Selectivity in cyclopropanations and 1,3-cycloadditions in transition metal-catalyzed decompositions of 2-diazocyclohexane-1,3-diones and the corresponding phenyliodonium ylides

Paul Müller,* Yves F. Allenbach, Maria Ferri, and Gérald Bernardinelli

Department of Organic Chemistry, University of Geneva, 30, Quai Ernest Ansermet, CH-1211 Geneva 4 Switzerland
E-mail: paul.muller@chiorg.unige.ch

Dedicated to Prof. E. A. McKervey on his 65th birthday

(received 28 Feb 03; accepted 14 Apr 03; published on the web 30 Apr 03)

Abstract

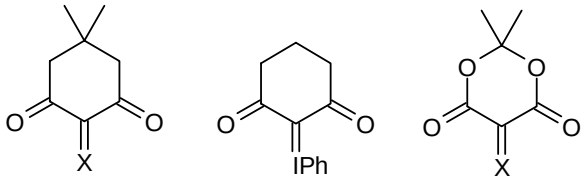
The cyclopropanation of olefins with 2-diazodimedone **1a** and the corresponding phenyliodonium ylide **1b** in the presence of selected chiral Cu(I)- and Rh(II)-catalysts proceeds without significant enantioselectivity. Contrary to previous reports in the literature, the cyclopropanation of styrene with **1a** in the presence of [Cu{(+)-facam}$_2$] is not enantioselective. While the transition metal catalyzed 1,3-dipolar cycloaddition of 2-diazodimedone (**1a**) to furan and dihydrofuran is equally non-selective, the introduction of heteroatoms and/or unsaturation in the carbene precursor results in slightly enhanced enantioselectivity.

Keywords: Transition metal-catalysts, carbene transfer, enantioselectivity, cyclopropanation, 1,3-dipolar cycloaddition, 2-diazo-1,3-diones, phenyliodonium ylide

Introduction

The decomposition of diazo compounds in the presence of chiral, non-racemic transition metal-catalysts affords metallocarbenes capable of asymmetric carbene transfer.[1] Impressive enantioselectivities have been reported for inter- and/or intramolecular cyclopropanations and CH-insertions with diazoacetates, diazoacetamides, and phenyl- or vinyl diazoacetate esters.[2] In addition, diazo ketones or ketoesters carrying electron-attracting substituents, such as ethyl diazoacetoacetate[3] ethyl diazopyruvate[4] or 2-diazocyclohexane-1,3-dione[5] may undergo formal 1,3-cycloaddition to polar or polarizable olefins. Enantioselective cycloadditions of 2-diazodimedone (**1a**) and 2-diazocyclohexane-1,3-dione (**2a**) to furan and dihydrofuran in the presence of chiral Rh(II)-catalysts have been reported, with ee's in the range of 50 to 95% according to the catalysts used (Scheme 1).[6,7] We have recently re-examined these reactions but

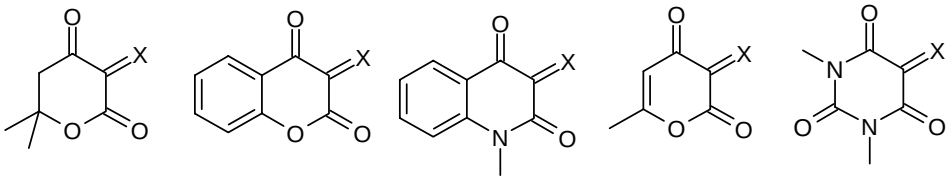
were unable to reproduce the reported results under the conditions described by the authors.[8] A considerable number of structurally different catalysts was screened for the cycloadditions with **1a** and **2a**, and the corresponding ylides **1b**, and **2b**, but no enantioselective cycloadditions could be realized. These negative results are even more striking in the light of our recent observation, that enantioselective Rh(II)-catalyzed carbene transfer with the ylide **3b** derived from Meldrum's acid proceed with ee's of up to 65%. The behaviour of **3b** is not directly comparable to that of **1** or **2**, since the metallocarbene derived from **3b** participates in cyclopropanations, while **1** and **2** typically afford products of 1,3-dipolar cycloaddition. Note that in the particular case of **3** reactions were carried out with the ylide **3b**, rather than the diazo compound **3a**, because the latter is quite resistant towards diazo decomposition and requires temperatures in the range of 80 °C, while reactions with the ylide **3b** may be conveniently carried out at room temperature.[9]



1a X = N_2 **2a** X = N_2 **3a** X = N_2
1b X = IPh **2b** X = IPh **3b** X = IPh
1c X = H_2 **2c** X = H_2 **3c** X = H_2

Scheme 1

The absence of enantioselectivity in the cycloadditions of **1a** and **1b** to furans may be attributed to various causes such as formation of a free ylide between the carbene and the oxygen atom of the furan, a possibly inherent low enantioselectivity of dipolar cycloadditions of metallocarbenes, or the poor selectivity of the carbene itself. At first glance, this latter point appeared unlikely, since enantioselective carbene transfer with **1a** has been reported: Matlin *et al*. observed enantioselective cyclopropanation of styrene with **1a** in the presence of chiral Cu(I)-catalysts at elevated temperatures in 21-48% yield and with 73.3-100% ee. The readily avaliable [Cu{(+)-facam}$_2$] produced the cyclopropane in 36% yield and with 91.7% ee.[10] However, details of the procedure have not been published, and the reported results have met some scepticisme.[11]



4a X = N_2 **5a** X = N_2 **6a** X = N_2 **7a** X = N_2 **8a** X = N_2
4b X = IPh **5b** X = IPh **6b** X = IPh **7b** X = IPh **8b** X = IPh
4c X = H_2 **5c** X = H_2 **6c** X = H_2 **7c** X = H_2 **8c** X = H_2

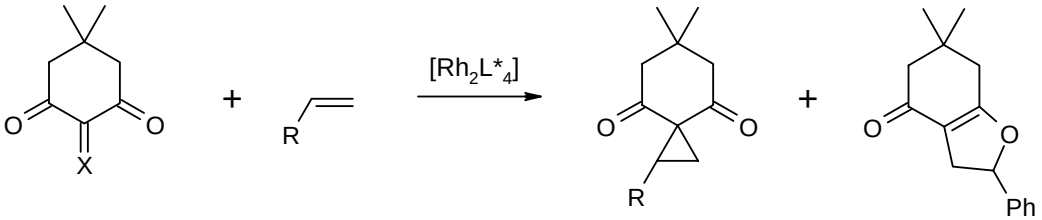
Scheme 2

In view of our difficulties with the reproduction of the enantioselectivity of the cycloadditions of **1a** and **1b** to furans, we have repeated the cyclopropanation of styrene with **1a** in the presence of [Cu{(+)-facam}$_2$], and we have investigated the cyclopropanation of terminal olefins with Rh(II)-catalysts. In addition, we have examined the influence of heteroatoms on the selectivity of the carbenes derived from the corresponding ylides **4b**-**8b** (Scheme 2) in the cycloaddition to furan and 2,3-dihydrofuran. The ylides were preferred over the corresponding diazo compounds owing to their generally higher reactivity in transition metal-catalyzed carbene transfer reactions.[8]

Results and Discussion

Cyclopropanation of styrene and apolar terminal olefins

The conditions of Matlin *et al*.[10] for cycloproanation of styrene consist in heating styrene neat or in toluene to reflux in the presence of **1a** and the appropriate Cu-catalyst. In our hands, these reaction conditions resulted in complete polymerization of styrene, and no cyclopropane could be isolated. Cyclopropanation did occur, however, in 53% yield with the phenyliodonium ylide **1b** and [Cu$_2$\{(+)-facam\}$_4$][12] but the cyclopropane (**9a**) was racemic (Scheme 3 and Table 1).



