Functionalised *cis*-Alkenes from the Stereoselective Decomposition of Diazo Compounds, Catalysed by [RuCl(η^5-C_5H_5)(PPh_3)$_2$]

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A catalytic amount of [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) (0.1 mol-%) at 60 °C stereoselectively decomposes α-diazo carbonyl compounds N_2CHCOR [R = EtO, Me, Et, *n*Pr, *i*Pr, Ph, $(CH_2)_{10}Me$, and $(CH_2)_{14}Me$] affording quantitatively RCOCH=CHCOR carbene dimers [R = EtO (**10**), Me (**11**), Et (**12**), *n*Pr (**13**), *i*Pr (**14**), Ph (**15**), $(CH_2)_{10}Me$ (**16**), and $(CH_2)_{14}Me$ (**17**)]. The *cis* isomer is formed in 95–99% purity, depending on the R group. Under the same experimental conditions, N_2CHCOR^1 and N_2CHCOR^2 react in equimolar amounts to give mixtures of unsymmetrical *cis*-$R^1COCH{=}CHCOR^2$ (**18**–**32**), and symmetrical *cis*-$R^1COCH{=}CHCOR^1$ and *cis*-$R^2COCH{=}CHCOR^2$ alkenes. The unsymmetrical *cis*-alkenes **23**–**32** are formed in about 50% yield from the reaction between two α-diazo ketones. The yield of the *cis*-$R^1COCH{=}CHCOR^2$ compounds **18**–**22** increases to ca. 60% when a mixture of α-diazo ketone and $N_2CHCOOEt$ is catalytically decomposed. Higher conversions into the unsymmetrical products have been obtained by treating N_2CHCOR and $N_2CHSiMe_3$, from which *cis*-$RCOCH{=}CHSiMe_3$ derivatives **34**–**41** are formed in 83–91% yield. The catalytic decomposition of α,ω-bis(diazo) ketones $N_2CHCO(CH_2)_nCOCHN_2$ (n = 4, 8, or 10) has also been investigated, and found to afford cyclic *cis*-alkenes arising from both intra- [n = 4 (**45**), 8 (**46**), and 10 (**47**)] and intermolecular carbene-carbene coupling processes.

Introduction

α-Diazo carbonyl compounds are capable of undergoing several metal-catalysed processes that are useful in organic synthesis. The majority of the work reported on this area has dealt with alkene cyclopropanation and carbene insertion into C−H or polar X−H bonds (X = O, N, or S).[1−3] Also, the carbene dimerisation process has been investigated, but it has received only minor interest. In fact, it is generally considered as an unwanted side-reaction in other processes involving the decomposition of diazo compounds.[3] Nevertheless, the carbene-carbene coupling reaction may be useful in producing suitably designed functionalised alkenes, if carried out with efficient stereocontrol of the process. Indeed, since the pioneering studies of Grundmann,[4] generally unsatisfactory results have been obtained with diazo ketones as starting material, both for inter- and intramolecular versions of the carbene coupling process.[5−8] More recently, good yields and high *cis*/*trans* selectivity have been obtained by using group-8 metal-porphyrin complexes such as [Ru(TMP)][9] and [Os(TTP)]$_2$,[10] which decompose ethyl diazoacetate (EDA) giving diethyl maleate in 94 and 96% yield, respectively. However, the highest stereoselectivity in diethyl maleate formation from EDA decomposition (99%) has been obtained by us using the commercially available catalyst [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**).[11,12] Furthermore, preliminary studies have shown the ability of complex **1** to promote the conversion of α-diazo ketones into *cis*-enediones.[11]

cis-Enediones are classically prepared by oxidative ring opening of 2,5-disubstituted furans,[13] though high yield and stereoselectivity have been obtained only in few cases. Furthermore, the difficulty in obtaining the desired 2,5-disubstituted furan precursors strongly limits this synthetic route. In this context, we present here the results of an extensive investigation into the carbene dimerisation process promoted by **1**. Indeed, this method constitutes a suitable entry to a variety of both symmetrical and unsymmetrical functionalised *cis*-alkenes. Of particular interest among these are *cis*-enediones, that can be used as starting materials in the synthesis of heterocyclic compounds,[14] flavouring agents for foods,[15] and substances useful as insecticides and antineoplastics.[16]

