

THE REACTIONS OF BREXADIENE - A NEW NORBORNENE-LIKE CAGED DIENE

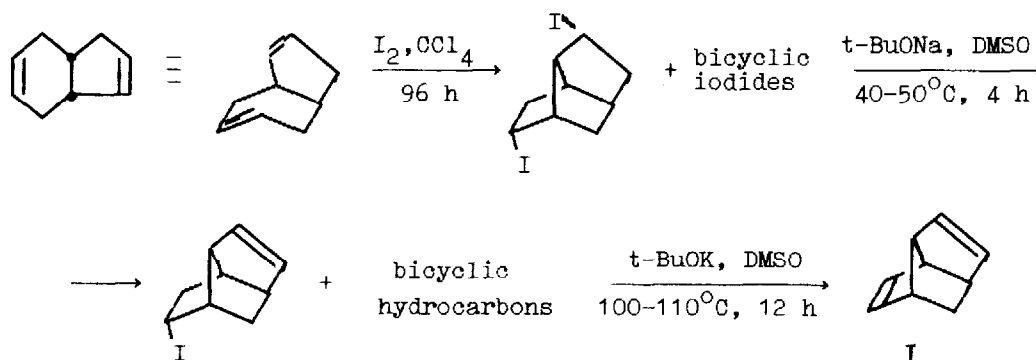
A.A.Bobylyova^a, N.F.Dubitskaya^a, A.V.Khoroshutin^a,
 T.I.Pehk^b, N.A.Belikova^a

^aPetroleum Chemistry Chair, Department of Chemistry,
 Moscow State University, Moscow, 119899, USSR

^bInstitute of Chemical and Biological Physics of the
 Estonian Academy of Sciences, Tallinn, 200001, USSR

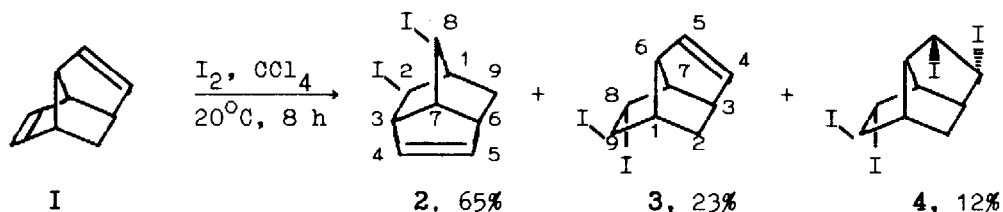
Summary: The reactions of brexadiene I with bromine, iodine, deuterio-tri-fluoroacetic and tetradeuteroacetic acid are described. These reactions proceed mainly as electrophilic exo-attack followed by Wagner-Meerwein rearrangement.

In the preceding paper¹ we reported the synthesis of a new norbornene-like caged diene, namely tricyclo[4.3.0.0^{3,7}]nona-4,8-diene (brexadiene), possessing C₂-symmetry. The scheme of the synthesis is as follows.

