Transition-Metal-Catalyzed Carbenoid Reactions of Sulfonium Ylides

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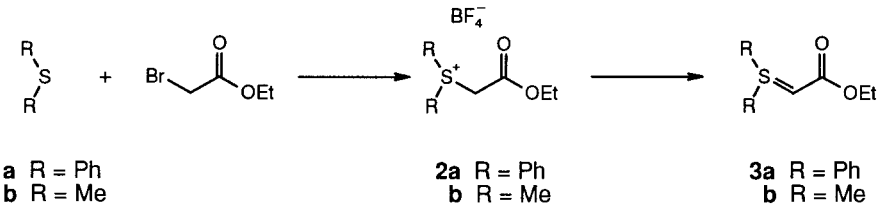
Olefins undergo cyclopropanation with diphenylsulfonium (ethoxycarbonyl)methylide (=diphenylsulfonium 2-ethoxy-2-oxoethylide; **3a**) in the presence of chiral Cu^{I} or Rh^{II} catalysts. *trans/cis* Ratios and ee's of the cyclopropanes **6** obtained with this ylide in the presence of a chiral Cu^{I} catalyst **7** are identical with those obtained with ethyl diazoacetate (**4**). In the case of catalysis with Rh^{II}, the *trans*/*cis* ratios of the cyclopropanes as well as the enantioselectivity change slightly upon going from the ylide **3a** to diazoacetate **4**.

1. Introduction. – Sulfur ylides react with carbonyl groups or with electron-deficient C=C bonds in a two-step reaction to afford epoxides or cyclopropanes, respectively [1]. With enantiomerically pure ylides, asymmetric cyclopropanation of C=O [2][3] and C=C bonds [4] is possible. In contrast, simple olefins are unreactive towards sulfur ylides. However, when decomposed in the presence of olefins under thermal or photochemical conditions, or in the presence of transition metals, sulfur ylides provide cyclopropanes possibly derived from intermediate carbenes or carbenoids [5]. Based on previous studies of *Cohen et al.* [6], *Cimetière* and *Julia* [7] recently proposed diphenylsulfonium (methoxycarbonyl)methylide as a substitute for methyl diazoacetate in copper-catalyzed cyclopropanations of olefins. The mechanism of the reaction of the ylide was not established, but the results imply a carbene or a carbenoid intermediate. Such intermediates have also been invoked to rationalize the formal intramolecular NH insertion resulting upon exposure of sulfoxonium ylides to $[Rh_2(OAc)_4]$ [8]. The generation of metal carbenoids from ylides is of interest in the context of asymmetric carbene transfer reactions [9], because it could allow the replacement of the potentially explosive, toxic, and/or carcinogenic diazo compounds [10] which are traditionally used as carbenoid precursors. In a previous communication, we have shown that Rh^{II}-catalyzed decomposition of diazo compounds and of the corresponding phenyliodonium ylides affords identical product mixtures and proceeds in both cases *via* Rh^{II} carbenoids [11]. Thus, phenyliodonium ylides may be substitutes for diazo compounds in metal-catalyzed carbenoid transformations. However, the use of iodonium ylides is limited. Phenyliodonium ylides must be stabilized by two electron-attracting substituents, such as carbonyl or sulfonyl groups, in order to be isolable. Monocarbonyliodonium ylides have only very recently been characterized; they are stable in THF below $-30°$, and no metal-catalyzed reactions of monocarbonyliodonium ylides have yet been reported [12]. Sulfur ylides do not suffer this limitation. They are isolable and well characterized, and may be manipulated at room temperature, even when stabilized by only one electron-attracting substituent [1][7]. We have now investigated the Cu^{I}- or Rh^{II}-catalyzed decomposition of diphenylsulfo-

nium (ethoxycarbonyl)methylide (= diphenylsulfonium 2-ethoxy-2-oxoethylide; **3a**) in the presence of olefins with the hope of developing a synthetic alternative for carbenoid olefin cyclopropanation. A comparison of the *trans*/*cis* ratios and enantiomeric excesses (ee's) of the resulting cyclopropanes with those obtained upon metal-catalyzed olefin cyclopropanation with ethyl diazoacetate (EDA, **4**) was expected to provide conclusive evidence for metal-carbenoid intermediates in the reaction of the ylide.

2. Results and Discussion. – 2.1. *Synthesis of Diphenylsulfonium (Ethoxycarbonyl)methylide* (**3a**) *and Dimethylsulfonium (Ethoxycarbonyl)methylide* (**3b**). Diphenylsulfonium (ethoxycarbonyl)methylide (**3a**) was prepared by a slightly modified version of the procedure originally proposed by *Nozaki et al.* [13]. Reaction of diphenyl sulfide (**1a**) with ethyl bromoacetate in the presence of $AgBF_4$ in the dark afforded the sulfonium salt **2a**, which was deprotonated with Et_3N in EtOH at 0° to afford **3a** in 75% yield (*Scheme 1*). The ylide **3a** is relatively stable. No change was detected in the ^{1}H-NMR spectrum after 24 h in $CDCl_3$ at 25°. After 4 days, signals of diphenyl sulfide, ethyl maleate, and ethyl fumarate (maleate/fumarate 6:1) started to appear. No decomposition occurred in CH_2Cl_2 within 13 h in the presence of $[Rh_2(OAc)_4]$ (1 mol-%) at 25°, and only trace amounts of cyclopropanes were formed upon attempted cyclopropanation of styrene (**5a**) with **3a** in the presence of $[Rh_2(OAc)_4]$ in refluxing CH_2Cl_2. Carbene addition occurred, however, upon slow addition (syringe pump, 16 h) of **3a** to olefins (10 equiv.) in refluxing 1,2-dichloroethane (DCE) containing 2 mol-% of $[Cu(acac)_2]$ or $[Rh_2(OAc)_4]$.

