# On the Enantioselectivity of Transition Metal-Catalyzed 1,3-Cycloadditions of 2-Diazocyclohexane-1,3-diones

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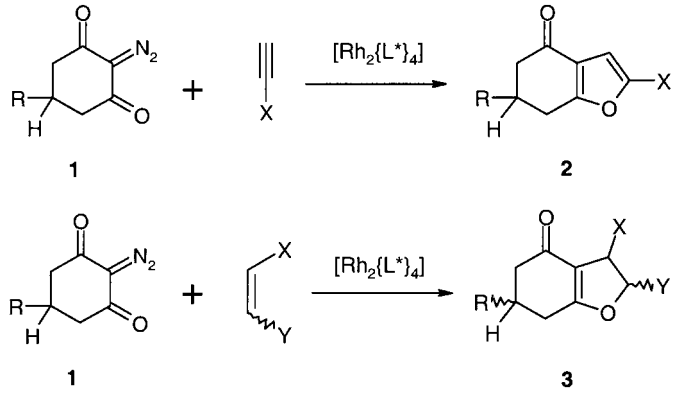
The formal 1,3-cycloaddition of 2-diazocyclohexane-1,3-diones **1a**–**1d** to acyclic and cyclic enol ethers in the presence of $Rh^{II}$-catalysts to afford dihydrofurans has been investigated. Reaction with a *cis/trans* mixture of 1-ethoxyprop-1-ene (**13a**) yielded the dihydrofuran **14a** with a *cis*/*trans* ratio of 85:15, while that with (*Z*)-1-ethoxy-3,3,3-trifluoroprop-1-ene (**13b**) gave the *cis*-product **14b** exclusively. The stereochemical outcome of the reaction is consistent with a concerted rather than stepwise mechanism for cycloaddition. The asymmetric cycloaddition of 2-diazocyclohexane-1,3-dione (**1a**) or 2-diazodimedone (=2-diazo-5,5-dimethylcyclohexane-1,3-dione; **1b**) to furan and dihydrofuran was investigated with a representative selection of chiral, nonracemic $Rh^{II}$ catalysts, but no significant enantioselectivity was observed, and the reported enantioselective cycloadditions of these diazo compounds could not be reproduced. The absence of enantioselectivity in the cycloadditions of 2-diazocyclohexane-1,3-diones is tentatively explained in terms of the *Hammond* postulate. The transition state for the cycloaddition occurs early on the reaction coordinate owing to the high reactivity of the intermediate metallocarbene. An early transition state is associated with low selectivity. In contrast, the transition state for transfer of stabilized metallocarbenes occurs later, and the reactions exhibit higher selectivity.

**Introduction.** – The desymmetrization of *meso*-compounds offers an attractive entry towards the synthesis of enantiomerically pure compounds, and a large number of approaches by enzymatic or chemical methods have been developed to this end. In the field of asymmetric carbene transfer, desymmetrization has been successfully applied towards inter- [1] and intramolecular cyclopropanations [2], and to intramolecular CH insertions of diazoacetate esters [3][4] and amides [5]. Cyclopropanation of olefins or acetylenes [6] is the most common pathway for transition metal-catalyzed decomposition of diazo compounds [7]. However, an alternative reaction consisting of formal 1,3-cycloadditions to olefins is available. It occurs with diazo esters or diazo ketones, which carry additional electron-attracting groups such as ethyl diazoacetoacetate [8], ethyl diazopyruvate [9], or 2-diazocyclohexane-1,3-dione [10], and it is favored with polar or polarizable olefins such as enol ethers and furans. Cycloadditions are also observed upon reaction of such diazo compounds or the corresponding phenyliodonium ylides with acetylenes [11][12], ketenes [13], nitriles [14], isocyanates [15], thioisocyanates [16], thiones [17], and heterocyclopentadienes [18]. Formal 1,3-dipolar cycloadditions have been reported upon photochemical decomposition of phenyliodonium ylides derived from dimedone (=5,5-dimethylcyclohexane-1,3-dione) and 1,3-cyclohexane-1,3-dione [19], and upon reaction of 2,2-dibromo 1,3-diketones with olefins in the presence of metallic Cu [20].

The 1,3-dipolar cycloaddition of 2-diazocyclohexane-1,3-diones to polar olefins leads to the formation of stereogenic centers and, therefore, is potentially enantiose-

lective. If the diketone carries a single substituent at C(5), C(5) becomes a stereogenic center in the product. Cycloaddition of **1** to an acetylene results in formation of a benzofuran derivative **2** with a single stereogenic center, while addition to an olefin leads to the creation of up to three stereogenic centers in the product **3**, as exemplified in *Scheme 1*. Since **1** is a *meso*-compound, the enantioselective cycloaddion to acetylenes or olefins constitutes a desymmetrization.

*Scheme 1*

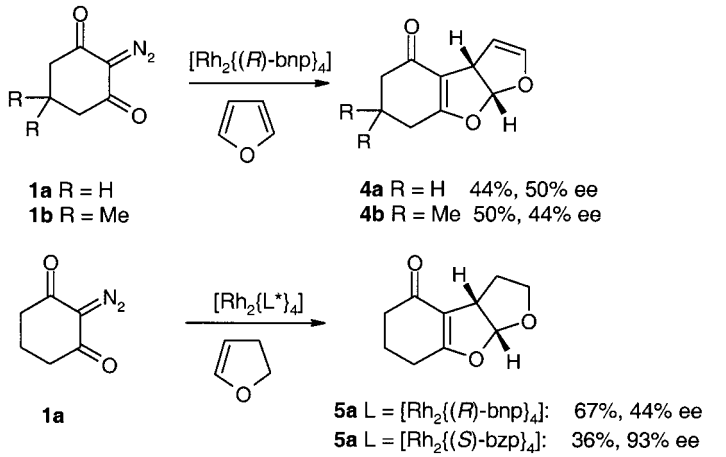



The feasibility of this approach may be illustrated by enantioselective cycloadditions with 2-diazo diones reported in the literature(*Scheme 2*). Thus, *Pirrung* and *Zhang* achieved enantioselectivities in the range of 44–50% upon decomposition of 2-diazocyclohexane-1,3-dione (**1a**) or 2-diazodimedone (=2-diazo-5,5-dimethylcyclohexane-1,3-dione; **1b**) to furan and 2,3-dihydrofuran with a chiral $Rh^{II}$ catalyst based on binol phosphate ($[Rh_2\{(R)\text{-bnp}\}_4]$, bnp = binolphosphate) [21]. More recently, *Ishitani* and *Achiwa* reported enantioselectivities of up to 93% for the addition of **1a** to 2,3-dihydrofuran with a $Rh^{II}$ catalyst having a benzoylated proline ligand, $[Rh_2\{(S)\text{-bzp}\}_4]$, and even 98% ee with 4-methoxybenzoylproline as ligand [22]. In view of the large structural variability of $Cu^{I}$ and $Rh^{II}$ catalysts, which are now available for enantioselective carbene transfer, it appeared possible to develop and generalize the enantioselective cycloadditions of 2-diazocyclohexane-1,3-diones.

This positive appreciation of the situation is, however, attenuated by the absence of any follow-up subsequent to the original reports on enantioselective cycloadditions [23]. Furthermore, the large majority of successful enantioselective carbene-transfer reactions uses diazo esters or diazo amides. Enantioselective carbene transfer with diazo ketones is, for unknown reasons, much less advanced [24], although some selective catalysts have been developed for this purpose [25][26].

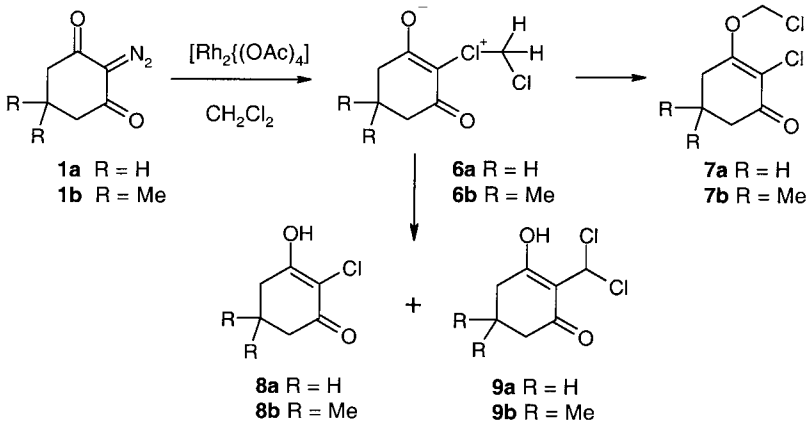
As will be described below, this original approach could not be realized. All cycloadditions tried afforded products without any significant enantioselectivity. This failure led us to investigate the $Rh^{II}$-catalyzed decomposition of 2-diazocyclohexane-1,3-diones in more detail, in the hope of finding its underlying reasons.

