

200. Rhodium(II)-Catalyzed Decomposition of β,γ -Unsaturated Diazo Compounds

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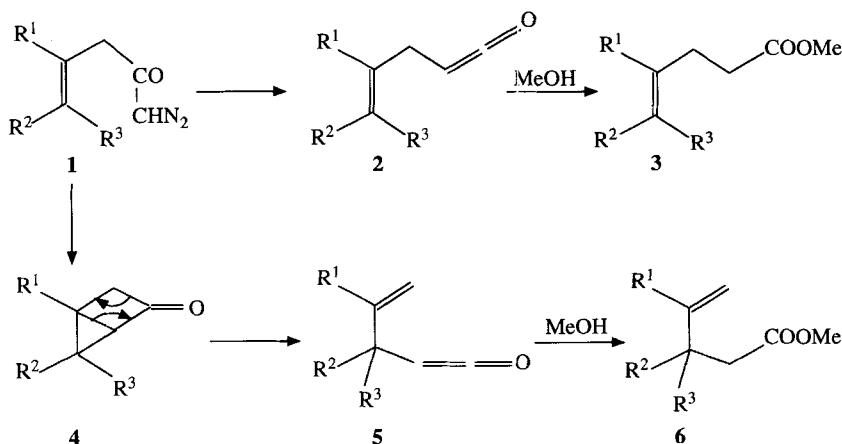
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The Rh^{II} -catalyzed decomposition of β,γ -unsaturated diazo ketones **1** in the presence of MeOH leads *via* vinylogous *Wolff* rearrangement to γ,δ -unsaturated esters **6** (Schemes 1 and 2). A modest asymmetric induction is achieved when the reaction is carried out with chiral tetrakis(pyrrolidinecarboxylato)- or tetrakis(oxazolidinonato)dirhodium(II) complexes. Vinyl and phenyl diazoacetates **11** and **20**, respectively, or 1-diazo-3-phenylpropan-2-one (**25**), when subjected to the same reaction conditions, react by OH insertion with MeOH (Schemes 3–5). In the absence of MeOH, phenyl diazoacetates **20** and **25** undergo intramolecular CH insertion to **22** and **26**, respectively. Intramolecular CH insertion occurs with *N*-aryldiazoamides **23** even in the presence of MeOH (Scheme 5).

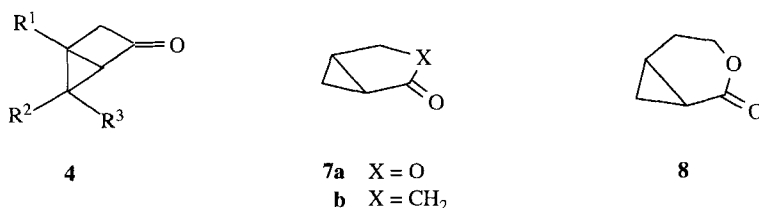
1. Introduction. – The best known reaction of diazo ketones is the *Wolff* rearrangement [1], which occurs under thermal [2] or photochemical [3] conditions, or in the presence of transition metals such as Ag_2O [4]. The normal reaction pathway involves formation of a ketene which is intercepted by an appropriate reagent such as an alcohol or an amine to yield the corresponding carboxylic-acid derivative. In the presence of certain metal catalysts such as Cu^{I} [5] or Rh^{II} [6] salts, the *Wolff* rearrangement may be entirely suppressed, and the putative metalcarbene intermediates react further *via* inter- or intramolecular insertions [7] or cyclopropane formation [8]. When β,γ -unsaturated diazo compounds **1** are decomposed in the presence of Cu^{II} salts and MeOH, the expected reaction *via Wolff* rearrangement to ketene **2** and, ultimately, to its interception product **3** does not occur (Scheme 1). The reaction follows a pathway involving intramolecular

Scheme 1



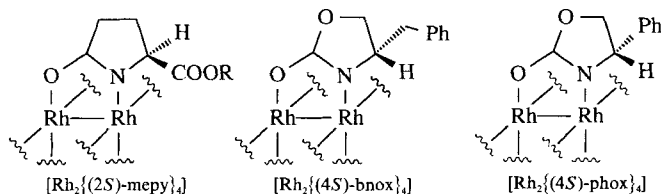
cyclopropane formation to give a bicyclo[2.1.0]pentan-2-one **4** which, in turn, suffers rearrangement to a ketene **5**, isomeric to **2**. Interception of **5** by MeOH, *e.g.*, affords the γ,δ -unsaturated ester **6**.

The overall reaction sequence converting diazo compound **1** to rearranged ester **6** was termed 'vinylogous *Wolff* rearrangement' [9]. Its mechanism was investigated [10] and the sequence exploited for the synthesis of several natural products [11]. Structural comparison between **1** and **6** shows that the vinylogous *Wolff* rearrangement may involve creation of an asymmetric center (C(γ)) from an achiral precursor, if the latter is appropriately substituted. The mechanism *via* the bicyclic intermediate **4** suggests the possibility of an asymmetric version of the reaction.



The vinylogous *Wolff* rearrangement is related to the intramolecular cyclopropane formation of homologous allylic [12] and homoallylic [13] diazo esters, which leads to stable 3-oxabicyclo[3.1.0]hexan-2-ones of type **7a** or 3-oxabicyclo[4.1.0]heptan-2-ones of type **8**. When these reactions are carried out in the presence of chiral carboxamido- or oxazolidinonatorrhodium(II) complexes, the intramolecular cyclopropane formation proceeds with a remarkable degree of asymmetric induction, which may reach 95% in selected cases. Because of the mechanistic similarity between the intramolecular cyclopropane formation and the vinylogous *Wolff* rearrangement, we initiated a study of this latter reaction in the hope of achieving comparable asymmetric inductions. Parts of the results of this investigation were reported in a preliminary communication [14].