Scheme 1



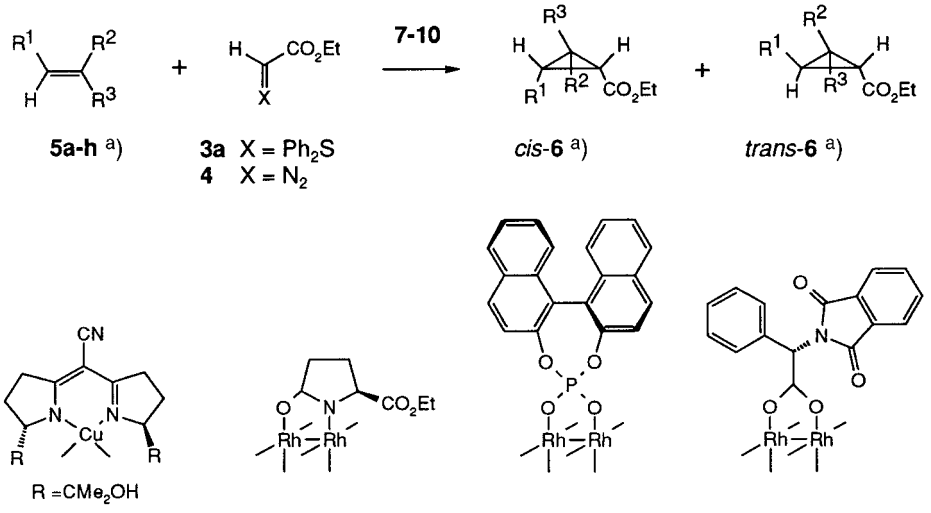
Dimethylsulfonium (ethoxycarbonyl)methylide (**3b**) was prepared by reaction of ethyl bromoacetate with dimethyl sulfide (**1b**), as described by *Johnson* and *Amel* for the corresponding methyl ester [14]. The resulting sulfonium salt **2b** was deprotonated with NaH to yield **3b**. Preliminary experiments, directed towards decomposition of **3b** with $[Rh_2(OAc)_4]$ in the presence of styrene (**5a**), provided none of the expected cyclopropanes. In the light of these negative results, the chemistry of **3b** was not further investigated.

2.2. *Copper(I)-Catalyzed Cyclopropanation of Olefins.* Some representative olefins were subjected to intermolecular cyclopropanation by syringe-pump addition of the ylide **3a** or ethyl diazoacetate (EDA; **4**) to a solution of olefin **5a**–**h** (10 equiv.) and 2% of the chiral Cu-semicorrin catalyst **7** of *Pfaltz* and co-workers [15] (*Scheme 2*). For practical reasons, the reactions of **3a** and **4** could not be carried out under exactly identical conditions: since **3a** reacted only at elevated temperature, the cyclopropanations were carried out in refluxing 1,2-dichloroethane (DCE), at 82°. At this

temperature, however, partial decomposition of the catalyst was observed in the reaction with EDA (**4**), as evidenced by a progressive decrease with time of the enantiomeric excess of the cyclopropanes **6** when samples were withdrawn from the reaction mixture during addition of EDA. This phenomenon was, however, not observed in the cyclopropanations with **3a**. Reactions with EDA (**4**) were, therefore, carried out at room temperature (23°), and those with **3a** at 82°. *Table 1* summarizes the principal results. The reactions of **3a** and **4** differ significantly with respect to the yield, which is always lower when the ylide is used as carbene precursor. Disubstituted olefins proved to be particularly unreactive in the Cu-catalyzed cyclopropanation with **3a**. Thus, (*E*)-*β*-methylstyrene (=(*E*)-(prop-1-enyl)benzene; **5e**; R^1 = Ph, R^2 = H, R^3 = Me) afforded only a 20% yield of cyclopropanes, and only traces of cyclopropanes were formed upon reaction of (*E*)-pent-2-ene (**5g**; R^1 = Et, R^2 = H, R^3 = Me) or (*Z*)-hex-3-ene in the presence of the chiral catalyst **7**. (*Z*)-*β*-Methylstyrene (**5h**; R^1 = Ph, R^2 = Me, R^3 = H) was equally unreactive and afforded only trace amounts of cyclopropanes with [Cu(acac)$_2$]. With these unreactive olefins, formation of the formal carbene dimers dimethyl fumarate and maleate predominated. When cyclopropanations with EDA (**4**) were performed at 50°, the enantioselectivity was significantly below that observed at 25°, and also below that resulting from reaction with the ylide **3a** at 82°.

The relative and absolute configurations of the cyclopropanecarboxylates **6** prepared in this study have been assigned previously by other investigators (see *Exper. Part*). The ylide **3a** and EDA (**4**) afforded cyclopropanes of identical absolute configurations with all of the olefins investigated. Despite the variation in reaction temperature, the variation of the *trans*/*cis* ratios of the cyclopropanes resulting from

Scheme 2



a) See *Tables 1* and *2* for R^1, R^2, and R^3.

Table 1. *Selectivity for Cyclopropanation of Olefins* **5** *with* $Ph_2S{=}CHCO_2Et$ (**3a**) *or EDA* (**4**) *Catalyzed by the Cu-Semicorrin Complex* **7**[a])

