77. Carbenoid Reactions in Rhodium(II)-Catalyzed Decomposition of Iodonium Ylides

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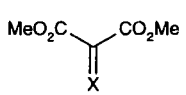
The intermediacy of metallocarbenes in decomposition reactions of iodonium ylides with $[Rh_2(OAc)_4]$ was established by comparison with reactions of the corresponding diazo compounds. The sensitivity of the Rh^{II}-catalyzed intermolecular cyclopropane formation from substituted styrenes and bis(methoxycarbonyl)(phenyliodono)methanide (**1a**) or dimethyl diazomalonate (**1b**) is identical. The *Hammett* plot (with σ^+) has a slope of –0.47. Iodonium ylides and diazo compounds afford the same products in $[Rh_2(OAc)_4]$-catalyzed cyclopropane formations, cycloadditions, and intramolecular CH insertions, and exhibit the identical selectivity in intramolecular competitions for cyclopropane formation and insertion. The intramolecular CH insertion of the ylide **20c**, when carried out in the presence of a chiral catalyst ($[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$), results in formation of **21a** having an ee of 67%, identical to the ee obtained with the diazo compound **20b**.

Introduction. – The decomposition of diazoketones and diazoesters in the presence of chiral transition-metal catalysts has a remarkable potential for asymmetric catalysis [1]. Cu-Based catalysts [2–5] found successful applications in intermolecular cyclopropane formation with olefins, while chiral Rh^{II}-complexes provided products of intramolecular cyclopropane formation [6], CH insertion [7–9], and intermolecular cyclopropene formation of acetylenes [10] having enantiomeric excesses in the range of 95% or more. The major drawback of these reactions is the requirement of diazo compounds as precursors which are potentially explosive, toxic, or/and carcinogenic [11].

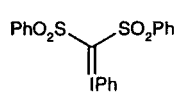
The transition-metal-catalyzed decomposition of diazo compounds leads to metallocarbenes which are not isolable, but transfer the carbene moiety to a suitable acceptor molecule or to an appropriate reactive site within the metallocarbene [1]. Thus, the use of diazo compounds might be avoided if it were possible to generate the metallocarbenes from other precursors. This investigation deals with the use of iodonium ylides [12–15] as precursors for metallocarbenes in view of their application to asymmetric catalysis.

The photochemical and transition-metal-catalyzed decomposition of iodonium ylides such as **1a** (bis(methoxycarbonyl)(phenyliodono)methanide) [13] and **2** ((phenyliodono)-bis(phenylsulfonyl)methanide) [14] [15] afforded products typical for carbenoid reactions, namely cyclopropanes in the presence of olefins [13–15] or arsonium or other ylides in the presence of triphenylarsine or other suitable acceptors [13] [16].



1a X = IPh

b X = N_2



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However, the involvement of metallocarbenes in such reactions has been questioned. The intramolecular cyclopropane formation of a series of iodonium ylides was recently investigated by *Moriarty* and coworkers [17]. Although the reaction was catalyzed by CuCl, it also occurred without catalyst although with lower yield. The authors concluded that the reaction mechanism involved a stepwise electrophilic addition of the iodonium center to the double bond to give a zwitterionic intermediate, or a stepwise radical mechanism involving an analogous biradical intermediate. The intermediacy of a metallocarbene was ruled out on the grounds of the absence of products derived from *Wolff* rearrangements of the postulated acylcarbene intermediates. The formation of live-membered heterocycles upon cycloaddition of iodonium ylides to CS_2, phenyl-isothiocyanate, acetonitrile, alkenes, and diphenylketene [18] was quoted as supporting evidence for the dipolar mechanism. The role of the Cu-catalyst in the intramolecular cyclopropane formation remained however obscure. An electron transfer from Cu^I to the iodonium species [19] was suggested as a mechanistic possibility. It should be noted, however, that, although *Wolff* rearrangement occurred when acylcarbenes were generated thermally [20], photochemically [21], or in the presence of Ag_2O [22], it did usually not take place during decomposition of diazo compounds in the presence of Cu or Rh^{II} catalysts [23].

The intermediacy of metallocarbenes upon metal-catalyzed decomposition of iodonium ylides is crucial for the realization of asymmetric syntheses, since dipolar or biradical mechanisms may proceed without strong interactions between reagent, substrate, and catalyst, and their stereochemistry will be difficult to control. We, therefore, investigated the decomposition of iodonium ylides in comparison to that of the corresponding diazo compounds under a variety of conditions, realizing cyclopropanation cyclopropenation, cycloaddition, and insertion reactions. The catalyst of choice was $[Rh_2(OAc)_4]$ because of the successful application of Rh^{II}-catalysts in asymmetric carbenoid reactions, and because these catalysts did not participate in electron-transfer reactions with diazo compounds [24], a reaction more likely to occur with Cu^I.

Results and Discussion. – 1. *Intermolecular Cyclopropanation of Olefins.* The ylide **1a** reacted with styrene and substituted styrenes **3a–e** in the presence of a catalytic amount of $[Rh_2(OAc)_4]$ or with $[Cu(acac)_2]$ (acac = pentane-2,4-dione) to the cyclopropanedicarboxylates **4a–e** in yields of 50–70% (see *Exper. Part*). The formal carbene dimer **5** was formed as side product in yields of 0–4% in reactions with **1a** and **1b** in the presence of $[Rh_2(OAc)_4]$.

Cyclopropanedicarboxylates **4a–e** were also formed upon decomposition of diazomalonate **1b** with $[Rh_2(OAc)_4]$, but no reaction occurred when **1b** was exposed to $[Cu(acac)_2]$. The relative reactivity of the styrenes was investigated by competition experiments using equimolar amounts of two styrenes in 10-fold excess over **1a** or **1b**, so that the relative rate constant could be directly obtained from the ratio of the cyclopropanedicarboxylates (see *Table*). Allylbenzene (**6**) as an example for a nonconjugated monosubstituted olefin and phenylacetylene (**8**) as a substrate for intermolecular cyclopropenation, were included in the investigation in order to extend it beyond polar substituent effects. Both reacted normally to the cyclopropanedicarboxylate **7** and the cyclopropenedicarboxylate **9**, respectively. *Fig. 1* shows a plot of the log of the relative rate constant for reaction of the olefins (including **8**) with the ylide **1a** *vs.* that of the reaction with diazomalonate **1b** in the presence of $[Rh_2(OAc)_4]$.