Results and Discussion

Symmetrical *cis*-Enediones

In chloroform solution at 60 °C, complex **1** catalytically (0.1 mol-%) decomposes N_2CHCOR compounds [R = EtO (**2**), Me (**3**), Et (**4**), *n*Pr (**5**), *i*Pr (**6**), Ph (**7**), $(CH_2)_{10}Me$ (**8**), and $(CH_2)_{14}Me$ (**9**)] to afford the corresponding RCOCH=CHCOR carbene dimers [R = EtO (**10**), Me (**11**), Et (**12**), *n*Pr (**13**), *i*Pr (**14**), Ph (**15**), $(CH_2)_{10}Me$ (**16**), and $(CH_2)_{14}Me$ (**17**)] (Scheme 1). ^1H NMR spectra taken of the reaction mixtures confirm the quantitative conversion of the starting material into *cis*/*trans*-enediones, the *cis* isomer being formed in 95−99% yield. All compounds were isolated as pure liquid (**10**−**14**) or solid (**15**−**17**) products in 70−85% yield.

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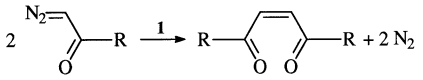
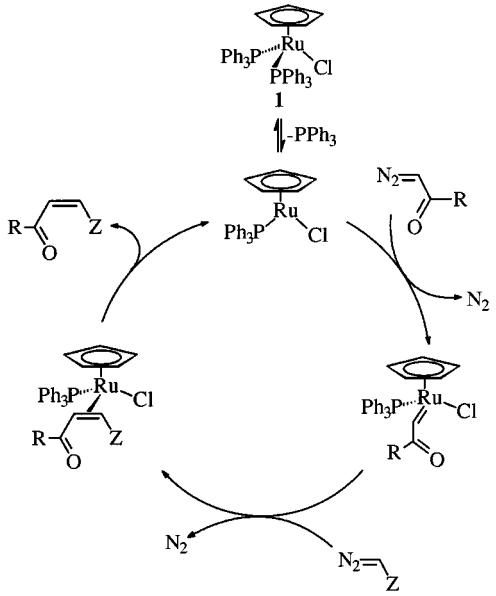


Scheme 1

We have studied, in detail, the mechanism of diethylmaleate formation from EDA decomposition catalysed by **1**. Though not directly detected in the reaction mixtures, the carbene complex [RuCl(η^5-C_5H_5)(=$CHCO_2Et$)(PPh_3)] has been proved to be the key-species in the catalytic cycle. Such a compound is formed by EDA attack on the 16-electron complex [RuCl(η^5-C_5H_5)(PPh_3)], generated from **1** upon thermally induced PPh_3 dissociation.[12] Most likely, an analogous mechanism and catalytic cycle can also account for the formation of *cis*-enediones **10**−**17** from precursors **3**−**9** (Scheme 2, Z = RCO).