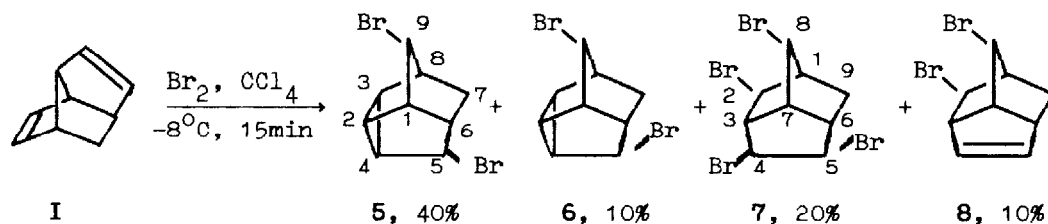


In this article we report some preliminary results concerning Ad_E-reactions of the diene I. The main product of its iodination was syn-8,exo-2-diiodobrend-4-ene 2. Besides, the mixture contained substantial amounts of endo-8,exo-9-diiodobrex 4-ene 3 and symmetrical tetraiodobrexane 4. The latter was poorly soluble in most organic solvents and was successfully recrystallized from the mixture of hexane, CHCl₃ and CH₂Cl₂ (1:2:2) to satisfactory elemental analysis. Structural and configurational assignments were made on the basis of ¹H and ¹³C NMR spectra on Bruker AM-500 instrument at 11.7T using results of previous studies², additivity of substituent effects and by means of 2D ¹H-¹H and ¹H-¹³C COSY experiments³. The 2 to 4 ratios were determined by GLC analysis of

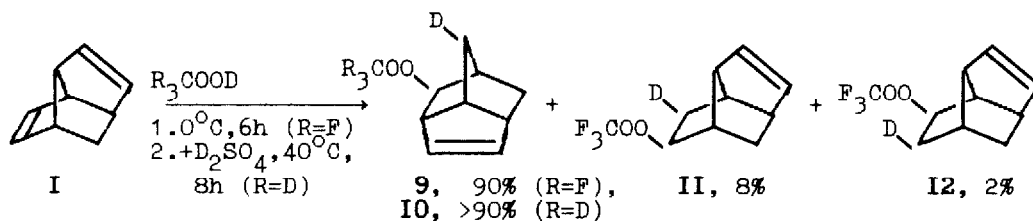
the reaction mixture reduced to hydrocarbons by LiAlH_4 .



The study of the mixture from the bromine addition revealed no compounds having brexane structure except unreacted brexadiene **I** (20%). Moreover, the main products were 5,9-dibromoisodeltacyclanes **5** and **6**, which indicates that the trapping of the internal nucleophile (the double bond) occurs prior to that of the external one (the bromine anion). One could infer, as to tetrabromobrendane **7**, that its formation is not the result of its hypothetical precursor bromination (i.e. dibromide, analogous to **3**) because of the reversed C-4 and C-5 substituents orientation expected for in that case.⁴

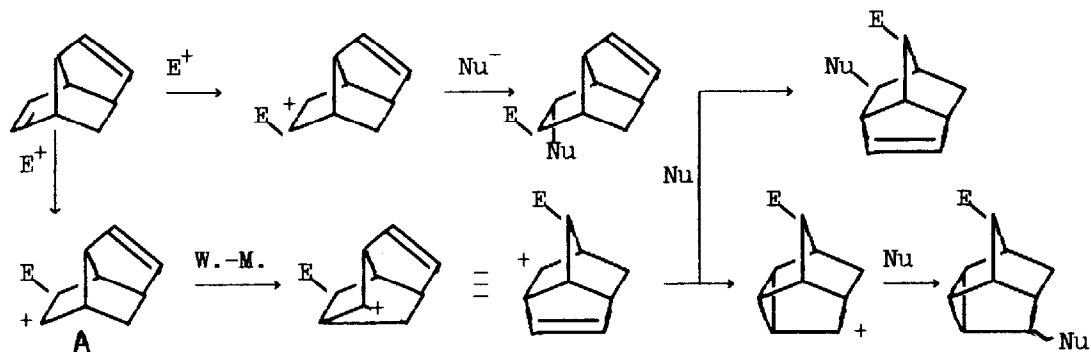


Deuterated organic acids react with brexadiene to form the mixture of esters with those of syn-8-deutero-exo-2-brend-4-enol **9**, **10** being predominant. Identifications of the minor products by NMR was successful only for trifluoroacetates.⁵ Deuterium orientation is consistent with ^2H NMR spectrum.



Thus, all the studied electrophiles attack the double bond from the exo side of the molecule with subsequent Wagner-Meerwein rearrangement of **A** to form predominantly derivatives of brendene and isodeltacyclane, the extent of rearrangement depending on the nature of electrophilic agent. For example, the difference in the addition of halogens could be at-

tributed to the lower nucleophilicity of bromide than that of iodide. (See next page)



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References and notes.