*Scheme 2*




**Results and Discussion.** – 1. *Decomposition of 2-Diazocyclohexane-1,3-dione* (**1a**) *and 2-Diazodimedone* (**1b**) *in* $CH_2Cl_2$. The decomposition of 2-diazocyclohexane-1,3-dione (**1a**) or 2-diazodimedone (**1b**) in the presence of $[Rh_2(OAc)_4]$ in $CH_2Cl_2$ affords 2-chloro-3-(chloromethoxy)cyclohex-2-en-1-ones **7a** and **7b** in 87 and 88% yields, respectively (*Scheme 3*). Evidence for the structures of **7a** and **7b** is provided by the 2-H *singlet* at 5.83 ppm in the $^1$H-NMR and the $CH_2$ signal in the $^{13}$C-NMR at 74.3 ppm. Compound **7** originates probably from the ylide **6**, which, in turn, results from reaction of the intermediate metallocarbene with the solvent. Ylide formation between 1,3-dioxocarbenes and benzyl or acyl halides to afford the corresponding haloenones is well documented, and has been preparatively exploited [27].

*Scheme 3*



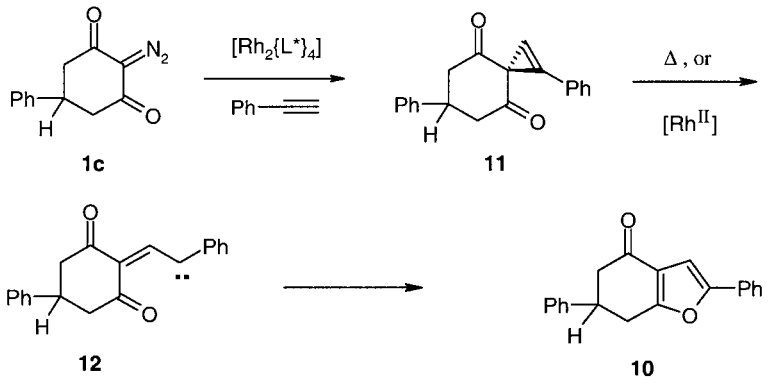

Our observations contrast with those of *Pirrung et al.* [10], who reported formation of 2-chlorocyclohexane-1,3-dione (**8a**, 80%) and 2-(dichloromethyl)cyclohexane-1,3-

dione (**9a**) upon decomposition of **1a** in $CH_2Cl_2$ although the latter product was not fully characterized. The formation of ylide **6a** was also invoked to account for the formation of **8a** and **9a**. However, in our experiments, **8a** and **9a** could not be detected. When the decomposition of **1a** and **1b** was carried out with the *N*-proline benzoate catalyst $[Rh_2\{(S)\text{-bzp}\}_4]$ in the presence of 2,3-dihydrofuran in $CH_2Cl_2$, the chloroenones **7a** and **7b** were formed in 70 and 80% yields, respectively, while the expected cycloadducts were formed in yields of only 14 and 15% (see below).

To prevent formation of these secondary products, the cycloadditions were carried out either with the substrate as solvent, or in trifluorotoluene, which does not react with the carbenes. *Pirrung et al.* have used fluorobenzene for such cycloadditions [18].

2. *Cycloaddition of 5-phenylcyclohexane-1,3-dione* (**1c**) *to phenylacetylene.* 2-Diazo-5-phenylcyclohexane-1,3-dione (**1c**) [28] underwent cycloaddition to phenylacetylene to afford a single product **10** in 84% yield (*Scheme 4*). The structure of **10**, unequivocally established by X-ray crystallography (*Fig.*), has the Ph substituent at C(2), and is consistent with that reported by *Pirrung et al.* for addition of **1a** to other acetylenes [11].

*Scheme 4*



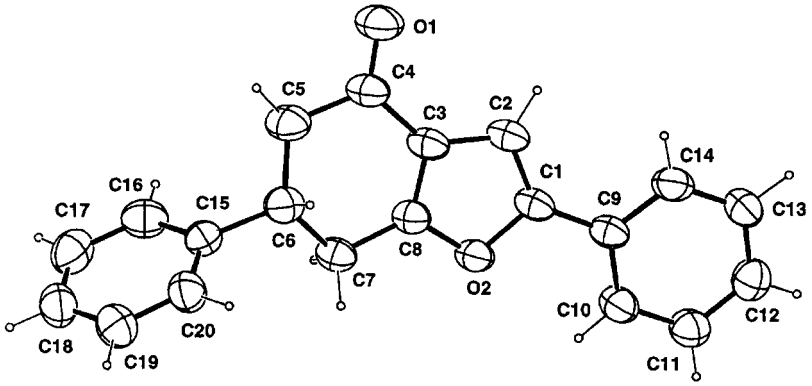




Figure. *Perspective view of the crystal structure of* **10** *with atom numbering.* Ellipsoids are represented with 40% probability.

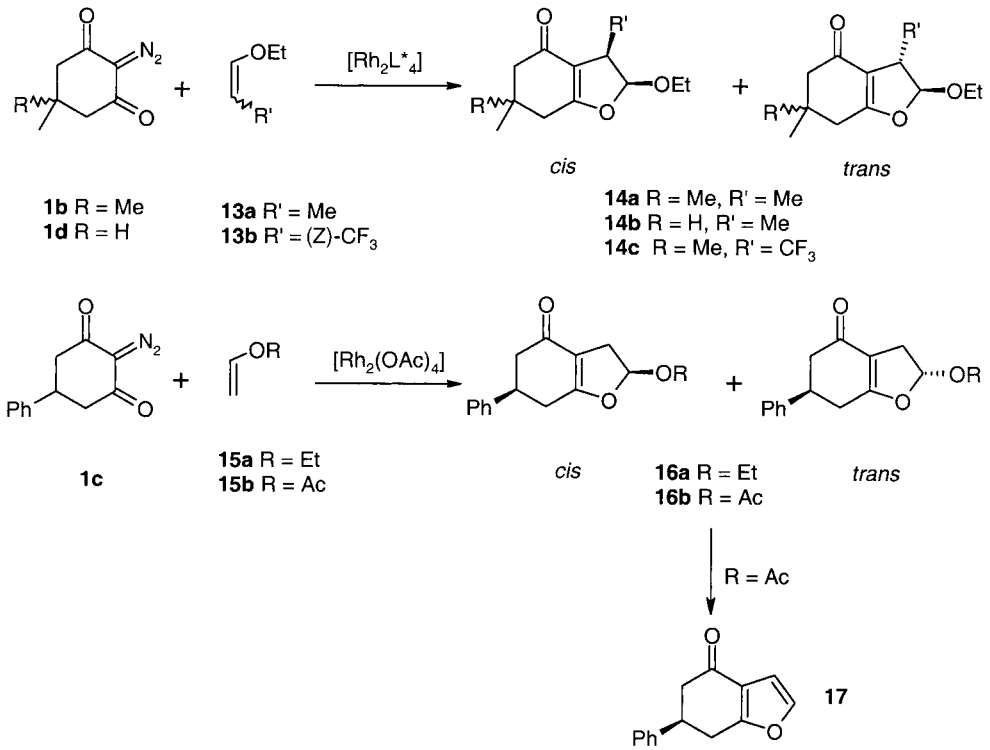
The reaction was carried out with three chiral catalysts, $[Rh_2\{(S)\text{-ptpa}\}_4]$, $[Rh_2\{(S)\text{-phsp}\}_4]$, and $[Rh_2\{(S)\text{-bnp}\}_4]$, with yields of 75, 68, and 73%, respectively. In all reactions, no enantioselectivity had been observed within experimental error.

Among the possible sources for the absence of enantioselectivity in these reactions, the possible intermediacy of a spirocyclic cyclopropene derivative **11** as proposed by *Pirrung et al.* [11] must be considered. The formation of cyclopropenes upon addition of carbenes to acetylenes is well-known [6], and thermal or transition metal catalyzed rearrangements of cycloprop-2-ene-1-carboxylates to furans [29][30] *via* intermediate vinylcarbenes [31][32] have been reported. In the present case, the postulated intermediate **11** may represent a *trans*/*cis* mixture of *meso*-compounds and the vinylcarbene **12** derived thereof *via* thermal rearrangement is necessarily racemic, so that the final product **10** is a racemate. We have recently shown that the products resulting from $Rh^{II}$-catalyzed rearrangement of achiral cycloprop-2-ene-1-carboxylates in the presence of chiral $Rh^{II}$ catalysts may be enantiomerically enriched [33]. Therefore, the absence of enantioselectivity in our experiments does not constitute conclusive evidence for a cyclopropene intermediate and could as well be due to an inappropriate choice of catalyst. Concievably, a concerted or stepwise cycloaddition could also proceed without enantioselectivity. To avoid possible ambiguities, the cycloaddition to acetylenes was not pursued, and the effort was concentrated on cycloadditions to olefins. In these latter reactions, the putative cyclopropane intermediates, if appropriately substituted, are chiral.