Olefin	R^1	R^2	R^3	**3a**, **4**		**6**			
				$X=$	T [°C]	Yield [%]	*trans*/*cis*	ee (*trans*) [%]	ee (*cis*) [%]
5a	Ph	H	H	N_2	23	75	75 : 25	78 (1*S*,2*S*)	54 (1*S*,2*R*)
5a	Ph	H	H	N_2	50	53	71 : 29	74 (1*S*,2*S*)	56 (1*S*,2*R*)
5a	Ph	H	H	Ph_2S	82	31	77 : 23	71 (1*S*,2*S*)	59 (1*S*,2*R*)
5b	C_5H_{11}	H	H	N_2	23	20	72 : 28	63 (1*S*,2*S*)	70 (1*S*,2*R*)
5b	C_5H_{11}	H	H	N_2	50	37	71 : 29	76 (1*S*,2*S*)	69 (1*S*,2*R*)
5b	C_5H_{11}	H	H	Ph_2S	82	20	68 : 32	72 (1*S*,2*S*)	59 (1*S*,2*R*)
5c	$H_2C{=}CH$	H	H	N_2	23	52	61 : 39	70 (1*S*,2*R*)	77 (1*S*,2*S*)
5c	$H_2C{=}CH$	H	H	N_2	50	57	58 : 42	37 (1*S*,2*R*)	41 (1*S*,2*S*)
5c	$H_2C{=}CH$	H	H	Ph_2S	82	24	60 : 40	76 (1*S*,2*R*)	80 (1*S*,2*S*)
5d	$Me_2C{=}CH$	H	H	N_2	23	65	58 : 42	45 (1*S*,2*R*)	65 (1*S*,2*S*)
5d	$Me_2C{=}CH$	H	H	Ph_2S	82	55	59 : 41	15 (1*S*,2*R*)	75 (1*S*,2*S*)
5e	Ph	H	Me	N_2	23	42	70 : 30	5 (1*S*,2*S*,3*S*)	48 (1*S*,2*R*,3*R*)
5e	Ph	H	Me	N_2	50	59	68 : 32	10 (1*S*,2*S*,3*S*)	32 (1*S*,2*R*,3*R*)
5e	Ph	H	Me	Ph_2S	82	20	65 : 35	7 (1*S*,2*S*,3*S*)	50 (1*S*,2*R*,3*R*)
5f	$-C_3H_6-$		Me_3SiO	N_2	23	50	30 : 70	18(1*R*,5*S*,6*S*)[b])	65 (1*S*,5*R*,6*S*)[b])
5f	$-C_3H_6-$		Me_3SiO	Ph_2S	82	28	28 : 72	30 (1*R*,5*S*,6*S*)[b])	64 (1*S*,5*R*,6*S*)[b])

[a]) 1.0 mmol of **3a** or **4** in 5 ml of DCE was added within 16 h to 10 mmol of olefin **5** in 10 ml of DCE at the temperature indicated. Initiation of the reaction of **3a** with a small amount of EDA [15]. [b]) Enantiomer of **6f**.

cyclopropanation with **3a** and **4** was small (1–5%). The enantioselectivities changed slightly more in going from **3a** to **4** (2–9%), but the variations were within the experimental uncertainties, and no clear trend could be identified.

These observations suggest that the Cu-catalyzed cyclopropanations with **3a** and **4** proceed by the same reaction mechanism. Since the intermediacy of a Cu-complexed carbene in the asymmetric olefin cyclopropanation with EDA is established [15], the same should hold for the reaction with **3a**. The formation of carbene dimers upon attempted cyclopropanation of 1,2-disubstituted olefins suggests an unfavorably high reactivity of **3a** towards the metal-complexed carbene in comparison to olefin reactivity. Carbene dimers are frequently found, even in carbenoid reactions of diazo compounds, but owing to the high olefin reactivity towards the metal carbenoid, it usually represents no serious problem in cyclopropanations. In the case of **3a**, however, the formation of carbene dimers becomes competitive even with terminal olefins, and this limits the potential of the system.

2.3. *Rhodium(II)-Catalyzed Cyclopropanation of Olefins.* No cyclopropanation took place when dimethylsulfonium ylide **3b** was exposed to $[Rh_2(OAc)_4]$ in the presence of olefins. However, slow addition (16 h) of the diphenyl derivative **3a** in refluxing DCE in the presence of $[Rh_2(OAc)_4]$ (2 mol-%) and styrene (**5a**) afforded cyclopropanes **6a** in 38% yield and with a *trans*/*cis* ratio of 52 : 48 (*Table 2*). All of the ylide had reacted after this time, and the yield of carbene dimers was below 3%. As in the case of the Cu-catalyzed cyclopropanation of styrene (**5a**), the yield with **3a** was lower than that obtained with EDA (**4**) in the reaction catalyzed with $[Rh_2(OAc)_4]$. The observation of reduced yields with **3a** applies generally, and was particularly significant with di- and trisubstituted olefins as substrates. In these reactions, formation

of formal carbene dimers predominated. The *trans*/*cis* ratio of the cyclopropanes **6a** derived from styrene deviated slightly, but reproducibly from that of 60:40 obtained with EDA under the same conditions, and from the 62:38 ratio reported for EDA (**4**) in CH_2Cl_2 at 25° [16]. Originally, we thought that this change was due to complexation of one of the vacant coordination sites of the rhodium complex by diphenyl sulfide (**1a**), which is liberated in the course of the reaction of the ylide **3a** [11b]. However, the *trans*/*cis* ratio of cyclopropanes derived from other olefins remained unchanged upon replacement of **3a** by **4**. The cyclopropanation of **5a** and some other olefins with **3a** and **4** was also carried out in the presence of Ph_2S with the expectation that this addition would result in modification of the *trans*/*cis* ratios, but no unambiguous results could be obtained from these experiments (see *Tables 2* and *3*). While the Rh^{II}-catalyzed reactions exhibited somewhat stronger variations in the diastereo- and enantioselectivities between **3a** and **4**, the origin of the trend could not be detected.

Table 2. *[$Rh_2(OAc)_4$]-Catalyzed Cyclopropanation of Olefins* **5** *with Ph_2S=CHCOOEt* (**3a**) *and EDA* (**4**)[a])

