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ASYMMETRIC RING OPENING OF *gem*-DIBROMOCYCLOPROPANES LEADING TO ALLENIC HYDROCARBONS

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We wish to report partial asymmetric synthesis of cyclic allenes from cycloolefin-dibromocarbene adducts proceeding *via* either chromium- or lithium-carbenoid whose asymmetric metal ligands behave as an inducing centre. An instance of asymmetric induction in copper-carbenoid reaction has been recorded (1).

Reduction of *gem*-dibromocyclopropane (I) with aqueous chromous sulphate affords allene IV along with monobromocyclopropane V and totally reduced cyclopropane VI in ratios varying with the length of the methylene chain R (2). The reaction intermediate was suggested to be α-bromoorganochromium (II) or cyclopropylidene-chromium complex (III) rather than free carbene species. In this paper, the reduction was carried out by means of chromous (+)-tartarate (3). Dibromides Ia,b were dissolved in 50% aqueous dimethyl-

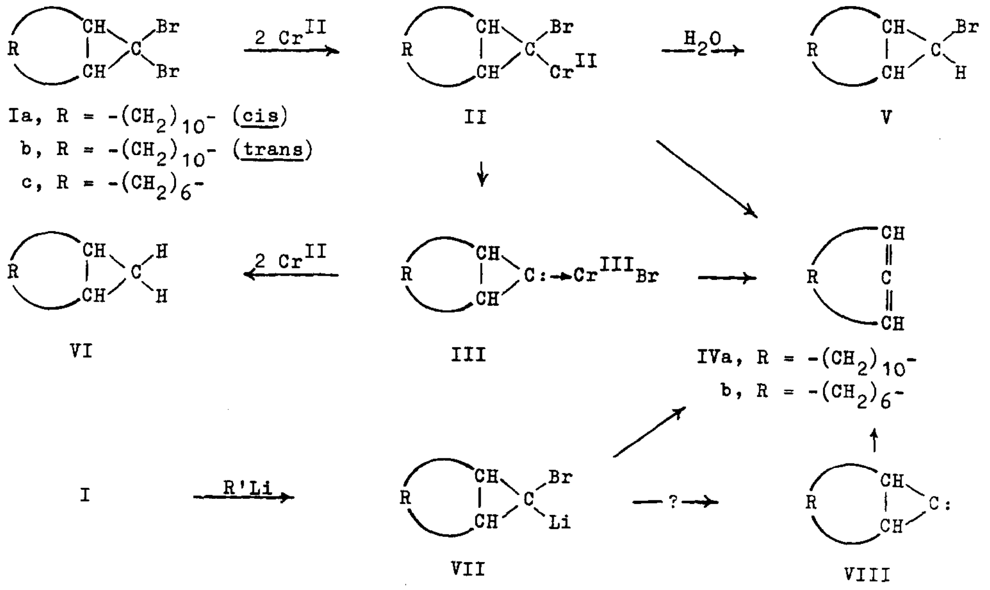


TABLE 1

Asymmetric Induction in Allenic Hydrocarbon Synthesis

Method	Dibromide	Product [a]	Yield, %	α_D^{25}, obsd [b]	*c*, g/100 ml	$[\alpha]_D^{25}$, deg
Cr(II)	Ia	(*S*)-IVa	51	+0.030	14.0	+0.43
Cr(II)	Ib	(*R*)-IVa	50	-0.035	15.8	-0.44
n-BuLi	Ia	(*S*)-IVa	70	+0.090	13.1	+1.4
n-BuLi	Ib	(*R*)-IVa	65	-0.190	13.8	-2.8
n-BuLi	Ic	(*S*)-IVb	34	+0.060	6.5	+1.9

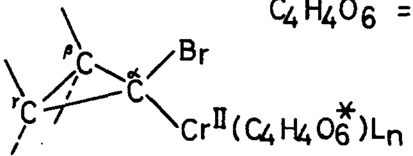
[a] All products gave correct elemental analyses. IR spectra were superimposable on those of authentic samples (Refs 2 and 4). The absolute configuration was assigned on the basis of the sign of optical rotation (Cf. Ref 5).

[b] All rotatory values were obtained in n-hexane solutions with 5 cm cells.

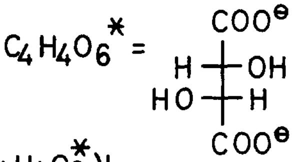
formamide and treated with four equivalents of chromous (+)-tartarate at 80° for 12 hr. Workup followed by gas chromatographic (GLC) purification yielded the corresponding allene IVa in optically active form. The results are summarized in Table 1. The optical yield has not been determined because of the difficulty in resolving the allenic hydrocarbon.

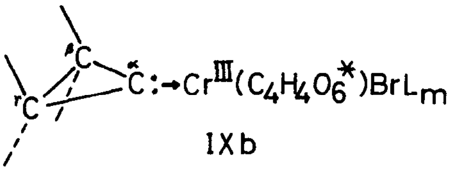
Such an asymmetric transformation has been successfully extended to the Skattebøl-Moore allene synthesis, which consists in the dehalogenation of *gem*-dihalocyclopropanes with alkyllithium (6). The mechanism involving the intermediacy of either α-halocyclopropyllithium (VII) or free cyclopropylidene (VIII) has been proposed. In view of the current interest in the reactivity of organolithium-tertiary amine complexes (7), we have tried the reaction in the presence of (-)-sparteine (8) as a bidentate ligand. *gem*-Dibromides Ia-c were treated with an equimolar mixture of n-butyllithium and (-)-sparteine in n-hexane at -70° for 1 hr. Chromatography on an alumina column followed by GLC separation gave optically active allenes IVa,b as shown in Table 1. It should be noted that treatment of racemic allene IVa,b with n-butyllithium and (-)-sparteine in the presence or absence of lithium bromide did bring about asymmetric consumption of the allenes. Under the conditions of the debromination, however, the extent of the kinetic resolution was not significant, the recovery in % and the specific rotation of allenes being IVa (44%) +0.15 (c, 13.2, n-hexane) and IVb (41%) +0.37 (c, 8.2, n-hexane).

Intermediacy of free cyclopropylidene must give rise to optically inactive products. The success of asymmetric induction implies that two ways of debromination proceed through chiral carbenoids (carbene-metal complexes). This interpretation is in accord with the recent findings by Skell and Engel that free cyclopropylidene in either ground state triplet or lowest singlet state does not isomerize to allene (9). The asymmetry-inducing species would be represented as IX (a or b) and X, respectively. Rotation in either a clockwise or a counterclockwise direction around C_α-C_β and C_α-C_γ bonds results in the formation of the respective enantiomeric allene. The selection would be determined by the tendency of minimizing non-bonded repulsion between the substituents on the cyclopropanes and on the metal ligands during the concerted conrotatory ring opening accompanying α-elimination (10). The configurational correlation appears to be unjustified at present.

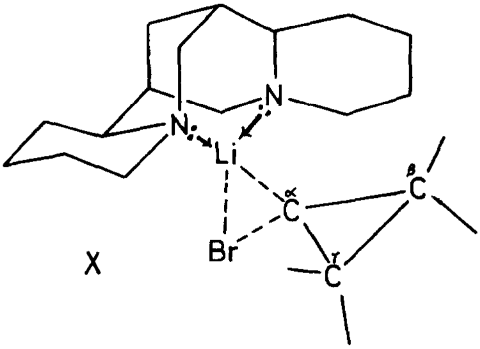


IXa





IXb



X

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