1a X = N_2
1b X = IPh

9a R = Ph
9b R = *n*-Pr
9c R = *n*-Bu
9d R = *t*-Bu

10a

Scheme 3

When the cyclopropanation of styrene was carried out with [$Rh_2(OAc)_4$] or [Rh$_2$\{(*S*)-nttl\}$_4$], the yield of cyclopropane **9a** varied in the range of 35-49%, and a formal cycloadduct **10a** was isolated in 22-35% yield as secondary product. The structure of **10a** was established by comparison of the spectral data with those of the known product resulting from reaction of 2,2-dibromodimedone with styrene in the presence of copper.[13] The origin of the cycloadduct is not clear. The stability of the cyclopropanes **9a** and **9c** under the conditions of the reaction was verified ([$Rh_2(OAc)_4$] in trifluorotoluene at r.t. for 72 h), and it was found that the cyclopropanes do not rearrange to the respective cycloadducts. Thus styrene may react with **1b** *via* two

competing pathways, namely *via* cyclopropanation or formal cycloaddition. The mechanism of the cycloaddition is not established, and may be concerted or stepwise. It is interesting to note, in this context, that the related cycloaddition of 2,2-dibromo-dimedone with *cis*- and *trans*-β-methylstyrene in the presence of copper is not stereospecific and, therefore, must proceed stepwise.[13]

Table 1. Cyclopropanation and Cycloaddition of terminal olefins with 2-diazo-dimedone (**1a**) and phenyliodonium ylide **1b**[a)]

Cpd	X	R	Catalyst/Solvent	Cyclopr. Yield (%)		ee (%)	Adduct (%)
1a	N_2	Ph	[Cu{(+)facam}$_2$]/styrene[(b)]	**9a**	36	91.7	0
1a	N_2	Ph	[Cu{(+)facam}$_2$]/styrene[(c)]	**9a**	0	-	0
1b	IPh	Ph	[Cu{(+)facam}$_2$]/$PhCH_3$	**9a**	53	0	0
1a	N_2	Ph	[$Rh_2(OAc)_4$]/styrene	**9a**	49	-	**10a** 22
1a	N_2	Ph	[Rh_2{(*S*)-nttl}$_4$]/$PhCH_3$	**9a**	35	0	**10a** 35
1b	IPh	Ph	[$Rh_2(OAc)_4$]/styrene	**9a**	49	-	**10a** 30
1b	IPh	Ph	[Rh_2{(*S*)-nttl}$_4$]	**9a**	37	0	**10a** 34
1a	N_2	*n*-Pr	[$Rh_2(OAc)_4$]/$PhCF_3$	**9b**	31	-	0
1a	N_2	*n*-Bu	[$Rh_2(OAc)_4$]/$PhCF_3$	**9c**	34	-	0
1b	IPh	*n*-Bu	[$Rh_2(OAc)_4$]/$PhCH_3$	**9c**	18	-	0
1a	N_2	*n*-Bu	[Rh_2{(*R*)-ntvl}$_4$]/hexene	**9d**	29	8	0
1a	N_2	*t*-Bu	[$Rh_2(OAc)_4$]/$PhCF_3$	**9d**	25	-	0
1a	N_2	*t*-Bu	[Rh_2{(*S*)-nttl}$_4$]/$PhCF_3$	**9d**	24	16	0

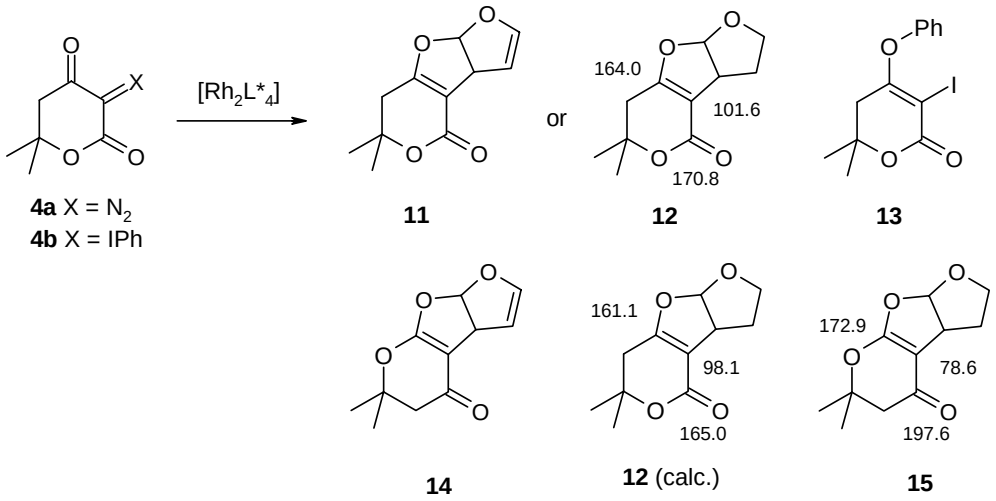
[(a)] Conditions: At 25 °C, with 5% of catalyst, 10 - 15-fold excess of olefin, unless indicated otherwise. [(b)] At reflux, ref.[10] [(c)] At reflux, this work.

The reaction of **1b** in the presence of [Rh_2{(*S*)-nttl}$_4$] resulted only in racemic cyclopropane **9a** and racemic cycloadduct **10a**. This compares unfavorably with the ee of 37% resulting from the cyclopropantion of styrene with the ylide **3b** using the same catalyst. Simple terminal olefins reacted also with 2-diazodimedone (**1a**) or the corresponding phenyliodonium ylide (**1b**), respectively, in the presence of [$Rh_2(OAc)_4$] to afford cyclopropanes **9b - d** in moderate yield (Table 1). However, no cycloadducts of type **10** were observed. Thus it appears that cycloaddition is restricted to polar or polarizable olefins with Rh(II)-catalysts. In the presence of [Rh_2{(S)-nttl}$_4$] the reactions proceeded with a small, but reproducible induction. It is interesting to note that the most hindered olefin (*t*-butylethylene) exhibited the highest ee in the series with 16%. No attempt was made at this point to improve the enantioselectivity by screening other catalysts.

Cycloaddition of 2,2-dimethyl-5-diazo-1-oxacyclohexane-4,6-dione (4a) and phenyliodonium ylide 4b to furan and dihydrofuran

The carbene precursor **4a**,**b** reacted in neat furan or 2,3-dihydrofuran, respectively, or in inert solvents such as fluorobenzene, trifluorotoluene or toluene in the presence of $[Rh_2(OAc)_2]$ to afford the adducts **11** and **12**, respectively (Scheme 4). The reaction was fully regioselective, with the addition involving the carbonyl group of the ketone rather than that of the ester function, and the regioisomers **14** and **15**, respectively, were not detected in the reaction mixture. The structure of the adducts is consistent with the higher polar character of the ketone group over that of the ester function. It was tentatively assigned for **12** on the grounds of ^{13}C NMR shift calculations using SpecTool.[14] The signals attributed to C(3b), C(4) and C(7a) of **12** appear at 101.6, 170.8 and 164.0 ppm, in good agreement with the calculated values of 98.1, 165.0 and 161.1 ppm. The chemical shifts of the isomer **15** are calculated at 78.6, 197.6, and 172.9 ppm. The X-ray structure of **12** confirms the tentative assignement. The structure of the addition product **11** resulting from reaction with furan was assigned by analogy. Compound **11** could not be fully characterized owing to its decomposition during work up to a mixture of two aldehydes of as yet unknown structure. A secondary product resulting from rearrangement of the ylide **4b** was observed in some reactions, but could not be fully identified owing to decomposition under the reaction conditions. The structure of **13** is tentatively assigned on the grounds of analogous rearrangements observed upon heating of phenyliodonium ylides.[15,16] The yields for the cycloadditions are acceptable for dihydrofuran (35 – 78%), but are poor for furan, which is less reactive.

The enantioselectivity of the reaction was tested with several Rh(II)-catalysts. In general, enantioselectivity was disappointingly low. For furan, the best result (22 %) was achieved with $[Rh_2\{(S)\text{-pttl}\}_4]$, and for 2,3-dihydrofuran (26%) with $[Rh_2\{(S)\text{-nttl}\}_4]$. Although this is not high, it is still much better than in the cycloaddition of diazodimedone.