Olefin	No.	**3a**,**4**	**6**		Comment
		X=	Yield [%]	*trans*/*cis*	
Styrene	**5a**	N_2	61	60:40	
Styrene	**5a**	Ph_2S	38	52:48	
Styrene	**5a**	N_2	–	60:40	1 equiv. of Ph_2S before addition
Styrene	**5a**	Ph_2S	–	57:43	1 equiv. of Ph_2S before addition
Hept-1-ene	**5b**	N_2	50	59:41	
Hept-1-ene	**5b**	Ph_2S	23	57:43	
Buta-1,3-diene	**5c**	N_2	36	45:55	
Buta-1,3-diene	**5c**	Ph_2S	30	43:57	
(*E*)-β-Methylstyrene	**5e**	N_2	51	77:23	
(*E*)-β-Methylstyrene	**5e**	Ph_2S	3	59:41	
1-(Me_3SiO)-cyclopentene	**5f**	N_2	42	47:53	
1-(Me_3SiO)-cyclopentene	**5f**	Ph_2S	9	45:55	
(*E*)-Pent-2-ene[b])	**5g**	N_2	43	56:44	
(*E*)-Pent-2-ene[b])	**5g**	Ph_2S	20	52:48	
(*Z*)-β-Methylstyrene[c])	**5h**	N_2	50	77:23	
(*Z*)-β-Methylstyrene[c])	**5h**	N_2	25	66:34	1 equiv. of Ph_2S before addition
(*Z*)-β-Methylstyrene[c])	**5h**	N_2	50	62:38	1 equiv. of Ph_2S during addition
(*Z*)-β-Methylstyrene[c])	**5h**	Ph_2S	3	69:31	

[a]) Conditions: Syringe-pump addition of **3a** or **4** (1 mmol) in DCE (5.0 ml) to olefin **5** (10 mmol) in refluxing DCE (10 ml) containing the catalyst (0.02 mmol). [b]) R^1 = Et, R^2 = H, R^3 = Me. [c]) R^1 = Ph, R^2 = Me, R^3 = H.

The cyclopropanation of several olefins with **3a** and EDA (**4**) was investigated with three chiral Rh^{II} catalysts, namely [Rh_2\{(2*S*)-mepy\}$_4$] (**8**), [Rh_2\{(−)-(*R*)-bnp\}$_4$] (**9**), and [Rh_2\{(−)-(*S*)-ptpa\}$_4$] (**10**) (*Table 3*). The enantioselectivity of the cyclopropanation was generally poor, except with [Rh_2\{(2*S*)-mepy\}$_4$], where the results with EDA (**4**) were consistent with reported data [16]. Again, we found some unexpected variations in the results obtained with **3a** and **4** for which there is no rationalization.

2.4. *Intramolecular Carbenoid Reactions with Diphenylsulfonium (Alkoxycarbonyl)methylides.* The most successful applications of chiral rhodium carboxamidate catalysts are found in the field of intramolecular cyclopropanation and CH insertion. Thus, allyl diazoacetate (**15**) undergoes cyclopropanation to **14** in the presence of

Table 3. *Cyclopropanation of Olefins* **5** *with* $Ph_2S{=}CHCOOEt$ (**3a**) *and EDA* (**4**) *in the Presence of Optically Active* Rh^{II} *Complexes*[a])

Olefin	No.	Catalyst	**3a**,**4**	**6**			
			X =	Yield [%]	*trans*/*cis*	ee (*trans*) [%]	ee (*cis*) [%]
Styrene	**5a**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	20	52 : 48	54 (1*S*,2*S*)	38 (1*S*,2*R*)
Styrene	**5a**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	59[b])	56 : 44[b])	58 (1*S*,2*S*)[b])	33 (1*S*,2*R*)[b])
Styrene	**5a**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	Ph_2S	34	67 : 33	48 (1*S*,2*S*)	34 (1*S*,2*R*)
Styrene	**5a**	$[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$	N_2	45	50 : 50	5 (1*R*,2*R*)[c])	3 (1*R*,2*S*)[c])
Styrene	**5a**	$[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$	Ph_2S	47	60 : 40	0	2 (1*S*,2*R*)
Styrene	**5a**	$[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$	N_2	57	47 : 53	2 (1*S*,2*S*)	2 (1*S*,2*R*)
Styrene	**5a**	$[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$	Ph_2S	35	52 : 48	0	2 (1*R*,2*S*)[c])
Hept-1-ene	**5b**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	41	54 : 46	42 (1*S*,2*S*)	40 (1*S*,2*R*)
Hept-1-ene	**5b**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	Ph_2S	14	49 : 51	13 (1*S*,2*S*)	19 (1*S*,2*R*)
Hept-1-ene	**5b**	$[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$	N_2	52	56 : 44	4 (1*S*,2*S*)	4 (1*S*,2*R*)
Hept-1-ene	**5b**	$[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$	Ph_2S	10	59 : 49	2 (1*S*,2*S*)	4 (1*S*,2*R*)
Buta-1,3-diene	**5c**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	25	44 : 56	39 (1*S*,2*R*)	44 (1*S*,2*S*)
Buta-1,3-diene	**5c**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	Ph_2S	21	42 : 58	34 (1*S*,2*R*)	39 (1*S*,2*S*)
Buta-1,3-diene	**5c**	$[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$	N_2	60	51 : 49	3 (1*S*,2*R*)	5 (1*S*,2*S*)
Buta-1,3-diene	**5c**	$[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$	Ph_2S	18	55 : 45	0	2 (1*S*,2*S*)
1-(Me_3SiO)-Cyclopentene	**5f**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	33	61 : 39	16 (1*R*,5*S*,6*S*)[d])	8 (1*S*,5*R*,6*S*)[d])
1-(Me_3SiO)-Cyclopentene	**5f**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	Ph_2S	5	55 : 45	23 (1*R*,5*S*,6*S*)[d])	39 (1*S*,5*R*,6*S*)[d])
(*E*)-Pent-2-ene[e])	**5g**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	N_2	21	58 : 42	15 (1*S*,2*S*,3*S*)	13 (1*S*,2*R*,3*S*)
(*E*)-Pent-2-ene[e])	**5g**	$[Rh_2\{(2S)\text{-mepy}\}_4]$	Ph_2S	13	56 : 44	13 (1*S*,2*S*,3*S*)	12 (1*S*,2*R*,3*S*)

[a]) Conditions: syringe-pump addition of **3a** or **4** (1.0 mmol) in DCE (5.0 ml) to olefin **5** (10 mmol) in refluxing DCE (10 ml) containing the catalyst. [b]) In CH_2Cl_2, under reflux. [c]) Enantiomer of **6a**. [d]) Enantiomer of **6f**. [e]) $R^1 = Et$, $R^2 = H$, $R^3 = Me$.