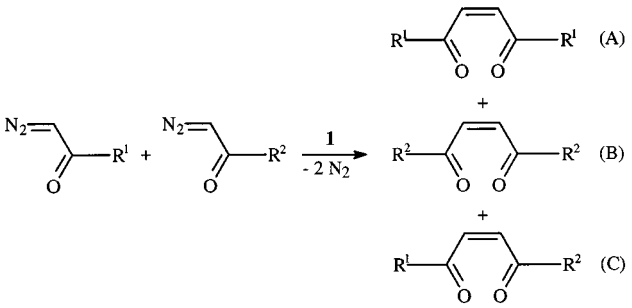


Scheme 2. Formation of *cis*-alkenes at the metal centre

Substrates **2**−**9**, that easily undergo decomposition, affording diethyl maleate and *cis*-enediones, possess the N_2CHCO moiety. In order to further explore the potential of **1** in the carbene dimerisation process, compounds with an R group on the α-carbon atom have also been tested. However, both ethyl diazoacetoacetate and $N_2C(CH_2CHMe_2)COOMe$ (methyl 2-diazo-4-methylpentanoate), chosen as model compounds, did not decompose in the presence of a catalytic amount of **1** at 60 °C in chloroform, and no evident evolution of N_2 was observed up to 90 °C in toluene solution. Although it is well known that diazoacetoacetates require higher temperatures for reactions with metal complexes than do diazoacetates,[3] the lack of catalytic activity shown by **1** with both substrates is still not fully understood, and studies directed at throwing light on this aspect are in progress.

Unsymmetrical *cis*-Alkenes

Unsymmetrical *cis*-alkenes can be obtained by "cross-coupling" of carbenes arising from two different N_2CHCOR compounds (Scheme 3). Reactions between couples of precursors **2**−**7** in a 1:1 molar ratio have been performed in $CDCl_3$ solution, and the resulting mixtures have been characterized by NMR and GC/MS. ^1H and $^{13}C\{^1H\}$ NMR data of the unsymmetrical products **18**−**32** are reported in Table 1 and 2, respectively. The spectra indicate that the reaction is stereoselective, as *trans*-enediones are generally formed below 5%. None of alkenes **18**−**32** have been isolated, but the novel compound ethyl (*Z*)-4-oxo-2-nonadecenoate (**33**) has been prepared in 49% yield by treating EDA with 1-diazo-2-heptadecanone.



Scheme 3

Symmetrical (A, B) and unsymmetrical (C) *cis*-enediones (see Scheme 3) are formed in molar ratios close to the expected 1:1:2 when the two substrates have similar electronic properties (Table 1, compounds **23**−**32**). On the other hand, in the reaction between EDA and α-diazo ketones (Table 1, compounds **18**−**22**) the unsymmetrical *cis*-alkene is formed in more-than-statistic yield[17] (about 60%). Thus, for example, in the reaction between EDA and $N_2CHCOMe$, diethyl maleate (**10**, ca. 21%), *cis*-3-hexen-2,5-dione (**11**, ca. 21%), *cis*-EtOCOCH=CHCOMe (**18**, ca. 58%), along with trace amounts of *trans* derivatives are obtained. The relative amounts of the products have been calculated by integration of the ^1H NMR spectrum. This result probably arises from different reactions rates of the two diazo compounds with **1**, and/or of the carbene intermediates (Scheme 2) with the diazo compounds. It should be noted, that as regards the rate of decomposition of EDA, N_2CHCO*n*Pr, and $N_2CHCOPh$ on **1**, the order is EDA >> N_2CHCO*n*Pr ≈ $N_2CHCOPh$.[18]

The formation of the unsymmetrical *cis*-alkenes becomes prevalent in the reaction between α-diazo carbonyl compounds and (trimethylsilyl)diazomethane. Thus, EDA and $N_2CHSiMe_3$ afford a mixture of **10** (5%), *cis*-Me_3SiCH=$CHSiMe_3$ (2.5%), *trans*-Me_3SiCH=$CHSiMe_3$ (2.5%), and *cis*-EtOCOCH=$CHSiMe_3$ (**34**, 90%). The combination of $N_2CHSiMe_3$ and α-diazo ketones also results in very high yields (> 83%) of *cis*-RCOCH=$CHSiMe_3$ compounds **35**−**41** (Table 3). On the basis of the catalytic cycle proposed for the carbene-carbene coupling reaction, this implies that EDA, or the α-diazo ketone, is the substrate that reacts faster with **1** to give the carbene intermediate, which is then almost selectively attacked by $N_2CHSiMe_3$ to form the unsymmetrical *cis*-alkene (Scheme 2, Z = $SiMe_3$). Indeed, comparative tests have confirmed that the two types of diazo compounds exhibit a very different reactivity with