Scheme 4

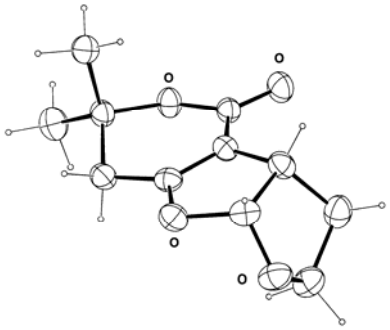


Figure 1. X-Ray crystal structure of **12**. Ellipsoids are represented with 40% probability level.

Table 2. Cycloaddition of **4a,b** to Furan and Dihydrofuran

Cpd	X =	Dipolarophile	Catalyst	Solvent	Adduct	ee
4a	N_2	Furan[(a)]	$[Rh_2(OAc)_4]$	$PhCF_3$	**11** 12%	-
4b	IPh	Furan[(a)]	$[Rh_2(OAc)_4]$	$PhCH_3$	**11** 18%	--
4a	N_2	Furan[(a)]	$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCF_3$	**11** 17%	22%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCF_3$	**12** 35%	24%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	**12** 71%	26%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-ptpa}\}_4]$	CH_2Cl_2	**12** 78%	1%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-dosp}\}_4]$	$PhCH_3$	**12** 47%	4%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-campha}\}_4]$	$PhCH_3$	**12** 63%	0%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(2S)\text{-mepy}\}_4]$	$PhCH_3$	**12** 52%	0%
4b	IPh	Dihydrofuran[(b)]	$[Rh_2\{(S)\text{-bnp}\}_4]$	$PhCF_3$	**12** 44%	0%

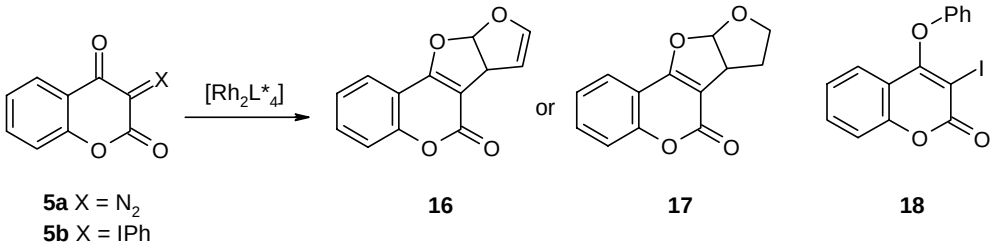
[(a)] Conditions: 0.50 mmol of **4a**,**b** 3.0 mL of furan, 6.0 mL of $PhCF_3$, 5 mol% of catalyst, 12 h reflux. [(b)]: 0.5 mmol of **4b**, 15 eq. of dihydrofuran in 8.0 mL of solvent, 5 mol% of catalyst, 12 h reflux.

Cycloaddition with the ylide derived from chromane-2,4-dione (5b)

The decomposition of the ylide **5b** required heating to 60 °C, and at this temperature **5b** rearranged partially to **18**. The cycloadditions to furan proceeded to **16** in yields of 6-36%, while those with dihydrofuran were more efficient and furnished **17** in up to 72% yield. In view of the poor yields of **16**, the cycloadditions with furan were not further investigated. However, it was noted that in the presence of the less reactive substrate, the yield of rearrangement product **18** increased, and that the rearrangement was accelerated by the catalyst. The rearrangement of phenyliodonium ylides to iodoethers is believed to be intramolecular.[14] Since the rate of ylide decomposition is independent of the substrate present, the lower yield of cycloadduct with the

less reactive substrate (furan) suggests, that formation of the metallocarbene from the ylide should be reversible.[17]

The cycloaddition is entirely regioselective. As before, only the carbonyl group of the ketone is involved in the reaction. The structure of the adduct **17** was confirmed by X-ray structure analysis. The enantioselectivities culminated at 31% ee for **16** and at 12% ee for **17**.



Scheme 5

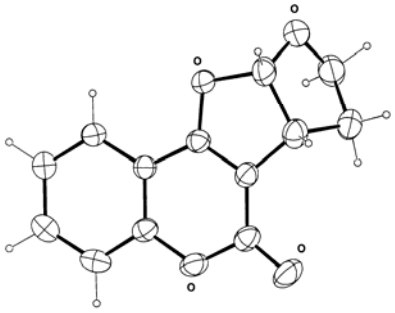


Figure 2. X-Ray crystal structure of **17**. Ellipsoids are represented with 40% probability level.

Table 3. Cycloaddition of ylide **5b** with furan and dihydrofuran[(a)]

Dipolarophile	Catalyst	Solvent	Adduct (%)	ee (%)
Furan	$[Rh_2(Oac)_4]$	Neat	**15**	--
Furan	$[Rh_2\{(S)\text{-pttl}\}_4]$	Neat	**15** 36	18
Furan	$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCH_3$	**15** 06	17
Furan	$[Rh_2\{(S)\text{-pttl}\}_4]$	CH_2Cl_2	**15** 06	10
Furan	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	**15** 08	31
Furan	$[Rh_2\{(S)\text{-tsin}\}_4]$	$PhCH_3$	**15** 15	0
Dihydrofuran	$[Rh_2(Oac)_4]$	$PhCH_3$	**16** 57	--
Dihydrofuran	$[Rh_2\{(S)\text{-nttl}\}_4]$	$PhCH_3$	**16** 72	10
Dihydrofuran	$[Rh_2\{(S)\text{-pttl}\}_4]$	$PhCH_3$	**16** 56	12
Dihydrofuran	$[Rh_2\{(5S)\text{-mepy}\}_4]$	$PhCH_3$	**16** 22	3
Dihydrofuran	$[Rh_2\{(S)\text{-tsop}\}_4]$	$PhCH_3$	**16** 41	0
Dihydrofuran	$[Rh_2\{(S)\text{-nbmatl}\}_4]$	$PhCH_3$	**16** 36	7
Dihydrofuran	$[Rh_2\{(S)\text{-tbsin}\}_4]$	$PhCH_3$	**16** 24	0

Dihydrofuran	$[Rh_2\{(S)\text{-tbsop}\}_4]$	$PhCH_3$	**16**	42	0
Dihydrofuran	$[Rh_2\{(S)\text{-dosp}\}_4]$	$PhCH_3$	**16**	46	0

[(a)] Conditions: At 60 °C, with 5% of catalyst.

Cycloadditions with ylides (6b-8b)

The decomposition of the ylides **6b**-**8b** with Rh(II)-catalysts afforded no characterizable products. This is surprising in the case of **6a**, because the corresponding diazo derivative **6a** adds normally to olefins.[18] The diazo analogue **7a** of ylide **7b** is not known in the literature; and attempts towards its preparation were not successful. In the case of **8a**,**b** both the diazo derivative and the ylide are too stable and may not be decomposed under normal conditions.

