REDUCTION OF 8,8-DIHALOBICYCLO [5.1.0]OCTANES AND 9,9-DIHALOBICYCLO[6.1.0]NONANES*

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The reduction of the readily available gem-dihalocyclopropanes is a convenient and simple method for the preparation of cyclopropane hydrocarbons and the corresponding monohalides [1, 3].

In the present paper, in order to obtain some bicyclo[n.1.0] alkanes (n = 5, 6) and their monohalides, we studied the complete and partial reduction of the 8,8-dihalobicyclo[5.1.0]octanes (I) and (II), and 9,9dihalobicyclo[6.1.0]nonanes (III) and (IV).



The partial reduction of 8,8-dibromobicyclo[5.1,0]octane (IIa) and its 1-substituted derivatives (IIb, c, d) was accomplished as described in [4] by treatment with CH₃MgBr in excess THF (mole ratio of dibromide: CH_3MgBr : THF = 1:1-1.2:14-23). The yields of the corresponding monobromides (V) were 35-80%; the ratio of the endo- and exo-isomers ranged from 1.1:1 to 1.8:1 (Table 1). The GLC and NMR methods were used to determine their isomeric composition. For the 8-bromobicyclo [5.1.0] octanes (V), as well as for the other (n + 3)-halobicyclo[n.1.0] alkanes, a distinct difference in the signals of the exoand endo-H atoms, attached to the same carbon as the halogen, is observed in the NMR spectra. Here in all cases the triplet or doublet, corresponding to the endo-halobicycloalkane that contains the H atom in the exo-position, is found further downfield ($\Delta \delta 0.7-0.35$ ppm), which is evidently associated with a different degree of shielding of these H atoms in the endo- and exo-isomers (see Table 1). In the GLC determination, using a column packed with 20% Rheoplex-400 deposited on Chromosorb R, the exo-8-bromobicyclo-[5.1.0]octanes [exo-(V)] in all cases, except 1-ethyl-8-bromobicyclo[5.1.0]octane [exo-(Vc)], had shorter retention times than the corresponding endo-isomers [endo-(V)]. A similar picture was observed by us [5] for the exo- and endo-isomers of the adducts of monochlorocarbene to cycloheptene and cis-cyclooctene.

*See also [1, 2].

(IIc)

(IId)

Yields of corresponding NMR spectrum: δ_{8-H}, ppm (J, Hz) Mole ratio of di-Starting reduction products, % bromide : dibromide CH₃MgBr:THF exo-(V) (VI) endo-(V) exo-(V) endo-(V) $\begin{array}{c} 2,53t \ (J=3,5) \\ 2,55 \ d(J=3) \\ 2,66 \ d(J=3) \\ 2,88 \ d(J=3) \end{array}$ $\begin{array}{l} 3,20 \ {\rm t} \ (J=7) \\ 2,90 \ {\rm d} \ (J=7) \\ 3,00 \ {\rm d} \ (J=7) \\ 3,28 \ {\rm d} \ (J=7) \end{array}$ 20 39 22 17 36 40 33 (IIa) 1:1,1:25,1 231:1:14,2 1:1:14,2 1:1:14,2 9,7 7,5 15 ίIIb

18.5

TABLE 1. Reduction of 8,8-Dibromobicyclo [5.1.0]octanes (II) by Treatment with CH₃MgBr in THF

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TABLE 2. Reduction of Dihalides (I)-(IV) with Na/NH₃ Solution

Starting dihalide	Mole ratio of dihalide Na	Concen- tration of Na/NH ₃ solution, %	Reduction products (yield, [%])
(Ia) (1b) (Ic)* (IId) (III) (IV)	1:4 1:5 1:4 1:5 1:4 1:5	3,8 6,5 3,6 6,7 3,8 6,9	(VIa) (75) (VIb) (77) (VIc)† (57) (VId) (75) (VII) (70) (VII) (53)

* As a mixture with 1-methyl-2,2-dichlorospiro [6.2] nonane (mole ratio 1: 1.7).

† As amixture with 1-methylspiro [6.2]-

nonane (mole ratio 1.1 :1).

As a result, in the starting dibromides the bromide atom, found in the exo-position, is predominantly reduced under the adopted conditions, which must be explained by its greater steric accessibility to attack by the reducing agent, in the given case, most probably by the methyl radical [1, 4]. In contrast to the data given in [4], in all cases, together with the monobromides (V), we observed the formation of the complete reduction products, the corresponding bicyclo[5.1.0]octanes (VI) in 7-23% yields, which may be associated with the somewhat more drastic reduction conditions adopted by us.