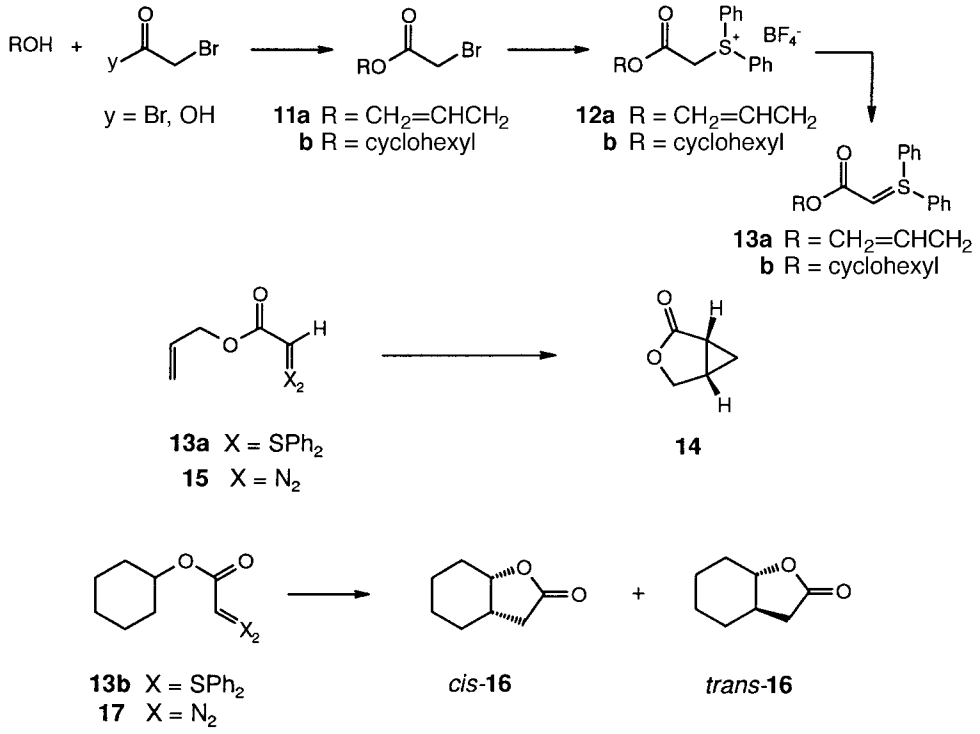
$[Rh_2\{(2S)\text{-mepy}\}_4]$ (**8**) in 75% yield and with 95% ee in CH_2Cl_2 at 25° [17] (see *Table 4*). As expected, the enantioselectivity of the reaction decreased to 80%, when it was carried out in refluxing DCE (*Table 4*). The allylic ylide **13a** was synthesized by reaction of bromoacetyl bromide with allyl alcohol (= prop-2-en-1-ol). The resulting ester **11a** was converted to the sulfonium salt **12a** with Ph_2S (**1a**) and $AgBF_4$, and **12a** was deprotonated with Et_3N [18]. The intramolecular cyclopropanation of **13a** with $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**8**) in refluxing DCE produced **14** in 40% yield and with 69% ee.

Table 4. *Intramolecular Carbenoid Reactions of Ylides* **13a** *and* **13b** *and Diazoacetates* **15** *and* **17**

No.	R	X	Catalyst	Conditions	Product	Yield [%]	*cis*/*trans*	ee [%]
13a	$CH_2{=}CHCH_2$	Ph_2S	$[Rh_2(OAc)_4]$	DCE, 82°	**14**	30	–	–
13a	$CH_2{=}CHCH_2$	Ph_2S	$[Rh_2\{(2S)\text{-mepy}\}_4]$	DCE, 82°	**14**	40	–	69 (1*R*,5*S*)
15	$CH_2{=}CHCH_2$	N_2	$[Rh_2\{(2S)\text{-mepy}\}_4]$	DCE, 82°	**14**	75	–	80 (1*R*,5*S*)
15	$CH_2{=}CHCH_2$	N_2	$[Rh_2\{(2S)\text{-mepy}\}_4]$	DCE, 82°, + 1 equiv. of Ph_2S	**14**	68	–	81 (1*R*,5*S*)
15	$CH_2{=}CHCH_2$	N_2	$[Rh_2\{(2S)\text{-mepy}\}_4]$	CH_2Cl_2, 25°	**14**	75[a])	–	95 (1*R*,5*S*)[a])
13b	Cyclohexyl	Ph_2S	$[Rh_2\{(2S)\text{-mepy}\}_4]$	DCE, 82°	**16**	8.5	73 : 27	93 (*cis*)[b]), 85 (*trans*)
17	Cyclohexyl	N_2	$[Rh_2\{(2S)\text{-mepy}\}_4]$	DCE, 82°	**16**	11	68 : 32	88 (*cis*), 77 (*trans*)
17	Cyclohexyl	N_2	$[Rh_2\{(2S)\text{-mepy}\}_4]$	CH_2Cl_2, 25°	**16**	65	75 : 25	97 (*cis*), 91 (*trans*)
17	Cyclohexyl	N_2	$[Rh_2(OAc)_4]$	CH_2Cl_2, 25°	**16**	46	40 : 60[c])	

[a]) See [17]. [b]) Absolute configuration (3a*S*,7a*S*) [17][27]. [c]) See [28].

Scheme 3



The enantioselectivity was not affected when the reaction of the diazo compound **15** was carried out in the presence of added Ph_2S. An attempt to repeat the above sequence with the ylide derived from 3-methylbut-2-en-1-ol failed. The reaction of 3-methylbut-2-en-1-ol with bromoacetyl bromide in the presence of $AgBF_4$ produced only decomposition products, and the desired sulfonium salt could not be obtained.