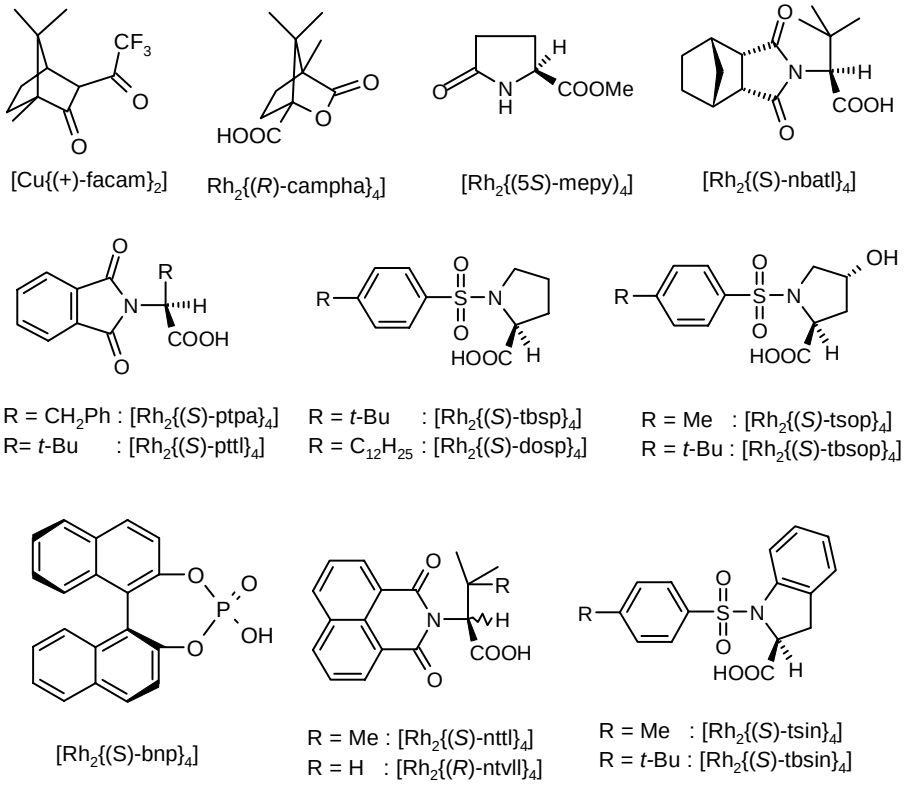
Discussion

We note that 2-diazodimedone (**1a**) and the ylide **1b** exhibit very poor enantioselectivity in cyclopropanations of terminal olefins. As reported elsewhere, the same is true for cycloadditions to furans. While in the case of the cycloadditions to furans, the hypothesis of formation of a free ylide between carbene and substrate provides a plausible explanantion for the absence of enantioselectivity, this argument cannot be invoked in the cyclopropanation of simple olefins. Introduction of oxygen atoms in the ring of **1a** results in a more selective carbene. Typically, the cyclopropanation of pentene and styrene proceed with ee's of 59 and 37%, respectively with $[Rh_2\{(S)\text{-nttl}\}_4]$, with the ylide derived from Meldrum's acid (**3b**).[9] A similar trend, although much less pronounced, may be seen in the cycloaddition to dihydrofuran, where the enantioselectivity reaches 26% with **4b** and 31% with **5b** when $[Rh_2\{(S)\text{-nttl}\}_4]$ is used as catalyst. The effect of a second oxygen atom on the cycloaddition could not be examined because **3b** does not undergo such reactions.

A tentative explanation for the low enantioselectivity of the diazodimedone (**1a**), or the corresponding phenyliodonium ylide **1b** may be advanced on the grounds of the investigations of Davies.[19] It was found that diazo esters carrying stabilizing substituents such as phenyl or vinyl groups, exhibit significantly higher ρ-values in the cyclopropanation of substituted styrenes than the unsubstituted diazoacetate esters. A higher ρ-value implies higher selectivity, owing to a transition state occurring later on the reaction coordinate. Interestingly, the more stabilized carbenes exhibit also higher enantioselectivities. Applying the same argument to carbenes derived from **1a**,**b**, the absence of selectivity may be attributed to their higher reactivity in comparsion, for example, to the carbene derived from **3a**,**b**, where the oxygen atoms provide some stabilization. The carbene derived from **4** and **5** are intermediate between these two, and exhibit intermediate enantioselectivity. This argument is consistent with the generally lower enantioselectivity for reactions involving diazo ketones[20] in comparison to diazo esters or diazo amides, although a few enantioselective catalysts for diazo ketones have been reported.[21,22]

Experimental Section

General: See ref.[23]



Scheme 6

Catalysts. The following chiral catalysts were synthesized according to procedures available in the literature: [Rh_2{(2*S*)-mepy}$_4$]: Ref.[24]; [Rh_2{(*R*)-campha}$_4$]: Ref.[25]; [Rh_2{(*S*)-bnp}$_4$]: Ref.[6], [Rh_2{(*S*)-ptpa}$_4$]: Ref.[26]; [Rh_2{(*S*)-pttl}$_4$]: Ref[27]; [Rh_2{(*S*)-dosp}$_4$]: Ref.[28]; [Rh_2{(*S*)-nttl}$_4$]: Ref.[9]. The synthesis of [Rh_2{(*S*)-tsop}$_4$],[29] [Rh_2{(*S*)-tbsop}$_4$],[29] [Rh_2{(*S*)-tsin}$_4$],[29] [Rh_2{(*S*)-tbsin}$_4$],[29] [Rh_2{(*S*)-nbmatl}$_4$],[30] and [Rh_2{(*R*)-ntvl}$_4$][30] will be reported elsewhere.

Synthesis of [Cu-{(+)-facam}$_2$]

To [$Cu(NO_3)_2 \cdot (H_2O)_3$] (1.565 g, 6.48 mmol) in H_2O was added aq. NH_3 (2.4 mL) dropwise, followed by 3-(trifluoroacetyl)-D-camphor (0.805 g, 3.24 mmol). The mixture was stirred until formation of a green precipitate. The aqueous layer was extracted with Etz_2O (3x20 mL), which was washed (satd. NaCl) and dried (Na_2SO_4). The solvent was evaporated, and the residue was recrystallized from hot EtOH to afford [Cu-{(+)-facam}$_2$] (802 mg, 88%) as green crystals, m.p. 151-152 °C; $[\alpha]_D^{20}$ = -10.4 (c = 0.125, $CHCl_3$). IR ($CHCl_3$): 2959*w*, 1626*s*, 1529*s*, 1479*w*, 1455*w*, 1440*w*, 1420*m*, 1392*w*, 1371*w*, 1329*m*, 1299*w*, 1285*w*, 1268*s*, 1224*s*, 1200*s*, 1178*s*, 1130*s*. MS: 559 (6), 557 (M^+, 11), 550 (16), 311 (14), 309 (100), 283 (10), 282 (11), 281 (13), 267 (16), 248 (23), 233 (11), 220 (12), 205 (11), 135 (12), 123 (10), 109 (10), 95 (16), 83 (20),

67 (10), 55 (23). HR MS: 557.1186 ($C_{24}H_{28}O_4{}^{63}CuF_6{}^+$; calc. 557.1188); 559.1197 ($C_{24}H_{28}O_4{}^{65}CuF_6{}^+$; calc. 557.1170).

Synthesis of diazocyclohexanediones 1a and **4a and phenyliodonium ylides (4b-b)**

The diazocyclohexanediones **1a** and **4a** were prepared from the respective diketones *via* diazo transfer with *p*-acetamidobenzenesulfonyl azide[31] in the presence of base. The procedure failed for **5a**, which is, however, available by the procedure of Taber.[32] The ylides **4b**-**8b**, in turn, were prepared from the hydrocarbons **4c**-**8c** *via* reaction with $PhI(OAc)_2$, according to Schank and Lick.[33]

Synthesis of 1-oxa-2,2-dimethyl-2,4-dioxo-5-(phenyliodonio)-cyclohexan-5-ide (4b). 1-Oxa-2,2-dimethylcyclohexane-4,6-dione (4c).[34] To NaH (1.92 g, 80 mmol) in anhydrous THF (200 mL) was added, at 0 °C methyl acetoacetate(9.28 g, 80 mmol) dropwise. After 10 min. of stirring BuLi (50 mL, 1.6M, 80 mmol) was added dropwise, and the orange solution was stirred at 0 °C for 10 more min. Dry acetone (7.5 mL, 82 mmol) was added at once, and the mixture was stirred for 10 min. at 0 °C. NaOH (80 mL, 2.5M) was then added, and the mixture was stirred at r.t. during 12 h, whereupon it was acidified (2.5M HCl) and extracted with ether (3x200 mL). The organic layer was washed (satd. NaCl) and dried (Na_2SO_4). After filtration, the solvant was evaporated. The residue was dissolved in a minimum of CH_2Cl_2, and **4c** (4.82 g, 42%) was precipitated with pentane as brownish solid, m.p. 126-127 °C. IR ($CHCl_3$): 2974*w*, 2361*s*, 2339*s*, 1647*m*, 1576*m*, 1342*m*, 1321*m*, 1236*m*, 1176*m*, 1110*m*, 999*m*. ^{1}H NMR (500 MHz, $CDCl_3$): 1.48 (*s*, 6H); 2.66 (*s*, 2H); 3.40 (*s*, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 28.3 (*q*); 44.9 (*t*); 50.4 (*t*); 79.1 (*d*); 167.3 (*s*); 200.6 (*s*). MS: 142 (M^+, 10), 127 (25), 85 (45), 84 (46), 83 (27), 70 (12), 59 (10), 56 (100), 55 (13). HR MS: 142.0618 ($C_7H_{15}O_3{}^+$; calc. 142.0630).