Scheme 1

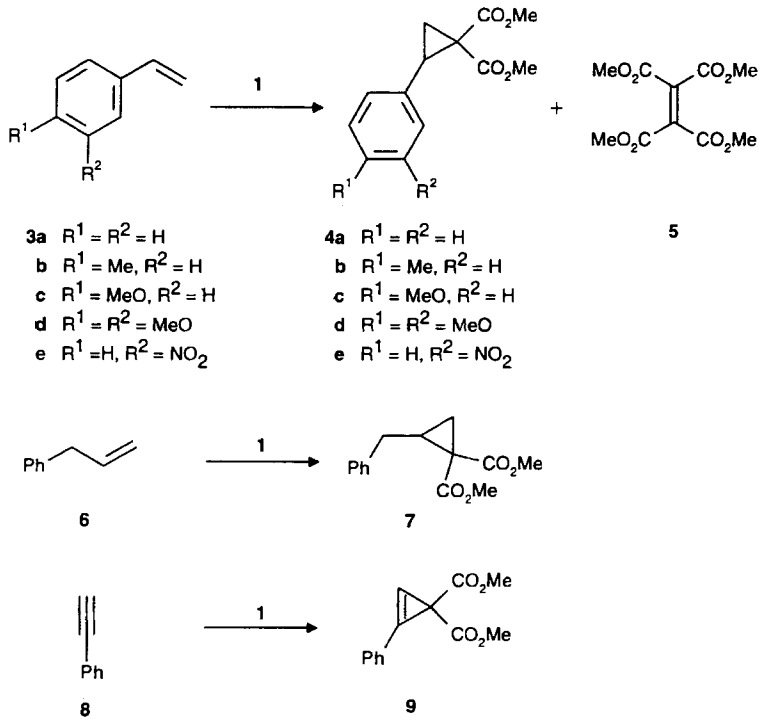


Table. *Product Composition for Metal-Catalyzed Decomposition of* **1a** *and* **1b** *in Competition Experiments*

Olefin	**1a** with $[Rh_2(OAc)_4]$		**1b** with $[Rh_2(OAc)_4]$		**1a** with $[Cu(acac)_2]$		σ^+
	Ratio[a])	$\log k_{rel}$[b])	Ratio[a])	$\log k_{rel}$[b])	Ratio[a])	$\log k_{rel}$[b])	
3a	–	0	–	0	0		0
b	57:43	0.12	58:42	0.14	67:33	0.31	−0.31
c	69:31	0.35	70:30	0.37	82:18	0.66	−0.78
d	62:38	0.21	66:34	0.29	80:20	0.60	−0.66
e	29:71	−0.39	30:70	−0.37	09:91	−1.00	0.71
6	10:90	−0.96	11:89	−0.91	05:95	−1.28	–
8	36:64	−0.25	27:73	−0.43	07:93	−1.12	–

[a]) Product ratio of cyclopropane **4a–e**, **7**, or cyclopropene **9** relative to **4a**.
[b]) Rel. to styrene (**3a**).

As *Fig. 1* shows, both reactions, with **1a** and **1b**, exhibit clearly similar selectivities, and this applies not only to the styrenes, but also to allylbenzene (**6**) and even to phenylacetylene (**8**). This suggests that the same reactive species should be responsible for attack with both **1a** and **1b**. The sensitivity of the reaction towards structural effects is, however, rather small. A *Hammett* plot for the relative rate constants of the cyclopropanation of styrenes and **1a** using σ^+ constants [25] has a slope of $\rho = -0.47$ (*Fig. 2*). The $[Cu(acac)_2]$-catalyzed reaction with **1a** is slightly more sensitive to polar effects and

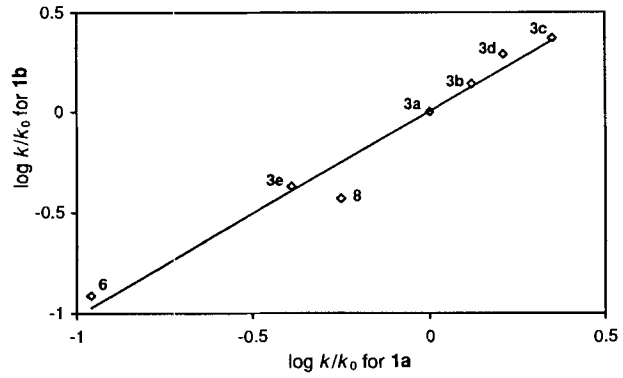


Fig. 1. *Plot of log* k_{rel} *for decomposition of* **1a** *with* $[Rh_2(OAc)_4]$ vs. *log* k_{rel} *for decomposition of* **1b** *with* $[Rh_2(OAc)_4]$

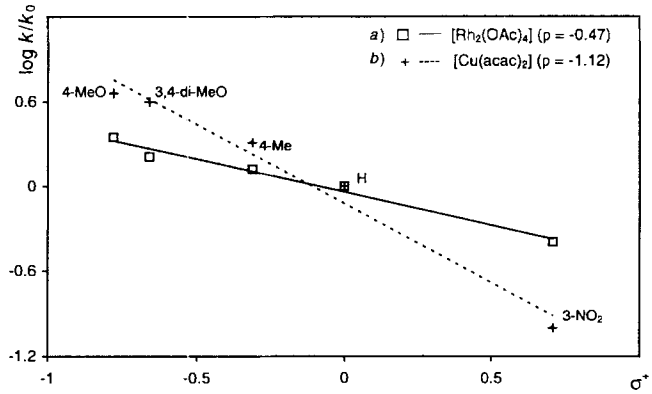


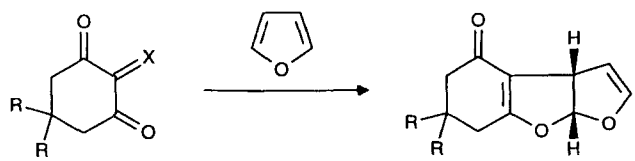
Fig. 2. a) Hammett *plot for log* k_{rel} *for reaction of* **1a** *with* $[Rh_2(OAc)_4]$ vs. σ^+. b) Hammett *plot for log* k *for reaction of* **1a** *with* $[Cu(acac)_2]$ vs. σ^+

exhibits a slope of −1.12 in the analogous plot. The results indicate that both reactions are characterized by development of partial positive charge on the styrene in the transition state, less for Rh^{II}, and more for Cu^{I}. Low sensitivity of Rh-catalyzed carbenoid reactions towards structural effects was observed in the past: *e.g.*, the relative reactivity of styrene and hex-1-ene towards $[Rh_2(AcO)_4]$-catalyzed cyclopropanation with ethyl diazoacetate was only 3.5 [26]. In addition, the stereoselectivity of these cyclopropanations was generally low. This has been attributed to an early transition state for carbene transfer. The low sensitivity of the Rh^{II}-catalyzed reaction of **1a** appears inconsistent with a dipolar mechanism for which more charge development would be expected. It is also inconsistent with a mechanism involving electron transfer from the metal to the olefin.