R = H (a), CH_3 (b), C_2H_5 (b), C_6H_5 (d)

The complete reduction of the adducts of the dichloro- and dibromocarbenes to cis-cyclooctene, cyclopentene and its derivatives was run as described in [6], by treatment with a 4-7% solution of Na in liquid NH₃ at \sim -70°C. Here either a stoichiometric amount of Na was used, or else a 25% excess. The yields of the obtained bicyclo[n.1.0]alkanes ranged from 55 to 80%, with a practically complete absence of hydrogenolysis products (Table 2).



The structure of the obtained bicyclo[n.1.0]alkanes and the corresponding monobromides (Table 3) is in complete agreement with the data of their IR, NMR, and mass spectra. In particular, the IR spectra of all of the compounds contained bands that testify to the presence of the cyclopropane ring, and specifically in the 800-875, 1000-1065, and 3030-3065 cm⁻¹ regions, while the spectra of the bromides (V), in addition, contained the bands of the C – Br bond (535-567, 750-758 cm⁻¹). The IR spectra of the isomeric bromides (Va) are given in Fig. 1, while those of the other synthesized compounds are given in [1]. A comparison of the IR spectra of the exo- and endo-isomers of (Va) (see Fig. 1) indicates that they are sharply different in the 500-800 cm⁻¹ region, and also that differences exist in the character and intensity of some of the other bands, which can be used in the analysis of the isomeric mixtures of these and similar compounds.

The NMR spectra of the obtained compounds, given in [1], lacked signals in the region of the olefinic protons of the CH₂ groups of either a 7- or an 8-membered ring. As was already mentioned, the signal of the cyclopropane proton at the C atom that contains bromine is most characteristic for the (V) bromides (see Table 1). In the spectra of the hydrocarbons of the bicyclo[n.1.0]-alkane (VI) and (VII) series are observed the characteristic signals of the CH₂ group of a three-carbon ring, which are located furthest up-field (δ ranges from -0.30 to 0.85 ppm). Thus, the NMR spectrum of cis-(VII), obtained from cis-cyclo-octene, contains for the endo-proton of this group (endo-9-H) a signal at δ -0.30 ppm (τ 10.3 ppm); the other three cyclopropane protons give a signal at δ 0.60 ppm. In addition, the signals of the CH₂ group of an 8-membered ring give a complex multiplet at δ 1.06 ppm. In addition, the signals of the protons of the corresponding substituent are also observed in the NMR spectra of the 1-alkyl(aryl)bicyclo[5.1.0]alkanes (VI).

The data of the mass spectra (see [1] and Table 3) are also found to be in complete agreement with the structure of the obtained compounds.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument as a thin layer of the compound. The NMR spectra were obtained at room temperature on RS-60 and Varian DA-60-IL spectrometers (60 MHz) either for the pure compounds or their $\sim 50\%$ solutions in CCl₄, using either TMS or HMDS as the internal standard. The mass spectra were taken on an MKh-1303 instrument, with insertion of the compound through the admittance cylinder (energy of ionizing electrons 50 eV; 150°C). The GLC analysis was run on LKhM-8M and Chrom-3 chromatographs (150-200 × 0.4 cm columns packed with 20% Rheoplex-400 deposited on

Products
f Reduction
Properties of
TABLE 3.