1-Oxa-2,2-dimethyl-2,4-dioxo-5-(phenyliodonio)-cyclohexan-5-ide (4b).[33] Prepared in 93% yield from **4c**. M.p. 133 °C. IR (film): 2990*w*, 1640*w*, 1558*s*, 1470*w*, 1428*w*, 1289*m*, 1168*w*, 1030*w*, 989*w*, 899*w*, 747*m*. ^{1}H NMR 500 MHz, $CDCl_3$): 1.46 (*s*, 6H); 2.69 (*s*, 2H); 7.38-7.57 (*m*, 3H); 7.85-7.87 (*m*, 2H). ^{13}C NMR (125 MHz, $CDcl_3$): 27.3 (*q*); 47.2 (*t*); 74.7 (*s*); 113.3 (*s*); 127.4 (*s*); 130.2 (*d*); 131.8 (*d*); 133.5 (*d*); 165.7 (*s*); 184.1 (*s*). MS: 344 (M^+, 9), 293 (19), 204 (75), 167 (12), 149 (87), 127 (18), 85 (17), 83 (11), 77 (100), 71 (28), 70 (13), 69 (11), 57 (25), 56 (10), 55 (12), 51 (46), 50 (24). HR MS: 343.9904 ($C_{13}H_{13}O_3I^+$; calc. 343.9910).

2,3-Benzo-4,6-dioxo-5-(phenyliodonio)-1-oxacyclohexan-5-ide (5b).[33] Prepared in 89 % yield from 4-hydroxycoumarin (**5c**). M.p. 142 °C (Lit. 135 °C). IR (film): 3050*w*, 1652*m*, 1591*m*, 1538*s*, 1460*w*, 1344*w*, 1283*m*, 1192*m*, 961*m*, 889*w*, 730*s*. ^{1}H NMR (300 MHz, $CDCl_3$): 7.22-7.25 (*m*, 2H); 7.39-7.60 (*m*, 4H); 7.95-8.07 (*m*, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 80.5 (*s*); 112.2 (*d*); 116.7 (*d*); 119.8 (*s*); 123.8 (*d*); 126.3 (*d*); 132.0 (*d*); 132.2 (*d*); 133.3 (*d*); 134.3 (*d*); 154.3 (*s*); 161.8 (*s*); 174.1 (*s*). MS: 364 (M^+, 23), 237 (20), 204 (100), 197 (12), 77 (94), 76 (10), 51 (37), 50 (22). HR MS: 363.9585 ($C_{15}H_9O_3I^+$; calc. 363.9597).

1-Methyl-2,3-benzo-4,6-dioxo-5-(phenyliodonio)-1-azacyclohexan-5-ide (6b). Pre-pared from (**6c**) in 99 %, yield; m.p. 130 °C. IR (film): 3000*w*, 1586*m*, 1513*s*, 1469*m*, 1411*w*, 1356*w*, 1314*m*, 1210*m*, 1156*w*, 1110*w*, 1070*w*, 1040*w*, 991*m*, 747*s*, 726*s*, 678*s*. ^{1}H NMR (400 MHz,

$CDCl_3$): 2.10 (*s*, 3H); 7.01-7.09 (*m*, 3H); 7.39-7.44 (*m*, 2H); 7.62-7.65 (*m*, 1H); 7.84-7.87 (*m*, 2H); 8.12-8.14 (*m*, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 302. (*q*); 112.5 (*s*); 113.8 (*d*); 114.2 (*s*); 121.3 (*s*); 121.5 (*d*); 127.3 (*d*); 130.2(*d*); 131.5 (*d*); 133.9 (*d*); 137.5 (*d*); 141.3 (*s*); 161.6 (*s*); 173.3 (*s*). MS: 377 (M^+, 100), 378 (16), 251 (15), 250 (93), 249 (10), 235 (22), 222 (13), 125 (22), 77 (17), 51 (11). HR MS: 376.9909 ($C_{16}H_{12}O_2NI^+$; calc. 376.9913).

6-Methyl-2,4-dioxo-3-(phenyliodonio)-1-oxacyclohexan-3-ide (7b).[33] Prepared in 82% yield from 4-hydroxy-6-methyl-4-pyrone (**7c**). M. p. 145 °C. IR (film): 3073*w*, 1651*s*, 1567*w*, 1532*s*, 1477*m*, 1441*m*, 1390*m*, 1365*m*, 129*m*, 1250*m*, 991*m*, 909*m*. ^{1}H NMR (500 MHz, $CDCl_3$): 2.15 (*d*, *J* = 0.6, 3H); 5.76 (*d*, *J* = 0.6, 1H); 7.39-7.49 (*m*, 2H); 7.56-7.59 (*m*, 1H); 7.91-7.93 (*m*, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 19.4 (*q*); 79.9 (*s*); 106.0 (*d*); 112.3 (*d*); 132.0 (*d*); 132.1 (*d*); 134.1 (*d*); 162.8 (*s*); 163.0 (*s*); 176.9 (*s*). MS: 328 (M^+, 89), 204 (66), 201 (38), 161 (45), 105 (22), 102 (10), 94 (37), 77 (100), 74 (10), 65 (13), 51 (48), 50 (27). HR MS: 327.9594 ($C_{12}H_9O_3I^+$; calc. 327.9597).

1,3-Dimethyl-2,4,6-trioxo-5-(phenyliodonio)-1,3-diazacyclohexan-5-ide (8b).[35] Prepared from 1,3-dimethylbarbituric acid (**8c**) according to Schank and Lick.[33] IR ($CHCl_3$): 1689, 1623. ^{1}H NMR (500 MHz, CD_2Cl_2): 3.15 (s, 6H); 7.44 (*m*, 2H); 7.59 (*tt*, *J* = 7.4, 1.0, 1H); 7.85 (*dd*, *J* = 8.5, 1.0, 2H). ^{13}C NMR (125 MHz, DMSO): 29.0 (*q*); 70.4 (*s*); 116.5 (*s*); 131.0 (*d*); 131.5 (*d*); 132.8 (*d*); 153.1 (*s*); 161.3 (*s*). MS: 358 (M^+, <1), 231 (2), 205 (7), 204 (100), 127 (6), 78 (7), 77 (96). HR MS: 357.9850 ($C_{12}H_{11}IN_2O_3^+$; calc. 357.9814).

Cyclopropanation and cycloaddition with diazo compounds and phenyliodonium ylides. General procedure

The carbene precursor (diazo compound or phenyliodonium ylide, respectively,1.00 mmol) and the appropriate olefin (10.0 mmol) were dissolved in were dissolved in the appropriate solvent (10 ml) indicated in the Tables. After addition of the catalyst (0.02 mmol) the mixture was stirred at the temperature indicated under N_2 overnight. The solvent was evaporated and the residue was purified by flash chromatography (SiO_2, EtOAc/pentane 1:4).