2. *1,3-Dipolar Cycloaddition to Furans.* Diazo compounds derived from cyclic 1,3-diketones such as **10a** and **11a** reacted in the presence of $[Rh_2(OAc)_4]$ with furan or 2,3-dihydrofurans to form *cis*-adducts **12** or the corresponding dihydro compounds which resulted from formal dipolar cycloaddition of an intermediate α-oxocarbene in

yields of *ca.* 50% [27]. The reaction proceeds propably *via* intermolecular cyclopropanation with the furan by an intermediate metallocarbene. The cyclopropane then undergoes sigmatropic rearrangement to **12**. With a chiral Rh^{II}-catalyst having 1,1′-binaphthyl-2,2′-diyl phosphate (bnp) ligands $[Rh_2\{(-)\text{-}(R)\text{-bnp}\}_4]$ [28], **12a** was formed in 44% yield and with an ee of 50%, for **12b** the yield was 50% and the ee 49% [29]. We repeated the synthesis of **12a** and **12b** according to the reported procedure. The ylides **10b** and **11b** were prepared from the appropriate diketones according to the method of *Schank* and *Lick* [30]. When **10b** was exposed to $[Rh_2(OAc)_4]$, adduct **12a** was produced, but the yield was only 37%. Reaction of **11b** afforded **12b** in 38% yield. With the chiral catalyst $[Rh_2\{(2S)\text{-mepy}\}_4]$ (mepy = methyl 2-oxopyrrolidine-5-carboxylate), almost no conversion of **10b** occurred (*ca.* 2% yield). No reaction, except partial decomposition occurred, when **10b** was exposed to $[Rh_2\{(R)\text{-bnp}\}_4]$.

Scheme 2

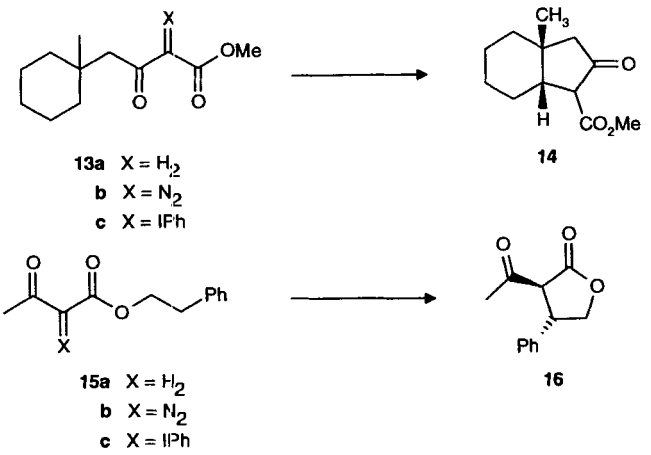


10a R = H, X = N_2
b R = H, X = IPh
11a R = Me, X = N_2
b R = Me, X = IPh

12a R = H
b R = Me

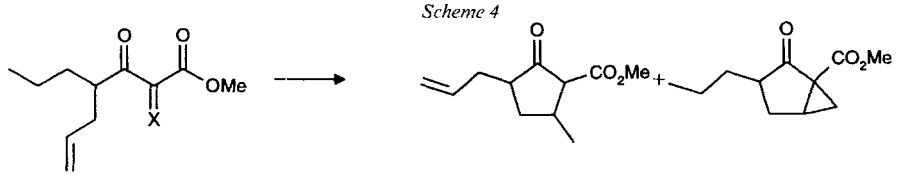
3. *Intramolecular CH Insertion.* Although cyclopropanations are reactions characteristic for carbenes, they are mechanistically sometimes ambiguous, since cyclopropane formation may proceed *via* stepwise pathways not involving carbenes. In this respect, CH insertions are more characteristic, and their occurrence provides strong evidence for carbenoid reactions. Rh^{II}-Catalyzed diazo decompositions led often to substantial amounts of insertion products when appropriate precursors were used [31]. The intramolecular insertion of diazo ester **13b** reportedly proceeded with $[Rh_2(OAc)_4]$ to the cyclic keto ester **14** in 95% yield [32]. The *cis*-isomer was formed exclusively, presumably owing to the presence of the angular Me group which hinders approach of the metallocarbene to that H-atom which leads to the *trans*-isomer [32]. Under comparable conditions, the ylide **13c** was cyclized in 56% yield. To our knowledge this is the first example of a CH insertion reported for a Rh^{II}-catalyzed decomposition of a iodonium ylide. Although formal insertion products were reported as by-products from decomposition reactions of iodonium ylides, [14] [33] their origin is unclear, since they could also be formed *via* ring opening of cyclopropanes. The yield of the reaction with **13c** was, however, lower than that achieved with **13b**. Nevertheless, the formation of **14** from both precursors suggests that in both reactions a carbene should be involved. This conclusion was corroborated by the observation of the *trans*-configurated insertion product **16** upon $[Rh_2(OAc)_4]$-catalyzed decomposition of **15b** (85% yield in refluxing benzene [34]; 41% in CH_2Cl_2, room temperature) and **15c** (28% in CH_2Cl_2, room temperature).

Scheme 3



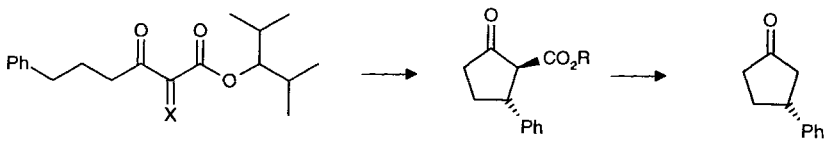
4. *Intramolecular Cyclopropanation* vs. *Insertion*. The selectivity of the Rh^{II}-mediated carbenoid reactions has been investigated in some detail. It depends markedly on the ligands [34–36]. The observation of identical selectivities for two different carbenoid pathways for decomposition of diazo compounds *vs.* ylides should provide strong evidence for identical reactive intermediates for a given catalyst. An appropriate system to study competing intramolecular cyclopropane formation and insertion was proposed by *Taber* and *Ruckle* [32]. Decomposition of the diazoacetoacetate **17b** with $[Rh_2(OAc)_4]$ afforded a mixture of insertion product **18** and cyclopropane **19** in a ratio of 29:71. The configuration of the products was not determined. Under our reaction conditions, **18** was present as a mixture of 3 stereoisomers (ratio 15:15:70) and **19** consisted of 2 stereoisomers (ratio 72:28). The spectral data of the major isomers were identical to those reported [32]. The **18**/**19** ratio was 27:73 with a total yield of 64%. The ylide **17c**, in turn, afforded with $[Rh_2(OAc)_4]$ a ratio of 23:77 (*ca.* 40%), when a freshly prepared sample of **17c** was used. However, the ratio changed to 10:90 with a sample of stored (−18°, 8 days) ylide **17c**. The change in product composition is best ascribed to partial spontaneous intramolecular cyclopropanation of **17c** during storage. Uncatalyzed intramolecular cyclopropanation of iodonium ylides has been reported previously [17]. The product ratio obtained in the Rh^{II}-catalyzed reaction from **17b** and **17c** was identical within experimental error and supports the hypothesis of identical reaction intermediates.