Table 1. ^{1}H NMR data for unsymmetrical *cis*-enediones $R^1COCH{=}CHCOR^2$ (in $CDCl_3$ solution); multiplicity given in parenthesis: d = doublet, t = triplet, q = quadruplet, sept = septuplet, tq = triplet of quadruplets, m = multiplet

Compound/ precursors	R^1	R^2	=CH[a]	CH_2 (R^1)	CH_3 (R^1)	CH	CH_2 (R^2)	CH_3 (R^2)	C_6H_5	Yield[b]
18/2,3	OCH_2CH_3	CH_3	6.02 (d), 6.48 (d) [12.1]	4.24 (q)	1.29 (t)			2.36		58%
19/2,4	OCH_2CH_3	CH_2CH_3	6.02 (d), 6.50 (d) [12.0]	4.22 (q)	1.29 (t)		2.62 (q)	1.14 (t)		60%
20/2,5	OCH_2CH_3	$CH_2CH_2CH_3$	6.02 (d), 6.48 (d) [12.2]	4.23 (q)	1.29 (t)		1.66 (tq), 2.56 (t)	0.96 (t)		58%
21/2,6	OCH_2CH_3	$CH(CH_3)_2$	6.05 (d), 6.61 (d) [12.1]	4.20 (q)	1.28 (t)	2.84 (sept)		1.17 (d)		59%
22/2,7	OCH_2CH_3	C_6H_5	6.25 (d), 6.86 (d) [12.1]	4.01 (q)	1.03 (t)				7.3−8.0 (m)	59%
23/3,4	CH_3	CH_2CH_3	6.31 (d), 6.34 (d) [12.0]		2.30		2.61 (q)	1.12 (t)		49%
24/3,5	CH_3	$CH_2CH_2CH_3$	6.30 (d), 6.35 (d) [12.0]		2.29		1.67 (tq), 2.53 (t)	0.95 (t)		49%
25/3,6	CH_3	$CH(CH_3)_2$	6.34 (d), 6.45 (d) [12.0]		2.29	2.74 (sept)		1.17 (d)		50%
26/3,7	CH_3	C_6H_5	6.56 (d), 6.86 (d) [12.1]		2.30				7.3−8.0 (m)	
27/4,5	CH_2CH_3	$CH_2CH_2CH_3$	6.31 (d), 6.34 (d) [11.9]	2.56 (q)	1.12 (t)		1.67 (tq), 2.52 (t)	0.95 (t)		48%
28/4,6	CH_2CH_3	$CH(CH_3)_2$	6.36 (d), 6.44 (d) [12.0]	2.56 (q)	1.12 (t)	2.71 (sept)		1.16 (d)		51%
29/4,7	CH_2CH_3	C_6H_5	6.58 (d), 6.84 (d) [12.0]	2.57 (q)	1.12 (t)				7.2−8.0 (m)	49%
30/5,6	$CH_2CH_2CH_3$	$CH(CH_3)_2$	6.33 (d), 6.43 (d) [11.8]	1.67 (tq), 2.52 (t)	0.95 (t)	2.77 (sept)		1.15 (d)		
31/5,7	$CH_2CH_2CH_3$	C_6H_5	6.57 (d), 6.81 (d) [12.0]	1.66 (tq), 2.51 (t)	0.94 (t)				7.3−8.0 (m)	48%
32/6,7	$CH(CH_3)_2$	C_6H_5	6.68 (d), 6.85 (d) [12.0]		1.12 (d)	2.75 (sept)			7.3−8.1 (m)	50%

[a] ^3J(H-H′) (Hz) in brackets. − [b] Calculated from the integration of the =CH resonances.

1. In the case of EDA the reaction takes place stereoselectively at 60 °C within seconds, while in the case of $N_2CHSiMe_3$ the rate of the reaction is significantly slower, and a mixture of *cis*- and *trans*-$Me_3SiCH{=}CHSiMe_3$ is obtained in about 1:1 molar ratio. It should be noted that $N_2CHSiMe_3$ is the only diazo compound among all those tested in this work that does not decompose stereoselectively in the presence of **1**.

