Solvolysis of β,β-Dialkylvinyliodonium Salt: Primary Vinyl Cation Intermediate and Alkyl Participation

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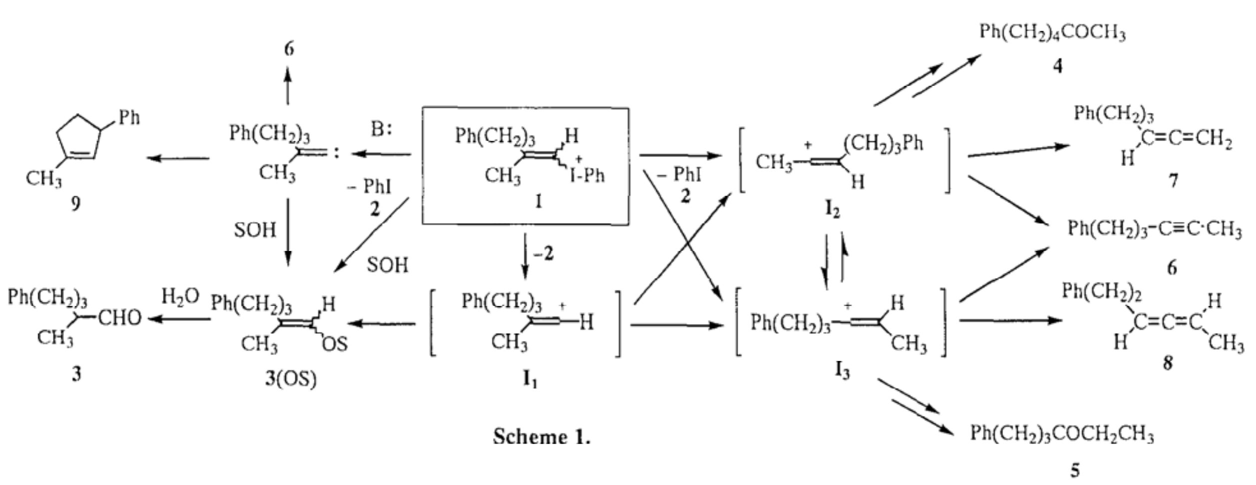
Solvolysis of both *E* and *Z* isomers of a β,β-dialkylvinyl(phenyl)iodonium salt gave extensively rearranged products. A mechanism involving a primary vinyl cation intermediate as well as the alkyl participation leading to secondary vinyl cations is proposed.

Vinyl cation is not so unstable as generally believed. The gas-phase thermochemical data show that the stability of vinyl cation is in-between methyl and ethyl cations,[1,2] and β,β-dimethylvinyl cation is estimated to be nearly as stable as ethyl cation from the gas-phase[1,2] and theoretical results.[3] So, a β,β-dialkylvinyl cation may be generated as a transient intermediate in a poorly nucleophilic medium from a precursor with a good leaving group. In fact, a primary vinyl cation was observed in a superacid,[4] and generated by photoexcitation[5] and by the nuclear decay.[6] Generation of cycloalkylidenemethyl cation was suggested for reaction of the triflate in aqueous solution.[7]

We have demonstrated that vinyl iodonium salts are good precursors for vinyl cations due to a high nucleofugality of the iodonio group.[8] A 1-cyclohexenyliodonium salt undergoes solvolysis through an intermediate formation of cyclohexenyl cation,[8] while solvolysis of styryliodonium salt takes place with the phenyl participation via vinylenebenzenium ion.[9] Primary 1-alkenyliodonium salts undergo a concerted S_N2 substitution with exclusive inversion but no sign of formation of primary vinyl cation was detected.[10] By contrast, we have now found that solvolysis of β,β-dialkylvinyliodonium salt, 2-methyl-5-phenyl-1-pentenyl(phenyl)iodonium tetrafluoroborate (**1**), results in extensive rearrangements to give both substitution and elimination products. Although this seems to suggest an intermediary formation of a primary vinyl cation stabilized by β-alkyl groups, an alternative mechanism involving the alkyl participation to lead directly to secondary vinyl cations cannot be excluded.[11]

Solvolysis of both isomers of **(*E*)-1** and **(*Z*)-1**[12] was examined in 2,2,2-trifluoroethanol (TFE), acetic acid, and methanol at 60 °C. The products were extracted with pentane containing tetradecane as an internal standard and determined by gas chromatography before and after treatments with aqueous hydrochloric acid. The products include iodobenzene (**2**), carbonyl compounds **3**-**5** (after hydrolysis) derived from the initial substitution products, enol ethers or esters, and elimination products **6**-**8** (Scheme 1).[14] Results are summarized in Table 1. The rearranged products must come from secondary vinyl cation, $\mathbf{I_2}$ or $\mathbf{I_3}$, which may be generated by migration of the β-alkyl group, 3-phenylpropyl or methyl, either from the primary vinyl cation $\mathbf{I_1}$ or directly from **1** (alkyl participation). The cyclic product **9** was also detected in methanol. This five-membered product is a typical one derived from the alkylidenecarbene generated by the α-elimination.[15] The carbene products were observed in the reaction in the presence of a base, e.g., 0.1 mol dm^{-3} sodium acetate in methanol (Table 1).