Scheme 4



5. *Asymmetric Induction in Intramolecular CH Insertion.* As a final test, we investigated the intramolecular CH insertion in the presence of a chiral catalyst. The compounds investigated so far were found unsuitable for this purpose, since the most efficient Rh^{II} catalyst for asymmetric insertion, $[Rh_2\{(2S)\text{-mepy}\}_4]$ [37] and similar carboxamido- and oxazolidinonato-rhodium(II) catalysts do not decompose diazo compounds having two electron-withdrawing substituents adjacent to the diazo function. On the other hand, iodonium ylides with only one such substituent are not isolable. We, therefore, used a system already described by *Ikegami* and coworkers [8] in which the diazo ketone **20b** underwent intramolecular CH insertion to **21a**, which was converted to ketone **22** for analysis *via* transesterification to **21b** followed by hydrolysis and decarboxylation. Thus with $[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$ (= dirhodium tetrakis(*N*-phthaloyl)-L-phenylalaninate), **21** was obtained in 86% yield as a single stereoisomer having *trans*-configuration, and with 76% ee (*R*) at C(3) (determined on (3*R*)-**22**) [8]. Under our reaction conditions, the yield with the diazo compound **20b** was 89% of **21a** having 69% ee (*R*) at C(3). The ylide **20c**, under the same reaction conditions, afforded **21a** in 78% yield with 67% ee (*R*) at C(3).

Scheme 5



20a X = H_2
b X = N_2
c X = IPh

21a R = $(i\text{-}Pr)_2CH$
b R = Me

22

Conclusion. – In all cases investigated we found identical product composition for Rh^{II}-catalyzed decomposition of diazo compounds and that of the corresponding iodonium ylides. Since the intermediacy of metallocarbenes is unequivocally established in the case of diazo decomposition, it follows, that metallocarbenes are also intermediates in the decomposition of iodonium ylides. This conclusion is further corroborated by a recent investigation which showed that iodonium ylides are possible alternatives for diazo compounds in the context of formation of carbonyl ylides [38]. It remains to be seen if the iodonium ylides will provide a practical advantage as diazo compound substitutes in asymmetric catalysis.

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Experimental Part

1. *General.* See [39].

2. *Intermolecular Cyclopropanation of Olefins.* 2.1. *Reactions of Iodonium Ylide* **1a**. 2.1.1. *Bis(methoxycarbonyl)(phenyliodonio)methanide* (**1a**) [30]. To KOH (10.0 g, 180 mmol) in MeOH (57 ml) at −10°, under N_2, was added dimethyl malonate (3.4 ml, 30 mmol) in MeOH (30 ml) at such a rate that the temp. remained below 0° (→white and sticky mixture). A soln. of (diacetoxyiodo)benzene (9.66 g, 30 mmol) in MeOH (230 ml) was added to the mixture at −10 to 0° (→transparent yellow soln.). After 4 h stirring between −10 and 0°, the soln. was poured into 250 ml of ice-water. The aq. phase was extracted with CH_2Cl_2 (5 × 75 ml) and the combined org. phase dried ($MgSO_4$) and evaporated: **1a** (5.6 g, 56%). The white solid was purified by dissolving in a minimum amount of $CHCl_3$ and precipitation with hexane. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.73 (*s*, 6 H); 7.39 (*tm*, *J* = 7, 2 H); 7.53 (*tm*, *J* = 7, 1 H); 7.73 (*dm*, *J* = 7, 2 H).

2.1.2. *Cyclopropa(e)nedicarboxylates* **4**, **7**, *and* **9**: *General Procedure.* To $[Rh_2(OAc)_4]$ (9.6 mg, 0.02 mmol) and the appropriate olefin (10 mmol) in CH_2Cl_2 (20 ml) was added ylide **1a** (334 mg, 1.0 mmol) in small portions at 25°. The mixture was stirred for 3–24 h, until all of **1a** was dissolved. The catalyst was removed by passing the soln. through a thin layer of silica gel, and the cyclopropane was purified by FC.

Dimethyl 2-Phenylcyclopropane-1,1-dicarboxylate (**4a**) [40]. Reaction time 3.2 h. FC (hexane/Et_2O 5:1) gave 144 mg (61%). Colorless oil. IR ($CHCl_3$): 3030*w*, 3010*w*, 2960*w*, 1725*s*, 1450*w*, 1440*m*, 1335*m*, 1275*m*, 1230*m*, 1220*w*, 1180*w*, 1140*m*, 700*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.74 (*dd*, *J* = 9.24, 5.2, 1 H); 2.19 (*dd*, *J* = 8.0, 5.2, 1 H); 3.22 (*dd*, *J* = 9.24, 8.0, 1 H); 3.35 (*s*, 3 H); 3.78 (*s*, 3 H); 7.13–7.33 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 19.0 (*t*); 32.4 (*d*); 37.1 (*s*); 52.1 (*q*); 52.7 (*q*); 127.4 (*d*); 128.0 (*d*); 128.3 (*d*); 134.5 (*s*); 166.9 (*s*); 170.1 (*s*). MS: 234 (0.4, M^+), 203 (0.7), 170 (17), 143 (13), 121 (64), 116 (20), 115 (100), 91 (15), 77 (14), 59 (21).

Dimethyl 2-(4-Methylphenyl)cyclopropane-1,1-dicarboxylate (**4b**) [40]. Reaction time 3.0 h. FC (hexane/Et_2O 5:1) gave 174 mg (69%). Colorless oil. IR ($CHCl_3$): 3028*w*, 3011*w*, 2954*w*, 1724*s*, 1519*w*, 1438*m*, 1373*w*, 1336*m*, 1283*m*, 1226*m*, 1196*w*, 1177*w*, 1133*m*, 909*w*, 830*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.72 (*dd*, *J* = 9.24, 5.1, 1 H); 2.18 (*dd*, *J* = 8.0, 5.1, 1 H); 2.29 (*s*, 3 H); 3.19 (*dd*, *J* = 9.24, 8.0, 1 H); 3.38 (*s*, 3 H); 3.78 (*s*, 3 H); 7.06 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 19.1 (*t*); 21.0 (*q*); 32.4 (*d*); 37.1 (*s*); 52.2 (*q*); 52.7 (*q*); 128.3 (*d*); 128.8 (*d*); 131.4 (*s*); 137.0 (*s*); 167.1 (*q*); 170.3 (*q*). MS: 248 (12, M^+), 217 (10), 216 (25), 189 (5), 188 (12), 185 (34), 184 (92), 135 (87), 129 (100), 128 (47), 115 (42), 91 (26), 77 (21), 59 (52).

