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MECHANISMS FOR THE CLEAVAGE OF CARBON–TIN BONDS VI*. A KINETIC AND STEREOCHEMICAL STUDY OF THE HALODEMETALLATION OF CYCLOPROPYLTRIALKYLTINS: THE SOLVENT EFFECT

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SUMMARY

The bimolecular halodemetallation of substituted cyclopropyltrialkyltins is stereospecific, and proceeds with retention of the configuration at carbon in methanol, acetic acid and chlorobenzene. The kinetic study confirms the hypothesis which was based on results for the $R'SnR_3$ series, and shows the participation of the ring orbitals in the rate determining step of the reaction.

A study of the selectivity in various media has revealed a surprising solvent effect.

INTRODUCTION

From the kinetic study of the halodemetallation reaction of symmetrical and mixed tetraalkyltin compounds a mechanism was proposed in which the stoichio-

$$R_4Sn + X_2 \xrightarrow{\text{solvent}} R_3SnX + RX$$

$$R_3SnR' + X_2 \longrightarrow \begin{cases} \rightarrow R_3SnX + R'X \\ \rightarrow R_2SnR'X + RX \end{cases}$$

metry, the polarity and the structure of the transition state are closely related to the nature of the solvent[3], and particularly to its nucleophilicity. In non-polar solvents, the assumed four-center transition state implies the retention of configuration at both carbon[4] and metal[5] atoms. On the contrary, the open structure proposed in polar solvents could give either retention[4] or inversion of configuration[6].

In the present work, we describe the kinetic and stereochemical results obtained for the halodemetallation of *cis*- and *trans*-1-(trimethylstannyl)-2-methylcyclopropanes in three different solvents. The same reactions have been studied for the unsubstituted cyclopropyltrialkyltins.

* A preliminary communication on this work has already appeared[2]. For part V see ref. 1.
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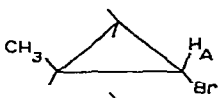
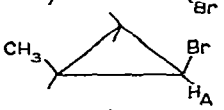
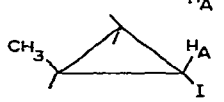
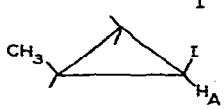
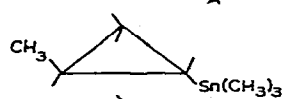
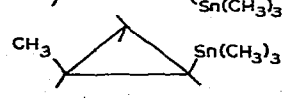
EXPERIMENTAL RESULTS

Structural analysis of cis- and trans-1-(trimethylstannyl)-, 1-iodo- and 1-bromo-2-methylcyclopropanes

PMR spectra recorded in CCl_4. The *cis*- or *trans*-structures of these compounds were assigned by examination of the PMR spectra. The trimethylenic cycle is a very good example for the application of the Karplus relationships correlating the coupling constant between *vicinal* protons with the dihedral angle between the CH bonds[7]. Although these relationships are sometimes only approximate, and since small variations of the angles[8,9] or of the electronegativities of the substituents[9] can modify the value of the coupling constants, the *vicinal* coupling constant between *trans* protons is always smaller than in *cis* pairs[10], and this provides an effective means of assigning the stereochemistries of cyclopropane derivatives. Unfortunately in all the cases considered here, the PMR spectra of the disubstituted cyclopropanes are especially complicated because of the numerous coupling constants between the different protons of the molecule. From the known examples of cyclopropanes for which the *cis* or *trans* structures have been unambiguously assigned on the basis of the calculated and experimental *vicinal* coupling constants[10,11], one can conclude that the cyclic protons are displaced upfield by alkyl and trialkylsilyl groups and halogens in *cis* positions. These effects are generally assigned to the anisotropy of the

