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Photosolvolysis of optically active 4-methyl-cyclohexylidenemethyl(aryl)iodonium tetrafluoroborate

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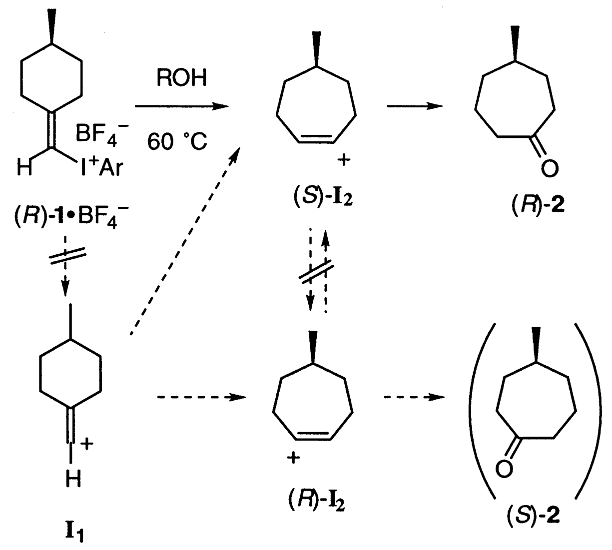
Abstract—The title reaction gives largely racemized 4-methylcycloheptanone, but the enantiomeric product in slight excess has a different form depending on the leaving group, ArI, of the iodonium salt. The results indicate that the photosolvolysis does not proceed via a completely achiral state. © 2002 Elsevier Science Ltd. All rights reserved.

The optically active 4-methylcyclohexylidenemethyliodonium salt **1** undergoes a stereospecific rearrangement to 4-methylcycloheptanone (**2**) during its thermal solvolysis, with complete retention of the optical purity in the product.[1] This indicates that in this reaction no primary vinyl cation intermediate $\mathbf{I_1}$ is involved. Such a linear and achiral intermediate would have led to racemic products, as shown in Scheme 1. This chirality probe approach was thus successful in definitely excluding the intermediacy of primary vinyl cations[2] in thermal reactions of vinyl iodonium salts. Here, the question is addressed: is it possible to generate primary vinyl cations upon irradiation? Photochemical generation of primary vinyl cations was reported in the irradiation of vinyl halides[3] and vinyl iodonium salts.[4] In order to examine the contribution of a primary vinyl cation to their photochemical pathway, we have employed the chirality probe approach[5] to the photosolvolysis of the vinyl iodonium salts **1**.



Scheme 1.

Irradiation of (*R*)- or (*S*)-4-methylcyclohexylidenemethyl(aryl)iodonium tetrafluoroborate ($\mathbf{1}\cdot BF_4^-$) in methanol ($\lambda_{exc} = 254$ nm) gave the mixture of products **2**–**7** depicted in Scheme 2.[6] The products **2**–**4** are the result of cleavage of the vinylic C–I bond, while **5**–**7** are those of cleavage of the phenylic C–I bond. The enantiomeric excess (ee) of products **2** and **5** was determined by GC measurements using chiral columns. The ee value of **2** is independent of the time of irradiation.[7] This suggests that secondary racemization of **2** due to its own photoreactivity does not proceed under the reaction conditions. Secondary reactions do occur: elongation of the time of irradiation results in a decrease in product yields, due to decomposition of the products. Product yields and ee values in the initial period of the photoreaction are summarized in Table 1. After 5 min of irradiation, ca. 20–10% of iodonium salt **1** still remained, and the ee of the remaining **1** equals that of the starting material **1**.[8] Thus, the decrease in ee of product **2** is associated with the photochemical reaction of **1** forming that product. Another potential substrate to use as chirality probe in photosolvolysis, (*R*)- or (*S*)-4-methylcyclohexylidenemethyl bromide (**8**), undergoes racemization faster than solvolysis product formation under the same conditions.[9]

Keywords: iodonium salt; vinyl cation; photosolvolysis.

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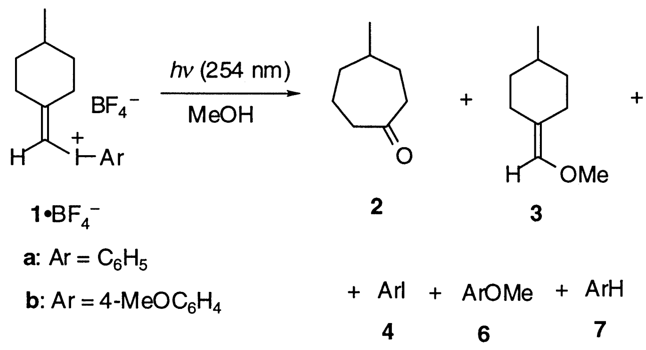

Scheme 2.