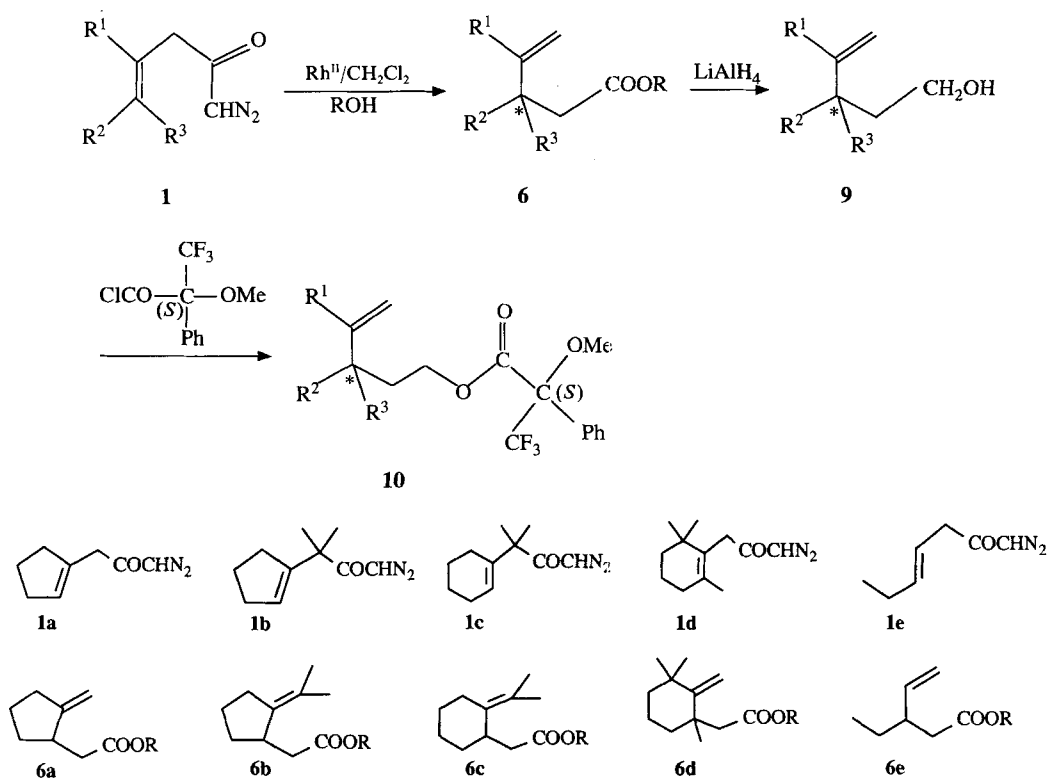
2. Results and Discussion. – 2.1. *Vinylogous Wolff Rearrangement with Chiral Rh^{II} Catalysts.* In the established version, the vinylogous *Wolff* rearrangement is carried out with Cu^{II} [10] catalysts, but we found [14] that reaction yields were as high or even better, when [Rh₂(OAc)₄] was used. The intermediate ketenes were efficiently trapped as esters with a *ca.* 3-fold excess of MeOH, which was present in the CH₂Cl₂ solution of catalyst, while the diazo compound was added slowly, by means of a syringe pump. Three chiral Rh^{II} catalysts were tested, namely [Rh₂{(2*S*)-mepy}₄] (= tetrakis[μ -(*S*)-methyl 5-oxopyrrolidine-2-carboxylato- $\kappa N, \kappa O^5$]dirrhodium(*Rh-Rh*)), [Rh₂{(4*S*)-bnox}₄] (= tetrakis-



[(4*S*)-4-benzoyloxazolidin-2-onato- $\kappa N, \kappa O^2$]dirhodium(*Rh-Rh*) [15] and $[\text{Rh}_2\{[(4*S*)-\text{phox}]\}_4]$ (= tetrakis[(4*S*)-4-phenyloxazolidin-2-onato- $\kappa N, \kappa O^2$]dirhodium(*Rh-Rh*) [16].

The reactions with the chiral catalysts were carried out by a slightly modified procedure. We observed that MeOH, when added in excess (for interception of the ketene) to the solution containing the catalyst, blocked the activity of the latter, presumably by complexation, which resulted in low reaction yields. Therefore, the diazo compound and 1 mol-equiv. of MeOH were added simultaneously in CH_2Cl_2 to a CH_2Cl_2 solution of the catalyst. After addition, the esters were isolated and reduced with LiAlH_4 to alcohols **9**. The latter were reacted with Mosher's acid chloride [17] to yield the corresponding esters **10** (Scheme 2). The diastereoisomeric excess of the esters **10**, which is equivalent to the

Scheme 2



enantiomeric excess (ee) of the primarily formed esters **6**, was determined by capillary gas chromatography (*Method A*), ^1H -NMR (*Method B*), or ^{19}F -NMR using $[\text{Eu}(\text{fod})_3]$ as shift reagent (*Method C*; see Table).

The Table shows that the vinylogous Wolff rearrangement proceeds with asymmetric induction, but the enantiomeric excess (ee) observed in these reactions is much below that achieved in the intramolecular cyclopropane formation of allylic and homoallylic diazo-

Table. *Asymmetric Induction in the Vinylogous Wolff Rearrangement of β,γ -Unsaturated Diazo Ketones Catalyzed with Chiral Rhodium Catalysts*

