[Chem. Pharm. Bull. 33(1) 41—47 (1985)]

Iodine(III)-Mediated Allylation of Aromatic Compounds and Alcohols Using Allylmetal (Group IVb) Compounds

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(Received April 23, 1984)

The reaction of allylmetal (group IVb) compounds with aromatic compounds and iodosylbenzene in the presence of BF_3–Et_2O afforded the corresponding allylation products. Allylation of alcohols was also carried out to give allyl ethers. The activation of iodosylbenzene by the coordination of BF_3–Et_2O was assumed to be one of the most important factors for the reaction. The involvement of the reactive allyliodine(III) compounds in these reactions is discussed.

Keywords——hypervalent organoiodine compound; iodosylbenzene; allylsilane; allylgermane; allylstannane; allyliodine(III) compound

Allymetal (group IVb) compounds usually act as species equivalent to allyl anion, and transfer the allyl group to various kinds of electrophiles in the presence of a Lewis acid.[1] Recently we reported that allylmetal (group IVb) compounds, on treatment with thallium(III) trifluoroacetate (TTFA) or arylthallium bis(trifluoroacetate), produced highly reactive allylorganothallium(III) compounds as transient intermediates by transmetalation. The allylthallium(III) compounds act as species equivalent to allyl cation, and react with a variety of nucleophiles.[2] The reaction was successfully applied to the synthesis of allylsubstituted aromatic compounds, *N*-allylamides, allyl ethers, allyl esters, and allyl nitrates.[3] Thus, the availability of the reaction has been well established. However, the use of the highly toxic thallium(III) compounds is undesirable, and consequently we wished to find alternative organometallic compounds with low toxicity or organic reagents without a heavy metal.

In the course of our investigation, we found hypervalent organoiodine compounds to be alternative and effective reagents for the allylation reaction. Thus, allyl-substituted aromatic compounds or allyl ethers were synthesized smoothly by the reaction of aromatic compounds or alcohols with allylmetal (group IVb) compounds and iodosylbenzene in the presence of BF_3–Et_2O, presumably *via* the formation of the reactive allyliodine(III) species, as shown in Chart 1.

M: Si, Ge, Sn

NuH: aromatic compound, alcohol

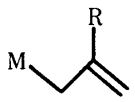
Chart 1

Results and Discussion

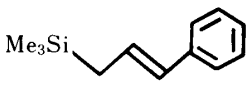
Hypervalent organoiodine compounds have been shown to be useful as mild oxidizing

reagents in organic synthesis[4] and biochemical model reactions, *e.g.* an epoxidation catalyzed by cytochrome P-450.[5] Oxidation of alcohols, sulfides, ketenes, and alkynes and α-hydroxylation of carbonyl compounds with iodosylbenzene have been reported.[6] Diaryliodonium salts are synthetically important owing to their reactivity with a variety of nucleophiles including halides, alkoxides, amines, Grignard reagents, and aryllithiums.[7] However, the synthetic utility of the alkyl- or allyl-aryliodine(III) compounds has not been much investigated because of their thermodynamic instability.[8]

Treatment of allyltrimethylsilane (**1a**) with one equivalent of iodosylbenzene in an excess amount of benzene did not afford any allylation product at all, even on heating to reflux (run 1). The result suggests that iodosylbenzene itself is not sufficiently reactive to nucleophilic attack of the allylsilane **1a**. Therefore activation of either iodosylbenzene or allylsilane **1a** is expected to be involved in the allylation of benzene. The iodine–oxygen bond of iodosylbenzene has been shown to be highly ionic and considerable positive and negative charges develop on the iodine and oxygen atoms, respectively.[4b] Thus, it seems reasonable that a Lewis acid may activate iodosylbenzene by coordination to the oxygen atom. The positive charge developed on the iodine atom of iodosylbenzene may be significantly enhanced by the complexation with a Lewis acid. As the Lewis acid, we selected boron trifluoride etherate for the following reasons: i) it is inexpensive; ii) it is easily handled; iii) it does not contain a nucleophilic ligand, which may react with allyl cationic species generated. In fact, boron trifluoride etherate was found to be suitable as a catalyst for the activation of iodosylbenzene. Allylbenzene was obtained in 73% yield from the reaction of allylsilane **1a** with iodosylbenzene and benzene in the presence of one equivalent of BF_3–Et_2O at −20 °C (run 3). The reaction also proceeded smoothly in the presence of a catalytic amount of BF_3–Et_2O (run 2). The results of allylation of various aromatic compounds are summarized in Table I.