3. *Cycloaddition to Acyclic Polar Olefins.* The $[Rh_2(OAc)_4]$-catalyzed decomposition of 2-diazodimedone (**1b**) in the presence of 1-ethoxyprop-1-ene (**13a**; 65:35 (*Z*)/(*E*)-mixture) afforded the cycloadduct **14a** in 70% yield as an unseparable 85:15 *cis*/*trans* mixture (*Scheme 5*). The relative configuration of the major component, *cis*-**14a**, follows from the vicinal coupling constant of 7.6 Hz of H-C(2)/H-C(3), while the vicinal coupling constant of the *trans*-isomer (*trans*-**14a**) was 2.8 Hz. The value for *cis*-**14a** agrees well with that of 7.3 Hz in the adduct **5b** of 2-diazodimedone (**1b**) to 2,3-dihydrofuran (see below). The preferential formation of *cis*-**14a** from from the (*Z*)/(*E*)-mixture of the dipolarophile indicates kinetic discrimination against the (*E*)-isomer of **13a** in the cycloaddition step, and is consistent with a concerted mechanism. For a stepwise cycloaddition, or for a process involving an intermediate cyclopropane, or for a thermodynamically controlled process, preferential formation of *trans*-**14a** would be expected. An analogous preference for the cycloaddition of *cis*-propenyl acetate has been reported by *Pirrung* and *Lee* [34]. Similarily, 2-diazo-5-methylcyclohexane-1,3-dione (**1d**) underwent preferential *cis*-cycloaddition to **13a** ((*Z*)/(*E*) 65:35) to afford **14b** as a 1:1 mixture of stereoisomers (with respect to the Me group at C(6)) and a *cis*/*trans* ratio of 91:9 (*cis*-**14b**: $^3J(H,H) = 7.5$ Hz, *trans*-**14b**: $^3J(H,H) = 2.7$ Hz). Thus, our expectation of stereochemical control by substituents at C(5) of the diazo compound could not be realized. To confirm the stereochemical course of the cycloaddition, **1b** was reacted with (*Z*)-1-ethoxy-3,3,3-trifluoropropene (**13b**) [35]. The cycloadduct *cis*-**14c** was isolated in 75% yield, with a *cis*/*trans* ratio $> 99:1$. The *cis*-configuration of **14c** was assigned again on the grounds of the vicinal coupling constant of 7.3 Hz of the dihydrofuran moiety. Although cycloaddition with the (*E*)-isomer of **13b**, which is not readily accessible [36], was not examined, the exclusive formation of *cis*-**14c** from **13b** supports the hypothesis of a concerted and stereospecific cyclo-

addition of **1** to polar olefins. A concerted cycloaddition mechanism has also been proposed for the stereospecific addition of diazopyruvate to (*E*)- and (*Z*)-dimethoxyethylene [9]. However, concertedness may not be general in these reactions, and, in other cases, a two-step mechanism involving either a cyclopropane intermediate, which subsequently rearranges, or a dipolar intermedate may take place.

*Scheme 5*




The cycloadducts *cis*-**14a** and *cis*-**14c** were isolated with ee values of 8 and 10%, respectively, when reactions were carried out with $[Rh_2\{(S)\text{-nttl}\}_4]$ (*Table 1*). 1,2-Dichloroethylene, in turn, failed to undergo cycloaddition to **1b**.

Table 1. *Cycloaddition of 2-Diazocyclohexane-1,3-diones* **1b** *and* **1d** *to Acyclic Olefins* (*Scheme 5*)[a])

| Diazo compound | | Olefin | | Catalyst | Adduct (Yield) | *cis/trans*[b]) | ee (*cis*)[c]) |
|---|---|---|---|---|---|---|---|
| No. | R | No. | R′ | | | | |
| **1b** | Me | **13a** | Me | $[Rh_2(OAc)_4]$ | **14a** (70%) | 85 : 15 | – |
| **1b** | Me | **13a** | Me | $[Rh_2\{(S)\text{-nttl}\}_4]$ | **14a** (65%) | 85 : 15 | 8% |
| **1d** | H | **13a** | Me | $[Rh_2(OAc)_4]$ | **14b** (56%)[d]) | 98 : 2 | – |
| **1b** | Me | **13b** | $CF_3$ | $[Rh_2(OAc)_4]$ | **14c** (75%) | > 99 : 1 | – |
| **1b** | Me | **13b** | $CF_3$ | $[Rh_2\{(S)\text{-nttl}\}_4]$ | **14c** (85%) | > 99 : 1 | 10% |

[a]) Conditions: neat, at r.t. in the presence of 0.60 mol-% of $Rh^{II}$ catalyst. [b]) With respect to C(2)/C(3). [c]) The ee value of *trans*-isomer not determined. [d]) 1 : 1 Mixture of stereoisomers with respect to Me group at C(6).

The cycloaddition of **1c** to 1-ethoxyethene (**15a**) in the presence of $[Rh_2(OAc)_4]$ produced an unseparable *cis/trans*-mixture of **16a** in a 1:1 ratio in quantitative yield, while ethenyl acetate (**15b**) afforded a 2:1 mixture of stereoisomers **16b** in 43% yield (*Scheme 5*). Heating **16b** in refluxing toluene in the presence of TsOH [37] afforded the benzofuran **17**. Attempts to eliminate EtOH from **16a** under a variety of conditions were not successful, however. No chiral catalysts were tested with **15a** and **15b** owing to the possibility of epimerization at the acetal function in the products **16a** and **16b**, respectively.

4. *Cycloaddition to Furan and Dihydrofuran* (*Scheme 6*). The original procedure for addition of 2-diazocyclohexane-1,3-dione (**1a**) or 2-diazodimedone (**1b**) to furan uses the substrate as solvent and $[Rh_2\{(S)\text{-bnp}\}_4]$ as catalyst. Decomposition of **1a** takes place at room temperature in 12 h. In our hands, these reaction conditions applied to **1b** produced only an insignificant ee value of the adduct **4b** (*Table 2*). Similarily, addition of **1a**, to 2,3-dihydrofuran in the presence of $[Rh_2\{(S)\text{-bnp}\}_4]$ afforded only the racemic adduct **5a** (*Table 3*). The method of preparation and the quality of the catalyst seem not responsible for this failure, since its optical rotation was found identical with that reported in the literature, and since we have used $[Rh_2\{(S)\text{-bnp}\}_4]$ in the past with success for other reactions [38]. Subsequently, the $[Rh_2\{(S)\text{-bzp}\}_4]$-catalyst was synthesized as described by *Ishitani* and *Achiwa*, and tested for the addition of **1a** to 2,3-dihydrofuran in $CH_2Cl_2$. However, the enantioselectivity of the reaction leading to the adduct **5a** was 0% rather than the reported 93%. In addition, **5a** was isolated in only 12% yield. The major reaction product was **7a** derived from reaction of the intermediate carbene with the solvent. The yield could be increased to 66% when the reaction was carried out in neat 2,3-dihydrofuran, but with only an insignificant ee value of 5%.

Table 2. *Cycloaddition of 2-Diazodimedone* (**1b**) *to Furan*[a])

| Catalyst | Adduct (**4b**) [%] | ee [%] | Remark |
|---|---|---|---|
| $[Rh_2(OAc)_4]$ | 34 | – | |
| $[Rh_2\{(S)\text{-bnp}\}_4]$ | 24 | 6 | |
| $[Rh_2\{(S)\text{-bnp}\}_4]$ | 50 | 49 | [21] |
| $[Rh_2\{(S)\text{-phsp}\}_4]$ | 42 | 9 | |
| $[Rh_2\{(S)\text{-ptpa}\}_4]$ | 36 | 9 | |
| $[Rh_2\{(S)\text{-nttl}\}_4]$ | 36 | 8 | |
| $[Rh_2\{(R)\text{-camph}\}]$ | 46 | 2 | |
| $[Rh_2\{(4S)\text{-bnaz}\}_4]$ | 0 | – | |
| $[Rh_2\{(4S)\text{-bnaz}\}_4]$ | 8[b]) | 0 | |

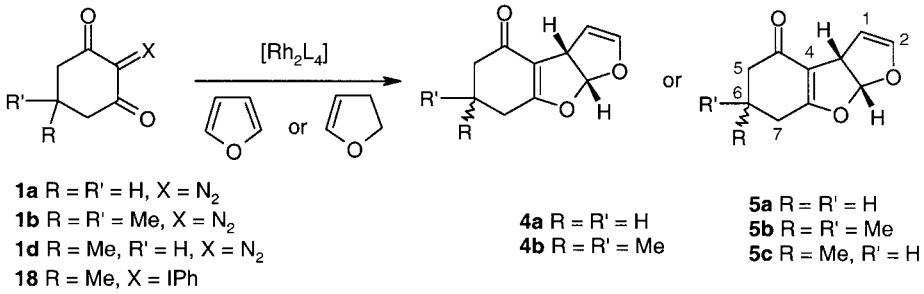
[a]) In neat furan, 25°. [b]) With phenyliodonium ylide **18** as substrate.