Diazo ketone	Products	Reaction conditions	Yields [%]	ee [%]
1a	6a	[Rh ₂ (AcO) ₄], MeOH	63	
		[Rh ₂ {(5 <i>S</i>)-mepy} ₄], MeOH	60	9 ^{a)}
1b	6b	[Rh ₂ (AcO) ₄], MeOH	90	
		[Rh ₂ {(5 <i>S</i>)-mepy} ₄], MeOH	54	16 ^{a)}
		[Rh ₂ {(4 <i>S</i>)-phox} ₄], MeOH	51	21 ^{a)}
		[Rh ₂ {(4 <i>S</i>)-bnox} ₄], MeOH	31	31 ^{a)}
		[Cu ^I {tetrahydro-methylenebis(oxazole)}], MeOH	42	7 ^{a)}
1c	6c	[Rh ₂ (AcO) ₄], MeOH	75	
		[Rh ₂ {(5 <i>S</i>)-mepy} ₄], MeOH	46	21 ^{a)}
1d	6d	[Rh ₂ (AcO) ₄], MeOH	17	
		[Rh ₂ {(5 <i>S</i>)-mepy} ₄], MeOH	12	17 ^{b,c)}
1e	6e	[Rh ₂ (AcO) ₄], BnOH	23	
		[Rh ₂ {(5 <i>S</i>)-mepy} ₄], MeOH	16	10 ^{b,c)}

^{a)} Determined by gas chromatography using a methylsilicone capillary column (*Method A*).

^{b)} Determined by ¹H-NMR using [Eu(fod)₃] as shift reagent (*Method B*).

^{c)} Determined by ¹⁹F-NMR using [Eu(fod)₃] as shift reagent (*Method C*).

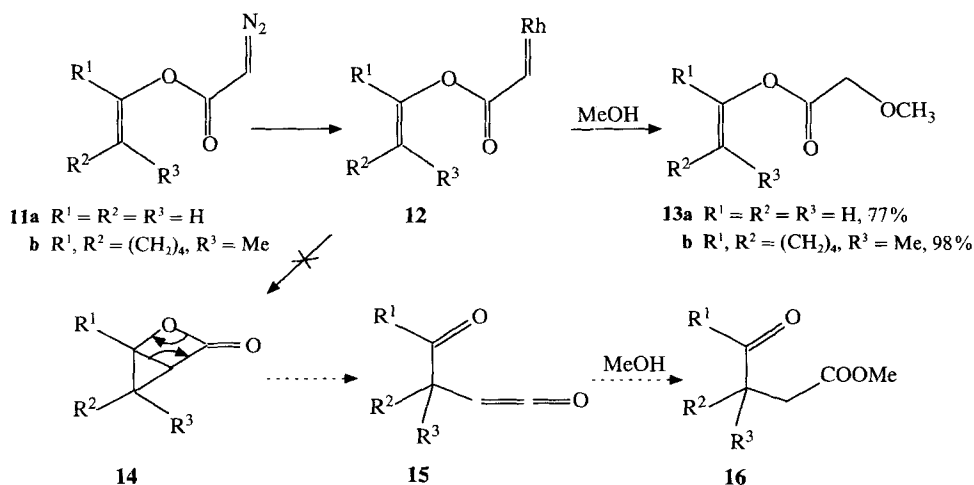
acetates. The best result, 31% ee, was obtained with **1b** and [Rh₂{(4*S*)-bnox}], while [Rh₂{(5*S*)-mepy}₄] produced only 16% ee. This is remarkable, since, in general, use of the mepy catalyst resulted in a higher degree of enantioselection in intramolecular cyclopropane formations than use of the oxazolidinone complexes [Rh₂(4-phox)₄] or [Rh₂(4-bnox)₄] [15] [16]. In the case of **1b**, Cu^I catalysis was also tried with a chiral bis(oxazole) complex (4,4'-di(*tert*-butyl)-4,4',5,5'-tetrahydro-2,2'-methylenebis(oxazole)copper(I)), which is very efficient in intramolecular cyclopropane formations [18], but the result was disappointing (7% ee).

The low enantioselectivity obtained in the Rh^{II}- and Cu^I-catalyzed reactions was explained by enhanced strain in the transition state of the vinylogous *Wolff* rearrangement leading to **6** in comparison to the transition states leading to **7** or **8** [14]. The cyclopropane formation is believed to proceed *via* a Rh-complexed carbene [19]. The enantioselectivity of the reaction is ascribed to the presence of the chiral center of the pyrrolidine or oxazolidinone ring of the ligand. Enhanced strain in the transition state corresponds to a transition state occurring late on the reaction coordinate, in which the carbene has moved away from the metal and closer to the double bond. The increased Rh–carbene bond length may lead to a diminished influence of the chiral center and thus to loss of enantioselectivity. In addition, our expectation of high enantioselectivity in the vinylogous *Wolff* rearrangement resulted from the ee obtained in intramolecular cyclopropane formations of allylic diazoacetates ($\rightarrow$ **7a**) and homoallylic diazoacetates ($\rightarrow$ **8**), which are probably not the best model for the intramolecular cyclopropane formation of β,γ -unsaturated diazoacetates. In fact, it was found that the intramolecular cyclopropane formation of γ,δ -unsaturated diazo ketones with chiral Rh^{II} catalysts leading to bicyclic ketones of type **7b**, which are structurally closer to the intermediate of the vinylogous *Wolff* rearrangement than **7a** and **8**, resulted only in modest asymmetric induction [20]. Apparently, the presence of an O-atom near the reacting double bond is essential for high enantioselectivity in intramolecular cyclopropane formations. The enantioselectivity was

also enhanced in intermolecular Rh^{II} -catalyzed cyclopropene formations, when an O-atom was situated near the reacting triple bond [21], and a similar effect was found in intramolecular CH insertions [22]. For this reason, we synthesized some alkenyl and phenyl diazoacetates analogous to **1**, but with an O-atom between the carbonyl group and the double bond. A reaction sequence analogous to the vinylogous *Wolff* rearrangement would afford an O-analogue of **4**, which upon fragmentation and interception with MeOH would yield a keto-ester having a chiral center in α position to the ketone function.