1a : R=H, M=$SiMe_3$
1b : R=H, M=$GeMe_3$
1c : R=H, M=$SnBu_3$
2 : R=$(CH_2)_2OAc$, M=$SiMe_3$



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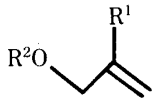
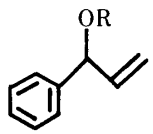


4a : R^1=H, R^2=Et
4b : R^1=$(CH_2)_2OAc$, R^2=Me
4c : R^1=$(CH_2)_2OAc$, R^2=Et
4d : R^1=$(CH_2)_2OAc$, R^2=$(CH_2)_2OMe$
4e : R^1=$(CH_2)_2OAc$, R^2=$CH_2C_6H_5$
5 : R^1=$(CH_2)_2OAc$, R^2=Ac



6a : R=Me
6b : R=Et

7a : R=Me
7b : R=Et

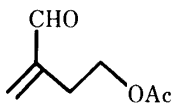


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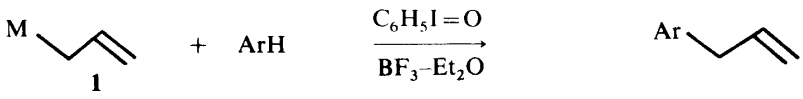
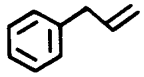
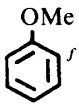
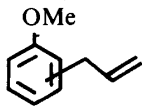
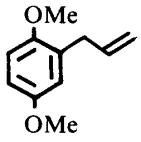
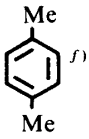
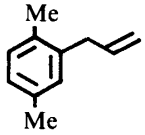
Chart 2

Allyltrimethylgermane (**1b**) was also shown to be an effective reagent, like allylsilane **1a** (run 4). However, the reaction with allyltributylstannane (**1c**) gave a much lower yield of allylbenzene (run 5). The poor result with **1c** may be attributable in part to its instability under the acidic conditions. As in the case of the allylation of anisole with allylmetal (group IVb) compounds by using TTFA as a reagent for transmetalation,[3d] a mixture of regio-isomeric products, *o*- and *p*-allylanisoles, was produced in this iodine-mediated reaction, though the *p*-

TABLE I. Allylation Reaction of Aromatic Compounds Using **1** and Iodosylbenzene[a]



Run	Aromatic compd.	**1** (M)	BF_3–Et_2O[b]	Reaction conditions (h)	Product	Yield[c] %
1	 [d]	**1a** ($SiMe_3$)	0	RT (1.5) then 80 °C (3)[e]		0
2		**1a** ($SiMe_3$)	0.25	10 °C (1)[e]		(67)
3		**1a** ($SiMe_3$)	1	−20 °C (1)		(73)
4		**1b** ($GeMe_3$)	1	−20 °C (1)		(74)
5		**1c** ($SnBu_3$)	1	−20 °C (1)		(25)
6	 [f]	**1a** ($SiMe_3$)	1	−20 °C (1)		(71)[g]
7	 [f]	**1a** ($SiMe_3$)	1	−78 °C (2) then −30 °C (1)		44
8	 [f]	**1a** ($SiMe_3$)	1	−20 °C (1)		42

a) See the experimental section for details. *b*) Mol eq to **1**.
c) Isolated yield and GLC yield (shown in parentheses).
d) 50 mol eq of benzene with respect to **1** was used.
e) Reactions were carried out in benzene.
f) 10 mol eq of aromatic compound with respect to **1** was used.
g) The ratio of *o*- to *p*-isomer was 1 : 3.4. RT = room temperature.

isomer was obtained as the major product (run 6).