Some other catalysts of a different type were also tested for cycloaddition of **1a** and **1b** to furan and 2,3-dihydrofuran, and the results are summarized in *Tables 2* and *3*. The catalysts are representative for the various structural types, which have been successfully used in enantioselective carbene transfer with diazo compounds. They were prepared according to published procedures. The $Rh^{II}$ carboxamidate catalysts of *Doyle*, such as $[Rh_2\{2S\text{)-mepy}\}_4]$ or $[Rh_2\{4S\text{)-bnaz}\}_4]$ failed to decompose the diazo compounds **1a** and **1b**, but reacted with the corresponding phenyliodonium ylide **18**

Table 3. *Cycloaddition of 2-Diazocyclohexane-1,3-diones* **1a**, **1b**, *and* **1d** *and Phenyliodonium Ylide* **18** *to Dihydrofuran* (*Scheme 6*)

| Compound | R, R′ | X | Catalyst | Solvent | Adduct (yield) | ee [%] | Remarks |
|---|---|---|---|---|---|---|---|
| **1a** | H | $N_2$ | [$Rh_2$(*S*-bnp}$_4$] | Neat | **5a** (67%) | 44 | [21] |
| **1a** | H | $N_2$ | [$Rh_2$(*S*-bnp}$_4$] | Neat | **5a** (60%) | 0 | This work |
| **1a** | H | $N_2$ | [$Rh_2$(*S*-bzp}$_4$] | $CH_2Cl_2$ | **5a** (36%) | 93 | [22] |
| **1a** | H | $N_2$ | [$Rh_2$(*S*-bzp}$_4$] | $CH_2Cl_2$ | **5a** (12%) | 0 | This work |
| **1a** | H | $N_2$ | [$Rh_2$(*S*-bzp}$_4$] | Neat | **5a** (66%) | 5 | |
| **1a** | H | $N_2$ | [$Rh_2$(*S*-tbsp}$_4$] | $PhCF_3$ | **5a** (8%) | 2 | |
| **1b** | Me | $N_2$ | [$Rh_2$(*S*-phsp}$_4$] | $CH_2Cl_2$ | **5b** (14%) | 0 | |
| **1d** | Me, H | $N_2$ | [$Rh_2(OAc)_4$] | Neat | **5c** (80%) | 0 | |
| **18** | Me | IPh | [$Rh_2$(*S*-nttl}$_4$] | $PhCF_3$ | **5b** (26%) | 0 | |
| **18** | Me | IPh | [$Rh_2$(2*S*-mepy}$_4$] | $PhCF_3$ | **5b** (26%) | 0 | |
| **18** | Me | IPh | [$Rh_2$(*S*-bnp}$_4$] | $PhCF_3$ | **5b** (60%) | 0 | |
| **18** | Me | IPh | [$Rh_2(O_2CF_3)_2(pc)_2$] (**22**) | $PhCF_3$ | **5b** (75%) | – | |
| **18** | Me | IPh | [$Rh_2(OAc)_2(pc)_2$] (**23**) | $PhCF_3$ | **5b** (69%) | – | |
| **18** | Me | IPh | (*P*)-[$Rh_2(O_2CF_3)_2(pc)_2$] (**24**) | $PhCF_3$ | **5b** (82%) | 0 | |

*Scheme 6*

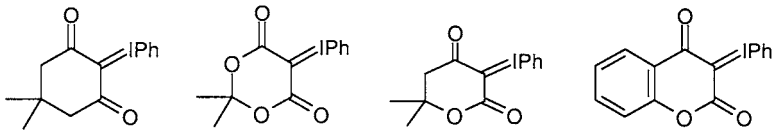



**1a** R = R' = H, X = $N_2$
**1b** R = R' = Me, X = $N_2$
**1d** R = Me, R' = H, X = $N_2$
**18** R = Me, X = IPh

**4a** R = R' = H
**4b** R = R' = Me

**5a** R = R' = H
**5b** R = R' = Me
**5c** R = Me, R' = H

[39]. However, despite large structural variations in the catalysts, no significant enantioselectivities were reached (*Scheme 6*). This failure is even more surprising considering the analogous carbene transfer with the phenyliodonium ylide derived from *Meldrum*'s acid, where we have observed ee values of up to 59% for intermolecular cyclopropanations of olefins [40].




**18** **19** **20** **21**

The addition of 2-diazo-5-methylcyclohexane-1,3-dione (**1d**) to 2,3-dihydrofuran afforded **5c** as a 1:1 mixture of stereoisomers (with respect to the Me group at C(6)). No chiral catalysts were tested with **1d**, however.

**Discussion.** – Two conclusions may be drawn from the present investigation: *i*) We were unable to reproduce the results of two independent reports on asymmetric cycloadditions of 2-diazocyclohexane-1,3-dione (**1a**) and 2-diazodimedone (**1b**) under the conditions applied by the authors, and *ii*) the cycloaddition of these diazo compounds or those of the corresponding phenyliodonium ylide **18** with catalysts that, in the past, have been successfully employed in asymmetric carbene transfer, are not enantioselective. While we cannot comment on the research of the other authors, we note that they have not followed up with applications on their original results. In addition, we have recently reinvestigated the cyclopropanation of styrene with 2-diazodimedone (**1b**) in the presence of [Cu{(+)-facam}$_2$] [41] and were unable to reproduce the high enantioselectivity reported by the authors. Other chiral $Rh^{II}$ catalysts were equally unselective [42]. In contrast, we have observed enantioselective cyclopropanations with the ylide **19** derived from *Meldrum*'s acid, which may be considered the dioxygen analogue of that derived from dimedone **18** [40], while some, although modest, enantioselectivity for cycloaddition to furan and 2,3-dihydrofuran was observed with the substituted ylides **20** and **21** [42].

The trend for enantioselective carbene transfer increases in the series **18** < **20** ≈ **21** < **19** is analogous to that in going from diazo ketones to diazo esters and diazo amides. Enantioselectivity is very difficult to control in reactions of diazo ketones, while numerous efficient systems for diazo esters and amides are known. We have recently argued that the reduced selectivity of diazo ketones may be ascribed to an early transition state in the carbene transfer step, which, in turn, is due to the higher reactivity of the intermediate carbene [24]. The same argument may be advanced for carbenes derived from 1,3-diones. The carbene derived from 2-diazodimedone (**1b**) is extremely reactive. As mentioned above, it reacts with $CH_2Cl_2$ *via* ylide formation, and with fluorobenzene *via* aromatic substitution or cycloaddition [10]. A *Hammett* study of *Davies* revealed that carbenes stabilized by electron-donating substituents are more susceptible towards electronic effects of the olefin than the more-electron-deficient counterparts. The stabilized carbenes exhibit larger negative $\rho$ values for cyclopropanations of substituted styrenes with [$Rh_2${(*S*)-dosp}$_4$] [43]. Thus, with ethyl diazoacetate, the styrenes showed no significant variation in reactivity upon changing the substituent. With diazomalonate, the $\rho$ value was $-0.2$, with diazoglutaconate $-0.7$, with phenyldiazoacetate and and vinyldiazoacetate $-1.0$, and with 4-methoxyphenyl acetate $-1.3$. The $\rho$ value for diazomalonate compares well with our previously reported value of $-0.49$ using [$Rh_2(OAc)_4$] [44]. *Davies* observed that the carbenes with higher negative $\rho$ values are not only more susceptible to electronic effects in the olefin, but, at the same time, exhibit higher enantioselectivities. This trend may be interpreted in terms of the *Hammond* postulate: the more-stabilized metallocarbenes pass through a later transition state, as evidenced by the higher $\rho$ value, and their selectivities increase. In contrast, for the carbenes derived from diazo ketones, and even more so from 2-diazo 1,3-diones, we expect an early transition state and, consequently, lower selectivity.