By analogy, the ylide **13b** was synthesized from cyclohexanol *via* **11b** and **12b**. Cyclohexyl diazoacetate (**17**) reportedly reacts with $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**8**) to form the corresponding lactone **16** as a 75:25 *cis*/*trans* mixture in 65% yield and with ee's of 97% (*cis*-**16**) and 91% (*trans*-**16**), respectively [9c] [19] (see *Table 4*). In refluxing DCE, the yield decreased dramatically to 11%, the *cis*/*trans* ratio changed to 68:32, and the ee decreased to 88% (*cis*-**16**) and 77% (*trans*-**16**) (see *Table 4*). Exposure of the ylide **13b** to $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**8**) afforded the lactone **16** in a poor 9% yield as a 73:27 *cis*/*trans* mixture with ee's of 93 (*cis*-**16**) and 85% (*trans*-**16**). Formation of carbene dimers predominated largely over the intramolecular insertion.

3. Conclusions. – The product distribution for the Cu^{I}- and Rh^{II}-catalyzed decomposition of diphenylsulfonium ylides and the corresponding diazo compounds is practically identical, which suggests that both types of compounds react *via* the same mechanism. The implication of metal carbenoids as reactive intermediates in both reactions follows from extensive studies on transition-metal-catalyzed diazo decom-

position. This hypothesis is supported by the observation of enantiomerically enriched insertion products upon reaction of the ylide **13b**. However, the reactions of the ylides suffer generally from significantly lower yields in comparison to those of diazo compounds, and this problem must be overcome in order to allow their use as substitutes for the latter.

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Experimental Part

1. *General*. See [20].

2. *Sulfonium Ylides*. 2.1. *Diphenylsulfonium 2-Ethoxy-2-oxoethylide* (**3a**). *(2-Ethoxy-2-oxoethyl)diphenylsulfonium Tetrafluoroborate* (**2a**) [18]. Solid $AgBF_4$ (5.0 g, 25 mmol) was added within 4 min to bromoacetate (16 ml, 10 equiv.) and Ph_2S (4.78 g, 25 mmol) in a round-bottomed flask wrapped with aluminum foil. The soln. was stirred at r.t. for 2 h. The precipitate of AgBr was removed by filtration through *Celite*. The residue of the filtrate was extracted with CH_2Cl_2 (15 ml) and the org. phase dried ($MgSO_4$) and evaporated. The residue was recrystallized from EtOH: **2a** (5.25 g, 56%) M.p. 108–110°. IR ($CHCl_3$): 3450*w*, 2465*m*, 1724*m*, 1617*s*, 1067*s*, 1580*m*, 1476*m*, 1443*m*, 1322*s*, 1134*s*. ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.13 (*t*, *J* = 7, 3 H); 4.15 (*q*, *J* = 7, 2 H); 5.18 (*s*, 1 H); 7.60–7.71 (*m*, 6 H); 7.97–8.05 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 13.6 (*q*); 47.3 (*t*); 63.8 (*t*); 124.1 (*s*); 130.5 (*d*); 131.4 (*d*); 134.6 (*d*); 162.8 (*s*). MS (electrospray): 273.1 (M^+). Anal. calc. for $C_{16}H_{17}BFSO_2$: C 53.36, H 4.76; found: C 53.24, H 4.87.

Ethylide **3a** [13]. To **2a** (2.92 g, 8.0 mmol) in EtOH (250 ml) at 0°, Et_3N (1.62 g, 16 mmol) in EtOH (50 ml) was added slowly. After 2 h of stirring, H_2O (700 ml) was added, the org. layer separated, the aq. phase extracted with CH_2Cl_2 (3 × 150 ml) and the combined org. phase dried and evaporated: **3a** (1.82 g, 83%). Yellowish oil. IR ($CHCl_3$): 3066*w*, 2995*m*, 1618*s*, 1580*m*, 1478*w*, 1444*w*, 1396*w*, 1371*s*, 1323*m*, 1233*w*, 1134*s*, 1062*w*, 1023*w*, 1023*w*, 1000*w*, 901*w*, 855*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.22 (*t*, *J* = 7.1, 3 H); 3.30–3.50 (br. *s*, 1 H); 4.09 (*q*, *J* = 7.1, 2 H); 7.40–7.59 (*m*, 10 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 14.9 (*q*); 58.5 (*t*); 77.2 (*d*); 127.9 (*d*); 130.8 (*d*); 136.6 (*s*); 170.0 (*s*).

2.2. *Dimethylsulfonium 2-Ethoxy-2-oxoethylide* (**3b**). The ylide was prepared according to [14].

2.3. *Diphenylsulfonium 2-Oxo-2-(prop-2-enyloxy)ethylide* (**13a**). *Prop-2-enyl Bromoacetate* (**11a**) [21]. To prop-2-en-1-ol (10.0 g, 170 mmol) in CH_2Cl_2 (60 ml) at −60°, bromoacetyl bromide (34.8 g, 170 mmol) was added within 2 h. The temp. was allowed to rise to 25°, and the mixture was stirred for 24 h and then treated with sat. $NaHCO_3$ soln. (100 ml). The org. layer was washed with H_2O (2 × 100 ml), dried (Na_2SO_4), and evaporated, and the crude product was distilled at 73°/10 Torr: **11a** (17.1 g, 56%). Colorless liquid. IR ($CHCl_3$): 2962*w*, 1738*s*, 1421*m*, 1279*s*, 1165*s*, 987*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.85 (*s*, 2 H); 4.42 (*d*, *J* = 5.7, 2 H); 5.20–5.50 (*m*, 2 H); 5.80–6.00 (*m*, 1 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 25.7 (*t*); 31.1 (*t*); 34.8 (*t*); 66.7 (*t*); 119.2 (*t*); 131.2 (*d*); 166.9 (*s*).