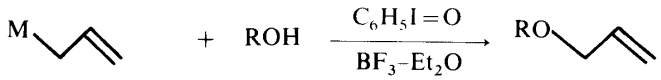
Alcohols also act as efficient nucleophiles in the reaction. The results of allylation of alcohols are summarized in Table II. The synthesis of allyl ethyl ether (**4a**) was achieved in high yields by utilizing the combination of iodosylbenzene and BF_3–Et_2O (runs 1—3).

Iodosylbenzene has been shown to oxidize alchols in dioxane on heating at reflux, yielding the corresponding aldehydes or ketones.[6a] The results of allylation of alcohols (Table II), however, clearly show that the allylmetal compounds are much more reactive than the primary alcohols toward iodosylbenzene activated by coordination with BF_3–Et_2O. In the synthesis of the allyl benzyl ether **4e**, oxidation of benzyl alcohol was observed, resulting in the formation of benzaldehyde in 7% yield (run 7). Reaction of cinnamyltrimethylsilane (**3**) with methanol or ethanol gave rise to a mixture of regio-isomeric products: in both cases, the rearranged allyl ethers **6a** and **6b** were concluded to be the major products, on the basis of analysis of the nuclear magnetic resonance (NMR) spectra of the crude reaction mixtures. The allylation reaction of alcohols was also applied to intramolecular cyclization, and 5- or 6-membered β-methylene cyclic ethers were obtained in good yields.[9]

Similarly, substitution of the trimethylsilyl group of the allylsilane **2** with an acetoxy group was carried out: treatment of **2** with iodosylbenzene and BF_3–Et_2O in acetic acid gave the desired allyl acetate **5** and α,β-enal **8** in 55 and 15% yields, respectively.[10]

It should be emphasized that one of the most important features in iodine-mediated allylation of aromatic compounds, alcohols, and acids may be the activation of iodosylben-

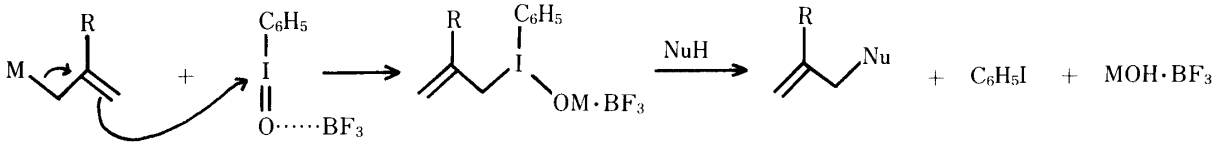
TABLE II. Allylation Reaction of Alcohols Using Allylmetal Compounds and Iodosylbenzene



Run	Allylmetal compd.	Alcohol	Reaction conditions (h)	Product	Yield[a] %
1	**1a**	EtOH	RT (2)	**4a**	(97)
2	**1b**	EtOH	RT (1.5)	**4a**	(91)
3	**1c**	EtOH	RT (1)	**4a**	(51)
4	**2**	MeOH	RT (0.5)	**4b**	87
5	**2**	EtOH	RT (1)	**4c**	80
6	**2**	MeO⌒OH	0 °C (2)	**4d**	84
7	**2**	$C_6H_5CH_2OH$[b,c]	RT (0.5)	**4e**	72[d,e]
8	**3**	MeOH	RT (0.75)	**6a**+**7a**[f]	93[d]
9	**3**	EtOH	RT (3.5)	**6b**+**7b**[g]	67[d]

a) Isolated yield and GLC yield (shown in parentheses).
b) 5 mol eq of benzyl alcohol with respect to **2** was used.
c) Dry dioxane was used as a reaction solvent. *d*) NMR yield.
e) Benzaldehyde was obtained in 7% yield.
f) The ratio of **6a** to **7a** was 64 : 36.
g) The ratio of **6b** to **7b** was 63 : 37. RT = room temperature.

