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REDUCTION OF GEM-DIHALOCYCLOPROPANES WITH SODIUM ALUMINIUM BIS (2-METHOXYETHOXY) HYDRIDE

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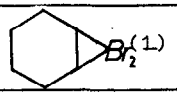
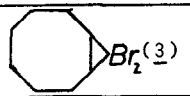
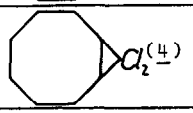
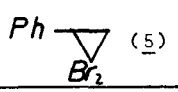
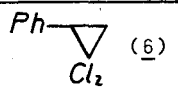
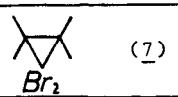
The reduction of one or both halogens of dihalocyclopropanes can be carried out successfully with a variety of reagents.[1] We want to report that the commercially available reagent sodium aluminium bis(2-methoxyethyoxy)hydride (SAH)[2] is useful for the same purpose.

Reductions with SAH (Table 1) were carried out in benzene solution under reflux (88°) until practically all the gem-dihalocyclopropane derivative had been consumed (2-5 hrs); an exception was the reduction of 9,9-dichlorobicyclo-[6,1,0]nonane (4) which was almost unreactive at this temperature and even at 110° for 3½ hrs only about 30% of reduced product was formed. The results clearly show that the monobromides are preferably formed in the anti or trans configuration with SAH as reducing agent while the syn- or cis-monohalide is the most abundant isomer when other reducing agents are used.[1] In addition our experiments yielded variable amounts of fully reduced compounds. This appears unavoidable, and with a four-fold molar excess of SAH at 110° compound 5 for example was completely converted after 11 hrs to the fully reduced compound e.g. phenylcyclopropane (12).

All evidence points to a radical mechanism for the tin hydride reductions of gem-dihalocyclopropanes.[5] Although similar stereochemistry is observed in reduction of gem-dihalocyclopropanes with lithium aluminium hydride, four-centre,[6] radical,[7] carbanion,[8] and S_N2[7] mechanisms have been claimed to accomodate the results. The fact that the opposite stereochemistry is observed in the SAH reductions of the dibromides renders a radical mechanism rather

TABLE 1

The Reduction of gem-Dihalocyclopropanes with Sodium Aluminium Bis(2-methoxyethoxy) Hydride (SAH)

gem-Dihalide	Hydride	Molar ratio[b]	Monohalide yield	Monohalide (ratio syn:anti)	Hydrocarbon	(yield)	Ratio hydrocarbon : monohalide
 (1)	SAH	0,5	65%	(0,35)	Bicyclo[4,1,0]heptane (8)	(35%)	
	BTH[a]	1,0	82%	(2,5)[3]			
 (2)	SAH	0,5	88%	(0,11)	Bicyclo[4,1,0]hept-2-ene (9)	(12%)	
	BTH	1,0	78%	(0,91)	Bicyclo[4,1,0]hept-2-ene (9)	(11%)	
 (3)	SAH	0,5	63%	(0,25)[e]	1,2-cyclononadiene (10)	(17%)	0,59
	BTH	0,9	85%	(6,7)	Bicyclo[6,1,0]nonane (11)	(20%)	
 (4)	SAH	0,5	26%	(1,56)	1,2-cyclononadiene (10)	(3,5%)	0,27
	BTH	1,0	72%	(2,2)[4]	Bicyclo[6,1,0]nonane (11)	(3,5%)	
 (5)	SAH	0,5	55%	(0,20)	Phenylcyclopropane (12)	(45%)	0,82
	BTH	1,0	70%	(1,85)			
 (6)	SAH	0,5	66%	(1,94)	Phenylcyclopropane (12)	(27%)	0,41
	BTH	1,0	75%	(1,5)			
 (7)	SAH	0,5	40%		c) d)		
	SAH	0,25	5%				

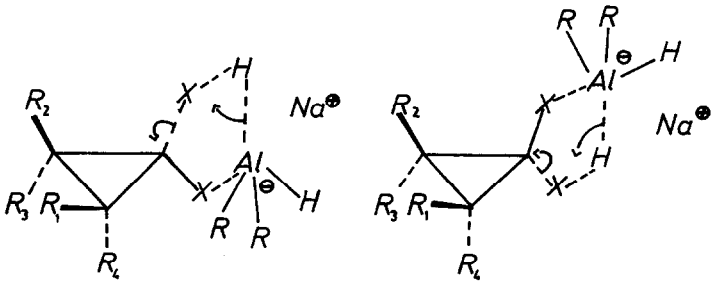
a) BTH = tri-n-butyltin hydride b) Molar ratio = gem-dihalide : SAH c) No hydrocarbon could be isolated because of the benzene used as solvent. d) With a molar ratio of 0,5 and 0,25, 2-(1-methylcyclopropyl)-2-propanol (13) was isolated in 10% and 30% yield, respectively. e) This reaction has previously been reported to yield exclusively the syn-isomer.[3]

unlikely. A direct nucleophilic attack by the hydride ion can also be ruled out since it demands a preferential approach from the most hindered side of the molecule. On the other hand, a four-centre type mechanism as well as one involving carbanions must be discussed.

Reaction of 9,9-dibromobicyclo[6,1,0]nonane (3) with SAH yielded a substantial amount of 1,2-cyclononadiene (10). This allene is the sole product from treatment of 3 with methyllithium,[9] an example of a general reaction which with certainty involves a carbanion type intermediate.[10] A similar reduction of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (7) yielded a small but significant amount of 2-(1-methylcyclopropyl)-2-propanol (13) an alcohol previously reported[11] as the product from acid-catalyzed addition of water to 1,2,2-trimethylbicyclo[1,1,0]butane (14). The latter is formed from dibromide 7 and methyllithium.[11] Acid is used during the isolation procedure for SAH reductions and the formation of carbinol 13 must be regarded as further evidence for a carbanion intermediate.

It seems that a carbanion is involved also in the reduction of other gem-halides. Thus treatment of bromoform with an excess of SAH in the presence of cyclohexene gave almost exclusively bicyclo[4,1,0]heptane (8) and 7-bromobicyclo[4,1,0]heptane (15) in a ratio of 3:2; the results are best explained by invoking a dibromomethyl anion which produces the product-forming monobromocarbene.

We suggest that the carbanion-forming step involves a cyclic transition state as depicted below.



16a 16b

R = $OCH_2CH_2OCH_3$

R_1,R_2 more bulky than R_3,R_4

Clearly, transition state 16a is sterically preferred and should lead to the anti-isomer on the assumption that the cyclopropyl carbanion retains its configuration; electronegative substituents on the carbon bearing the charge enhance the rate of inversion[12] but we have not been able to observe any inversion of monobromocyclopropanes under conditions favouring carbanion formation.

Several mechanisms will account for the subsequent reduction of the monobromides. At least in the case of 9-bromobicyclo[6,1,0]nonane the anti-isomer reacted faster than the syn-isomer, indicating a steric effect in the transition state.

The stereochemistry of the SAH-reduction products from gem-dichlorocyclopropanes is similar to that observed with tri n-butyltin hydride (Table 1). The formation of a small amount of 1,2-cyclononadiene from the chloride 4 indicates a carbanion intermediate for this reaction also; however, further mechanistic discussions must await additional studies which are in progress.

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