Dimethyl 2-(4-Methoxyphenyl)cyclopropane-1,1-dicarboxylate (**4c**) [40]. Reaction time 3.0 h. FC (hexane/Et_2O 5:1) gave 139 mg (52%). Colorless oil. IR ($CHCl_3$): 3028*w*, 3010*w*, 2954*w*, 2839*w*, 1723*s*, 1613*w*, 1517*m*, 1438*m*, 1374*w*, 1336*w*, 1283*m*, 1261*m*, 1227*m*, 1197*w*, 1133*m*, 1094*w*, 1039*w*, 906*w*, 934*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.71 (*dd*, *J* = 9.3, 5.2, 2 H); 2.15 (*dd*, *J* = 8.0, 5.2, 1 H); 3.17 (*dd*, *J* = 9.3, 8.0, 1 H); 3.38 (*s*, 3 H); 3.76 (*s*, 3 H); 3.77 (*s*, 3 H); 6.79 (*dm*, *J* = 8.8, 2 H); 7.11 (*dm*, *J* = 8.8, 2 H). ^{13}C-NMR ($CDCl_3$): 19.1 (*t*); 32.1 (*d*); 37.0 (*s*); 52.1 (*q*); 52.6 (*q*); 55.0 (*q*); 113.5 (*d*); 126.2 (*s*); 129.5 (*d*); 158.8 (*s*); 167.0 (*s*); 170.2 (*s*). MS: 264 (16, M^+), 233 (8), 232 (21), 205 (13), 204 (22), 201 (26), 200 (67), 173 (17), 157 (11), 151 (56), 146 (20), 145 (100), 131 (14), 115 (17), 103 (30), 102 (24), 91 (23), 77 (38), 65 (16), 63 (15), 59 (49), 51 (29).

Dimethyl 2-(3,4-Dimethoxyphenyl)cyclopropane-1,1-dicarboxylate (**4d**) [40]. Reaction time 3.2 h. FC (hexane/Et_2O 1:1) gave 211 mg (74%). Yellowish oil. IR ($CHCl_3$): 3026*m*, 2955*w*, 2840*w*, 1724*s*, 1591*w*, 1519*m*, 1465*m*, 1438*m*, 1254*m*, 1142*m*, 1028*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.73 (*dd*, *J* = 9.2, 5.1, 1 H); 2.16 (*dd*, *J* = 8.1, 5.1, 1 H); 3.19 (*dd*, *J* = 9.2, 8.1, 1 H); 3.41 (*s*, 3 H); 3.79 (*s*, 3 H); 3.84 (*s*, 3 H); 3.85 (*s*, 3 H); 6.70–6.80 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$): 19.3 (*t*); 32.4 (*d*); 37.0 (*s*); 52.2 (*q*); 52.7 (*q*); 55.68 (*q*); 55.72 (*q*); 110.6 (*d*); 111.7 (*d*); 120.3 (*d*); 126.9 (*s*); 148.3 (*s*); 148.4 (*s*); 167.1 (*s*); 170.2 (*s*). MS: 295 (5.3, $[M + 1]^+$), 294 (26, M^+), 263 (5), 262 (5), 236 (5), 235 (33), 234 (19), 231 (17), 230 (33), 203 (11), 181 (57), 176 (13), 175 (62), 173 (12), 161 (11), 160 (15), 145 (11), 133 (12), 131 (19), 115 (17), 89 (20), 77 (24), 59 (100). HR-MS: 294.1088 ($C_{15}H_{18}O_6^+$; calc. 294.1103).

Dimethyl 2-(3-Nitrophenyl)cyclopropane-1,1-dicarboxylate (**4e**). Reaction time 3.0 h. FC (hexane/Et_2O 2:1) gave 165 mg (58%). Pale-yellow oil. IR ($CHCl_3$): 3028*w*, 3007*w*, 2955*w*, 2849*w*, 1728*s*, 1533*m*, 1438*m*, 1352*m*, 1289*m*, 1225*m*, 1134*m*, 991*w*, 898*w*. 809*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.82 (*dd*, *J* = 9.2, 5.4, 1 H); 2.23 (*dd*, *J* = 8.0, 5.4, 1 H); 3.18 (*dd*, *J* = 9.2, 8.0, 1 H); 3.41 (*s*, 3 H); 3.81 (*s*, 3 H); 7.40–7.58 (*m*, 2 H); 8.04–8.15 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 19.0 (*t*); 31.2 (*d*); 37.1 (*s*); 52.4 (*q*); 52.9 (*q*); 122.4 (*d*); 123.4 (*d*); 129.1 (*d*); 134.6 (*d*); 137.0 (*s*); 148.0 (*s*); 166.4 (*s*); 169.4 (*s*). MS: 279 (8.6, M^+), 248 (11), 247 (26), 216 (15), 187 (10), 166 (89), 150 (52), 145 (24), 144 (11), 129 (14), 128 (10), 120 (17), 116 (15), 115 (72), 114 (39), 113 (20), 103 (19), 102 (20), 89 (27), 77 (27), 65 (16), 63 (37), 59 (100), 51 (22). HR-MS: 279.0788 ($C_{13}H_{13}NO_6^+$; calc. 279.0743).

Dimethyl 2-(Phenylmethyl)cyclopropane-1,1-dicarboxylate (**7**). From allylbenzene (**6**). Reaction time 3.0 h. FC (hexane/Et_2O 5:1) gave 131 mg (53%). Colorless oil. IR ($CHCl_3$): 3029*m*, 2954*w*, 2848*w*, 1724*s*, 1495*w*, 1438*m*, 1337*m*, 1279*m*, 1224*m*, 1139*m*, 887*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.50 (*dd*, *J* = 9.2, 4.8, 1 H); 1.59 (*dd*, *J* = 7.7, 4.8, 1 H); 2.24 (*m*, 1 H); 2.49 (*dd*, *J* = 14.7, 8.5, 1 H); 2.86 (*dd*, *J* = 14.7, 5.9, 1 H); 3.72 (*s*, 3 H); 3.74 (*s*, 3 H);

7.15–7.35 (*m*, 5 H). ^{13}C-NMR ($CDCl_3$): 21.4 (*t*); 28.9 (*d*); 34.0 (*s*); 34.3 (*t*); 52.5 (*q*); 52.6 (*q*); 52.6 (*q*); 126.4 (*d*); 128.2 (*d*); 128.3 (*d*); 139.5 (*s*); 168.6 (*s*); 170.5 (*s*). MS: 248 (1.5, M^+), 217 (7), 216 (11), 188 (19), 184 (58), 156 (22), 129 (33), 128 (52), 113 (25), 104 (100), 91 (55), 65 (21), 59 (27). HR-MS: 248.1043 ($C_{14}H_{16}O_4^+$; calc. 248.1049).