The reaction between EDA and $N_2CHSiMe_3$ in $CDCl_3$ was conveniently followed by ^{1}H NMR spectroscopy (details are reported in the Experimental Section). The reaction products **10**, **34**, and *cis*- and *trans*-$Me_3SiCH{=}CHSiMe_3$, were already detected in the first sample, which was removed from the bath and cooled at 0 °C just after the formation of the first N_2 bubbles. In all other samples analysed by ^{1}H NMR, the relative percentage of the four reaction products (see above) was the same.

Finally, it should be noted that both ethyl diazoacetoacetate and methyl 2-diazo-4-methylpentanoate, which are not decomposed by complex **1**, are also unreactive when treated with equimolar EDA in the presence of the catalyst. In both cases, ^{1}H NMR analysis revealed the formation of diethyl maleate (99%) and diethyl fumarate only.

Catalytic Decomposition of α,ω-Bis(diazo) Ketones

The decomposition in $CDCl_3$ solution of three different $N_2CHCO(CH_2)_nCOCHN_2$ compounds [n = 4 (**42**), 8 (**43**), and 10 (**44**)] catalysed by **1** has been investigated by ^{1}H NMR and GCMS techniques. In each reaction mixture, different *cis*-olefinic products have been identified [δ(=CH) in the range 6.25−6.40], along with *trans*-olefins in very low amount (< 5%). The relative percentage of the reaction products have been found to strongly depend on the procedure adopted. Thus, the addition of catalyst **1** to a concen-

Table 2. $^{13}C\{^1H\}$ NMR data ($CDCl_3$ solution) for unsymmetrical *cis*-enediones $R^1COCH{=}CHCOR^2$

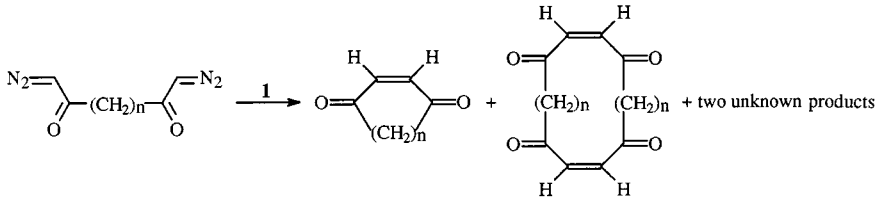
Compound precursors	R^1	R^2	=CH	CH_2 (R^1)	CH_3 (R^1)	CH	CH_2 (R^2)	CH_3 (R^2)	C_6H_5	CO
18/2,3	OCH_2CH_3	CH_3	124.4, 141.6	61.0	13.8			29.6		165.1, 201.2
19/2,4	OCH_2CH_3	CH_2CH_3	124.5, 141.7	61.1	13.9		35.8	7.2		165.2, 204.1
20/2,5	OCH_2CH_3	$CH_2CH_2CH_3$	124.6, 141.5	61.0	13.9		16.7, 44.4	13.5		
21/2,6	OCH_2CH_3	$CH(CH_3)_2$	125.1, 141.1	60.9	13.8	40.3		17.5		165.2, 207.0
22/2,7	OCH_2CH_3	C_6H_5	126.0, 140.9	61.0	13.6				128.5, 128.6, 133.8, 136.0	164.7, 194.0
23/3,4	CH_3	CH_2CH_3	135.4, 135.9		29.5		35.6	7.4		198.3, 200.8
24/3,5	CH_3	$CH_2CH_2CH_3$	135.1, 136.0		29.6		16.8, 44.3	13.5		200.3, 202.8
25/3,6	CH_3	$CH(CH_3)_2$	134.3, 136.7		29.5	40.4		17.6		200.7, 206.0
26/3,7	CH_3	C_6H_5	135.3, 136.1		29.7				128.6, 128.8, 133.5, 135.9	193.2, 199.2
27/4,5	CH_2CH_3	$CH_2CH_2CH_3$	135.2, 135.6	35.6	7.4		17.1, 44.3	13.5		202.6, 202.8
28/4,6	CH_2CH_3	$CH(CH_3)_2$	134.3, 135.4	35.6	7.4	40.4		17.7		203.5, 206.3
29/4,7	CH_2CH_3	C_6H_5	135.3, 135.6	35.8	7.4				128.5, 128.7, 133.5, 135.9	
30/5,6	$CH_2CH_2CH_3$	$CH(CH_3)_2$	134.8, 135.5	16.9, 44.3	13.5	40.4		17.7		202.8, 206.3
31/5,7	$CH_2CH_2CH_3$	C_6H_5	135.5, 137.8	16.8, 44.2	13.5				128.5, 128.6, 133.4, 136.0	
32/6,7	$CH(CH_3)_2$	C_6H_5								