TABLE 1

60 MHz PMR SPECTRA OF 1,2-DISUBSTITUTED CYCLOPROPANES: SOLVENT EFFECT

Compound	Protons	δ (Hz)[a] CCl_4	δ (Hz)[a] C_6D_6	$\Delta\delta$ $\delta(CCl_4)-\delta(C_6D_6)$ (Hz)
(F_1'') 	H_A	148	134	+14
	CH_3	67	40	+27
(F_2'') 	H_A	178	158	+20
	CH_3	73	64	+ 9
(F_1') 	H_A	119	99	+20
	CH_3	68	39	+29
(F_2') 	H_A	155	132	+23
	CH_3	70	58	+12
(F_1) 	CH_3	68	67	0
(F_2) 	CH_3	62	61	0

[a] Downfield from TMS.

bonds, and can be evaluated by the McConnell relationship[12], which is a rather rough approximation[13], especially since bond anisotropies are not accurately known[14]. The upfield shift of *cis*-methyl and of *cis*-cyclic protons under the influence of Group IVB trialkylmetal substituents, observed in the propenyltrialkylmetal series[15], might be expected for the analogous cyclopropyltrialkyltin case.

It is thus possible to assign unambiguously the structures of the organotin compounds (see Table 1). The notations F_1 and F_2 for the isomers denote the peak sequence always observed by GLC. It may be pointed out that the methyl protons of the *cis*- or *trans*-cyclopropyl halides are weakly deshielded by a *cis*-halogen, as in the analogous vinylic derivatives[16].

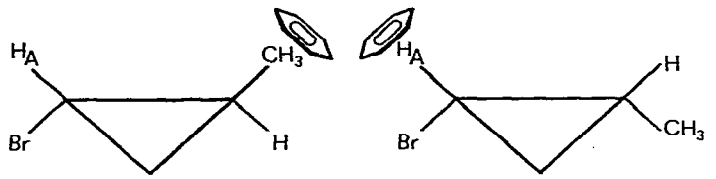


Fig. 1. Solvation of cyclopropylic bromides by benzene.

Solvent effects on the PMR spectra of 1-halo-2-methylcyclopropanes. The NMR spectra of the 1-bromo- and 1-iodo-2-methylcyclopropanes show an upfield shift for all the protons when carbon tetrachloride is replaced by perdeuteriobenzene. However, the cyclic protons are not all equally sensitive to the solvent effect. The H_A proton of the F_2 isomer is more sensitive than the H_A proton of the F_1 isomer, however, the methyl protons of the F_1 isomer are more sensitive than the corresponding protons of the F_2 isomer. These effects are observed with the bromides and with the iodides, and the differential specific effect observed here can be used to assign a structure to such disubstituted cyclopropanes. It is difficult to interpret solvent–solute associations quantitatively in terms of well defined geometries; but it seems well established that the solvation effect due to benzene is more important when the protons concerned are accessible to the solvent in terms of steric interactions with the α-substituent for the H_A or for the methyl protons. The most favourable solvated forms are depicted in Fig. 1. Consequently, one can confirm the *trans* structure of F_1 and the *cis* configuration of F_2. Analogous effects have already been mentioned for cyclopropylic[17] and olefinic[18] derivatives.

TABLE 2

HALODEMETALLATION OF (METHYLCYCLOPROPYL)TRIALKYLTINS AT 20° STRUCTURE OF THE FORMED CYCLOPROPYL HALIDES

Organometallic compound	Structure of halides CH_3–C_3H_4–X obtained in halodemetallation using the systems			
	I_2/CH_3OH	I_2/CH_3CO_2H	Br_2/CH_3CO_2H	Br_2/C_6H_5Cl
cis-CH_3–C_3H_4–$Sn(CH_3)_3$	>95% *cis*	>99% *cis*	>99% *cis*	>99% *cis*
trans-CH_3–C_3H_4–$Sn(CH_3)_3$	>95% *trans*	>99% *trans*	>99% *trans*	>99% *trans*

Structure of the reaction products

The reaction products have been isolated by GLC; their structures have been assigned by comparison with those of reference compounds. In all the cases studied (see Table 2), the action of iodine or bromine on the *cis*- and *trans*-1-(trimethylstannyl)-2-methylcyclopropanes gives, along with the methyl halide always present, only the 2-methyl-cyclopropyl halides having the same structure as the starting organometallic compound. All the demetallations studied thus proceed stereospecifically with complete retention of configuration at the attacked carbon atom.