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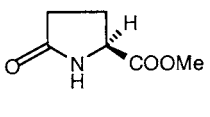
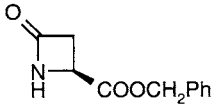
## Experimental Part

1. *General:* See [45]. The chiral catalysts were synthesized according to literature procedures: $[Rh_2\{(2S)\text{-mepy}\}_4]$: [46]; $[Rh_2\{(4S)\text{-bnaz}\}_4]$: [47]; $[Rh_2\{(R)\text{-campha}\}_4]$, $[Rh_2\{(S)\text{-phsp}\}_4]$, and $[Rh_2\{(S)\text{-tbsp}\}_4]$: [48]; $[Rh_2\{(S)\text{-bnp}\}_4]$: [21]; $[Rh_2\{(S)\text{-nttl}\}_4]$: [42], $[Rh_2\{(S)\text{-ptpa}\}_4]$: [49].

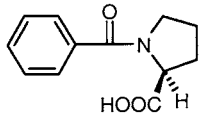
2. *Synthesis of [Rh$_2$[(*S*)-bzp]$_4$] (Tetrakis-*N*-benzoyl-L-prolinate dirhodium(II))* [22]. To $NaHCO_3$ (253 mg, 3.0 mmol) in $H_2O$ (33 ml)/EtOH (2.0 ml) was added *N*-benzoyl-L-proline [50] (657 mmg, 3.00 mmol), followed by $RhCl_3$ (263 mg, 1.00 mmol). The soln. was heated to reflux for 1 h. The solvent was evaporated, and the residue was purified by FC (Alox basic; $Et_2O$/EtOH 4 : 1). The eluates were concentrated, and the residue was treated with MeCN to afford a violet solid (220 mg, 38%). An anal. sample was dissolved in $CHCl_3$ (30 ml), washed with 5% $NaHCO_3$ ($2 \times 10$ ml), dried ($Na_2SO_4$), and concentrated almost to dryness. The product was then precipitated with an excess of hexane and filtered. $[\alpha]_D^{20} = -237$ ($c = 0.04$, $CHCl_3$). IR (film): 2928*w*, 1729*w*, 1595*s*, 1402*s*, 1300*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.49 – 1.54 (*m*, 1 H); 1.65 – 1.75 (*m*, 1 H); 1.89 – 2.00 (*m*, 2 H); 3.20 – 3.38 (*m*, 2 H); 4.33 (br. *t*, *J* = 8.7, 1 H); 7.43 (*s*, 5 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 25.9 (*t*); 30.1 (*t*); 50.4 (*t*);



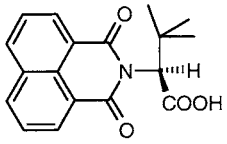

$[Rh_2\{(5S)\text{-mepy}\}_4]$



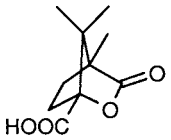

$[Rh_2\{(4S)\text{-bnaz}\}_4]$



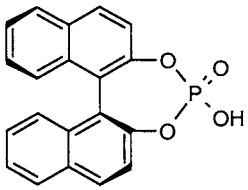

$[Rh_2\{(S)\text{-bzp}\}_4]$



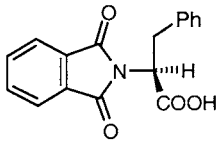

$[Rh_2\{(S)\text{-nttl}\}_4]$



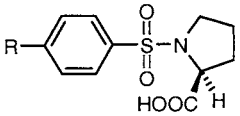

$[Rh_2\{(R)\text{-campha}\}_4]$



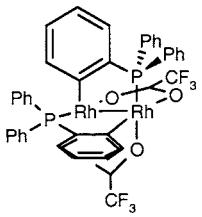

$[Rh_2\{(R)\text{-bnp}\}_4]$



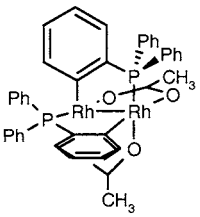

$[Rh_2\{(S)\text{-ptpa}\}_4]$



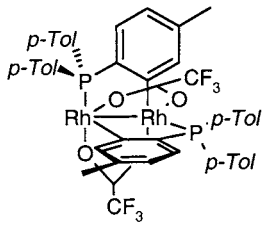

R = H : $[Rh_2\{(S)\text{-phsp}\}_4]$
R = *t*-Bu : $[Rh_2\{(S)\text{-tbsp}\}_4]$




*rac*-$[Rh_2(O_2CF_3)_2(pc)_2]$ (**22**)




*rac*-$[Rh_2(OAc)_2(pc)_2]$ (**23**)




(*P*)-$[Rh_2(O_2CF_3)_2(pc)_2]$ (**24**)

61.1 (*d*); 127.8 (*d*); 129.2 (*d*); 130.7 (*d*); 138.3 (*s*); 169.4 (*s*); 193.4 (*s*). ES-MS: 1183.1 ($C_{52}H_{54}N_6NaO_{12}Rh_2^+$ ($[Rh_2L_4(MeCN)_2]^+$)), 1101.0 ($C_{48}H_{48}N_4NaO_{12}^+$, $[Rh_2L_4Na]^+$).

3. *Synthesis of Diazo Ketones* **1a**–**1d** *and Phenyliodonium ylide* **18**. The 2-diazocyclohexane-1,3-diones **1a**–**1d** were prepared *via* diazo transfer with 4-acetamidobenzenesulfonyl azide to the appropriate dione in the presence of $Et_3N$ [51], and the ylide **18** *via* reaction of dimedone with diacetoxyiodobenzene, according to *Schank* and *Lick* [52].

4. *Decomposition of* **1a** *in* $CH_2Cl_2$. *2-Chloro-3-(chloromethoxy)cyclohex-2-en-1-one* (**6a**). To *2-diazocyclohexane-1,3-dione* (**1a**; 72.2 mg, 0.52 mmol) in $CH_2Cl_2$ (4.0 ml) was added activated (by heating *in vacuo*) $[Rh_2(OAc)_4]$ (5.3 mg, 0.01 mmol) in $CH_2Cl_2$ (1.0 ml) dropwise. The mixture was stirred at r.t. during 1 h. The solvent was evaporated, and the residue was purified by flash chromatography (FC; $SiO_2$, AcOEt/pentane 3:7) to afford **6a**. Yellow oil (90.0 mg, 88%). IR (film): 3320*w*, 3067*w*, 3001*w*, 1960*w*, 2929*w*, 1655*s*, 1597*s*, 1425*m*, 1370*m*, 1292*m*, 1279*m*, 1182*s*, 1074*s*, 1043*s*, 1015*s*. $^1$H-NMR (300 MHz, $CDCl_3$): 2.14 (*quint.*, $J = 6.2$, 2 H); 2.69 (*t*, $J = 7.0$, 2 H); 2.89 (*t*, $J = 6.2$, 2 H); 5.87 (*s*, 2 H). $^{13}$C-NMR (75 MHz, $CDCl_3$): 20.1 (*t*); 25.9 (*t*); 36.9 (*t*); 74.5 (*t*); 116.0 (*s*); 167.0 (*s*); 191.1 (*s*). MS: 195 (9, $M^+$), 194 (100), 170 (10), 168 (61), 166 (94), 161 (21), 160 (10), 159 (164), 158 (16), 148 (13), 146 (42), 138 (29), 133 (16), 131 (64), 130 (14), 129 (63), 128 (16), 123 (16), 120 (28), 118 (80), 110 (22), 108 (29), 105 (14), 104 (24), 103 (31), 102 (47), 101 (18), 100 (12), 95 (16), 91 (13), 89 (44), 76 (11), 75 (29), 74 (11), 73 (35), 67 (33), 66 (20), 65 (50), 63 (11), 61 (19), 55 (65), 54 (26), 53 (31), 49 (39). HR MS: 193.9942 ($C_7H_8O_2{}^{35}Cl_2^+$; calc. 193.9901); 195.9879 ($C_7H_8{}^{37}Cl^{37}ClO_2^+$; calc. 195.9872).

*2-Chloro-3-(chloromethoxy)-5,5-dimethylcyclohex-2-en-1-one* (**6b**). Same procedure. Yield 87%. IR (film): 1680*s*, 1613*s*, 1067*s*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.14 (*s*, 6 H); 2.42 (*s*, 2 H); 2.69 (*s*, 2 H); 5.83 (*s*, 2 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 28.0 (*q*); 32.2 (*s*); 39.3 (*t*); 50.5 (*t*); 74.3 (*t*); 115.0 (*s*); 165.1 (*s*); 190.0 (*s*). MS: 222 (52, $M^+$), 196 (18), 194 (28), 170 (11), 169 (10), 168 (64), 167 (18), 166 (100), 157 (17), 138 (24), 136 (37), 110 (11), 108 (18), 104 (10), 103 (15), 102 (32), 101 (11), 83 (17), 77 (10), 73 (11), 67 (18), 55 (14). HR MS: 222.0217 ($C_9H_{12}{}^{35}Cl_2O_2^+$; calc. 222.0214).