Table 3. ^1H NMR data for *cis*-$RCOCH{=}CHSiMe_3$ compounds **35−41** (in $CDCl_3$ solution); multiplicity given in parenthesis: d = doublet, t = triplet, q = quadruplet, sept = septuplet, tq = triplet of quadruplets, m = multiplet

Compound	R	$Si(CH_3)_3$	=CH[a]	CH	CH_2	CH_3	C_6H_5	Yield[b]
35	CH_3	0.15	6.36 (d), 6.88 (d) [14.0]		2.23			90%
36	CH_2CH_3	0.15	6.35 (d), 6.87 (d) [14.0]		2.53 (q)	1.10 (t)		83%
37	$CH_2CH_2CH_3$	0.15	6.34 (d), 6.87 (d) [14.1]		1.66 (tq), 2.48 (t)	1.27 (t)		89%
38	$CH(CH_3)_2$	0.10	6.34 (d), 6.89 (d) [14.1]	2.63 (sept)		1.06 (d)		84%
39	C_6H_5	0.21	6.63 (d), 7.63 (d) [14.2]				7.3−8.0 (m)	91%
40	$(CH_2)_{10}CH_3$	0.15	6.35 (d), 6.88 (d) [14.0]		1.2−1.6 (m), 2.49 (t)	0.95 (t)		83%
41	$(CH_2)_{14}CH_3$	0.15	6.34 (d), 6.88 (d) [14.0]		1.2−1.6 (m), 2.49 (t)	0.95 (t)		88%

[a] ^3J(H-H′) (Hz) in brackets. − [b] Calculated from the integration of the =CH resonances.

trated solution of each substrate **42−44** resulted in the formation of a mixture of four *cis*-alkenes. The cyclic monomers **45−47**, arising from the intramolecular carbene-carbene couplings, were obtained in rather low yield. A second cyclic product, generated by the intermolecular coupling of two $CHCO(CH_2)_nCOCH$ units, was undoubtedly identified for $n = 4$ (**48**) and, though not unequivocally established by MS analysis, it seems reasonable that precursors **43** and **44** also afforded cyclic dimers. The formation of the cyclic *cis*-alkenes from substrates **42−44** is depicted in Scheme 4. As indicated above, the structure of two of the four products identified in the ^1H NMR spectra of the reaction mixtures were not determinable. The conversion into the monomeric product was strongly enhanced when a very dilute chloroform solution of **42−44** was slowly added to that of **1**. By adopting this procedure, the



Scheme 4

cyclic monomer *cis*-2-cycloocten-1,4-dione (**45**) has been prepared and isolated in pure form, in 64% yield.