Kinetic study of the halodemetallation of the cyclopropyltrialkyltins

Iododemetallations in methanol and in acetic acid. These reactions were followed by spectrophotometry at the absorption maximum of I_3^- in methanol (365 nm) and of iodine in acetic acid (470 nm)[19]. The concentration of the organometallic compound is always much larger than the analytical concentration of iodine, and the kinetics are pseudo first-order. The observed rate constants (Table 3) in methanol can be described by the equation: rate $= k_2^{exp} \cdot [Sn] \cdot [I_2]$.

In acetic acid, the formation of trimethyltin acetate indicates that an equation taking into account the protolysis by the solvent must be used, *viz.* rate $= k_2^{exp} \cdot [SN] \cdot [I_2] + k_2' \cdot [SN]$

TABLE 3

IODODEMETALLATION IN METHANOL (IONIC STRENGTH: $\mu = 0{,}1$; $\varepsilon = 26.800$ AT 365 nm) AND IN ACETIC ACID ($\varepsilon = 800$ AT 470 nm) AT 20° (C_3H_5 = CYCLOPROPYL)

Compounds	In methanol		In acetic acid		
	$[Sn] \times 10^2$	k_2^{20} methanol) ($l \cdot mole^{-1} \cdot sec^{-1}$)	$[Sn] \times 10^2$	k_2' (sec^{-1})	k_2^{exp} ($l \cdot mole^{-1} \cdot sec^{-1}$)
$C_3H_5Sn(CH_3)_3$	9.48	4.0	5.48	$4.8 \cdot 10^{-5}$	0.105
	9.48	4.1			0.103
	7.31	4.0			0.101
	7.31	4.1			0.104
					0.106
					0.103
$C_3H_5Sn(C_2H_5)_3$	8.94	0.64	9.30	$3.3 \cdot 10^{-5}$	0.034
	8.94	0.61			0.034
	10.08	0.59			0.032
	10.08	0.60	11.0	$3.7 \cdot 10^{-5}$	0.031
					0.034
					0.033
					0.032
$C_3H_5Sn(i\text{-}C_3H_7)_3$	10	~0.01	10.9	Very slow	~0.0025
			13.5		~0.0031
trans-CH_3–C_3H_4–$Sn(CH_3)_3$	4.48	4.9	4.09	$3.4 \cdot 10^{-4}$	0.145
	4.48	5.2	4.02		0.152
	4.48	5.2			
	4.48	5.2			
cis-CH_3–C_3H_4–$Sn(CH_3)_3$	4.96	2.65	4.01	$6.2 \cdot 10^{-5}$	0.058
	4.96	2.58	4.01		0.061
	4.46	2.72	3.82	$7.0 \cdot 10^{-5}$	0.059
	4.46	2.62	3.82		0.057

TABLE 4

BROMODEMETALLATION IN CHLOROBENZENE AT 20° (ε=232 AT 410 nm)

Compounds	D_0[a]	D'_0	k_2^{exp} ($l \cdot mole^{-1} \cdot sec^{-1}$)
$C_3H_5Sn(CH_3)_3$	1.34	7.46	2.58
	1.81	8.98	2.42
	1.36	7.73	2.52
$C_3H_5Sn(C_2H_5)_3$	1.28	9.90	13.2
	1.12	11.20	12.9
	1.07	9.50	13.2
	1.60	7.65	13.2
	1.35	13.37	12.9
	1.20	8.91	13.2
	1.02	8.26	13.5
trans-CH_3–C_3H_4–$Sn(CH_3)_3$	1.77	8.72	10.0
	1.05	12.00	9.6
	2.00	13.57	10.3
cis-CH_3–C_3H_4–$Sn(CH_3)_3$	0.98	11.53	5.5
	0.50	13.09	5.5
	1.90	16.60	5.2

[a] $D'_0=\varepsilon \cdot l \cdot [Sn]$, $D_0=\varepsilon \cdot l \cdot [I_2]$.