5. *Cycloaddition of 2-Diazocyclohexane-1,3-diones* **1** *and Phenyliodonium ylide* **18**.

5.1. *Addition of 2-Diazo-5-phenylcyclohexane-2,5-dione* (**1c**) *to Phenylacetylene. 4,5,6,7-Tetrahydro-2,6-diphenylbenzofuran-4-one* (**10**). Composing **1c** (214 mg, 1.00 mmol) in phenylacetylene (10 ml) was stirred at r.t. under $N_2$ with $[Rh_2(OAc)_4]$ (4.8 mg, 0.01 mol) for 6 h. After evaporation of the solvent, the residue was purified by FC ($SiO_2$; $Et_2O$/pentane 35:65) to afford pure **10** (243 mg, 84%). Solid. M.p. 110°. IR ($CHCl_3$): 3026*w*, 3015*m*, 2875*w*, 1673*s*, 1456*m*, 1438*m*, 1221*m*, 1213*m*. $^1$H-NMR (400 MHz, $CDCl_3$): 2.78–2.88 (*m*, 2 H); 3.16 (*dd*, $J = 11.1$, 17.4, 1 H); 3.29 (*dd*, $J = 5.3$, 17.4, 1 H); 3.59–3.70 (*m*, 1 H); 6.94 (*s*, 1 H); 6.29–7.35 (*m*, 4 H); 7.38–7.44 (*m*, 4 H); 7.67–7.70 (*m*, 2 H). $^{13}$C-NMR (100 MHz, $CDCl_3$): 31.2 (*t*); 41.2 (*d*); 44.9 (*t*); 100.8 (*d*); 122.8 (*s*); 123.9 (*d*); 126.7 (*d*); 127.2 (*d*); 128.2 (*d*); 128.9 (*d*); 129.7 (*s*); 142.4 (*s*); 154.7 (*s*); 165.7 (*s*); 193.0 (*s*). MS: 288 (58, $M^+$), 289 (13), 185 (13), 184 (98), 156 (53), 105 (100), 77 (34). HR-MS: 288.1159 ($C_{20}H_{16}O_2^+$; calc. 288.1150). Enantiomer separation by HPLC (*OD-H* column, i-PrOH/hexane 1:9, 0.5 ml/min; $\tau_1 = 32.6$, $\tau_2 = 37.3$ min).

*Crystal-Structure Analysis of* **10**. $C_{20}H_{16}O_2$; $M_r$ 288.4; $\mu = 0.08$ mm$^{-1}$, $d_x = 1.256$ g·cm$^{-3}$, monoclinic, *C*2/*c*, $Z = 8$, $a = 19.5015(10)$, $\beta = 6.3772(3)$, $c = 24.6135(13)$ Å, $b = 94.810(6)°$, $V = 3050.3(3)$ Å$^3$. Crystal size: 0.076 × 0.21 × 0.24 mm. Cell dimensions and intensities were measured at 200 K on a *Stoe IPDS* diffractometer with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda = 0.71073$ Å), 10962 measured reflections, 2962 unique reflections of wich 1387 were observables ($|F_o| > 4\sigma(F_o)$); $R_{int}$ for 7446 equivalent reflections 0.059. Data were corrected for *Lorentz* and polarization effects and for absorption ($T_{min,max} = 0.9790, 0.9943$). The structure was solved by direct method (SIR97) [53], all other calculations were performed with XTAL system [54]. Full-matrix least-squares refinement based on *F* using weight of $1/(\sigma^2(F_o) + 0.0002(F_o^2))$ gave final values $R = 0.046$, $\omega R = 0.045$, and $S = 1.76(4)$. The maximum shift/error on the last cycle was $0.35 \cdot 10^{-3}$. H-Atoms were observed and refined with a fixed value of their isotropic displacement parameters. The final difference electron-density map showed a maximum of + 0.76 and a minimum of − 0.34 eÅ$^{-3}$. CCDC-205856 contains supplementary crystallographic data for this paper. These data can be obtained, free of charge, *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre,* 12 Union Road, Cambridge CB21EZ, UK (fax: Int. + 44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)).

5.2. *Addition to Acyclic Vinyl Ethers.* cis-*2-Ethoxy-2,3,4,5,6,7-hexahydro-3,6,6-trimethylbenzofuran-4-one* (**14a**). To *2-diazo-5,5-dimethylcyclohexane-1,3-dione* (**1b**, 360 mg, 2.16 mmol) in *1-ethoxyprop-1-ene* (**13a**; 5.0 ml, 85:15 (*Z*)/(*E*) mixture) was added $[Rh_2(OAc)_4]$ (6.6 mg, 0.014 mmol), and the mixture was stirred for 1 h at r.t. under $N_2$. The solvent was evaporated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 2:3) to afford **14a** (341 mg, 70%) as a 17:3 mixture of unseparable stereoisomers. IR ($CHCl_3$): 2959*w*, 1638*s*, 1401*m*, 1169*w*, 1137*w*, 1032*w*. $^1$H-NMR 500 MHz, $CDCl_3$): 1.07 (*s*, 3 H); 1.11 (*s*, 3 H); 1.19 (*d*, $J = 7.3$, 3 H); 1.26 (*t*, $J = 7.3$, 3 H); 2.15–2.14 (*m*, 4 H); 3.19–3.26 (*m*, 2 H); 3.58–3.95 (*m*, 2 H); 5.65 (*d*, $J = 7.6$, 1 H). $^{13}$C-NMR (125 MHz,

$CDCl_3$): 11.3 (*q*); 14.9 (*q*); 28.5 (*q*); 28.8 (*q*); 33.9 (*s*); 37.4 (*d*); 37.8 (*t*); 51.3 (*t*); 66.1 (*t*); 110.5 (*d*); 115.6 (*s*); 173.8 (*s*); 194.7 (*s*). MS: 225 (16), 224 (100, $M^+$), 196 (11), 195 (69), 180 (26), 179 (96), 178 (51), 177 (10), 168 (13), 167 (24), 165 (21), 153 (20), 140 (17), 139 (17), 137 (13), 135 (14), 125 (20), 123 (14), 122 (36), 112 (19), 111 (47), 107 (22), 98 (15), 97 (52), 96 (10), 95 (17), 94 (12), 93 (11), 84 (13), 83 (62), 69 (33), 67 (19), 66 (17), 65 (14), 57 (15), 55 (34), 53 (15). HR-MS: 224.1404 ($C_{13}H_{20}O_3^+$; calc. 224.1413). Enantiomer separation by GC (γ-Dex, isothermal at 150°, $\tau_1 = 18.1$, $\tau_2 = 19.1$ min).

*2-Ethoxy-2,3,4,5,6,7-hexahydro-3,6-dimethylbenzofuran-4-one* (**14b**). To *2-diazo-5-methylcyclohexane-1,3-dione* (**1d**; 152 mg, 1.00 mmol) in **13a** (2.5 ml, (*E*)/(*Z*) mixture) was added [$Rh_2(OAc)_4$] (3.3 mg, 0.0069 mmol), and the mixture was stirred for 1 h at r.t. under $N_2$. The solvent was evaporated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 3:7) to afford **14b** (118 mg, 56%) as 11.2:1 mixture of *cis*/*trans* isomers with respect to C(2)/C(3). Colorless oil. IR ($CHCl_3$): 2983*w*, 1628*s*, 1455*w*, 1403*m*, 1380*w*. $^1$H-NMR (500 MHz, $CDCl_3$, *cis*-isomer at C(2)/C(3)): 1.01–1.04 (*m*, 3 H); 1.12–1.14 (*m*, 3 H); 1.16–1.21 (*m*, 3 H); 1.94–2.45 (*m*, 5 H); 3.11–3.19 (*m*, 1 H); 3.51–3.60 (*m*, 1 H); 3.76–3.89 (*m*, 1 H); 5.56 (*d*, $J = 7.3$, 0.5 H); 5.59 (*d*, $J = 7.3$, 0.5 H). $^{13}$C NMR (125 MHz, $CDCl_3$): [10.9 (*q*), 11.6 (*q*)]; 14.9 (*q*); [20.9 (*d*), 21.1 (*d*)]; [29.5 (*q*), 29.9 (*q*)]; [31.9 (*t*), 32.1 (*t*)]; 37.4 (*d*), 37.6 (*d*)]; [45.3 (*t*), 45.7 (*t*)]; 65.9 (*t*), 66.1 (*t*)]; [110.3 (*d*), 110.5 (*d*)]; [116.2 (*s*); 116.9 (*s*)]; [174.4 (*s*), 174.6 (*s*)]; [194.9 (*s*); 195.1 (*s*). MS: 210 (100, $M^+$), 181 (66), 165 (88), 164 (46), 163 (15), 154 (10), 153 (36), 151 (20), 140 (13), 136 (10), 135 (11), 125 (11), 122 (28), 122 (28), 121 (12), 112 (17), 111 (21), 109 (10), 98 (10), 97 (27), 95 (15), 94 (10), 93 (33), 85 (12), 84 (13), 83 (15), 79 (11), 69 (66), 67 (22), 65 (12), 57 (10), 55 (25), 53 (16), 45 (10). HR MS: 210.1306 ($C_{12}H_{18}O_3^+$; calc. 210.1256).