Possible substitution products must include three pairs of geometrical isomers of enol ethers or esters, but we could only identify the unrearranged ones **3**(OS) because of a poor separation of GC peaks of the minor products. The rearranged substitution products were identified and determined as ketones after acid hydrolysis. The yield of unrearranged aldehyde **3** is quite small in TFE and acetic acid, and the % rearrangements are greater than 90% (Table 1). The *E* isomer of **1** seems to rearrange more readily than **(*Z*)-1**. Migration of the 3-phenylpropyl group leads to **4**, **6**, and **7** through the cation $\mathbf{I_2}$, while that of the methyl group affords **5**, **6**, and **8** through $\mathbf{I_3}$. The group *trans* to the leaving iodonio group migrates more



Scheme 1.

Table 1. Product distribution for the solvolyis of **1** at 60 °C[a]

struct. of **1**	solv.	reaction time/h	product yield/%								(**4** + **7**)/(**5** + **8**)
			2	**3** (Z/E)[b]	**4**	**5**	**6**	**7**	**8**	**9**	
E	TFE	30	85	0.9 (nd)	15	8.9	30	0.5	0.2	0	63/37
Z	TFE	80	62	2.9 (nd)	11	17	34	0.3	0.4	0	39/61
E	AcOH	40	63	2.0 (0/0.3)	21	3.4	50	2.7	(1)[c]	0	84/16
Z	AcOH	80	70	9.0 (1.0/3.9)	7.7	22	47	0.5	(3)[c]	0	25/75
E	MeOH	16	80	26 (6.2/16)	12	trace	25	7.0	0.3	2.8	large
Z	MeOH	46	68	61 (10.3/31)	trace	3.7	12	trace	2.7	5.4	small
E(*Z*)[d]	MeOH	1	79	80 (17/47)	0	0	1.7	0	0	9.3	

[a] Products were determined by gas chromatography after treatments with aqueous hydrochloric acid. [b] Percent yields of ***Z*-3**(OS) and ***E*-3**(OS) before the acid treatments. [c] Partially overlapped with another peak. [d] Reactions were carried out in the presence of 0.1 mol dm^{-3} sodium acetate, and both (***E***)- and (***Z***)**-1** gave essentially the same results.

readily than the *cis* group. Furthermore, the phenylpropyl group seems to show slightly higher tendency to migrate than the methyl group in the same stereochemical arrangement, judging from the magnitudes of (**4** + **7**)/(**5**+ **8**) value for the *E* and *Z* isomers as well as their total rearranging tendencies. The fraction of rearrangement is smaller in methanol, but the unrearranged products must mostly be formed through α-elimination followed by solvent insertion to the carbene intermediate.

The *trans* alkyl group migrates more than the *cis* group, but not exclusively. The observed migration of the *cis* group implies either the intermediary formation of the primary vinyl cation $\mathbf{I}_1$, in which both β-alkyl groups can migrate, or the alkyl participation leading directly to $\mathbf{I}_2$ and $\mathbf{I}_3$ (respectively from (*E*)**-1** and (*Z*)**-1**), followed by a rapid but still partial 1,2-shift of hydride between them. Since theoretical calculations show that the 1,2-hydride shift of 1-methyl-1-propenyl cation occurs essentially without barrier,[16] neither of the processes can be excluded.

The unrearranged products may be formed from trapping of the primary cation $\mathbf{I}_1$ or by the vinylic S_N2 reaction if the α-elimination-insertion (carbene) process is unlikely in acetic acid as well as in TFE. Stereochemistry of the substitution observed in acetic acid, where an appreciable amount of the retained product **3**(OAc) is formed (Table 1), is incompatible with the exclusive S_N2 pathway. Substitution with retention may occur via an addition-elimination[17] or ligand coupling pathway.[9b,18] Both of these pathways are unlikely for such a poor nucleophile like acetic acid. In the present reaction in TFE and acetic acid, primary vinyl cation $\mathbf{I}_1$ must be involved, and this may be taken as more direct evidence for generation of a primary vinyl cation in solvolysis.[11] A question remains, however, if the lifetime of this unstable vinyl cation as an intermediate can be rationalized. A β,β-dialkylvinyl cation may be as stable as ethyl cation,[1] and the latter cation cannot have enough lifetime in aqueous solution.[19] However, it may survive during a few bond vibrations in a less basic and less nucleophilic solvent.

In conclusion, primary β,β-dialkylvinyl cation is formed in poorly nucleophilic media, and the secondary vinyl cations are formed by rearrangement of the primary cation as well as through the direct alkyl participation during the solvolysis of the β,β-dialkylvinyliodonium salt.

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