TABLE 5

RATIOS OF MOLAR AREAS (CATHAROMETER GLC) (C_3H_5=CYCLOPROPYL)

Alkyl iodides		Alkyl bromides	
Compounds	Ratio of molar areas	Compounds	Ratio of molar areas
CH_3I/C_3H_5I	0.77	CH_3Br/C_3H_5Br	0.74
C_2H_5I/C_3H_5I	0.92	C_2H_5Br/C_3H_5Br	0.95
CH_3I/*trans*-CH_3–C_3H_4–I	0.78	CH_3Br/*trans*-CH_3–C_3H_4–Br	0.64
CH_3I/*cis*-CH_3–C_3H_4–I	0.78	CH_3Br/*cis*-CH_3–C_3H_4–Br	0.67

TABLE 6

RATE CONSTANTS FOR THE IODODEMETALLATION OF CYCLOPROPYLTRIALKYLTINS IN METHANOL AND IN ACETIC ACID AT 20°

Compounds	In methanol			In acetic acid		
	k_2^{exp}	k(R)	k(Δ)	k_2^{exp}	k(R)	k(Δ)
$C_3H_5Sn(CH_3)_3$	4.06	1.4±0.15	0.0085	0.103	0.032	0.007
$C_3H_5Sn(C_2H_5)_3$	0.609	0.19	0.018	0.033	0.0069	0.012
trans-CH_3–C_3H_4–$Sn(CH_3)_3$	5.18	1.7	0.10	0.148	0.040	0.026
cis-CH_3–C_3H_4–$Sn(CH_3)_3$	2.64	0.86	0.043	0.059	0.016	0.011

Bromodemetallation in chlorobenzene. The reactions of bromine with the cyclopropyltrialkyltins are rather fast, and were followed in 10 cm-cells containing dilute solutions. The optical density variation curve was recorded, and the value of the experimental rate constants calculated, and shown to fit perfectly the second-order relationship (Table 4).

Specific rate constant values. The experimental rate constant, k_2^{exp}, results from the combination of two specific rate constants describing the cleavage of the cyclopropyl–tin [$k_2(\Delta)$] and the alkyl–tin bond [$k_2(R)$], respectively.

$$R_3SnC_3H_5 + X_2 \xrightarrow{k_2^{exp}} \begin{cases} \xrightarrow{k_2(\Delta)} R_3SnX + C_3H_5{-}X \\ \xrightarrow{k_2(R)} R_2(C_3H_5)SnX + R{-}X \end{cases}$$

To determine the value of the specific rate constants one has to solve the equations:

$$\begin{cases} k_2^{exp} = 3k_2(R) + k_2(\Delta) \\ \dfrac{k_2(\Delta)}{3k_2(R)} = \dfrac{[C_3H_5{-}X]}{[R{-}X]} \end{cases}$$

The $[C_3H_5{-}X]/[R{-}X]$ ratio was obtained from the relative concentrations of cyclopropyl and alkyl halides determined by GLC, as described before (see Table 5)[19].

The specific rate constants are gathered together in Tables 6 and 7. Rate constants have not been determined for the *bromo*dementallation in acetic acid, but the reactivity ratios have been measured (see Table 8).

