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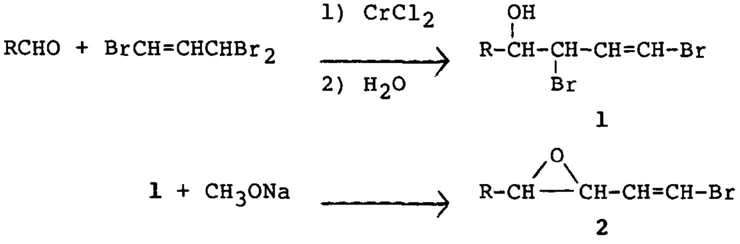
A CONVENIENT AND STEREOSELECTIVE CONVERSION OF ALDEHYDES INTO β-BROMOVINYLOXIRANES MEDIATED BY CHROMIUM(II) CHLORIDE

Jacques Augé
Institut de Chimie Moléculaire d'Orsay, Laboratoire de Chimie Organique
Multifonctionnelle, Université de Paris-Sud, Bt 420, F91405 Orsay Cédex

Abstract. The monoreduction of 1,3,3-tribromopropene by chromium(II) chloride gave a chromium(III) species converting aldehydes into β-bromovinyloxiranes. The stereochemistry of this new reaction is mainly temperature dependent.

The conversion of aldehydes into vinyloxiranes can be mediated by sulfur,[1] selenium[2] or organometallic[3] species. More difficult seems to be the preparation of β-bromovinyloxiranes.[4] These compounds should be good intermediates in carbon-carbon coupling reactions, but difficulties to obtain pure stereoisomers have prohibited their use. This led us to investigate a chromium(II) methodology.

The reduction of allyl halides or gem-diiodoalkanes (but not gem-dibromoalkanes) by chromium(II) chloride gives chromium or geminal dichromium species which undergo highly selective additions on aldehydes, leading respectively to homoallyl alcohols[5,6] or (E)-olefins.[7] We took advantage of these results and studied the reduction of 1,3,3-tribromopropene[8] by chromium(II) chloride in the presence of an aldehyde. Bromohydrins 1 were isolated as mixtures of stereoisomers, then allowed to react with a base:



$$\mathrm{RCHO + BrCH{=}CHCHBr_2 \xrightarrow[2)\ H_2O]{1)\ CrCl_2} R\text{-}\overset{\displaystyle OH}{\overset{|}{C}H}\text{-}\underset{\displaystyle Br}{\underset{|}{C}H}\text{-}CH{=}CH\text{-}Br}$$

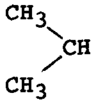
1

$$\mathrm{1 + CH_3ONa \longrightarrow R\text{-}CH\overset{O}{\frown}CH\text{-}CH{=}CH\text{-}Br}$$

2

Bromovinyloxiranes 2 were separated by preparative HPLC and identified by NMR spectroscopy.[9] The percentage of each stereoisomer was dependent on experimental conditions (see following table).

The salient features of the process are as follows:
(1) the (trans,Z) stereoisomer is always the major product in THF solution,
(2) temperature is a key factor for stereoselectivity (runs 3, 4, 5 and 6).

Run	R	Method	Temp. °C	Time	Isolated yield %	% Products trans,E	trans,Z	cis,Z	cis,E
1	Ph	B	-28	6 h	66	17	63		20
2	Ph	A	-28	3 h	76	11	80		9
3	Ph	A	-28	5 h	81	14	75		11
4	Ph	A	-12	35 min	88	6	83	7	4
5	Ph	A	0	30 min	67	3	83	13	1
6	Ph	A	+20	30 min	51	4	59	36	1
7	$CH_3(CH_2)_6$	A	-25	3 h	79	22	66	1	11
8	$Ph(CH_2)_2$	A	-12	6 h	40	10	79	7	4
9		A	-12	5 hr	57		90		

Method A: addition of tribromopropene to an aldehyde-$CrCl_2$ (2:1:4 molar ratio) suspension in THF.

Method B : addition of aldehyde-tribromopropene mixture to a $CrCl_2$ (1:2:2 molar ratio) suspension in THF.

We expect the trans/cis ratios in bromovinyloxiranes **2** to reflect the anti/syn ratios in bromhydrins **1**. Thus the trans selectivity in THF may be interpreted in terms of a chair transition state.[6] When an aldehyde-$CrCl_2$ complexe is preformed (method A), the coordination may be the origin of both the rate enhancement and the trans selectivity[11] (compare runs 1 and 2).

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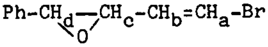
References and notes

1. J.C. Paladini and J. Chuche, Bull. Soc. Chim. Fr. **1974**, 192.
   M. Pohmakotr, K.H. Geiss and D. Seebach, Chem. Ber. **1979**, 112, 1420.
2. D. Van Ende and A. Krief, Tetrahedron Lett. **1976**, 17, 457.
3. J. Augé and S. David, Tetrahedron Lett. **1983**, 24, 4009 and references cited therein.
4. J.P. Bény, J.C. Pommelet and J. Chuche, Bull. Soc. Chim. Fr. **1981**, II-369.
5. Y. Okude, S. Hirano, T. Hiyama and H. Nozaki, J. Am. Chem. Soc. **1977**, 99, 3179.
6. T. Hiyama, K. Kimura and H. Nozaki, Tetrahedron Lett. **1981**, 22, 1037.
7. T. Okazoe, K. Takai and K. Utimoto, J. Am. Chem. Soc. **1987**, 109, 951.
8. This new compound was easily prepared from 1-bromopropene and 2 equivalents of N-bromosuccinimide; the mixture was refluxing overnight in CCl_4 in presence of a radical initiator. Distillation (bp_{16} = 88-92°C) gave 1,3,3-tribromopropene (E/Z = 50:50, 69% yield). The composition found (C, H, Br) was satisfactory for the formula $C_3H_3Br_3$.
9. NMR-^1H (250 MHz, $CDCl_3$) parameters for  $Ph\text{-}CH_d\text{—}CH_c\text{-}CH_b\text{=}CH_a\text{-}Br$ (with O bridging CH_d and CH_c) were given as an example:

   (trans,E): J_{ab} = 13.8 Hz, J_{cd} = 2 Hz; (cis,E): J_{ab} = 13.8 Hz, J_{cd} = 4.2 Hz
   (trans,Z): J_{ab} = 7.5 Hz, J_{cd} = 2 Hz; (cis,Z): J_{ab} = 7.5 Hz, J_{cd} = 2 Hz

   Identical J_{cd} coupling constants were observed for the (trans,Z) and (cis,Z) stereoisomers; this problem was resolved by converting (trans,Z)β-bromovinyloxirane into (trans)ethynyloxirane. Indeed the ethynyloxirans display a 2 Hz coupling constant for the trans isomer and a 4 Hz coupling constant for the cis one.[10]
10. J.P. Bény, J.C. Pommelet and J. Chuche, Bull. Soc. Chim. Fr. **1981**,II-377.
11. When DMF, which is an effective ligand for chromium(II)[6,7], was used as the solvent, yield is low and selectivity is reverse; (cis,Z) is the major product.

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