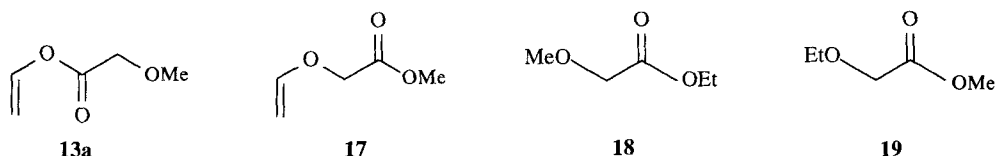
2.2. Decomposition of Heteroatom-Containing β,γ -unsaturated Diazo Ketones, viz. Diazoacetates and Diazo Amides. Vinyl and Phenyl Diazoacetates. When vinyl diazoacetates **11** were decomposed by $[\text{Rh}_2(\text{OAc})_4]$ in the presence of MeOH, the course of the reaction changed, and only vinyl 2-methoxyacetates **13**, derived from interception of the intermediate metalcarbenes **12** by insertion in the O–H bond of the alcohol, were formed (*Scheme 3*) [23]. The reaction was generally very clean and produced high yields of insertion products.

Scheme 3



An attempt was made to suppress the undesired OH insertion of the metalcarbene by using less acidic or less nucleophilic solvents such as *t*-BuOH or $\text{CF}_3\text{CH}_2\text{OH}$, etc., but the reaction course could not be diverted in favor of **14** $\rightarrow$ **15** $\rightarrow$ **16**. In addition, no identifiable products were formed when the reaction was carried out in the absence of any intercepting reagent.

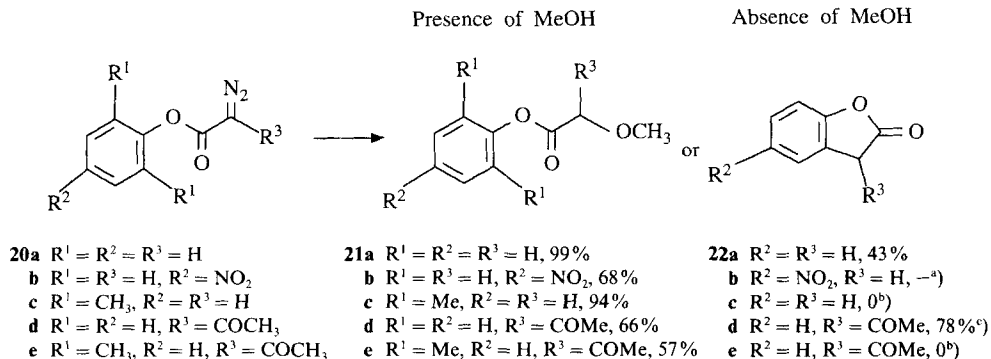
The insertion product **13a** is a structural isomer of **17**, the expected product resulting from O-migration in the normal *Wolff* rearrangement of diazo esters. This reaction occurred when the diazo decomposition was carried out under photolytic conditions [24]. Since the NMR pattern of the rearranged product **17** is the same as that of the unrearranged **13a**, and since no data of both compounds were reported so far, the structures of the reaction products are not unambiguously established. Although O-migration in Rh^{II} -catalyzed decomposition of diazo esters was, to our knowledge, never reported, we verified its absence under our reaction conditions by decomposing ethyl diazoacetate in the presence of MeOH and by comparing the ^1H -NMR data of the insertion product **18** with



methyl ethoxyacetate (**19**) [24] [25], synthesized from commercial ethoxyacetic acid and diazomethane. The signal of the MeO group of **18** was found at δ 3.46 (that of **13a** at δ 3.47) shifted upfield by 0.31 ppm with respect to that of **19**, while that of the α -methylene group of **18** occurred at δ 4.03 (**13a** at δ 4.11). The α -methylene group of **19** resonated at 4.07 ppm. This established that the reaction product has structure **13a** rather than **17**.

The phenyl diazoacetates **20a–c** and diazoacetoacetates **20d, e** reacted smoothly upon exposure to $\text{Rh}^{\text{II}}/\text{MeOH}$ to **21a–e** by intermolecular insertion into the O–H bond (Scheme 4). The structure of **21a** was established by independent synthesis [24], those of the other compounds followed from analogy of the spectral data. When the reaction with **20a** and **20d** was carried out in the absence of MeOH, intramolecular CH bond insertion into the *o*-position of the aromatic ring took place [26] and gave **22a, d**. Blocking of the *o*-positions by Me groups (see **20c, e**) produced no change in the reaction with MeOH, but blocked the intramolecular CH insertion when the reaction was carried out without MeOH. In this case, no identifiable products could be separated from the reaction mixture.

Scheme 4



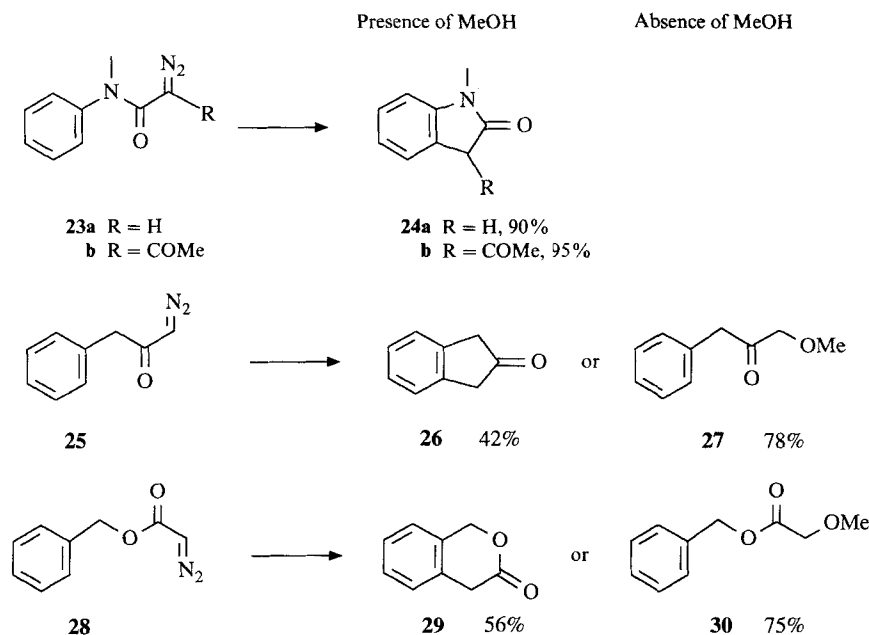
a) Not investigated. b) No product identified. c) See [26].