cis-*2-Ethoxy-2,3,4,5,6,7-hexahydro-6,6-dimethyl-3-(trifluoromethyl)benzofuran-4-one* (**14c**). To **1b** (86 mg, 0.52 mmol) in *(Z)-1-ethoxy-3,3,3-trifluoroprop-1-ene* [25] (**13b**; 1.0 ml) was added [$Rh_2(OAc)_4$] (9.2 mg, 0.019 mmol), and the mixture was stirred under $N_2$ for 4 h at r.t. After evaporation of the solvent, the residue was purified by FC ($SiO_2$; AcOEt/pentane 3:7) to afford **14c**. Yellow solid (109 mg, 75%). IR ($CHCl_3$): 2963*w*, 1659*s*, 1630*s*, 1400*m*, 1259*m*, 1195*m*, 1137*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.10 (*s*, 3 H); 1.14 (*s*, 3 H); 1.31 (*t*, $J = 7.3$, 3 H); 2.23 (*d*, $J = 16$, 1 H); 2.29 (*d*, $J = 18$, 1 H); 2.23 (*d*, $J = 16$, 1 H); 2.42 (*d*, $J = 18$, 1 H); 3.75 (*dq*, $J = 8.5$, 9.6, 1 H); 3.80 (*quint.*, $J = 7.6$, 1 H); 5.83 (*d*, $J = 7.3$, 1 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 14.8 (*q*); 28.1 (*q*); 28.8 (*q*); 33.5 (*s*); 33.5 (*s*); 37.9 (*t*); 46.3 (*d*); 51.1 (*t*); 67.7 (*t*); 107.8 (*s*); 108.2 (*d*); 124.3 (*s*); 177.5 (*s*); 192.1 (*s*). MS: 278 (54, $M^+$), 258 (10), 234 (10), 233 (17), 230 (25), 229 (11), 215 (34), 213 (39), 202 (45), 196 (55), 194 (23), 179 (19), 177 (18), 176 (18), 176 (16), 174 (75), 166 (16), 165 (100), 159 (16), 154 (16), 162 (32), 151 (12), 148 (14), 146 (38), 140 (20), 86 (41), 84 (68), 83 (33), 69 (32). HR MS: 278.1120 ($C_{13}H_{17}O_3F_3^+$; calc. 278.1129). Enantiomer separation by GC (γ-Dex, isothermal, at 160°, $\tau_1 = 15.9$, $\tau_2 = 16.8$ min).

*2-Ethoxy-2,3,4,5,6,7-hexahydro-6-phenylbenzofuran-4-one* (**16a**). Same procedure with **1c** and 1-ethoxyethene (**15a**) as solvent. FC ($SiO_2$; hexane/AcOEt 60:40) afforded **16a** as a 1:1 mixture of *cis/trans* isomers. Yield 100%, oil. IR ($CHCl_3$): 3024*w*, 3015*m*, 2984*w*, 2938*m*, 1632*s*, 1405*m*, 1347*m*, 1257*m*, 1189*m*, 1108*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.28–1.32 (*m*, 3 H); 2.61–2.81 (*m*, 4 H); 2.99–3.06 (*m*, 1 H); 3.42–3.48 (*m*, 1 H); 3.51–3.57 (*m*, 1 H); 3.66–3.73 (*m*, 1 H); 3.91–3.99 (*m*, 1 H); 5.81–5.84 (*m*, 1 H); 7.28–7.41 (*m*, 5 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 15.0 (*q*); [31.4 (*t*), 31.6 (*t*)]; 38.2 (*t*); [40.1 (*d*), 40.5 (*d*)]; [43.6 (*t*), 44.0 (*t*)]; [65.1 (*t*), 65.3 (*t*)]; [108.9 (*d*), 109.2 (*d*)]; [112.2(*s*), 112.5 (*s*)]; 126.7 (*d*); [127.0 (*d*), 127.1 (*d*)]; [128.8 (*d*), 128.8 (*d*)]; [142.6 (*s*); 142.7 (*s*)]; [174.8 (*s*), 174.9 (*s*)]; [193.7 (*s*), 193.8 (*s*)]. MS: 258 (100, $M^+$), 213 (19), 154 (26), 126 (50, 125 (23), 111 (10), 108 (17), 104 820), 103 (15), 98 (38), 97 (39), 91 (16), 84 (23), 83 (15), 82 (14), 81 (10), 77 (14), 70 (11), 69 (32), 55 (21), 53 (13), 51 (12). HR MS: 258.1235 ($C_{16}H_{18}O_3^+$; calc. 258.1256).

*2-Acetoxy-2,3,4,5,6,7-hexahydro-6-phenylbenzofuran-4-one* (**16b**). Same procedure with **1c** in vinyl acetate. Purification by FC ($SiO_2$; AcOEt/cyclohexane 35:65) gave a 2:1 mixture of *cis/trans* stereoisomers of **16b** in 43% yield as colorless solid. IR ($CHCl_3$): 3028*w*, 3015*m*, 1759*s*, 1644*s*, 1404*m*. $^1$H-NMR (500 MHz, $CDCl_3$): 2.06 (*s*, 1 H); 2.08 (*s*, 2 H); 2.60–2.80 (*m*, 5 H); 3.03–3.09 (*m*, 1 H); 3.34–3.48 (*m*, 1 H); 7.17–7.31 (*m*, 5 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): [21.0 (*q*), 21.0 (*q*)]; [31.0 (*t*), 31.2 (*t*)]; [32.0 (*t*), 32.0 (*t*)]; [40.2 (*d*), 40.5 (*d*)]; [43.8 (*t*), 44.1 (*t*)]; [98.9 (*d*), 99.1 (*d*)]; [112.3 (*s*), 112.5 (*s*)]; [126.7 (*d*), 126.7 (*d*)]; [127.3 (*d*), 127.3 (*d*)]; [128.9 (*d*)]; [142.2 (*s*);, 142.3 (*s*)]; [169.4 (*s*), 169.5 (*s*)]; [174.5 (*s*), 174.6 (*s*)]; [193.7 (*s*); 193.7 (*s*)]. MS: 272 (< 1, $M^+$), 244 (10), 213 (20), 212 (55), 203 (10), 202 (72), 108 (28), 104 (14), 98 (100), 97 (21), 69 (16). HR MS: 272.1062 ($C_{16}H_{16}O_4^+$; calc. 272.1049).

*4,5,6,7-Tetrahydro-6-phenylbenzofuran-4-one* (**17**). The acetate **16b** (200 mg, 0.7 mmol) and TsOH (18 mg) were heated to reflux in toluene under $N_2$ for 3 h. The solvent was evaporated *in vacuo*, and the residue was purified by FC ($SiO_2$, $EtO_2$/pentane 35:65) to afford **17** (120 mg, 77%). Colorless liquid. IR ($CHCl_3$): 3030*m*, 3022*m*, 2957*w*, 2908*w*, 1674*s*, 1601*m*, 1516*m*, 1498*m*, 1450*s*, 1413*m*, 1120*m*, 1039*m*, 996*m*, 908*s*. $^1$H-NMR (500 MHz, $CDCl_3$): 2.77–2.84 (*m*, 2 H); 3.08 (*ddd*, $J = 0.6$, 11.1, 17.1, 1 H); 3.21 (*dd*, $J = 5.1$, 17.1, 1 H); 6.73 (*d*, $J = 1.9$, 1 H); 7.28–7.40 (*m*, 6 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 31.2 (*t*); 41.3 (*d*); 45.0 (*t*); 106.5 (*d*); 121.0 (*s*);

126.7 (*d*); 127.2 (*d*); 128.9 (*d*); 142.4 (*s*); 143.1 (*d*); 166.3 (*s*); 193.0 (*s*). MS: 212 (24, $M^+$), 108 (100), 86 (14), 84 (32), 80 (32), 52 (14). HR MS: 212.0848 ($C_{14}H_{12}O_2^+$; calc. 212.0837).