Dimethyl 2-Phenylcycloprop-2-ene-1,1-dicarboxylate (**9**) [41]. From phenylacetylene (**8**). Reaction time 3.0 h. FC (hexane/Et_2O 4:1) gave 87 mg (37%). Orange solid. M.p. 67–70°. IR ($CHCl_3$): 3160*w*, 3026*m*, 2954*w*, 2846*w*, 1732*s*, 1436*m*, 1290*s*, 1068*m*, 987*w*, 956*w*, 909*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.73 (*s*, 6 H); 6.90 (*s*, 1 H); 7.43 (*m*, 3 H); 7.62 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 32.8 (*s*); 52.3 (*q*); 95.2 (*d*); 112.2 (*s*); 123.9 (*s*); 128.9 (*d*); 130.3 (*d*); 130.5 (*d*); 171.1 (*s*). MS: 232 (19.6 M^+), 217 (100), 173 (66), 145 (79), 121 (70), 115 (54), 114 (37), 113 (36), 105 (99), 102 (55), 91 (35), 77 (60), 59 (52), 51 (47). HR-MS: 232.0723 ($C_{13}H_{12}O_4^+$; calc. 232.0736).

2.2. *Competition Experiments.* To a soln. of catalyst [$Rh_2(OAc)_4$] or [Cu(acac)$_2$] (0.02 mmol) in CH_2Cl_2 (20.0 ml) was added olefin A (5.0 mmol) and olefin B (5.0 mmol). Ylide **1a** was added in small portions within 1 min. The mixture was stirred for 3 h at r.t. The catalyst was removed by filtration through a thin layer of silica gel. Products were identified by NMR and the product ratios determined by GC (methylsilicone column). The data in *Table 1* represent average values from several runs with a reproducibility of 1%.

For the addition of dimethyl diazomalonate (**1b**), the amount of CH_2Cl_2 was 16.0 ml, and **1b** was added in CH_2Cl_2 (4.0 ml) within 30 s.

3. *Cycloaddition of Iodonium Ylides to Furan.* 3.1. cis-*3a,6,7,8a-Tetrahydrofuro[2,3-b]benzofuran-4(5H)-one* (**12a**) [27]. To [$Rh_2(OAc)_4 \cdot 2H_2O$] (9.56 mg, 0.020 mmol) in furan (20 ml) was added iodonium ylide **10b** [30] (317 mg, 1.01 mmol) in small portions in 1 min. The suspensions was stirred for 24 h at r.t. The catalyst was removed by filtration through a plug of silica gel, and **12a** (68 mg, 37%) was purified by FC (hexane/Et_2O 1:1). M.p. 86–87°. IR ($CHCl_3$): 3010*w*, 1641*s*, 1455*w*, 1402*m*, 1224*m*, 1125*w*, 1046*w*, 1017*w*, 978*m*, 926*w*, 842*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.04 (*m*, 2 H); 2.34 (*m*, 2 H); 2.51 (*m*, 2 H); 4.30 (*m*, 1 H); 5.38 (*t*, J = 2.6, 1 H); 6.39 (*dd*, J = 2.8, 2.1, 1 H); 6.59 (*d*, J = 7.54, 1 H). ^{13}C-NMR ($CDCl_3$): 21.4 (*t*); 23.5 (*t*); 36.4 (*t*); 47.8 (*d*); 103.4 (*d*); 112.4 (*d*); 116.1 (*s*); 144.1 (*d*); 175.9 (*s*); 194.6 (*s*). MS: 178 (35, M^+), 150 (56), 122 (100), 108 (11), 94 (45), 79 (13), 77 (13), 66 (39), 65 (20), 52 (27). HR-MS: 178.0637 ($C_{10}H_{10}O_3^+$; calc. 178.0630).

3.2. cis-*3a,6,7,8a-Tetrahydro-6,6-dimethylfuro[2,3-b]benzofuran-4(5H)-one* (**12b**). The same procedure, starting wiht ylide **11b** [30] (347 mg, 1.01 mmol) afforded **12b** (63 mg, 30%), after FC (hexane/Et_2O 1:1). Colorless oil. IR ($CHCl_3$): 3009*w*, 2964*w*, 2872*w*, 1640*s*, 1402*m*, 1357*w*, 1280*w*, 1229*w*, 1168*w*, 1146*w*, 1126*w*, 1108*w*, 1038*w*, 979*w*, 924*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.05 (*s*, 3 H); 1.09 (*s*, 3 H); 2.20 (*d*, J = 2.1, 2 H); 2.34 (*d*, J = 1.6, 2 H); 4.29 (*m*, 1 H); 5.37 (*t*, J = 2.6, 1 H); 6.37 (*dd*, J = 2.8, 2.1, 1 H); 6.59 (*d*, J = 7.5, 1 H). ^{13}C-NMR ($CDCl_3$): 28.3 (*q*); 28.6 (*q*); 34.0 (*s*); 37.3 (*t*); 47.7 (*d*); 50.9 (*t*); 103.4 (*d*); 112.7 (*d*); 114.7 (*s*); 144.2 (*d*); 174.8 (*s*); 193.9 (*s*). MS: 207 (68, $[M + 1]^+$), 206 (17, M^+), 178 (24), 122 (100), 94 (38), 66 (37), 65 (28), 55 (33), 53 (30), 52 (32), 51 (24). HR-MS: 206.0942 ($C_{13}H_{12}O_4^+$; calc. 206.0943).

4. *Intramolecular Insertions.* 4.1. *Insertion of Iodonium Ylide* **13c**. *1-(Methoxycarbonyl)-3-(1-methylcyclohexyl)-2-oxo-1-(phenyliodonio)propan-1-ide* (**13c**). To **13a** [32] (2.12 g, 10.0 mmol) in cooled (−15°) MeOH (10 ml) were added below −10°, successively KOH (3.33 g, 59 mmol) in MeOH (25 ml) and a suspension of $PhI(OAc)_2$ (3.23 g, 10.0 mmol) in MeOH. The mixture was stirred for 2 h between −10 and 0° and then poured into 100 ml of ice-water. After extraction with CH_2Cl_2 (3 × 30 ml), the org. layer was dried ($MgSO_4$) and evaporated. The crude ylide **13c** (3.98 g), a yellow oil, could not be further purified. Purity (NMR) *ca.* 90%. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.99 (*s*, 3 H); 1.2–1.6 (*m*, 10 H); 3.04 (*s*, 2 H); 3.61 (*s*, 3 H); 7.36 (*m*, 2 H); 7.50 (*m*, 1 H); 7.76 (*m*, 2 H).