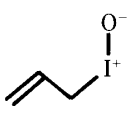
zene by coordination of BF_3–Et_2O to the oxygen atom.[11] The reaction process shown in Chart 3 seems to be plausible. The first step of the reaction is presumably the nucleophilic attack of the allylmetal compound on the highly electron-deficient iodine atom of the activated iodosylbenzene, yielding the highly reactive allyliodine(III) compound **9** as a transient intermediate, which can act as an allyl cation equivalent. Substitution of **9** with a nucleophile produces the allylation product **10**, with the concomitant loss of iodobenzene. Transformation of allyl iodide to allyl alcohol by using organic peracids was reported recently by Nagata and co-workers. It was assumed that the reaction proceeded *via* [2, 3] sigmatropic rearrangement of the reactive intermediate, the allyliodine(III) compound **11**.[12]



9 **10**

M = $SiMe_3$, $GeMe_3$, $SnBu_3$

Chart 3



11

Chart 4

Thus, we have developed a new and convenient method for the allylation of aromatic compounds and alcohols, based on a combination of an allylmetal (group IVb) compound with iodosylbenzene activated by the coordination of BF_3–Et_2O.

Experimental

Infrared (IR) spectra were recorded with a JASCO IR-A-1 spectrophotometer. Nuclear magnetic resonance (NMR) spectra were obtained with a JEOL JNM-FX 100 or Hitachi R40 spectrometer. Chemical shifts are reported relative to internal tetramethylsilane. Mass spectra (MS) were determined on a Hitachi RMU-7L spectrometer. Analytical gas-liquid chromatography (GLC) was performed on a Shimadzu GC-4CM gas chromatograph with 20% Silicone GE SE-30 or 20% Silicone DC-200 on Chromosorb W. Preparative thin layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, Silica gel F-254). Kieselgel 60 (Merck) was used for column chromatography.

Materials——Allyltrimethylsilane (**1a**) is commercially available (Shin-Etsu Silicon Chem.). Allylmetal compounds **1b**, **1c**, **2**, and **3** were prepared by the methods described previously.[3d,13] Iodosylbenzene was prepared by oxidation of iodobenzene with peracetic acid followed by hydrolysis with sodium hydroxide.[14] BF_3–Et_2O was freshly distilled from calcium hydride under nitrogen.

General Procedure for Allylation of Aromatic Compounds——BF_3–Et_2O was added dropwise to a stirred suspension of an allylmetal compound **1**, iodosylbenzene (one molar equivalent with respect to **1**), and an aromatic compound in dichloromethane under nitrogen. The mixture was stirred under the conditions described in Table I. The reaction mixture was poured into an aqueous sodium bicarbonate solution and extracted with ether. The extract was washed with water and with brine. After being dried, the pure products were isolated by silica gel column chromatography [hexane–ethyl acetate (30 : 1)] and preparative TLC [hexane–ethyl acetate (20 : 1)]. The yields are given in Table I. After the addition of appropriate internal standards, the yields were determined by analytical GLC in some experiments.

1-Phenyl-2-propene[3c]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1645, 1605, 1500, 1455, 1000, 920. NMR ($CDCl_3$) δ: 3.35 (2H, d, J=6 Hz), 4.8–5.3 (2H, m), 5.6—6.3 (1H, m), 7.0—7.5 (5H, m).

1-(2-Methoxyphenyl)-2-propene[3c]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1645, 1605, 1500, 1470, 1035, 920. MS *m/e*: 148 (M^+, base peak), 133, 119, 117, 115, 105, 91, 77. NMR ($CDCl_3$) δ: 3.38 (2H, d, J=6 Hz), 3.82 (3H, s), 4.8—5.3 (2H, m), 5.7–6.3 (1H, m), 6.7—7.4 (4H).