5.3. *Cycloaddition of* **1b** *to Furan. 4,5,6,7-Tetrahydro-6,6-dimethyl-3a*H*-furo[2,3-*b*]benzofuran-4-one* (**4b**). Compound **1b** (396 mg, 2.38 mmol) was dissolved in furan (20 ml, freshly distilled over KOH). [$Rh_2(OAc)_4$.2 MeOH] (15.2 mg, 0.028 mmol) was added, and the mixture was stirred for 45 min under $N_2$. The solvent was evaporated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 2:3) to afford **4b** (171 mg, 34%). Yellowish oil. IR ($CHCl_3$): 3013*m*, 2963*m*, 2890*w*, 1640*s*, 1402*s*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.07 (*s*, 3 H); 1.11 (*s*, 3 H); 2.19 (*d*, *J* = 16.4, 1 H); 2.25 (*d*, *J* = 16.4, 1 H); 2.33–2.40 (*m*, 2 H); 5.38 (*t*, *J* = 2.2, 1 H); 6.39 (*d*, *J* = 2.2, 2 H); 6.60 (*d*, *J* = 7.5, 1 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 28.3 (*q*); 28.7 (*q*); 34.1 (*s*); 37.4 (*t*); 47.7 (*d*); 50.9 (*t*); 103.4 (*d*); 112.7 (*d*); 114.8 (*s*); 144.2 (*d*); 174.9 (*s*); 194.1 (*s*). MS: 206 (25, $M^+$), 178 (20), 150 (14), 123 (10), 122 (100), 121 (10), 94 (16), 66 (14), 55 (12), 52 (10). HR-MS: 206.0952 ($C_{12}H_{14}O_3^+$; calc. 206.0943). Enantiomer separation by GC ($\gamma$-Dex, isothermal at 150°, $\tau_1 = 25.2$, $\tau_2 = 26.2$ min).

5.4. *Cycloaddition of* **1a** *and* **1d** *to 2,3-Dihydrofuran. 2,3,4,5,6,7-Hexahydro-3*H*-3a*H*-furo[2,3-*b*]benzofuran-4-one* (**5a**). To 2,3-dihydrofuran (2.5 ml) and **1a** (139.6 mg, 1.01 mmol) was added activated [$Rh_2(OAc)_4$] (18.5 mg, 0.039 mmol), and the mixture was stirred under $N_2$ at r.t. for 16 h. The solvent was evaporated *in vacuo*, and the residue was purified by distillation (150°/0.2 Torr) to afford **5a** (137 mg, 75%). Colorless oil. IR (film): 2946*w*, 2877*w*, 2358*w*, 1623*s*, 1450*w*, 1401*m*, 1364*w*, 1289*w*, 1240*m*, 1176*w*, 1079*s*, 1000*w*, 947*s*, 895*s*, 806*s*. $^1$H-NMR (400 MHz, $CDCl_3$): 2.00–2.10 (*m*, 4 H); 2.32–3.35 (*m*, 2 H); 2.39–2.55 (*m*, 2 H); 3.60–3.66 (*m*, 1 H); 4.00–4.10 (*m*, 1 H); 6.23 (*d*, *J* = 5.9, 1 H). $^{13}$C-NMR (100 MHz, $CDCl_3$): 21.6 (*t*); 23.7 (*t*); 30.3 (*t*); 36.6 (*t*); 43.8 (*d*); 67.9 (*t*); 112.8 (*d*); 113.7 (*s*); 177.5 (*s*); 195.2 (*s*). MS: 180 (86, $M^+$), 165 (74), 152 (17), 151 (70), 137 (100), 135 (11), 134 (13), 124 (60), 123 (11), 110 (11), 109 (17), 96 (59), 95 (39), 91 (11), 82 (21), 81 (37), 79 (18), 78 (13), 77 (16), 71 (13), 69 (14), 68 (34), 67 (26), 66 (17), 65 (13), 57 (10), 55 (73), 54 (18), 53 (57), 52 (18). HR MS: 180.0794 ($C_{10}H_{12}O_3^+$; calc. 180.0786). Enantiomer separation by GC ($\beta$-Dex, isothermal, at 150°, $\tau_1 = 26.0$, $\tau_2 = 27.6$ min).

cis/trans-*2,3,4,5,6,7-Hexahydro-6-methyl-3a*H*-furo[2,3-*b*]benzofuran-4-one* (**5c**). The same procedure, starting from **1d** (304 mg, 2.00 mmol) afforded **5c** as a 1:1 mixture of *cis*- and *trans*-stereoisomers (311 mg, 80%). Yellowish oil. IR ($CHCl_3$): 2959*w*, 2247*w*, 1628*s*, 1421*w*, 1405*w*, 1363*w*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.09 (*d*, *J* = 8.2, 0.5 H); 1.10 (*d*, *J* = 8.2, 0.5 H); 1.89–2.57 (*m*, 7 H); 3.56–3.65 (*m*, 1 H); 3.66–3.72 (*m*, 1 H); 4.05–4.09 (*m*, 1 H); 6.22 (*d*, *J* = 7.6, 0.5 H); 6.23 (*d*, *J* = 7.3, 0.5 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): [20.8 (*d*), 20.9 (*d*)]; 29.5 (*q*), 29.8 (*q*))]; [30.0 (*t*), 30.5 (*t*)]; [31.6 (*t*), 31.7 (*t*)]; [43.6 (*d*), 43.7 (*d*)]; 45.1 (*t*); [67.9 (*t*), 67.8 (*t*)]; [112.9 (*d*), 113.1 (*d*)]; [113.0 (*s*), 113.3 (*s*)]; [177.0 (*s*), 177.1 (*s*) ]; [194.7 (*s*), 1948 (*s*)]. MS: 194 (100, $M^+$), 180 (10), 179 (93), 166 (10), 165 (28), 153 (28), 152 (23), 151 (23), 151 (99), 133 (14), 124 (67), 123 (12), 109 (15), 96 (49), 95 (28), 82 (19), 81 (25), 79 (12), 77 (11), 69 (42), 68 (19), 67 (16), 66 (10), 65 (10), 54 (11), 53 (42), 52 (12), 51 (11). HR-MS: 194.0930 ($C_{11}H_{14}O_3^+$; calc. 194.0943).

5.4. *Cycloaddition of Ylide* **18** *to 2,3-Dihydrofuran. 2,3,4,5,6,7-Hexahydro-6,6-dimethyl-3a*H*-furo[2,3-*b*]benzofuran-4-one* (**5b**). The ylide **18** (342 mg, 1.00 mmol) was suspended in trifluorotoluene (3.0 ml) containing 2,3-dihydrofuran (15–20 equiv.). The catalyst (1.5 mol-%) in trifluorotoluene (2.0 ml) was added, and the mixture was stirred at 30–40° for 12 h, when all of the ylide was dissolved. The solvent was evaporated, and the residue was purified by FC ($SiO_2$; AcOEt/pentane 3:7) to give **5b**. Yellowish solid. M.p. 98–99°. IR (film): 2955*w*, 2866*w*, 1357*m*, 1650*s*, 1627*s*, 1403*s*, 1356*m*, 1221*m*, 1069*s*, 1035*m*, 943*m*, 922*m*, 881*s*. $^1$H-NMR (500 MHz, $CDCl_3$): 1.08 (*s*, 3 H); 1.10 (*s*, 3 H); 2.10–2.14 (*m*, 2 H); 2.19 (*d*, *J* = 16.1, 1 H); 2.24 (*d*, *J* = 16.1, 1 H); 2.31 (*dd*, *J* = 17.7, 2.3, 1 H); 2.36 (*dd*, *J* = 17.1, 1.0, 1 H); 3.62 (*ddd*, *J* = 12.0, 8.8, 5.1 1 H); 3.72 (br. *t*, *J* = 7.0, 1 H); 4.08–4.12 (*m*, 1 H); 6.26 (*d*, *J* = 5.7, 1 H). $^{13}$C-NMR (125 MHz, $CDCl_3$): 28.2 (*q*); 28.8 (*q*); 30.4 (*t*); 33.9 (*s*); 37.5 (*t*); 43.7 (*d*); 51.0 (*t*); 67.8 (*t*); 112.1 (*s*); 113.0 (*d*); 176.2 (*s*); 194.4 (*s*). MS: 208 (85, $M^+$), 194 (11), 193 (100), 180 (15), 179 (35), 166 (13), 165 (100), 152 (19), 147 (17), 137 (15), 125 (11), 124 (87), 123 (16), 110 (13), 109 (20), 97 (11), 96 (75), 95 (32), 82 (28), 81 (29), 79 (12), 77 (19), 71 (10), 69 (30), 68 (22), 67 (20). HR MS: 208.1091 ($C_{12}H_{16}O_3^+$; calc. 208.1099). Enantiomer separation by GC, $\gamma$-Dex, isothermal, at 150°, $\tau_1 = 26.7$, $\tau_2 = 27.3$ min.

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