[2-Oxo-2-(prop-2-enyloxy)ethyl]diphenylsulfonium Tetrafluoroborate (**12a**). To **11a** (18 g, 100 mmol) and Ph_2S (4.78 g, 25.7 mmol) under N_2, anh. $AgBF_4$ (5.00 g, 25 mmol) was added within 2 min at −40°. The brown suspension was stirred at r.t. for 14 h, then diluted with CH_2Cl_2, and filtered through *Celite*. After evaporation of the solvent, the excess of **11a** was eliminated by flash distillation. The solid residue was isolated after filtration and dissolved in a minimum quantity of hot EtOH, the soln. was filtered, the filtrate allowed to cool slowly, and the precipitated colorless crystals filtered off: **12a** (5.63 g, 59%). M.p. 84–86°. IR ($CHCl_3$): 3563*w*, 3034*s*, 1740*s*, 1448*w*, 1311*w*, 1189*m*, 1069*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.59 (*d*, *J* = 6, 2 H); 5.14–5.23 (*m*, 4 H); 5.79 (*ddt*, *J* = 6, 10, 17, 1 H); 7.61–7.72 (*m*, 6 H); 7.96–8.03 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 47.3 (*t*); 68.0 (*t*); 119.9 (*t*); 124.0 (*s*); 130.3 (*d*); 130.6 (*d*); 131.5 (*d*); 134.7 (*d*); 162.7 (*s*). MS (electrospray): 284.7 (M^+). Anal. calc. for $C_{17}H_{17}BF_4SO_2$: C 54.86, H 4.60; found: C 54.72, H 4.72.

Ethylide **13a**. The general procedure of [13] was used: To **11a** (1.00 g, 2.70 mmol) in EtOH (80 ml), Et_3N (1.5 ml, 10.8 mmol) in EtOH (50 ml) was added dropwise at 0°. The resulting mixture was kept at 0° for 2 h and then poured on ice-water (500 g). The white suspension was extracted with CH_2Cl_2 (3 × 100 ml) and the extract dried ($MgSO_4$) and evaporated: **13a** (66 mg, 86%). Viscous, yellowish oil which solidified at −18°. IR ($CHCl_3$): 3086*w*, 2955*m*, 1698*s*, 1550*m*, 1435*w*, 1376*w*, 1331*m*, 1233*w*, 1134*m*, 1052*w*, 1012*w*, 1004*w*, 755*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.50 (br. *s*, 1 H); 4.53–4.59 (*m*, 2 H); 5.20 (*dd*, *J* = 30, 16, 2 H); 5.85–6.10 (*m*, 1 H); 7.39–7.60 (*m*, 10 H). ^{13}C-NMR: 46.2 (*t*); 65.9 (*d*); 116.4 (*t*); 127.9 (*d*); 129.6 (*d*); 130.8 (*d*); 134.5 (*d*); 136.5 (*s*); 169.9

(*s*). MS: 188(6), 187(18), 186(100), 185(58), 184(27), 183(5), 152(6), 109(5), 99(12), 92(12), 77(9), 77(13), 65(7), 51(17), 50(5).

2.4. *Diphenylsulfonium 2-(Cyclohexyloxy)2-oxoethylide* (**11b**). *Cyclohexyl Bromoacetate* (**11b**). Phosphotungstic acid ($H_3[P(W_3O_{10})_4]\cdot H_2O$; 0.20 g, 0.07 mmol), bromoacetic acid (500 ml), and cyclohexanol (65.1 g, 0.65 mol) were refluxed in toluene (50 ml) under a *Dean-Stark* trap for 4.5 h [21]. The mixture was then washed with H_2O (100 ml), sat. $NaHCO_3$ soln. (2 × 100 ml), and H_2O (100 ml), dried ($MgSO_4$), and evaporated and the crude product distilled at 50–60°/0.3 Torr: **11b** (85.4 g, 78%). Colorless liquid. IR ($CHCl_3$): 2894*s*, 2861*m*, 1726*s*, 1450*w*, 1421*w*, 1289*s*, 1224*w*, 1174*m*, 1111*w*, 1036*w*, 1010*m*, 971*w*, 892*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.20–1.60 (*m*, 6 H); 1.65–1.80 (*m*, 2 H); 3.80 (*s*, 2 H); 4.75–4.85 (*m*, 1 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 23.5 (*t*); 25.2 (*t*); 26.4 (*t*); 74.7 (*d*); 166.6 (*s*).

[2-(Cyclohexyloxy)-2-oxoethyl]diphenylsulfonium Tetrafluoroborate (**12b**). To Ph_2S (4.55 g, 24.4 mmol) in **11b** (45.7 g, 250 mmol) under N_2, anh. $AgBF_4$ (5.00 g, 25 mmol) was added within 2 min. The resulting suspension was stirred in the dark for 50 h and then for 4 d in the daylight (to allow decomposition of traces of unreacted $AgBF_4$). After dilution with CH_2Cl_2, the mixture was filtered through *Celite*, the filtrate evaporated, and the resulting mixture of crystals and liquid cooled to 4°. The crystals were separated by filtration and purified by recrystallization from EtOH: 6.634 g (66%) or **12b**. M.p. 142–144°. IR ($CHCl_3$): 3564*w*, 3029*m*, 2942*m*, 1730*s*, 1448*m*, 1309*m*, 1227*w*, 1210*s*, 1066*s*, 912*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.10–1.40 (*m*, 5 H); 1.41–1.48 (*m*, 1 H); 1.54–1.62 (*m*, 2 H); 4.70–4.79 (*m*, 1 H); 5.15 (*s*, 2 H); 7.61–7.71 (*m*, 6 H); 7.97–8.04 (*m*, 4 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 23.3 (*t*); 24.9 (*t*); 30.9 (*t*); 47.3 (*t*); 77.3 (*d*); 124.1 (*s*); 130.5 (*d*); 131.5 (*d*); 134.6 (*d*); 162.0 (*s*). MS (electrospray): 327.1 (M^+). Anal. calc. for $C_{20}H_{23}BF_4SO_2$: C 57.95, H 5.59; found: C 57.81, H 5.71.