TABLE 7

RATE CONSTANTS FOR THE BROMODEMETALLATION OF CYCLOPROPYLTRIALKYLTINS IN CHLOROBENZENE AT 20°

Compounds	k_2^{exp}	$k(R)$	$k(\Delta)$
$C_3H_5Sn(CH_3)_3$	2.5	0.081	2.27
$C_3H_5Sn(C_2H_5)_3$	13.2	0.36	11.9
trans-$CH_3{-}C_3H_4{-}Sn(CH_3)_3$	10	0.089	9.75
cis-$CH_3{-}C_3H_4{-}Sn(CH_3)_3$	5.42	0.056	5.25

TABLE 8

SELECTIVITY: SOLVENT EFFECT ON THE REACTIVITY RATIOS $k(\Delta)/k(R)$ AT 20°

Compounds	Reactivity ratios $k(\Delta)/k(R)$ in the systems			
	$MeOH/I_2$	$AcOH/I_2$	$AcOH/Br_2$	C_6H_5Cl/Br_2
$C_3H_5Sn(CH_3)_3$	0.0063	0.10	3.7	28
$C_3H_5Sn(C_2H_5)_3$	0.091	1.81	11.1	33
trans-$CH_3{-}C_3H_4{-}Sn(CH_3)_3$	0.059	0.65	12.3	109
cis-$CH_3{-}C_3H_4{-}Sn(CH_3)_3$	0.050	0.68	8.5	93

DISCUSSION

Stereochemistry

The experimental results show clearly that electrophilic substitution occurs

with full retention of configuration, independent of the nature of the solvent or of the halogen. These conclusions are completely different from those published by Sisido[20] for the iodo- and *bromo*demetallation, of the optically active (1-methyl-2,2-diphenylcyclopropyl)trimethyltin in CCl_4. They observe "racemization" at carbon, and describe the reaction as a radical process; on the contrary, the protodemetallation with HBr in methanol proceeds with retention of configuration. A recent short communication[21] has resolved the controversy: when the reaction is carried out in the dark with very pure reagents, as we suggested[2], the halodemetallation proceeds with retention.

The retention of configuration observed here might be compared with the same stereochemical result obtained in the vinylic series[22], and perhaps also with those observed for bimolecular electrophilic substitutions at saturated carbon atoms studied either on main group element organometallics[23] or on transition metal complexes[24]. It must however be noticed that an inversion mechanism is strongly disfavoured with cyclopropylic substrates. The retention of configuration described in this work may thus certainly not be used as evidence to support a general picture of bimolecular displacements at saturated carbon atoms always occurring with retention of configuration. Nevertheless, the stereochemical result considered along with the high reactivity of cyclopropyltin compounds towards halogens suggests that retention of configuration is not unusual for this type of reaction.

Kinetic study and solvent effect

Structure–reactivity correlations in the cyclopropyltrialkyltin series

Reactivity of the alkyl groups: $k(R)$. The experimental reactivity sequences are identical in methanol and in acetic acid and, when the substituted alkyl group is kept constant, the rate constant is higher in methanol than in acetic acid. The presence on the tin atom of an electron-withdrawing cyclopropyl group [$\sigma^*(C_3H_5) = +0.110$], which can also inhibit the solvation at tin by steric hindrance, leads to a small decrease of the reactivity; thus $k_{Me}(Me_3SnC_3H_5)$ is 1.35 while $k_{Me}(Me_4Sn)$ is 1.80 in methanol; the corresponding values are 0.032 and 0.060 in acetic acid. Again $k_{Et}(Et_3SnC_3H_5)$ is 0.19 while $k_{Et}(Et_4Sn)$ is 0.22 in methanol; in acetic acid, the values are 0.007 and 0.020. The introduction of a *trans* methyl group on the cyclopropyl ring weakly increases the reactivity, whereas the introduction of a *cis* methyl group decreases the reactivity.

These results are in complete agreement with the view that the determining influences on the rate of reaction are the ability of the substituted group to accept the electrons of the carbon–metal bond and the electronic effect of the SnR_3 group.

Reactivity of the cyclopropyl group: $k_2(\Delta)$. In all three solvents, the reactivity sequences are similar: $k_2(\Delta)(C_3H_5SnEt_3) > k_2(\Delta)(C_3H_5SnMe_3)$ and $k_2(\Delta)(trans\text{-}CH_3\text{–}C_3H_4\text{–}SnMe_3) > k_2(\Delta)(cis\text{-}CH_3\text{–}C_3H_4\text{–}SnMe_3) > k_2(\Delta)(C_3H_5\text{–}SnMe_3)$. The first sequence can be understood in terms of a better stabilization of the $SnEt_3^+$ than of the $SnMe_3^+$ leaving group. The second shows the importance of the pseudo-π cyclopropane ring orbital participation in the reaction mechanism (see Fig. 2).

