^{1}H-NMR(100 MHz, CCl_4, see also Fig. 1):δ 2.02(t, $J_{1(7),2}=J_{1(7),6}=2.0$ Hz, H-1,7), 3.07(dtd, $J_{6,2}=4.8$ Hz, $J_{6,1(7)}=2.0$ Hz, $J_{6,arom.}\simeq 0.5$ Hz, H-6), 5.07(dt, $J_{2,6}=4.8$ Hz, $J_{2,1(7)}=2.0$ Hz, H-2), 6.4-7.0(m, arom)]. The FT ^{13}C-NMR spectrum[9] of *2c* was most informative and consists signals depicted in Fig. 2. Assignments are based upon comparison to *2a* and *2b*, and off-resonance spectrum.

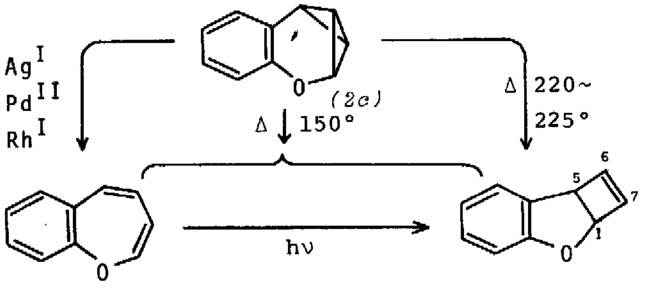


(*2c*) (*2b*) (*2a*)

Fig. 2. ^{13}C-Nmr parameters of (*2c*) compared with those of (*2b*) and (*2a*).

Chemical shifts are δ-values relative to tetramethylsilane. Coupling constants with directly bonded hydrogens are given in parentheses (Hz).

When a solution of *2c* in benzene was treated with silver perchlorate at room temperature for 30 min clean conversion was observed with the formation of 1-benzoxepin (*1c*)[10,11,12], the nmr and ir spectra of which were identical with those in the literature. In contrast to the case of *2a*[1], reaction of *2c* with π-allylpalladium chloride dimer or rhodium dicarbonyl chloride dimer in chloroform afforded again *1c* in 95% yield. These valence isomerizations of *2c* promoted by transition metal catalysts constitute a convenient synthesis of the heterocycle (*1c*)[10,11,12].



(*1c*) (*3c*)

The thermal reaction of *2c* was examined by heating a carbon tetrachloride solution of *2c* at 150°C. After 45 min the reaction proceeded smoothly giving 86% of a 1:1 mixture of *1c* and new isomer, 3, 4 -benz-2-oxabicyclo[3.2.0]hepta-3,6-diene (*3c*)[7], whereas when *2c* was subjected thermolysis in carbon tetrachloride at 220-225°C for 10 min *3c* was obtained as a sole product in 95% yield. Assignment of structure of *3c*, pale yellow oil, rests on elemental analysis and spectroscopic data [UV, λ_{max}(cyclohexane): 217 nm (log ε 3.71), 285(3.56), 291(3.56); ^{1}H-NMR, δ($CDCl_3$):4.34(bd, $J_{5,7}$=0.8 Hz, H-5), 5.47(dd, $J_{1,5}$=1.8 Hz, $J_{1,6}$=1.3 Hz, H-1), 6.08(dd, $J_{7,6}$=1.4 Hz, $J_{7,5}$=0.8 Hz, H-7), 6.59(t, $J_{6,1}$=1.3 Hz, $J_{6,7}$=1.4 Hz, H-6), 6.68-7.26(m, arom.)]. Finally *3c* was also obtained by irradiation of *1c* in tetrahydrofuran with 100-w high pressure Hg lamp.

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7) Satisfactory elemental analyses were obtained for new compounds described in this paper.

8) ^{1}H-nmr of (*5*) : δ 2.39(2H, d, J=1.0 Hz), 3.24(2H, dd, J=7.4, 3.9 Hz), 3.44 (2H, dd, J=7.4, 4.6 Hz), 5.22(2H, ddd, J=4.6, 3.9, 1.0 Hz), 6.6-7.2(8H, m).

9) ^{13}C-FT-nmr spectra were taken with a Varian XL-100-15 FT-NMR spectrometer at 25.2 MHz.

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