In all examples investigated so far, the diazoacetates, having an O-atom adjacent to the carbonyl group, failed to undergo the vinylogous *Wolff* rearrangement and reacted by OH insertion in the presence of MeOH or *via* intramolecular CH insertion in the absence of MeOH in the case of phenyl derivatives carrying no substituents at the *o*-positions. The behavior of the phenyl diazoacetates is understandable, since the double bond which would be attacked in the intramolecular cyclopropane formation is part of an aromatic system and, therefore, less susceptible to attack, so that CH insertion takes place. It should be noted, however, that the homologous diazo ketones, derived from 3-arylpropionic acids [27], underwent intramolecular cyclopropane formation to cycloheptatrienes quite readily. The failure of the vinyl diazoacetates to participate in the vinylogous *Wolff*

rearrangement is more surprising considering the facility with which the reaction proceeds with the β,γ -unsaturated C-counterparts. The presence of the acyloxy function at the double bond is, by itself, compatible with intermolecular cyclopropane formation. E.g., vinyl acetate reacted with ethyl diazoacetate in the presence of $[\text{Rh}_2(\text{OAc})_4]$ in acceptable yield (59%) under cyclopropane formation [28]. The replacement of the CH_2 group in **1** by an O-atom is accompanied by slight changes in molecular geometry owing to different bond lengths and different ideal bond angles, however, the force constants for bending the $\text{C}-\text{CH}_2-\text{C}(\text{O})$ as compared to that of the $\text{C}-\text{O}-\text{C}(\text{O})$ bond vary only by *ca.* 20–30% [29]. This appears insufficient to explain the reactivity difference of the O-derivatives in the light of the intensivity of the intramolecular cyclopropane formation of allyl and homoallyl diazoacetates to ring strain. Other investigators observed a marked selectivity difference upon Rh^{II} -catalyzed decomposition of unsaturated diazoketones and diazoesters [30]: α -diazo ketones reacted preferentially *via* intramolecular cyclopropane formation, whereas closely related α -diazo- β -keto-esters inserted into CH bonds. This trend is consistent with our results. Apparently, the presence of the O-atom adjacent to the diazoketone modifies the properties of the intermediate metalcarbene and thus provokes a change in chemoselectivity.

N-Aryldiazoamides. The Rh^{II} (and *Nafion-H*)-catalyzed decomposition of 2-diazo-*N*-methyl-*N*-phenylacetamide (**23a**) and of its aceto derivative **23b** was reported to furnish 1*H*-indol-2(3*H*)-ones **24** in the absence of MeOH (Scheme 5) [31]. However, with these compounds, addition of MeOH had no influence on the course of the reaction: the intramolecular CH insertion products were isolated almost in the same yields with or without MeOH. In this series, intramolecular CH insertion is clearly favored over

Scheme 5



intermolecular OH insertion, which is just the opposite of the tendencies found with aryl diazoacetates.

In view of the selectivity changes between aryl diazo esters and aryl diazo amides, we also investigated the behavior of the analogous aryl-substituted diazo ketones. Some years ago, *Nakatani* [32] reported the formation of indan-2-one (**26**) in 42% yield upon decomposition of **25** with $[\text{Rh}_2(\text{OAc})_4]$. We repeated the reaction in the presence of MeOH and found only the OH-insertion product **27** in the reaction mixture. No products of vinylogous *Wolff* rearrangement or of intramolecular CH insertion into the *o*-position of the aromatic ring were found. In addition, when benzyl diazoacetate (**28**) was decomposed in the absence of MeOH, only intramolecular CH insertion occurred, leading to **29**. The preferential formation of **29** rather than of a cycloheptatriene (by intramolecular cyclopropane formation) was noted previously [33]. This contrasts with the decomposition of the analogous 1-diazo-4-phenylbutan-2-ones [27], where cycloheptatrienes were formed. As in the case of phenyl diazoacetates, the presence of the O-atom in **28** changes the selectivity in favor of CH insertion, and it is remarkable that even formation of a 6-membered ring is preferred over intramolecular cyclopropane formation. In the presence of MeOH, however, the reaction of **28** was again diverted to the OH-insertion product **30**.

3. Conclusions. – The Rh^{II} -catalyzed decomposition of unsaturated diazo ketones in the presence of MeOH is extremely sensitive to structural variations. The β,γ -unsaturated diazoketones **1** react *via* intramolecular cyclopropane formation to yield the products **6** of the vinylogous *Wolff* rearrangement with modest enantioselectivity when chiral (pyrrolidinonato)- or (oxazolidinonato)rhodium complexes are used. No reaction of the intermediate metallocarbenes with MeOH is found. In contrast, the aliphatic and aromatic O-analogues react exclusively by OH insertion. *N*-Aryl-diazoacetamides, in turn, undergo intramolecular CH insertion. When the double bond of the unsaturated β,γ -unsaturated diazo ketone is part of an aromatic ring, the preferred pathway consists in reaction with MeOH, and the intramolecular CH-insertion (to indan-2-one) is only observed in the absence of MeOH.