Cyclopropanation of terminal olefins

6,6-Dimethyl-1-phenylspiro[2.5]octane-4,8-dione (9a). Yield 33 % for $[Rh_2OAc)_4]$. M.p. 127 - 120°. IR (KBr): 3361*w*, 3063*w*, 2951*m*, 2871*m*, 1700*s*, 1679*s*. ^{1}H NMR (500 MHz, $CDCl_3$): 0.97 (*s*, 3 H); 1.06 (*s*, 3 H); 2.10 - 2.30 (*m*, 2 H); 2.25 (*dd*, *J* = 9.2, 3.8, 1 H); 2.46 (*dd*; J = 8.8, 3.9, 1 H); 2.48- 2.58 (*m*, 2 H); 7.14 - 7.22 (*m*, 5 H). ^{13}C NMR (125 MHz, $CDCl_3$): 22.1 (*z*); 27.9 (*q*); 29.3 (*q*); 30.5 (*s*); 48.5 (*d*); 48.7 (*s*); 53.2 (*t*); 54.0 (*t*); 128.0 (*d*); 128.1 (*d*); 129.5 (*d*); 133.2 (*s*); 201.7 (*s*); 205.6 (*s*). MS: 242 (100), 241 (11), 186 (18), 184 (64), 171 (47), 158 (15), 157 (12), 144 (41), 129 (13), 116 (22), 115 (41), 105 (16), 104 812), 91 (12), 83 (40), 55 (20). HR MS: 242.1313 ($C_{16}H_{18}O_2^+$; calc. 242.1307). Enantiomer separation: HPLC, OD-H, isopropanol /hexane 1:9, 0.3 mL/min. τ_1 = 28.4, τ_2 = 30.8 min.

6,6-Dimethyl-2-phenyl-3,4,6,7-tetrahydro-2*H*-benzofuran-4-one (10a). Yield 19 %, oil. IR ($CHCl_3$): 1630*s*. ^{1}H NMR (500 MHz, $CDCl_3$): 1.15 (*s*, 3 H); 1.16 (*s*, 3 H); 2.27 (*d*, *J* = 16.0, 1 H); 2.18 - 2.39 (*m*, 2 H); 2.31 (*d*, *J* = 16.0, 1 H); 2.89 (*ddt*, *J* = 16.4, 7.9, 1.9, 1 H); 3.30 (*ddt*; *J* = 16.4, 10.7, 1.9, 1 H); 5.78 (*dd*, *J* = 10.4, 7.9, 1 H); 7.29 - 7.41 (*m*, 5 H). ^{1}C NMR (125 MHz,

CDCl3): 28.6 (*q*); 28.8 (*q*); 33.9 (*t*); 34.2 (*s*); 37.8 (*t*); 51.0 (*t*); 86.5 (*d*); 111.4 (*s*); 125.8 (*d*); 128.5 (*d*); 128.8 (*d*); 140.7 (*s*); 176.0 (*s*); 194.7 (*s*). MS: 242 (M^+,100), 241 (12), 186 (19), 185 (56), 171 (40), 158 (14), 157 (11), 144 (33), 129 (10), 116 (16), 115 (30),105 (13), 83 (32), 55 (15). HR MS: 242.1328 ($C_{16}H_{18}O_2^+$; calc. 242.1307). Enantiomer separation: HPLC, OD-H, isopropanol /hexane 1:9, 0.3 mL/min. τ_1 = 24.5, τ_2 = 39.5 min.

6,6-Dimethyl-1-propylspiro[2.5]octane-4,8-dione (9b). Yield 34 %. IR ($CHCl_3$): ^{1}H NMR (500 MHz, $CDCl_3$): 0.88 (*t*, *J* = 7.3, 3 H); 1.06 (*s*, 3 H); 1.18 - 1.37 (*m*, 2 H); 1.44 - 1.58 (*m*, 3 H); 1.85 (*dd*, *J* = 8.5, 2.5, 1 H); 2.01 (*dd*, *J* = 8.5, 2.5, 1 H); 2.04 - 2.09 (*m*, *m*, 1 H); 2.48 - 2.58 (*m*, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): 13.7 (*q*); 22.5 (*t*); 27.2 (*t*); 27.6 (*q*); 28.5 (*t*); 29.4 (*q*); 30.5 (*s*); 45.5 (*s*); 46.5 (*d*); 53.1 (*t*); 54.3 (*t*); 204.9 (*s*); 206.9 (*s*). MS: 208 (M^+, 40), 193 (19), 179 (32), 166 (20), 165 (54), 153 (60), 152 (26), 141 (11), 137 (37), 124 (29), 123 (32), 110 (18), 109 (29), 98 (11), 97 (100), 96 (10), 95 (35), 83 (29), 82 (22), 81 (27), 79 (11), 77 (11), 69 (45), 68 (23), 67 (27), 57 (10), 56 (19), 55 (68), 54 (18), 53 (40). HR MS: 208.1461 ($C_{13}H_{20}O_2^+$; calc. 208.1463).

1-*n*-Butyl-6,6-dimethylspiro[2.5]octane-4,8-dione (9c). Yield 31 %. IR ($CHCl_3$): 2961*w*, 1675*s*, 1371*w*, 1339*w*, 1256*w*. $^+$H NMR (400 MHz, $CDCl_3$): 0.87 (*t*, *J* = 6.8, 3 H); 1.06 (*s*, 3 H); 1.16 (*s*, 3 H); 1.17 - 1.35 (*m*, 4 H); 1.44 - 1.61 (*m*, 2 H); 1.85 (*dd*, *J* = 8.1, 2.0, 1 H); 2.48 - 2.58 (*m*, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): 13.9 (*q*); 22.2 (*t*); 26.1 (*t*); 27.2 (*t*); 27.5 (*q*); 29.3 (*q*); 30.4 (*s*); 31.4 (*t*); 45.5 (*s*); 46.6 (*d*); 53.1 (*t*); 54.2 (*t*); 204.8 (*s*); 206.8 (*s*). MS: 223 (13); 222 (M^+, 66), 207 (17), 193 (54), 180 (27), 179 (34), 167 (12), 166 (38), 165 (60), 154 (27), 153 (77), 151 (18), 141 (16), 138 (13), 137 (45), 124 (20), 123 (29), 110 (10), 109 (16), 98 (26), 97 (100), 96 (16), 95 (28), 83 (51), 82 (28), 81 (25), 79 (10), 77 (10), 70 (11), 69 (32), 68 (14), 67 (21), 56 (11), 55 (55), 54 (13), 53 (23). HR MS: 222.1625 ($C_{14}H_{22}O_2^+$; calc. 222.1620). Enantiomer separation: GC, β-Dex, isothermal at 150 °C; τ_1 = 27.6, τ_2 = 28.2 min.

1-*t*-Butyl-6,6-dimethylspiro[2,5]octane-4,8-dione (9d). Yield 25 %. IR ($CHCl_3$): 2960*w*, 1672*s*, 1334*w*. ^{1}H NMR (500 MHz, $CDCl_3$): 0.96 (*s*, 9 H); 0.97 (*s*, 3 H); 1.18 (*t*, *J* = 9.6, 1 H); 1.97 (*dd*, *J* = 9.6, 3.3, 1 H); 2.20 (*dd*, *J* = 9.6, 3.3, 1 H); 2.46 - 2.67 (*m*, 4 H). ^{13}C NMR (125 MHz, $CDCl_3$): 21.7 (*t*); 26.6 (*q*); 29.8 (*q*); 30.2 (*q*); 30.7 (*s*); 32.3 (*s*); 47.0 (*s*); 53.2 (*t*); 55.5 (*t*); 58.5 (*d*); 204.9 (*s*); 206.(*s*). MS: 222 (M^+, 5), 207 (19), 179 (56), 165 (13), 97 (41), 83 (11), 70 (100), 69 (14), 55 (37). HR MS: 222.1611 ($C_{14}H_{22}O_2^+$; calc. 222.1620). Enantiomer separation: GC, β-Dex, isothermal at 120 °C; τ_1 = 29.5, τ_2 = 30.4 min.

Cycloaddition to furan and dihydrofuran with 4a,b

6,6-Dimethyl-3a,6,7,8a-tetrahydro-1,5,8-trioxacyclopenta[*a*]inden-4-one (11). ^{1}H NMR (200 MHz, $CDCl_3$): 1.47 (*s*, 3H); 1.49 (*s*, 3H); 2.59 (*d*, *J* = 1.8, 2H); 4.35-4.38 (*m*, 1H); 5.42-5.44 (*m*, 1H); 6.42-6.44 (*m*, 1H); 6.67 (*d*, *J* = 7.5, 1H). Enantiomer separation by GC, β-dex, isothermal, 150 °C, τ_1 = 34.1, τ_2 = 34.8 min.