These schemes are very similar to those proposed in the vinyltrialkyl series, where the same types of substituent effects have been observed[22].

Importance of the solvent for the orientation of reaction (*Table* 8). The selectivities $k_2(\Delta)/k_2(R)$ are quite different in a polar solvent such as methanol for which

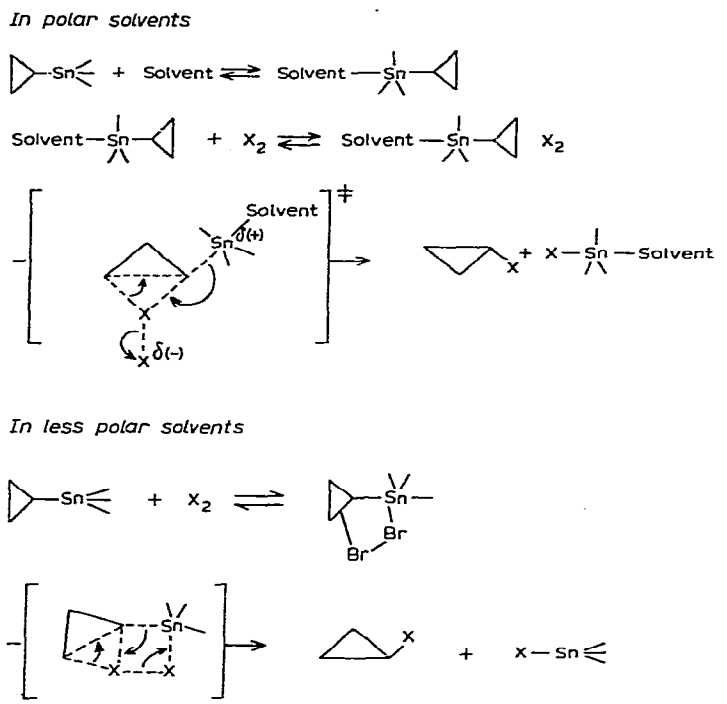


Fig. 2. Proposed reaction mechanisms for the halodemetallation of cyclopropyltin compounds in polar and in less polar solvents.

$k_2(\Delta)/k_2(R) \ll 1$, than in a less nucleophilic solvent like chlorobenzene, for which $k_2(\Delta)/k_2(R) \gg 1$. Furthermore, the selectivity is lower for bromine than iodine, which is another example of the selectivity–reactivity relationship[3,19].

The high reactivity of the cyclopropyl group observed in chlorobenzene is entirely justified by the electronic structure of cyclopropane, which withdraws the electrons through its exocyclic orbitals[25] and stabilizes the electrons of the carbon–metal bond much more efficiently than the R groups.

The very low reactivity of the ring observed in methanol can only be interpreted in terms of some special property associated with the nucleophilic power of the solvent. If a predetermining nucleophilic catalysis by the solvent at the tin atom is assumed, one has to consider a pentacoordinate complex with a trigonal bipyramidal geometry[26] having an apical solvent molecule and either an apical cyclopropyl group or an apical alkyl group. The two possible solvated intermediates are depicted in Fig. 3. It may be further assumed that only an apical group can be used as leaving

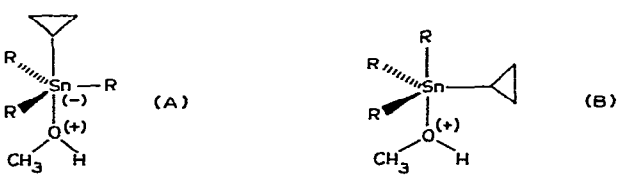


Fig. 3. Possible solvation of cyclopropyltrialkyltins by methanol.