Ethylide **13b**. To a suspension of **12b** (2.10 g, 5.0 mmol) in EtOH (200 ml), Et_3N (2.8 ml, 20 mmol) in EtOH (100 ml) was added dropwise at 0° within 30 min. The mixture was kept at 0° for 90 min with stirring and then poured into ice-water (900 g). The white suspension was extracted with CH_2Cl_2 (3 × 150 ml) and the extract dried ($MgSO_4$) and evaporated: **13b** (1.65 g, 100%). Pale-yellowish viscous liquid which solidified after 1 h to afford a colorless solid. IR ($CHCl_3$): 3066*w*, 2998*s*, 2936*s*, 1610*s*, 1477*w*, 1377*w*, 1335*s*, 1301*m*, 1133*s*, 1053*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10–2.02 (*m*, 10 H); 3.40 (br. *s*, 1 H); 4.60–4.75 (*m*, 1 H); 7.38–7.60 (*m*, 10 H). ^{13}C-NMR (50 MHz, $CDCl_3$): 24.2 (*t*); 25.7 (*t*); 32.5 (*t*); 70.3 (*d*); 73.8 (*d*); 127.9 (*d*); 129.5 (*d*); 130.7 (*d*); 136.7 (*s*); 169.4 (*s*). MS 326 (1, M^+), 199(5), 188(5), 187(16), 186(100), 185(50), 184(23), 152(6), 117(13), 109(5), 100(5), 99(9), 92(9), 83(22), 77(13), 69(5), 65(7), 55(14), 51(18), 50(5). HR-MS: 326.1338 ($C_{20}H_{22}O_2S^+$; calc. 326.1340).

3. *Transition-Metal-Catalyzed Cyclopropanation of Olefins*. 3.1. *Catalysts*. $[Rh_2(OAc)_4]$ was purchased from *Pressure Chemical Company*, Pittsburgh. The chiral Cu-semicorrin catalyst **7** was synthesized as described in [22]. The synthesis of the chiral Rh^{II} catalysts has been described: The procedure of [23] was used for $[Rh_2\{(2S)\text{-mepy}\}_4]$ (**8**); $[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$ (**9**) was prepared as described in [24] and $[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$ (**10**) according to [25].

3.2. *General Method for Olefin Cyclopropanation*. To a soln. of catalyst (0.02 mmol) and olefin (10 mmol) in 1,2-dichloroethane (DCE, 10 ml) at the appropriate temp., **3a** or **4** (1.00 mmol) in DCE (5.0 ml) was added dropwise within 16 h, by means of a syringe pump. In the case of the Cu-catalyzed reactions with **3a**, the catalyst was activated with a drop of EDA (**4**). After the addition, the mixture was stirred for an additional 4 h under reflux. The mixture was filtered through a thin layer of silica gel to remove the catalyst, the filtrate evaporated, and the mixture directly analyzed by GC to determine the product and enantiomer composition.

3.3. *Separation and Characterization of Cyclopropanecarboxylates*. The cyclopropane carboxylates **6a–g** were identified by comparison of their spectral data and GC retention times with data available from previous studies in this laboratory [16][26] or available in the literature (see also *Table 5*).

4. *Intramolecular Cyclopropanation of Ylide* **13a**: *(1R,5S)-3-Oxabicyclo[3.1.0]hexan-2-one* (**14**). To $[Rh_2\{(2S)\text{-mepy}\}_4]$ (19 mg, 0.02 mmol) in refluxing DCE (10 ml), **13a** (0.35 g, 1.20 mmol) in DCE (5.0 ml) was added dropwise by means of a syringe pump within 14 h. The crude mixture was filtered through a thin layer of silica gel. Flash chromatography (silica gel, petroleum ether/AcOEt 3:1) afforded **14** (47 mg, 40%), with an ee of 69% (with *LIPODEX E*, 120°). For results under different reaction conditions, and with allyl diazoacetate (**15**), and determination of absolute configuration [27], see *Table 4*.

5. *Intramolecular CH Insertion of Ylide* **13b**: *Hexahydrobenzofuran-2(3H)-one* (**16**). The previously dried (activated molecular sieves) **13b** (0.31 g, 0.96 mmol) in DCE (5.0 ml) was added dropwise within 3.25 h to $[Rh_2\{(2S)\text{-mepy}\}_4]$ (18 mg, 0.02 mmol) in refluxing DCE (20 ml). After the addition, the mixture was refluxed for an additional hour. The catalyst was filtered off. GC analysis of the crude mixture revealed the presence of *cis*- and *trans*-**16** as a 73:27 mixture. Flash chromatography (silica gel, hexane/Et_2O 5:1 afforded 11.5 mg (8.5%)

Table 5. *Diastereomer and Enantiomer GC Separation of Cyclopropanation Products* **6** *and* **14**, *and of Insertion Product* **16**

No	Product	GC Column	*T*	Ref.
6a	Ethyl 2-phenylcyclopropanecarboxylate	*Supelco β-DEX 120*	120°	[29]
6b	Ethyl 2-pentylcyclopropanecarboxylate	*Macherey Nagel LIPODEX E*	50°	[29]
6c	Ethyl 2-vinylcyclopropanecarboxylate	*Supelco β-DEX 120*	55°	[29]
6d	Ethyl 2-(2-methylprop-1-en-yl)cyclopropanecarboxylate	*Supelco β-DEX 120*	80°	[29]
6e	Ethyl 2-methyl-3-phenylcyclopropanecarboxylate (2,3-*trans*)	*Supelco β-DEX 120*	110°	[30]
6f	Ethyl 1-(trimethylsilyloxy)bicyclo[3.1.0]hexane-6-carboxylate	*Supelco β-DEX 120*	80°	[31]
6g	Ethyl 2-ethyl-3-methylcyclopropanecarboxylate (2,3-*trans*)	*Supelco β-DEX 120*	55°	[29]
14	3-Oxabicyclo[3.1.0]hexan-2-one	*Macherey Nagel LIPODEX E*	120°	[27]
16	Hexahydrobenzofuran-2(3*H*)-one	*Macherey Nagel LIPODEX E*	120°	[28]

of **16** with an ee of 93 (*cis*-isomer; (3a*S*,7a*S*)) and 85% (*trans*-isomer), as determined by GC (*LIPODEX E*). For results under different reaction conditions, and with cyclohexyl diazoacetate (**17**) [9c][28], see *Table 4*.

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