1-(4-Methoxyphenyl)-2-propene[3c]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1645, 1615, 1590, 1515, 1470, 1040, 1000, 920. MS *m/e*: 148 (M^+, base peak), 133, 121, 117, 105, 91, 77. NMR ($CDCl_3$) δ: 3.33 (2H, d, J=6 Hz), 3.78 (3H, s), 4.8—5.3 (2H, m), 5.6—6.3 (1H, m), 6.6—7.3 (4H).

1-(2,5-Dimethoxyphenyl)-2-propene[3c]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1605, 1595, 1505, 1470, 1050, 918. MS *m/e*: 178 (M^+, base peak), 163, 135, 91, 77. NMR ($CDCl_3$) δ: 3.35 (2H, d, J=6 Hz), 3.73, 3.76 (each 3H, s), 4.9—5.2 (2H, m), 5.7—6.2 (1H, m), 6.6—6.9 (3H).

1-(2,5-Dimethylphenyl)-2-propene[3c]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1635, 1605, 1505, 990, 915. MS *m/e*: 146 (M^+), 131 (base peak), 91, 77. NMR ($CDCl_3$) δ: 2.24, 2.29 (each 3H, s), 3.32 (2H, d, J=6 Hz), 4.8—5.2 (2H, m), 5.6—6.4 (1H, m), 6.8—7.3 (3H).

General Procedure for Allylation of Alcohols——BF_3–Et_2O (1.2 mmol) was added dropwise to a stirred suspension of an allylmetal compound (1 mmol) and lodosylbenzene (1.2 mmol) in an alcohol (50—100 mmol) under nitrogen. The mixture was stirred under the conditions described in Table II. The reaction mixture was poured into an aqueous sodium bicarbonate solution and extracted with ether. The extract was washed with brine. After being dried, the pure products were isolated by preparative TLC [hexane–ethyl acetate (7 : 1)]. The yields are given in Table II. After the addition of appropriate internal standards, the yields were determined by analytical GLC or from the NMR spectrum in some experiments.

1-Ethoxy-2-propene (4a)[3e]——bp 65—67 C. NMR ($CDCl_3$) δ: 1.22 (3H, t, J=7 Hz), 3.51 (2H, q, J=7 Hz), 3.97 (2H, d, J=6 Hz), 5.1—5.4 (2H, m), 5.7—6.2 (1H, m). The physical and spectral data were identical with those of an authentic sample prepared from allyl bromide by reaction with sodium ethoxide.

1-Acetoxy-3-(methoxymethyl)-3-butene (4b)[3e]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1660, 1455, 1370, 1230, 1100, 1040, 910. MS *m/e*: 157, 142, 130, 112, 83 (base peak), 55. NMR ($CDCl_3$) δ: 2.03 (3H, s), 2.40 (2H, t, J=7 Hz), 3.31 (3H, s), 3.88 (2H, s), 4.21 (2H, t, J=7 Hz), 4.98, 5.10 (each 1H, s).

1-Acetoxy-3-(ethoxymethyl)-3-butene (4c)[3e]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1660, 1370, 1230, 1100, 1040, 910. MS *m/e*: 131, 121 (base peak), 112, 103, 99, 81, 71, 43. NMR ($CDCl_3$) δ: 1.20 (3H, t, J=7 Hz), 2.03 (3H, s), 2.40 (2H, t, J=7 Hz), 3.46 (2H, q, J=7 Hz), 3.92 (2H, s), 4.20 (2H, t, J=7 Hz), 4.96, 5.10 (each 1H, s).

1-Acetoxy-3-[(2-methoxyethoxy)methyl]-3-butene (4d)——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1655, 1365, 1230, 1090, 1035, 910. MS *m/e*: 201, 156, 142, 127, 99, 83, 59 (base peak). NMR ($CDCl_3$) δ: 2.01 (3H, s), 2.39 (2H, t, J=7 Hz), 3.37 (3H, s), 3.53 (4H, s), 3.97 (2H, s), 4.19 (2H, t, J=7 Hz), 4.96, 5.08 (each 1H, s). *Anal.* Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.14; H, 8.81.