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Experimental Part

1. *General.* CH_2Cl_2 and 1,2-dichloroethane were distilled from CaH_2 and P_2O_5 , respectively, just prior to use. Dirhodium(II) tetraacetate was obtained from *Fluka*. $[\text{Rh}_2\{(2S)\text{-mepy}\}_4]$ [15], $[\text{Rh}_2\{(4S)\text{-bnox}\}_4]$ [15], $[\text{Rh}_2\{(4S)\text{-phox}\}_4]$ [16], and 4,4'-di(*tert*-butyl)-4,4',5,5'-tetrahydro-2,2'-methylenebis(oxazole)copper(I) [18] [34] were prepared according to published procedures. The purity of the compounds was verified by TLC with plastic plates, covered with silica gel 60 F_{254} (*Merck*); detection by UV lamp (254 and 366 nm) and by treatment with phosphomolybdic acid (5%) in EtOH. Column chromatography (CC): silica gel 60, 230–400 mesh. GC: *Hewlett-Packard*-5890 instrument, flame-ionization detector; He as carrier. IR Spectra (cm^{-1}): *Perkin-Elmer*-681 and *Polaris-FTIR* spectrometers; CHCl_3 solns., NaCl cells. NMR Spectra: *Varian-XL-200* (^1H at 200 MHz; ^{13}C at 50 MHz with ^1H decoupling; ^{19}F at 188 MHz) or *Bruker WH-360* (^1H at 360 MHz); CDCl_3 solns.; chemical shifts δ in ppm rel. to Me_4Si (^1H and ^{13}C) or hexafluorobenzene ($=0$ ppm). MS: *Varian-EM-60*, *Finnigan-4000*, and *VG-70-70* instruments.

2. *Vinylogous Wolff Rearrangement of β,γ -Unsaturated Diazo Ketones.* The β,γ -unsaturated diazo ketones **1a–e** were prepared according to [9–11] and purified by CC just prior to use.

2.1. *$[\text{Rh}_2(\text{OAc})_4]$ -Catalyzed Decomposition of Diazo Ketones **1a–e**: General Procedure.* A soln. of diazo ketone **1** (1.0 mmol) in dry CH_2Cl_2 (5.0 ml) was added dropwise over 24 h, *via* syringe pump, to a mixture of $[\text{Rh}_2(\text{OAc})_4]$

(10.0 mg, 2.5 mol-%) and MeOH (96 mg, 3.0 mmol) in CH_2Cl_2 (25 ml). The soln. was stirred for 1 additional h and then filtered through a 1-cm plug of silica gel. The silica gel was washed with CH_2Cl_2 (50 ml). The combined CH_2Cl_2 soln. was evaporated and the residue purified by CC (silica gel, CH_2Cl_2) or by bulb-to-bulb distillation to afford the corresponding γ,δ -unsaturated esters **6a–e** (for chemical yields, see Table). Spectral data: identical to those reported [9–11].

2.2. Decomposition of Diazo Ketones 1a–e with Chiral Rh^{II} Catalysts: General Procedure. A soln. of the diazoketone **1** (1.0 mmol) and MeOH (1.0 mmol) in dry CH_2Cl_2 (5.0 ml) was added, over 24 h, by means of a syringe pump to the chiral Rh^{II} catalyst (2.5 mol-%) in CH_2Cl_2 (25 ml). The resulting soln. was stirred for 1 additional h at r.t. and then worked up as above to yield the corresponding γ,δ -unsaturated esters **6a–e** (for chemical yields, see Table).

2.3. Bis(oxazole)copper(I)-Catalyzed Decomposition of 1b. Freshly prepared 4,4'-di(*tert*-butyl)-4,4',5,5'-tetrahydro-2,2'-methylenebis(oxazole)copper(I) [34] (0.01 mmol) was combined with MeOH (3.0 mmol) in 1,2-dichloroethane (5.0 ml) at r.t. and activated with 1% phenylhydrazine soln. in MeOH (0.05 ml). After 10 min, **1b** in 1,2-dichloroethane (5.0 ml) was added within 24 h. The soln. was evaporated and the residue purified by bulb-to-bulb distillation: **6b** in 42% yield.

2.4. (+)- α -Methoxy- α -(trifluoromethyl)phenylacetates (= 3,3,3-Trifluoro-2-methoxy-2-phenylpropanoates) 10a–e [17]. To a cooled (0°) soln. of **6** (0.2 mmol) in anhyd. THF (5.0 ml) was added LiAlH_4 (0.1 mmol) in one portion. The mixture was stirred for 1 h at r.t. under N_2 and then quenched with H_2O (5.0 ml). The product was extracted with Et_2O and the extract dried (MgSO_4). The γ,δ -unsaturated alcohols **9** thus prepared were used in the subsequent step without further purification.

(+)-(*R*)-MTPA (= 3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid; Aldrich) was converted to the acyl chloride [17] and distilled. To a soln. of dry pyridine (300 ml, 300 mg) in anhyd. CCl_4 (2.0 ml), (+)-MTPA-Cl (26 ml, 35 mg, 0.14 mmol) and **9** (0.10 mmol) were added at r.t. under N_2 . The mixture was stirred for 5 min, allowed to stand at r.t. for 10 min, then treated with an excess of *N,N*-dimethylpropane-1,3-diamine (ca. 24 ml, 20 mg, 0.20 mmol), and allowed to stand for 5 min. It was then diluted with Et_2O , the Et_2O phase washed (cold dil. HCl, cold sat. Na_2CO_3 , and sat. NaCl soln.), dried, and evaporated, and the residue purified by bulb-to-bulb distillation.

2.5. Determination of the Enantiomeric Excess of 10a–e. The three methods used were tested on racemic esters **10a–e** to determine the most effective method. *Method A*: Anal. GLC using a crosslinked methylsilicone (25 m, 0.2 mm, 0.33 μl) column. *Method B* and *C*: ^1H -NMR and ^{19}F -NMR examination, respectively, in CDCl_3 in the presence of up to 0.4 equiv. of $[\text{Eu}(\text{fod})_3]$. At this $[\text{Eu}(\text{fod})_3]$ concentration, the peak separations were sufficient to permit accurate signal integration. Results: Table.

