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Further evidence of SET mechanism during the LAH reduction of optically active 1-bromo 1-methyl 2,2-diphenyl cyclopropane.

J.Hatem, J.M.Meslem and B.Waegell.

Laboratoire de Stéréochimie, associé au CNRS, UA 109, Université
d'Aix-Marseille, rue H.Poincaré, 13397 Marseille Cédex 13.

Abstract : The stereochemical outcome of the reduction of 1(-) (R) with TBTH, SMEAH or LAH shows that with the latter a radical intermediate is involved.

Our early report (1) where we showed that the LAH dehalogenation of gem dihalocyclopropanes proceeds via a radical intermediate had been a matter of controversy : an anionic (2) and a four centre (3) mechanism had been proposed as other possibilities. Since then, the occurence of single electron transfer in the reduction of organic halides (4) and gem dibromocyclopropanes (5) by LAH has been demonstrated.

It is now clearly established that the cyclopropyl radical inversion rate depends on the nature of the cyclopropane substituent geminated with the halogen which is going to be reduced (6). On the other hand it has been shown by Walborsky that the cyclopropyl radical produced from 1 racemizes easily (6) whereas the corresponding carbanion is able to retain its configuration (7).

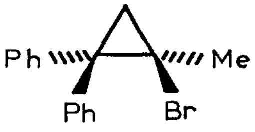
It was therefore of interest to compare the behaviour of optically active 1-bromo 1-methyl 2,2-diphenyl cyclopropane 1 (8) towards various reducing agents : TBTH known for its ability to generate radical species (9), SMEAH which favors the formation of cyclopropyl anions (10) and LAH.

The corresponding results are reported in the present paper. Compound 1 (-)(R), prepared according to Walborsky's procedure (8) with a 74% optical purity, was submitted to reduction with TBTH, SMEAH and LAH under experimental conditions giving comparable chemical yields.

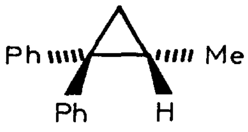
Substrate 1(-)(R)	Reducing agent mmole for 1 mmole of 1	Solvent °C	Reaction time (hours)	Chemical yield %	Product 2(+)S[c] 2(-)R $[\alpha]^D_{24}$	Optical purity %	Overall stereochemical outcome of the reaction
$[\alpha]^D_{24} = -79°$[a]	TBTH (1) +AIBN	hexane 68°	48	45	+ 1.2	1.3	racemisation
Optical purity 74,5%[b]	SMEAH (3.4)	toluene 110°	24	40	+ 68.4[d]	72,4	retention
	LAH (7)	diglyme 100°	65	66	+ 7.9	8,4	racemisation

a : all the [α] are taken in chloroform and are given with a precision of ±1°
b : pure 1 (-) R has an $[\alpha]^D_{24}$ = -106° (ref.7)
c : pure 2 (+) has an $[\alpha]^D_{24}$ = +126.8 (ref.11)
d : considering the 74% optical purity of the starting material 1, the retention ratio is equal to

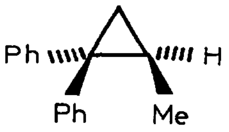
$$\frac{68,4}{0,745 \times 126,8} = 72,4\%$$



1(-) R



2 (+) S



2(-) R

≠TBTH : tri butyl tin hydride; SMEAH : sodium methoxy ethoxy aluminium hydride; LAH : lithium aluminium hydride.

The major observation which results from the examination of the Table is that TBTH and LAH, give both essentially rise to racemisation. It was clearly shown that the reduction of 1 with TBTH proceeds via a cyclopropyl radical intermediate which inverts rapidly and is therefore unable to retain its configuration (12, 13). Based on the stereochemical outcome of the reduction, the mechanism involved with LAH should be similar, and is most likely to involve an intermediate radical species.This is certainly the case as the racemisation observed with LAH is in contrast with the retention observed when 1 is reduced with SMEAH. In the later case the carbanionic species which is known to be involved (10), invert much more slowly (7).

In conclusion, the comparison of the stereochemical behaviour of various reducing reagents towards cyclopropyl halide 1 shows that the LAH reduction proceeds via a radical intermediate, and most likely via a SET mechanism

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