6,6-Dimethyl-2,3,3a,6,7,8a-hexahydro-1,5,8-trioxacyclopenta[*a*]inden-4-one (12). Yield 48 %, m.p. 125 - 126 °C. IR (film): 2972*w*, 2867*w*, 1727*w*, 1687*s*, 1664*s*; 1438*w*, 1406*m*, 1363*m*, 1239*s*, 1202*w*, 1181*m*, 1114*s*, 1083*s*, 1045*s*, 934*s*, 905*m*, 880*s*. ^{1}H NMR (300 MHz,

$CDCl_3$): 1.47 (*s*, 6H); 2.00-2.23 (*m*, 2H); 2.49-2.63 (*m*, 2H); 3.64-3.73 (*m*, 1H); 3.78 (*tbr*, *J* = 7, 1H); 4.14 (*t*, 1H); 6.32 (*d*, *J* = 5.8, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 28.0 (*q*); 28.1 (*q*); 30.3 (*t*); 34.1 (t); 44.4 (*d*); 68.1 (*t*); 79.4 (*s*); 101.6 (*s*); 113.6 (*d*); 164.0 (*s*); 170.8 (*s*). MS: 210 (M^+, 20), 192 (29), 177 (15), 155 (18), 154 (63), 149 (24), 137 (12), 136 (24), 126 (20), 110 14), 109 (20), 108 (19), 105 (14), 98 (18), 97 (15), 95 (12), 91 (15), 85 (17), 83 (1009, 82 (17), 81 (21), 80 (12), 79 (10), 77 (10), 71 (26), 70 (21), 69 (42), 68 (10), 67 (11), 58 (11), 57 (37), 56 (26), 55 (51), 54 (13), 52 (10), 51 (10). HR MS: 210.0911 ($C_{11}H_{14}O_4^+$; calc. 210.0892). Enantiomer separation by GC, β-dex, isothermal, 150 °C, τ_1 = 44.1, τ_2 = 45.9 min.

Crystallographic data for 12. $C_{11}H_{14}O_4$; M_r = 210.3; μ = 0.10 mm^{-1}, d_X = 1.370 $g{\cdot}cm^{-3}$, monoclinic, $P\ \bar{1}$, Z = 2, a = 6.9812(15), b = 8.855(2), c = 8.854(2) Å, α = 107.93(3), β = 99.44(3), γ = 93.80(3)º, V = 509.7(3)$Å^3$; Data were collected at 200K on a Stoe IPDS diffractometer. Hydrogen atoms were observed and refined. *R* = 0.036, ω*R* = 0.033, *S* = 1.24(3). Crystallographic data for **12** (excluding structure factors) have been deposited to the *Cambridge Crystallographic Data Base* as supplementary publication number CCDC 204495. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. + 44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Cycloaddition of furan and dihydrofuran with 6b

6,7-Benzo-3a,8a-dihydro-1,5,8-trioxacyclopenta[*a*]inden-4-one (16). M.p. 135 °C. IR (film): 2919*br*, 1710*s*, 1646*m*, 1614*w*, 1569*w*, 1496*w*, 1410*m*, 1326*w*, 1229*w*, 1126*w*, 1006*w*, 977*w*, 914*m*, 898*m*, 759*s*. ^{1}H NMR (500 MHz, $CDCl_3$): 4.66 (*d*, *J* = 5.0, 1H); 5.53-5.54 (*m*, 1H); 6.51-6.52 (*m*, 1H); 6.91-6.92 (*m*, 1H); 7.32-7.34 (*m*, 1H); 7.39-7.40 (*m*, 1H); 7.58-7.59 (*m*, 1H); 7.72-7.74 (*m*, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 29.7 (*s*); 30.9 (*s*); 48.8 (*d*); 102.6 (*d*); 104.9 (*s*); 112.0 (*s*); 113.8 (*d*); 117.0 (*d*); 123.2 (*d*); 124.2 (*d*); 132.8 (*d*); 145.3 (*d*); 160.0 (*s*). MS: 228 (M^+, 40), 201(12), 200 (93), 199 (38), 171 (16), 144 (14), 121 (100), 120 (11), 118 (10), 115 (24), 108 (37), 93 (19), 92 (23), 89 (10), 80 (13), 79 (10), 77 (13), 73 (16), 71 (14), 69 (15), 65 (23), 64 (17), 63 (25), 62 (10), 60 (14), 57 (32), 56 (10), 55 (26), 53 (12), 52 (12), 51 (19), 50 (14). HR MS: 228.0434 ($C_{13}H_8O_4^+$; calc. 228.0423). Enantiomer separation: HPLC, OD-H column, isopropanol/hexane 1:9, 0.5 mL/min.; τ_1 = 23.3, τ_2 = 25.9 min.

6,7-Benzo-2,3,3a,8a-tetrahydro-1,5,8-trioxacyclopenta[*a*]inden-4-one (17). M.p. 137 °C. IR (film): 3056*w*, 2956*br*, 1715*m*, 1643*w*, 1499*w*, 1416*w*, 1264*m*, 1156*w*, 1075*m*, 1003*w*, 942*w*, 862*w*, 732*s*, 702*m*. ^{1}H NMR (500 MHz, $CDCl_3$): 2.13-2.15 (*m*, 1H); 2.25-2.27 (*m*, 1H); 3.65-3.68 (*m*, 1H); 3.98-3.99 (*m*, 1H); 4.11-4.15 (*m*, 1H); 6.50 (*d*, *J* = 5.8, 1H); 7.20-7.24 (*m*, 1H); 7.29-7.30 (*m*, 1H); 7.48-7.52 (*m*, 1H); 7.61-7.63 (*m*, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 30.1 (*t*); 44.8 (*d*); 68.3 (*t*); 102.4 (*s*); 111.8 (*s*); 114.5 (*d*); 116.9 (*d*); 123.2 (*d*); 124.1 (*d*); 132.7 (*d*); 154.9 (*s*); 159.9 (*s*); 166.5 (*s*). MS: 230 (M^+, 46), 215 (15), 202 (18), 201 (11), 187 (45), 121 (100), 120 (11), 108 (10), 93 (12), 92 (17), 82 (26), 65 (13), 64 (12), 63 (13), 57 (10), 53 (15). HR MS: 230.0586 ($C_{13}H_{10}O_4^+$; calc. 230.0579). Enantiomer separation: HPLC, OD-H column, isopropanol/hexane 1:9, 0.5 mL/min.; τ_1 = 27.6, τ_2 = 31.0 min.

Crystallographic data for 17. $C_{13}H_{10}O_4$; M_r = 230.2; μ = 0.11 mm^{-1}, d_X = 1.458 $g \cdot cm^{-3}$, monoclinic, *P* $2_1/c$, Z = 4, a = 10.4043(10), b = 8.7026(9), c = 12.5505(13) Å, β = 112.635(11)º, V = 1048.8(2)$Å^3$; Data were collected at 200K on a Stoe IPDS diffractometer. Hydrogen atoms were observed and refined. *R* = 0.031, ωR = 0.030, *S* = 1.21(3). Crystallographic data for **17** (excluding structure factors) have been deposited to the *Cambridge Crystallographic Data* Base as supplementary material, publication number CCDC 204496.

5,6-Benzo-3-iodo-5-phenoxy-1-oxacyclohex-3-en-2-one (18). M.p. 131 °C. IR (film): 3011*br*, 1739*m*, 1719*s*, 1606*m*, 1555*m*, 1483*m*, 1339*s*, 1083*w*, 1033*w*, 978*w*, 775*w*. ^{1}H NMR 300 MHz, CDC_3): 6.95-6.99 (*m*, 2H); 7.15-7.22 (*m*, 2H); 7.34-7.46 (*m*, 3H); 7.53-7.61 (*m*, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 80.5 (*s*); 115.9 (*d*); 116.3 (*s*); 116.9 (*d*); 123.7 (*d*); 123.9 (*d*); 124.6 (*d*); 130.1 (*d*); 133.0 (*d*); 153.4 (*s*); 155.4 (*s*); 155.7 (*s*); 165.0 (*s*). MS: 364 (M^+, 100), 365 (17), 238 (16), 237 (94), 236 (10), 209 (14), 197 (42), 193 (16), 181 (17), 165 (41), 152 (13), 116 (15), 88 (27), 77 (25), 76 (17), 62 (16), 51 (19), 50 (10). HR MS: 363.9602 ($C_{15}H_9O_3I^+$; calc. 363.9597).