1-Acetoxy-3-(benzyloxymethyl)-3-butene (4e)——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1605, 1370, 1250, 1070, 915. MS *m/e*: 234, 233, 188, 174, 128, 107, 91, 68 (base peak). NMR ($CDCl_3$) δ: 2.00 (3H, s), 2.42 (2H, t, J=7 Hz), 3.97 (2H, s), 4.20 (2H, t, J=7 Hz), 4.48 (2H, s), 4.99, 5.13 (each 1H, s), 7.2—7.5 (5H, s). *Anal.* Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.63; H, 7.53.

1-Methoxy-1-phenyl-2-propene (6a)[15]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1455, 1090, 990, 930. NMR ($CDCl_3$) δ: 3.33 (3H, s), 4.63 (1H, d, J=6 Hz), 5.1—5.45 (2H, m), 5.75—6.2 (1H, m), 7.25—7.45 (5H, m).

1-Ethoxy-1-phenyl-2-propene (6b)[16]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1600, 1450, 1305, 1070, 990, 930. NMR ($CDCl_3$) δ: 1.23 (3H, t, J=6 Hz), 3.3—3.7 (2H, m), 4.75 (1H, d, J=7 Hz), 5.1—5.4 (2H, m), 5.8—6.2 (1H, m), 7.2—7.5 (5H, m).

1-Methoxy-3-phenyl-2-propene (7a)[15]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1600, 1455, 1380, 1120, 970. NMR ($CDCl_3$) δ: 3.40 (3H, s), 4.12 (2H, d, J=6 Hz), 6.28 (1H, dt, J=15, 6 Hz), 6.65 (1H, d, J=15 Hz), 7.2—7.5 (5H, m).

1-Ethoxy-3-phenyl-2-propene (7b)[17]——Colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1600, 1495, 1450, 1375, 1350, 1100, 965. NMR ($CDCl_3$) δ: 1.25 (3H, t, J=7 Hz), 3.56 (2H, q, J=7 Hz), 4.15 (2H, d, J=6 Hz), 6.28 (1H, dt, J=16, 6 Hz), 6.65 (1H, d, J=16 Hz), 7.2—7.5 (5H, m).

Synthesis of 3-Acetoxymethyl-3-buten-1-yl Acetate (5)——BF_3–Et_2O (27 mg, 0.19 mmol) was added dropwise to a stirred suspension of allylsilane **2** (38 mg, 0.19 mmol) and iodosylbenzene (42 mg, 0.19 mmol) in acetic acid (1.1 ml, 19 mmol) at room temperature under nitrogen. The mixture formed a clear, yellow solution and stirring was continued for 1 h at room temperature. The reaction mixture was poured into an aqueous sodium bicarbonate solution and extracted with ether. The organic layer was washed with brine, dried, and concentrated to give an oil. On preparative TLC [hexane–ethyl acetate (5 : 1)], the allyl acetate **5** (19.6 mg, 55%) and the conjugated enal **8** (4 mg, 15%) were isolated. **5**: colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1750, 1665, 1370, 1230, 1035, 915. MS *m/e*: 126, 84 (base peak), 72, 43. NMR ($CDCl_3$) δ: 2.06, 2.12 (each 3H, s), 2.42 (2H, t, J=7 Hz), 4.22 (2H, t, J=7 Hz), 4.56 (2H, s), 5.04, 5.15 (each 1H, s). *Anal.* Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 57.98; H, 7.57. **8**: colorless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2830, 2710, 1740, 1705, 1370, 1250, 1040, 950. NMR ($CDCl_3$) δ: 2.03 (3H, s), 2.62 (2H, t, J=6 Hz), 4.19 (2H, t, J=6 Hz), 6.08, 6.32 (each 1H, s), 9.57 (1H, s).

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