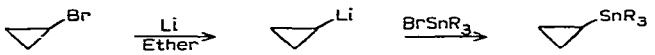
group and be attacked by an electrophile.

A careful examination of the models shows very clearly that the interactions between the ring and the alkyl groups are much more important in A than in B, and still more important with an α-methyl group in the *cis*-position. This seems to be a rather attractive explanation for the low $k(\Delta)/k(R)$ ratio in polar solvents. This is also entirely consistent with the high reactivity observed for the protodemetallation of dicyclopropylmercury in water[27]: this linear molecule might be less sensitive to nucleophilic oxygen, since mercury is a weak acid; furthermore, the steric requirements for a pentacoordinate organotin complex and for a probably tricoordinate mercury one are quite different. Another explanation might be that the normal stereochemistry in methanol is inversion of configuration, which is rather unfavourable for the cyclopropyl group.

EXPERIMENTAL

Syntheses

Organometallic derivatives. The cyclopropyltrialkyltin derivatives were prepared in good yields by the usual route:



The identity of each compound was confirmed by its demetallation products, and its purity (>99%) was checked by GLC.

The (*cis*-α-methylcyclopropyl)- and (*trans*-α-methylcyclopropyl) trimethyltins were prepared from the corresponding mixture of bromides and isolated by preparative GLC (column: 5m × 3/4 inch, chromosorb P 60–80 mesh + carbowax 20M, 75–220°, 80/20 N_2/He mixture, 3 kg/cm^2, 700 ml/min, retention temperature: 106° for the *trans* isomer; 116° for the *cis* isomer).

Cyclopropyl halides. The cyclopropyl bromides were made by bromodecarboxylation with mercuric oxide[28] and isolated by fractional distillation. The *cis*- and *trans*-α-methylcyclopropyl bromides were prepared by Applequist and Peterson's method[29]. Reaction of iodine with the organolithium compounds in ether gives the iodides which can be isolated by GLC (column: 3m × 1/4 inch, chromosorb P 100–120 mesh, diisodecyl phthalate 33% weight, 120° progr. 1°/min, H_2, 2 kg/cm^2, 40 ml/min, retention time: 32 min for the *trans* iodide; 35 min for the *cis* iodide; for the analogous bromides, analogous conditions are used: isoth. 87°, H_2, 60 ml/min, retention time: 12 min for the *trans* bromide, 16 min for the *cis*-bromide).

Solvents and reagents

Methanol (U.C.B., P.A.); chlorobenzene (Merck, P.A.); acetic acid (U.C.B., P.A.) and sodium iodide (Merck, P.A.) were used as such. Sodium perchlorate (Riedel–De Haen) was dried at 200° for 12 h. Iodine was sublimed three times before use. Bromine was distilled twice after drying over $CaCl_2$.

Methods

The reactions were followed on a Beckman-B (cell: 1.001 cm), a Zeiss (5.001

cm-cell) or on a Cary 15 (10 cm-cell) spectrophotometer, the temperature being regulated at 20° (Haake-thermostat).

The NMR spectra of 5% solutions were recorded with a 60 MHz Varian A60, with tetramethylsilane as internal standard.

Analytical GLC was carried out with a F & M 500 Chromatograph. For the preparative GLC we used a F & M 770 apparatus.

GLC, reaction products and stereochemistry

The reaction conditions for the stereochemical study were identical to those chosen for the kinetic experiments. The concentration of the organometallic compound did not exceed 5% in weight, and the halogen was added slowly to the organometallic solution at 20° with exclusion of light. The reaction products were analyzed by GLC, the peak areas being measured with good precision by planimetry. The sensitivity of the analysis is determined by the area of the 2-methylcyclopropyl halide peak, which is not very important when the reaction is studied in methanol. The reaction products were isolated by GLC, trapped at low temperature and analyzed by NMR and IR spectroscopy (on Perkin–Elmer PE 21 and PE 125 spectrophotometers).

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