3. Decomposition of Vinyl and Phenyl Diazoacetates. **3.1. Synthesis of Diazo Esters 11a, b and 20a–c.** Vinyl diazoacetate (**11a**), and 2-methylcyclohex-1-enyl diazoacetate (**11b**) were synthesized from vinyl chloroformate (Fluka) and 2-methylcyclohex-1-enyl chloroformate [35], respectively, and a 3-fold excess of freshly distilled ethereal diazomethane (from Diazald). The diazo esters were purified by CC immediately before use. The same procedure was used for phenyl diazoacetate (**20a**) and 4-nitrophenyl diazoacetate (**20b**) with the corresponding commercially available chloroformates. The chloroformate required for the synthesis of 2,6-dimethylphenyl diazoacetate (**20c**) was prepared by reaction of 2,6-dimethylphenol with an excess (3.0 equiv.) of phosgene in toluene [35].

11a: Yield 72%. IR: 3127 m , 3025 m , 2112 s , 1704 s , 1646 s , 1363 s , 1294 w , 1236 s . ^1H -NMR: 7.30 (q , 1 H); 4.85 (dd , 1 H); 4.55 (dd , 1 H). ^{13}C -NMR: 164.0; 140.9; 96.9; 40.3.

11b: Yield 77%. IR: 2937 w , 2116 s , 1993 m , 1373 m , 1339 m , 1210 s , 1174 w . ^1H -NMR: 4.80 (s , 1 H); 4.80 (s , 1 H); 1.98–2.18 (m , 2 H); 1.55–1.80 (m , 2 H); 1.53–1.56 (m , 3 H). ^{13}C -NMR: 164.83; 141.56; 120.93; 46.01; 29.95; 27.21; 23.01; 22.27; 15.83. MS: 180 (5.94, M^+), 112 (100), 97 (34), 84 (16), 69 (12), 55 (13).

20a: Yield 87%. IR: 3126 m , 2121 s , 1707 s , 1592 w , 1491 m , 1369 s , 1233 s , 1194 s , 1151 s . ^1H -NMR: 7.10–7.45 (m , 5 H); 4.95 (s , 1 H). See [24].

20b: Yield 68%. IR: 3127 w , 3026 w , 2127 s , 1716 s , 1527 m , 1370 m , 1345 s , 1218 m , 1144 s . ^1H -NMR: 8.34–8.22 (m , 2 H); 7.40–7.28 (m , 2 H); 5.03 ($br.$ s , 1 H). ^{13}C -NMR: 155.19; 145.17; 125.13; 122.26; 47.23.

20c: Yield: 60%. IR: 3025 w , 2118 s , 1709 s , 1475 w , 1369 s , 1237 w , 1166 s . ^1H -NMR: 7.05 (s , 3 H); 5.05–4.95 ($br.$ s , 1 H); 2.19 (s , 6 H). ^{13}C -NMR: 148.52; 130.59; 128.55; 125.97; 46.21; 16.24. MS: 190 (10.64, M^+), 122 (100), 107 (19), 91 (12), 77 (14).

3.2. Synthesis of Diazoacetates 20d, e. Phenyl 2-diazo-3-oxobutanoate (**20d**) and 2,6-dimethylphenyl 2-diazo-3-oxobutanoate (**20e**) were prepared by transacetoacetylation of the corresponding phenol with *tert*-butyl acetoacetate (= *tert*-butyl 3-oxobutanoate) [36], followed by diazo transfer [37] according to established procedures.

20d: Yield 78%. IR: 3027 w , 2144 s , 1733 s , 1656 m , 1492 w , 1367 m , 1324 s , 1248 m , 1190 s . ^1H -NMR: 7.10–7.50 (m , 5 H); 2.52 (s , 3 H). See [26].

20e: Yield 85%. IR: 2143s, 1730s, 1656m, 1476w, 1367w, 1325s, 1246w, 1161s. ¹H-NMR: 7.09 (s, 3 H); 2.53 (s, 3 H); 2.19 (s, 6 H). ¹³C-NMR: 189.60; 159.15; 147.22; 130.34; 128.76; 126.43; 28.24; 16.32. MS: 232 (10.98, *M*⁺), 204 (6), 161 (12), 122 (100), 111 (31), 91 (22), 83 (21), 77 (26).

3.3. [*Rh*₂(*OAc*)₄]-Catalyzed Decomposition of Vinyl and Phenyl Diazoacetates **11a**, **b** and **20a–e**: General Procedure. To a blue soln. of [*Rh*₂(*OAc*)₄] (0.01 mmol) and MeOH (1.0 mmol) in CH₂Cl₂ (20 ml) under N₂ was added diazoester **11a**, **b** or **20a–e** (1.0 mmol) in CH₂Cl₂ (5.0 ml) dropwise over 24 h. After the addition, the catalyst was filtered off through a 1-cm plug of silica gel, and the silica gel was washed with additional CH₂Cl₂ (50 ml). The solvent was evaporated under reduced pressure and the residue purified by CC (silica gel, CH₂Cl₂).

Vinyl 2-Methoxyacetate (**13a**): Yield 77%. B.p. 72–75°/20 Torr. IR: 3030w, 1769m, 1649w, 1212m, 1186m, 1131m. ¹H-NMR: 7.31 (q, 1 H); 4.94 (dd, 2 H); 4.64 (dd, 1 H); 4.11 (s, 2 H); 3.47 (s, 3 H). ¹³C-NMR: 166.5; 139.6; 97.6; 68.3; 58.5.

2-Methylcyclohex-1-enyl 2-Methoxyacetate (**13b**): Yield 98%. B.p. 75–80°/20 Torr. IR: 3022m, 2937s, 2862m, 1759s, 1450m, 1263m, 1186s, 1124s. ¹H-NMR: 4.12 (s, 2 H); 3.47 (s, 3 H); 2.15–1.95 (m, 2 H); 1.80–1.50 (m, 2 H); 1.58–1.50 (m, 3 H). ¹³C-NMR: 168.26; 141.38; 120.64; 69.56; 59.26; 26.99; 23.02, 22.31; 15.99. MS: 184 (7.99, *M*⁺), 156 (15), 126 (8), 111 (8), 82 (8), 55 (9), 45 (100). HR-MS: 184.1098 (C₁₀H₁₆O₃⁺, calc. 184.1099).