Compound	Bp, °C(p,	50	,20	Щ.	ound, 1/2		Empirical	Ca	lculated	°/0	Mass spectrum (m/e)
	mm of Hg)	un Un	aq	IJ	н	Br	formula	υ	н	Br	
a) [7]	38(20)	1,4625	0,8494	87,20	12,79		C_8H_{14}	87,19	12,81	1	M ⁺ 110, main peak 67
[8] (q	45-46(10)	1,4570	0,8373	86,98	13,05	1	C ₉ H ₁₆	87,01	12,99		ver
c) *	5657(10)	1,4620	0,8514	86,93	13,00	1	C10H18	86,95	13,05		1
d)	8384(1)	1,5400	0,9842	90,28	9,72		C14H18	90,26	9,74	l	. and a
[6] (I	56-56,5(14)	1,4700	0,8731	86,76	12,90	1	C9H16	87,01	12,99	1	M ⁺ 124, main peak 67
-(Va) [10]	I	1,5048	1	42,30	6,89	50,80	C ₈ H ₁₃ Br	42,33	6,88	50,79	M ⁺ 188 (190), main peak 67
o-(Va) [10]	1	1,5150	I	42,32	6,87	50,79	C ₈ H ₁₃ Br	42,33	6,88	50,79	M ⁺ 188 (190), main peak 67
/endo =1:1,2)	5657(2)	1,5080	1,2652	53,22	7,34	39,25	C9H15Br	53,21	7,44	39,35	M ⁺ 202 (204), main peak 81
() $(=1.1,75)$	5152(1)	1,5085	1,2267	55,37	7,94	36,63	$C_{I0}H_{17}Br$	55,36	7,88	36,76	1
) /endo = 1:1,8)	124-125(1,5)	1,5700	1,2807	63,35	6,45	30,18	C14H17Br	63,40	6,46	30,14	M ⁺ 264 (266), main peak 185
	· · ·	-	_		-				_	-	

* As a mixture with 1-methylspiro[6.2] nonane (ratio 1.1:1).



Fig. 1. Infrared spectra of exo-(a) and endo-(b) isomers of (Va).

Chromosorb R, 10% poly(ethylene glycol adipate) deposited on Risorb, or 15% squalane deposited on silanized Celite-545; 90-185°C; carrier gas = helium). The preparative separation of the (Va) isomers was run on a Perkin – Elmer Auto-Prep chromatograph (200×0.4 cm column packed with 20% Rheoplex-400 deposited on silanized Celite-545; 125°C). The synthesis and properties of the starting dihalides (I)-(IV) are given in [11].

<u>Reduction of 8,8-Dibromobicyclo[5.1.0]octanes (II) with Methylmagnesium Bromide in THF.</u> With rapid stirring, a solution of 0.034 mole of dibromide (IIa) in 20 ml of absolute THF was added (~20°C, 10 min) in a N₂ atmosphere to 0.04 mole of CH₃MgBr in 50 ml of absolute THF. Then the mixture was stirred for another hour at ~20°C, 3-4 min at 50-52°C, and ~1 h again at ~20°C (a white precipitate deposits). After hydrolysis with saturated NH₄Cl solution and the usual workup the product was fractionally distilled to give 4.7 g of a fraction with bp 42-54°C (1 mm), n_D^{20} 1.5040-1.5090, which, based on the GLC data, contained three substances in a 1:1.16:2.19 ratio (in the order of increasing retention time). After the separation of this mixture by preparative GLC the compound with the shortest retention time was identified as being bicyclo[5.1.0]octane (VIa) (n_D^{20} 1.4605, 23% yield), while the compounds following it were identified as being exo-8-bromobicyclo[5.1.0]octane [exo-(Va)] (n_D^{20} 1.5048, yield 20%, purity 99.3%) and its endo-isomer [endo-(Va)] (n_D^{20} 1.5150, yield 36%, purity 99.2%). Hydrocarbon (VIa) proved to be identical with that obtained by the reduction of dichloride (Ia) with a solution of Na in NH₃ (see Tables 2 and 3).

The reduction of the other dibromides was run in a similar manner (see Table 1). The properties and analysis data of the obtained products are given in Tables 1 and 3.

Reaction of 8,8-Dihalobicyclo[5.1.0]octanes (I) and (II), and 9,9-Dihalobicyclo[6.1.0]nonanes (III) and (IV), with Sodium in NH₃. To a solution of 0.144 g-atom of Na in 108 ml of liquid NH₃, cooled to -70° C, was added a solution of 0.036 mole of dichloride (III) in 95 ml of absolute ether in 20 min. After additional stirring at the same temperature for ~30 min the mixture was treated with 0.07 mole of NH₄Cl, the excess NH₃ was evaporated through a cooled trap, and the residues was worked up in the usual manner. Distillation gave 3.1 g (70%) of bicyclo[6.1.0]nonane (VII), purity 99.9% (GLC).

The same procedure was used to reduce the other dihalides to the corresponding [n.1.0] alkanes (see Table 2), the properties and analysis data of which are given in Table 3.

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CONCLUSIONS

A study was made of the partial and complete reduction of some 8,8-dihalobicyclo[5.1.0]octanes and 9,9-dihalobicyclo[6.1.0]nonanes to the corresponding monohalides and hydrocarbons of the bicyclo[n.1.0]-alkane series.

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