Methyl 2,3,3aα4,5,6,7,7aα-Octahydro-3aα-methyl-2-oxo-1H-indene-1-carboxylate (**14**) [32]. To [$Rh_2(OAc)_4 \cdot 2H_2O$] (9.73 mg, 0.02 mmol) in CH_2Cl_2 (15 ml) was added a soln. of **13c** (439 mg, 1.06 mmol) in CH_2Cl_2 (10 ml) in 2 min. The mixture was stirred for 3 h. The catalyst was removed by filtration through a plug of silica gel. Purification of the crude product by FC (hexane/Et_2O 15:1) afforded **14** (184 mg, 82%) which was not further purified. (The analogous reaction of diazo compounds **13b** afforded **14** in 95% yield.) IR ($CHCl_3$): 3027*w*, 2934*m*, 2862*w*, 1753*s*, 1725*s*, 1436*w*, 1306*w*, 1277*w*, 1243*w*, 1166*w*, 1118*w*, 1033*w*, 981*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.00–2.55 (*m*, 11 H); 1.18 (*s*, 3 H); 3.32 (*d*, J = 12.1, 1 H); 3.69 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 19.7 (*t*); 21.5 (*t*); 22.5 (*t*); 23.9 (*q*); 33.7 (*t*); 35.8 (*s*); 45.2 (*d*); 52.3 (*q*); 55.1 (*t*); 56.5 (*d*); 169.8 (*s*); 210.7 (*s*). MS: 210 (11, M^+), 195 (10), 182 (20), 179 (20), 167 (9), 163 (11), 154 (11), 151 (22), 150 (15), 136 (14), 135 (14), 133 (7), 128 (9), 123 (7), 122 (17), 121 (12), 113 (89), 111 (7), 109 (30), 108 (70), 107 (13), 100 (15), 96 (19), 95 (100), 81 (35), 67 (45), 55 (49).

4.2. *Insertion of Iodonium Ylide* **15c**. *2-Oxo-1-[(2-phenylethoxy)carbonyl]-1-(phenyliodonio)propan-1-ide* (**15c**). As described for **13c**, with **15a** [34] (2.07 g, 10.0 mmol), MeOH (10 ml, at −20°), KOH (3.26 g, 58 mmol), MeOH (25 ml), $PhI(OAc)_2$ (3.22 g, 10.0 mmol), and MeOH (25 ml). Addition below 0°, then 1 h at −10 to 0°. Workup with 80 ml of ice-water and CH_2Cl_2 (4 × 25 ml). Crude **15c** (3.95 g, 97%; *ca.* 75% pure) was isolated as

yellow, transparent oil which solidified at −18° and was used without further purification. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.53 (*s*, 3 H); 2.91 (*t*, *J* = 6.7, 2 H); 4.32 (*t*, *J* = 6.7, 2 H); 7.13–7.62 (*m*, 10 H).

trans-*3-Acetyl-4,5-dihydro-4-phenylfuran-2-(3*H*)-one* (**16**) [34]. As described for **14**, with $[Rh_2(OAc)_4 \cdot 2H_2O]$ (4.40 mg, 0.01 mmol), CH_2Cl_2 (10.0 ml), **15c** (409 mg, 1.0 mmol), and CH_2Cl_2 (4.0 ml). Addition in 1 min, then 20 h at r.t. FC (hexane/Et_2O 5:1) yielded 58 mg (28%) of **16**. IR ($CHCl_3$): 3030*w*, 1773*s*, 1723*s*, 1496*w*, 1455*w*, 1360*w*, 1225*w*, 1149*m*, 1022*w*, 700*m*. ^{1}H-NMR ($CDCl_3$): 2.43 (*s*, 3 H); 3.80 (*d*, *J* = 8.3, 1 H); 4.18–4.50 (*m*, 2 H); 4.58–4.78 (*m*, 1 H); 7.12–7.46 (*m*, 5 H).

4.3. *Insertion of Iodonium Ylide* **17c**. *1-(Methoxycarbonyl)-2-oxo-1-(phenyliodonio)-3-propylhex-5-en-1-ide* (**17c**). As described for **13c**, with **17a** [34] (1.98 g, 10.0 mmol), MeOH (10 ml; at −15°), KOH (3.35 g, 60 mmol) in MeOH (25 ml), $PhI(OAc)_2$ (3.22 g, 10.0 mmol) in MeOH (25 ml). Addition below −10°, then 2 h at −5 to 0°. Workup with 100 ml of ice-water and CH_2Cl_2 (4 × 25 ml). The crude **17c** (3.56 g; 50–80% pure by NMR), an orange-brown transparent oil, was used without further purification. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.84 (*m*, 3 H); 1.15–1.87 (*m*, 4 H); 1.95–2.60 (*m*, 3 H); 3.63 (*s*, 3 H); 4.82–5.14 (*m*, 2 H); 5.60–5.89 (*m*, 1 H); 7.34 (*m*, 2 H); 7.50 (*m*, 1 H); 7.73 (*m*, 2 H).

Decomposition of **17c** *with [$Rh_2(OAc)_4$]*. As described for **14**, with $[Rh_2(OAc)_4 \cdot H_2O]$ (9.19 mg, 0.02 mmol), CH_2Cl_2 (15 ml), freshly prepared **17c** (406 mg, 1.03 mmol), and CH_2Cl_2 (5.0 ml). Addition in 1 min, then 3 h, at r.t. The crude product (*ca.* 40%) was subjected to GC analysis (cross-linked methylsilicon gum): **18**/**19** 23:77 (**18**: 3 stereoisomers, ratio 15:15:70; **19**: 2 stereoisomers, ratio 72:28), identified by independent synthesis from diazo compound **17b** and by comparison with reported spectral data [32]. A sample of **17c** stored at −18° for several days yielded **18**/**19** 10:90.

Decomposition of diazo compound **17b** with $[Rh_2(OAc)_4]$ afforded **18**/**19** 27:73 (50% yield).