Phenyl 2-Methoxyacetate (**21a**): Yield 99%. B.p. 77–80°/0.1–0.15 Torr ([24]: 99–101°/0.6–0.7 Torr). ¹H-NMR: 7.45–7.10 (m, 5 H); 4.29 (s, 2 H); 3.54 (s, 3 H). See [24].

4-Nitrophenyl 2-Methoxyacetate (**21b**): Yield 68%. M.p. 55–56° ([38]: 56–58°). ¹H-NMR: 8.28 (d, 2 H); 7.32 (d, 2 H); 4.32 (s, 2 H); 3.54 (s, 3 H). See [38].

2,6-Dimethylphenyl 2-Methoxyacetate (**21c**): Yield 94%. B.p. 95–97°/0.30–0.35 Torr. IR: 3025m, 2929m, 1771s, 1474s, 1377s, 1266s, 1239s, 1179s, 1124s. ¹H-NMR: 7.06 (s, 3 H); 4.34 (s, 2 H); 3.55 (s, 3 H); 2.15 (s, 6 H). ¹³C-NMR: 168.12; 147.66; 129.99; 128.69; 126.09; 60.39; 59.50; 16.33. MS: 194 (17.44, *M*⁺), 166 (35), 136 (10), 121 (11), 91 (12), 77 (11), 45 (100). HR-MS: 194.0930 (C₁₁H₁₄O₃⁺, calc. 194.0942).

Phenyl 2-Methoxy-3-oxobutanoate (**21d**): Yield 66%. B.p. 80–85°/0.35–0.40 Torr. IR: 3026w, 2930w, 1756s, 1729s, 1529w, 1492m, 1261m. ¹H-NMR: 7.55–7.20 (m, 5 H); 4.50 (s, 1 H); 3.58 (s, 3 H); 2.36 (s, 3 H). ¹³C-NMR: 201.44; 165.67; 150.13; 129.57; 126.40; 121.16; 86.83; 58.83; 26.37. MS: 208 (2.77, *M*⁺), 180 (21), 166 (48), 152 (13), 137 (81), 121 (7), 108 (53), 94 (95), 87 (18), 77 (98), 65 (100), 59 (31). HR-MS: 208.0734 (C₁₁H₁₂O₄⁺, calc. 208.0735).

2,6-Dimethylphenyl 2-Methoxy-3-oxobutanoate (**21e**): Yield 57%. B.p. 105–110°/0.35–0.40 Torr. IR: 3026w, 2928w, 1764m, 1728s, 1474w, 1358w, 1263m, 1158s, 1121m. ¹H-NMR: 7.06 (s, 3 H); 3.61 (s, 3 H); 2.39 (s, 3 H); 2.14 (s, 6 H). ¹³C-NMR: 209.81; 168.56; 164.78; 147.62; 129.90; 128.75; 126.31; 86.87; 58.80; 26.38; 16.44. MS: 236 (9.54, *M*⁺), 208 (9), 194 (8), 165 (78), 136 (10), 122 (53), 107 (14), 105 (45), 91 (47), 87 (62), 77 (54), 72 (16), 65 (17), 59 (100), 51 (16), 45 (17). HR-MS: 236.1045 (C₁₃H₁₆O₄⁺, calc. 236.1048).

3.4. [*Rh*₂(*OAc*)₄]-Catalyzed Decomposition of **20a** and **20d** in the Absence of MeOH. The procedure was identical to *Exper.* 3.3, except that no MeOH was present.

Benzofuran-2(3H)-one (**22a**): Yield 43% from **20a**. Spectral data: identical to those reported [39].

3-Acetylbenzofuran-2(3H)-one (**22d**): Yield 78% from **20d**. Spectral data identical to those reported [26].

4. Decomposition of N-Aryldiazoamides. 2-Diazo-N-methyl-3-oxo-butanamide-N-phenyl [31] (**23b**) was prepared from N-methylaniline by acetoacetylation with *tert*-butyl acetoacetate [36] and diazo transfer [37] according to published procedures. The 2-diazo-N-methyl-N-phenylacetamide (**23a**) was obtained by deacylation [40] of **23b** in MeCN/H₂O with KOH (3.0 equiv.). The decomposition with and without MeOH were carried out as described in 3.3 and 3.4.

1-Methyl-1H-indol-2(3H)-one (**24a**) and 3-Acetyl-1-methyl-1H-indol-2(3H)-one (**24b**): Yield 90% from **23a** and 95% from **23b**, respectively. Spectral data: identical to those reported [31].

5. Decomposition of Diazo Ketone **25** and Diazo Ester **28**. 1-Diazo-3-phenylpropan-2-one (**25**) [41] and benzyl diazoacetate (**28**) [42] were synthesized by treatment of phenylacetyl chloride (*Fluka*) and benzyl chloroformate (*Fluka*), respectively, with an excess (3 equiv.) of diazomethane according to established procedures [8] [9]. The decompositions were carried out in the presence and absence of MeOH as described in 3.3 and 3.4.

Indan-2-one (**26**): Yield 42% from **25** in the absence of MeOH. Spectral data: identical to those reported [43].

1-Methoxy-3-phenylpropan-2-one (**27**): Yield 78% from **25** in the presence of MeOH. Spectral data: identical to those reported [44].

1H-2-Benzopyran-3(4H)-one (**29**): Yield 56% from **28** in the absence of MeOH. Spectral data: identical to those reported [45].

Benzyl 2-Methoxyacetate (**30**): Yield 75% from **28** in the presence of MeOH. Spectral data: identical to those reported [42].

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