Table 1. Products of photosolvolysis of iodonium **1** in alcohol at room temperature

Run	Substrate (% ee)	Solvent	Time (min)	% Yield (% ee)					
				2	**3**[a]	**4**	**5**	**6**	**7**
1	**1a** (*R*, 69)	MeOH	4	3 (*R*, 7)	<1	>1	20 (*R*, 50)	<1	[b]
2	**1a** (*S*, 79)	MeOH	4	2 (*S*, 13)	<1	>2	13 (*S*, 66)	<1	[b]
3	**1b** (*R*, 70)	MeOH	5	2 (*S*, 17)	<1	12	5 (*R*, 53)	1	1
4	**1b** (*R*, 70)	MeOH	10	3 (*S*, 19)	3	27	6 (*R*, 53)	2	5
5	**1b** (*R*, 70)	MeOH	15	3 (*S*, 17)	<1	21	9 (*R*, 48)	2	4
6	**1b** (*S*, 81)	MeOH	10	3 (*R*, 21)	4	24	11 (*S*, 60)	<1	6
7	**1b** (*R*, 70)	MeOH/H_2O[c]	5	6 (*S*, 7)		8	2 (*R*, 45)		<1
8	**1b** (*S*, 81)	MeOH/H_2O[c]	5	6 (*R*, 10)		8	2 (*S*, 52)		1
9	**1b** (*S*, 81)	CF_3CH_2OH	10	8 (*R*, 11)		12	2 (*S*, 66)		5

[a] The ee value could not be determined accurately because of low yield, but it was largely racemized.

[b] Not determined due to the volatility.

[c] 50% vol.

The ee values of the cycloheptanones **2** are much smaller than that of the starting iodonium salts **1** but are not zero. It is noteworthy that the phenyl iodonium salts *R*- and *S*-**1a** preferentially give *R*- and *S*-**2** (runs 1 and 2), while the *p*-methoxyphenyl iodonium salts *R*- and *S*-**1b** preferentially give *S*- and *R*-**2** (runs 3–9), respectively. The phenyl iodonium salt **1a** gives preferentially the same enantiomer as the thermal solvolysis, while the excess enantiomer obtained in the photosolvolysis of **1b** is opposite to that in the thermal solvolysis. The results cannot be explained from contamination of the thermal reaction.

That is, the slight excess of enantiomer of **2** formed in the photosolvolysis depends on the leaving group, ArI, of the iodonium salt. The primary vinyl cation $\mathbf{I}_1$ of Scheme 1 as product-forming intermediate in the photoreaction would result in racemization of **2**, but cannot explain the incomplete racemization nor the stereodivergent product formation depending on the leaving group. The mechanism for the thermal stereospecific formation of *R*-**2** from *R*-**1** is established to involve participation of the *trans*-β-alkyl group in the departure of ArI.[1] The decrease of the ee value of **2** may well be the overall result of a combination of photochemical vinyl cation formation and alkyl participation. A tentative explanation for the chirality results reported here is that the photoreaction occurs not (only) via the free primary vinyl cation $\mathbf{I}_1$, but via an ion-molecule complex of $\mathbf{I}_1$, ArI and a solvent molecule within a solvent cage (cf. Ref. 4). The exact constitution of this complex and orientation of the constituents depend on the nature of the leaving group ArI, for example because the complex is formed from free **1** or from methanol-coordinated **1**.[4] The residual asymmetry in the ion-molecule(s) complexes leads to preferential migration of one of the two β-alkyl groups.

In conclusion, the chirality probe approach shows that photosolvolysis does not proceed via a completely achiral state. The primary vinyl cation involved is very probably not in a free, dissociated form.

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6. Tetrafluoroborate salt of *R*- or *S*-**1** (1 mg) was dissolved in 1 mL of methanol in a quartz cell and irradiated using a low-pressure mercury lamp (30 W) for 5–15 min at room temperature. The products were extracted with ether and washed with water. The yields of products were determined by GC using tetradecane as an internal standard.
7. At low conversion, the vinyl iodide **5** essentially maintained the ee value of **1**, and thus the configuration of **1**. In the course of the photoreaction the ee value of **5** slightly decreased. The racemization may be attributed to a secondary photoreaction due to irradiation of **5** (e.g. *E*/*Z* isomerization).
8. The amount and the ee value of the remaining iodonium salt **1** were determined by GC after transforming **1** into bromide **8** because of the instability of **1**. See also Ref. 1.
9. The photosolvolysis of **8** was carried out in the same way as that of **1**, although it required longer times of irradiation.