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²A.A.Bobylyova, E.V.Golubeva, N.F.Dubitskaya, T.I.Pehk, N.A.Belikova, *Zh.Org.Khim.*, 21(3), p.680, (1985); N.F.Dubitskaya, E.A.Khaibullina, T.I.Pehk, Yu.K.Grishin, N.A.Belikova, A.A.Bobylyova, *Zh.Org.Khim.*, 21(8), p.1738, (1985); V.A.Arbuzov, G.G.Gevorkyan, T.I.Pehk, A.A.Bobylyova, N.A.Belikova, *Zh.Org.Khim.*, 20(6), p.1226, (1984); G.G.Gevorkyan, M.D.Orudbadi, Tesfaye Lemma, T.I.Pehk, N.A.Belikova, S.N.Anfilogova, A.A.Bobylyova, *Zh.Org.Khim.*, 21(9), p.1891, (1985), see also ref.¹

³NMR chemical shifts for **2** to **4** (reported from H(C)-1 to H(C)-9; methylene groups protons chemical shifts:exo(syn)/endo(anti)): ¹H NMR (CDCl₃) δ **2**: 2.79, 3.83, 3.15, 6.16, 6.08, 2.47, 3.11, 4.16, 1.65/1.35; **3**: 2.13, 1.60/0.92, 2.52, 6.14, 6.00, 3.38, 2.35, 4.48, 4.62; **4**: 2.57, 1.55, 2.57, 4.29, 4.77, 3.03, 3.03, 4.77, 4.29 ¹³C NMR (CDCl₃) δ **2**: 54.5, 28.4, 56.5, 137.3, 139.2, 40.0, 62.7, 27.0, 38.2; **3**: 44.6, 34.5, 46.8, 137.5, 130.6, 49.7, 66.8, 31.2, 40.6; **4**: 52.7, 31.7, 52.7, 35.0, 31.4, 52.4, 31.4, 35.0

⁴Identified compounds make up about 90% of the reaction mixture. NMR chemical shifts of bromides **5** to **8**: ¹H NMR (C₆D₆) δ **5**: 2.77, 2.46, 1.47, 1.89, 4.26, 2.11, 0.80/0.39, 2.14, 3.68; **6**: 2.21, 2.06, 1.38, 1.69, 4.32, 1.81, 0.76/1.99, 2.46, 3.70; **7**: 2.13, 3.25, 3.33, 4.05, 4.34, 1.62, 2.64, 3.46, 0.95/1.23; **8**: 2.57, 3.66, 3.26, 5.82, 5.61, 1.83, 2.88, 3.79, 1.02/0.78; ¹³C NMR (CDCl₃) δ **5**: 50.2, 34.6, 31.8, 41.5, 64.0, 45.7, 37.3, 44.5, 68.1; **6**: 48.5, 31.6, 25.9, 38.5, 59.1, 39.3, 29.7, 44.5, 68.9; **7**: 48.6, 51.6, 63.6, 57.7, 61.4, 42.3, 53.7, 52.2,

32.9; **8**: 55.1, 53.3, 56.3, 137.0, 139.3, 39.8, 61.1, 53.0, 37.1. Carbon atoms C-2,3,4 in **5** and **6** have $^1J_{CH}$ values about 170 Hz confirming the presence of 3-membered ring.

⁵Identified compounds make up about 95% of trifluoroacetates and about 90% of trideuteroacetates. 2H NMR ($CDCl_3$) δ **9**: H-8=1.98; **II**: H-5=1.52; **I2** H-4=1.77; 1H NMR ($CDCl_3$) δ **9** H-8_{syn}=1.98, H-8_{anti}=1.54; **II**: H-5_{exo}=1.52, H-5_{endo}=1.78; **I2** H-4_{exo}=1.77, H-4_{endo}=2.46

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