Methyl 5-Methyl-2-oxo-3-(prop-2-enyl)cyclopentanecarboxylate (**18**; major isomer) [32]. IR ($CHCl_3$): 3020*w*, 2958*m*, 2921*w*, 2867*w*, 1749*s*, 1726*s*, 1460*w*, 1437*m*, 1324*m*, 1288*w*, 1215*m*, 1192*w*, 1123*m*, 995*w*, 914*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.16 (*d*, *J* = 6.3, 3 H); 1.92–2.65 (*m*, 6 H); 2.72 (*d*, *J* = 11.6, 1 H); 3.75 (*s*, 3 H); 4.94–5.13 (*m*, 2 H); 5.60–5.86 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 19.2 (*q*); 33.7 (*t*); 34.1 (*t*); 35.6 (*d*); 50.1 (*d*); 52.4 (*q*); 63.0 (*d*); 116.9 (*t*); 135.2 (*d*); 169.5 (*s*); 211.8 (*s*). MS: 196 (27, M^+), 181 (19), 178 (32), 165 (38), 164 (47), 149 (18), 136 (42), 123 (28), 119 (35), 101 (41), 69 (100). HR-MS: 196.1097 ($C_{11}H_{16}O_3^+$; calc. 196.1099).

Methyl 2-Oxo-3-propylbicyclo[3.1.0]hexane-1-carboxylate (**19**; major isomer) [32]. IR ($CHCl_3$): 3025*m*, 2958*m*, 2874*m*, 1753*s*, 1729*s*, 1439*m*, 1377*m*, 1326*m*, 1266*m*, 1203*m*, 1174*m*, 1051*w*, 943*w*, 883*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.81–0.95 (*m*, 3 H); 1.07–2.58 (*m*, 10 H); 3.74 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 13.8 (*q*); 20.2 (*t*); 23.1 (*t*); 28.4 (*t*); 31.3 (*d*); 32.0 (*t*); 37.6 (*s*); 42.7 (*d*); 52.1 (*q*); 168.9 (*s*); 207.9 (*s*). MS: 196 (5, M^+), 165 (23), 154 (96), 153 (50), 122 (100), 113 (28). HR-MS: 196.1093 ($C_{11}H_{16}O_3^+$; calc. 196.1099).

4.4. *Insertion of Iodonium Ylide* **20c**. *1-{[2-Methyl-1-(1-methylethyl)propoxy]carbonyl}-2-oxo-5-phenyl-1-(phenyliodonio)pentan-1-ide* (**20c**). As described for **13c**, with **20a** [8] (3.04 g, 10.0 mmol), MeOH (10 ml; at −20°), KOH (3.30 g, 59 mmol) MeOH (10 ml), $PhI(OAc)_2$ (3.23 g, 10.0 mmol), and MeOH (25 ml). Addition below −10°, then 1.25 h at −10 to 0°. Workup with ice-water (80 ml) and CH_2Cl_2 (3 × 30 ml): crude **20c** (5.04 g, 99%) as yellow semi-solid of *ca.* 90% purity (NMR). ^{1}H-NMR (200 MHz, $CDCl_3$): 0.78 (*d*, *J* = 6.7, 6 H); 0.83 (*d*, *J* = 6.8, 6 H); 1.68–2.10 (*m*, 4 H); 2.66 (*m*, 2 H); 3.09 (*m*, 2 H); 4.57 (*t*, *J* = 6.2, 1 H); 7.03–7.77 (*m*, 10 H).

2-Methyl-1-(1-methylethyl)propyl 2-Oxo-5-phenylcyclopentanecarboxylate (**21a**) [8]. To dirhodium(II) tetrakis[*N*-phthaloyl-L-phenylalaninate] ($[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$) [8] (13.44 mg, 0.01 mmol) in CH_2Cl_2 at r.t. was added **20c** (504 mg, 1.00 mol) in CH_2Cl_2 (5.0 ml) in 1 min. The mixture was stirred for 1 h at r.t. Evaporation and FC (hexane/Et_2O 10:1) gave **21a** (236 mg, 78%). Colorless solid. ^{1}H-NMR: 0.64 (*d*, *J* = 6.7, 3 H); 0.69 (*d*, *J* = 6.8, 3 H); 0.85 (*d*, *J* = 6.7, 6 H); 1.78–2.12 (*m*, 3 H); 2.35–2.80 (*m*, 3 H); 3.39 (*d*, *J* = 12.0, 1 H); 3.79 (*dt*, *J* = 12.1, 6, 1 H); 4.57 (*t*, *J* = 6.2, 1 H); 7.10–7.40 (*m*, 5 H).

Reaction of diazo ester **20b** with $[Rh_2\{(-)\text{-}(S)\text{-ptpa}\}_4]$ afforded **21a** in 93% yield ([8]: 86%).

Methyl 2-Oxo-5-phenylcyclopentanecarboxylate (**21b**). Ester **21a** (236 mg, 0.78 mmol) was heated in MeOH (45 ml) in a *Carius* tube at 100° for 20.5 h with stirring. Evaporation and FC (hexane/Et_2O 4:1) gave **21b** (148 mg, 87%). Colorless solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.88–2.19 (*m*, 1 H); 2.35–2.70 (*m*, 3 H); 3.35 (*d*, *J* = 11.6, 1 H); 3.70 (*s*, 3 H); 3.80 (*dt*, *J* = 12.1, 6, 1 H); 7.10–7.40 (*m*, 5 H).

3-Phenylcyclopentanone (**22**). Keto ester **21b** (148 mg, 0.68 mmol) was heated in H_2O (3.6 ml) and DMSO (0.40 ml) at 120° for 13 h. After cooling, the mixture was extracted (hexane/CH_2Cl_2 5:1, 3 × 20 ml) and the org. layer washed with H_2O (3 × 15 ml), dried ($MgSO_4$), and evaporated. FC (hexane/Et_2O 5:1) gave **22** (99 mg, 91%). Colorless oil. Enantiomeric excess (ee) 67%, determined by GC (*Macherey-Nagel Lipodex-B* column, 150°). IR ($CHCl_3$): 3013*m*, 2970*w*, 1738*vs*, 1495*m*, 1453*w*, 1404*m*, 1233*w*, 1136*w*, 700*m*, 666*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.87–2.11 (*m*, 1 H); 2.18–2.55 (*m*, 4 H); 2.66 (*dd*, *J* = 18, 8, 1 H); 3.30–3.52 (*m*, 1 H); 7.18–7.42 (*m*, 5 H). ^{13}C-NMR

($CDCl_3$): 31.0 (*t*); 38.6 (*t*); 42.0 (*d*); 45.6 (*t*); 126.6 (*d*); 128.5 (*d*); 143.0 (*s*); 217.7 (*s*). MS: 160 (91, M^+), 131 (13), 117 (41), 104 (100), 91 (17), 78 (15), 77 (14). HR-MS: 160.0887 ($C_{11}H_{12}O^+$; calc. 160.0888).

The sequence starting with diazo compound **20b** afforded **22** having $[\alpha]_D^{21.5} = +68.6$ ($c = 2.45$, $CHCl_3$) for ee 65% ([8]: $[\alpha]_D^{22} = +69.4$ ($c = 1.42$, $CHCl_3$) for (*R*)-**22**, with ee 76%).

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