Supporting Information Available. Crystal data, intensity measurement and structure refinement, atomic coordinates, displacement parameters, bond distances and bond angles for **12** and **17** and CIF files.

Acknowledgments

This work was supported by the Swiss National Science Foundation (Projects No. 20-52581.97 and 2027-048156) and by the European Commission for Science, Research and Development (COST Action D12). The authors are indebted to A. Pinto and J.-P. Saulnier for the NMR spectra, D. Klink for the mass spectra, and E. Robert for the preparation of **8b**.

References

1. (a) Müller, P.; Boléa, C. *Helv. Chim. Acta* **2001**, *84*, 1093. (b) Müller, P.; Boléa, C. *Synlett* **2001**, 826. (c) Müller, P.; Fernandez, D. *Helv. Chim. Acta* **1995**, *78*, 947. (d) Müller, P.; Fernandez, D.; Nury, P.; Rossier, J.-C. *J. Phys. Org. Chem.* **1998**, *11*, 321.
2. (a) Lydon, K. M.; McKervey, M. A. In *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N.; Pfaltz, A.; Yamamoto, Eds; H. Springer: Berlin, 1999; Vol. II, p 539. (b) Doyle, M. P.; McKervey, M. A. *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley: New York, 1997. (c) Doyle, M. P.; Forbes, D. C. *Chem. Revs*. **1998**, *98*, 911.
3. (a) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Chou, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 4778. (b) Alonso, M. E.; Morales, A.; Chitty, A. W. *J. Org. Chem*. **1982**, *47*, 3747.
4. (a) Alonso, M. E.; Jano, P.; Hernandez, M. L.; Greemberg, R. S.; Wenkert, E. *J. Org. Chem*. **1983**, *48*, 3047. (b) Wenkert, E.; Alonso, M. E.; Buckwalter, B. L.; Sanchez, *J. Am. Chem.*

Soc. **1983**, *105*, 2021. (c) E. Wenkert, T. P. Anantanarayan, V. F. Ferreira, M. G. Hoffmann, H.-S. Kim, E. L. *J. Org. Chem*. **1990**, *55*, 4975.
5. Pirrung, M. C.; Zhang, J.; McPhail, A. T. *J. Org. Chem*. **1991**, *56*, 6269.
6. Pirrung, M. C.; Zhang, J. *Tetrahedron Lett*. **1992**, *33*, 5987.
7. Ishitani, H. Achiwa, K. *Heterocycles* **1997**, *46*, 153.
8. Müller, P.; Allenbach, Y.; Ferri, M. *Helv. Chim. Acta* **2003**, in preparation.
9. Müller, P.; Allenbach, Y.; Robert, E. *Tetrahedron: Asymmetry* **2003** in the press.
10. Matlin, S. A. ; Lough, W. J.; Chan, L.; Abram, D. M. H.; Zhou, Z. *J. Chem. Soc. Chem. Commun*. **1994**, 1038.
11. Pfaltz, A. In *Comprehensive Asymmetric Catalysis*, Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H. Eds; Springer, Berlin, 1999; Vol. II, p 513.
12. Kurganov, A. A.; Zhuchova, L. YA.; Davankov, V. A. *Tetrahedron* **1983**, *2*, 37.
13. Yoshida, J.; Yano, S.; Ozawa, T.; Kawabata, N. *J. Org. Chem.* **1985**, *50*, 3467.
14. SpecTool 2.1 A Hypermedia Book for Structure Elucidation of Organic Compounds with Spectroscopic Methods. Gloor, A.; Cadisch, M.; Bürgin-Schaller, R.; Farkas, M.; Kocsis, T.; Clerc, J. T.; Pretsch, E.; Aeschimann, R.; Badertscher, M.; Brodmeier, T.; Fürst, A.; Hediger, H.-J.; Junghans, M.; Kubinyi, H.; Munk, M. E.; Schriber, H.; Wegmann, D.; Kiedorf, U.; Moll, R. Chemical Concepts GmbH, P.O. Box 10 02 02, D-69442 Weinheim.
15. Takaku, M.; Hayasi, Y.; Nozaki, H. *Tetrahedron* **1970**, *26*, 1243.
16. Neilands, O. *Latvian J. Chem.* **2002**, 27.
17. Moriarty, R. M.; Bailey, B. R.; Prakash, O.; Prakash, I. *J. Am. Chem. Soc*. **1985**, *107*, 1375.
18. Pirrung, M. C.; Blume, F. *J.Org. Chem.* **1999**, *64*, 3642.
19. Davies, H. M. L.; Panaro, S. A. *Tetrahedron* **2000**, *56*, 4871.
20. Müller, P.; Maîtrejean, E. *Coll. Czech. Chem. Commun*. **1999**, *64*, 1807.
21. (a) Tokunoh, R.; Fähndrich, B.; Pfaltz, A. *Synlett*. **1995**, 491. (b) Piqué, C.; Tomiyana, H.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett*. **1996**, *37*, 2449. (c) Doyle, M. P.; Eismont, M. Y.; Zhou, Q.-L. *Russ. Chem. Bull*. **1977**, *46*, 955.
22. (a) Estevan, F.; Herbst, K.; Lahuerta, P.; Barberis, M.; Pérez-Prieto, J. *Organometallics* **2001**, *20*, 950. (b) Barberis, M.; Lahuerta, P.; Pérez-Prieto, J.; Sanaú, M. *J. Chem. Soc. Chem. Commun*. **2001**, 439. (c) Barberis, M.; Pérez-Prieto, J.; Stribia, S.-E.; Lahuerta, P. *Org. Lett*. **2001**, *3*, 3317.
23. Müller, P.; Nury, P. *Helv. Chim. Acta* **2001**, *84*, 662.
24. Doyle, M. P.; Winchester, W. R.; Protopopova, M. N.; Kazala, A.; Westrum, L. *Org. Synth.* **1996**, *73*, 13.
25. Roos, G. H. P.; McKervey, M. A. *Synth. Comm.* **1992**, *22*, 1751.
26. (a) Hashimoto, S.-I.; Watanabe, N.; Ikegami, S. *Tetrahedron Lett.* **1990**, *31*, 5173. (b) Hashimoto, S.; Watanabe, N.; Sato, T.; Shiro, M.; Ikegami, S. *Tetrahedron Lett.* **1993**, *34*, 5109. (c) Hashimoto, S.-I.; Watanabe, N.; Ikegami, S. *Synlett* **1994**, 353. (d) Watanabe, N.; Anada, M.; Hashimoto, S.; Ikegami, S. *Synlett.* **1994**, 1031.
27. Watanabe, N.; Ogawa, T.; Ohtake, Y.; Ikegami, S.; Hashimoto, S. *Synlett* **1996**, 85.

28. Davies, H. L. M.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc*. **1996**, *118*, 6897.
29. D'Augustin, M. DEA Thesis, University of Geneva, 2002.
30. Ferri, M. Diploma Thesis, University of Geneva, 2002.
31. Davies, H. M. L.; Cantrell, W. R.; Romines, K. R.; Baum, S. S. *Org. Synth*. **1992**, *70*, 93.
32. (a) Lee, R. R.; Suk, J. Y.; Kim, B. S. *Tetrahedron Lett*. **1999**, *40*, 6603. (b) Taber, D. F.; Ruckle, Jr. R. E. *J. Org. Chem*. **1986**, *51*, 4077.
33. Schank, K.; Lick, C. *Synthesis* **1983**, 392.
34. Arnett, E. M.; Harrelson, J. A.; *J. Am. Chem. Soc*. **1987**, *109*, 809.
35. Neilands, O. Y.; Neiman, D. E. *J. Org. Chem. USSR (English translation)* **1970**, *6*, 2522.