Although the catalytic decomposition of each of the three $N_2CHCO(CH_2)_nCOCHN_2$ precursors tested affords several products, the ^1H NMR spectra of the reaction mixtures unequivocally indicate that *trans*-alkenes are present in the reaction mixture below 5%. Therefore, independent of the chain length of the bis(diazo) compound, catalyst **1** promotes the stereoselective formation of cyclic *cis*-alkenes. These results can be compared with those reported by Kulkowit and McKervey on the decomposition of **42**−**44** and related compounds catalysed by $Cu(acac)_2$.[7] Their studies revealed that the reaction is stereoselective only for **42** (n = 4), as for the product 2-cycloocten-1,4-dione the reported *cis*/*trans* ratio is 20:1. Conversely, mixtures of cyclic enediones were obtained for substrates with $n > 7$, the *trans* isomer being predominant (*trans*/*cis* ratios in the range 3−10). Also the formation of *cis*-2-cycloheptene-1,4-dione from $N_2CHCO(CH_2)_3COCHN_2$ decomposition by copper-bronze catalyst has been reported.[6] Apparently, with the copper-based catalysts, the formation of cyclic *cis*-alkenes is favoured only for the $N_2CHCO(CH_2)_nCOCHN_2$ precursors whose short chain length (n = 3 or 4) prevents the formation of the *trans* product, for steric reasons.

Conclusion

The commercially available complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) is an excellent catalyst for the stereoselective formation of both symmetrical and unsymmetrical *cis*-enediones from α-diazo carbonyl compounds. On a laboratory scale, the method described here is useful for preparing *cis*-enediones that cannot be obtained by the oxidative ring opening of 2,5-disubstituted furans. Furthermore, though the decomposition of $N_2CHSiMe_3$ promoted by **1** is not stereoselective, the combination of such precursor with an α-diazo carbonyl compound leads mainly to the *cis*-RCOCH=CHSiMe$_3$ derivative. We have also proved that $N_2CHCO(CH_2)_nCOCHN_2$ precursors decompose in the presence of **1** to give cyclic oligomers showing only the *cis* geometry around the C=C bond, independent of the $(CH_2)_n$ chain length.

Experimental Section

General Information and Physical Measurements: Solvents were purified by standard methods and stored over molecular sieves under argon. Ethyl diazoacetate, ethyl diazoacetoacetate, (trimethylsilyl)diazomethane (2 M hexanes solution), and the chemicals used for the preparation of diazo ketones were purchased from Aldrich Chemical Co. $N_2C(CH_2CHMe_2)COOMe$ has been prepared according to the literature.[19] The diazo ketones were prepared from the corresponding acyl chlorides and diazomethane by the Arndt−Eistert method.[20] Liquid N_2CHCOR compounds [R = Me (**3**), Et (**4**), *n*Pr (**5**), and *i*Pr (**6**)] were purified by vacuum distillation. $N_2CHCOPh$ (**7**), $N_2CHCO(CH_2)_nCH_3$ [n = 10 (**8**) 14 (**9**)] and $N_2CHCO(CH_2)_nCOCHN_2$ [n = 4 (**42**), 8 (**43**), 10 (**44**)] spontaneously separated from the solution as pale yellow crystals on cooling at −4 °C. Complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) was prepared according to a literature procedure.[21]

^1H (200.13 MHz) and $^{13}C\{^1H\}$ (50.32 MHz) NMR spectra were recorded with a Bruker AC 200 F QNP spectrometer, both ^1H and ^{13}C chemical shifts are referenced to $SiMe_4$. IR spectra were recorded with a Nicolet-FT 550 spectrophotometer. GCMS analyses were performed with a Fisons TRIO 2000 gas chromatograph/mass spectrometer working in the positive-ion 70-eV electron-impact mode. Injector temperature was kept at 260 °C and the column (Supelco® SE-54, 30 m long, 0.32 mm i.d., coated with a 0.25-μm phenyl methyl silicone rubber film); temperature was programmed from 50 to 300 °C with a gradient of 10 °C/min. Elemental analyses were carried out at the Microanalytical Laboratory of our Department.

Syntheses of *cis*-Enediones 10−17: All manipulations were performed under argon with exclusion of atmospheric oxygen and moisture, since solutions of **1** are sensitive to oxygen. In a typical synthesis, a solution of the diazo compound (5 mmol) in chloroform (20 mL) was added dropwise to a solution of **1** (5 mg; ca. 7 μmol) in chloroform (10 mL) at 60 °C within 10 min. For compounds **10**−**14**, after removal of the solvent in vacuo, pure samples were obtained by distillation under reduced pressure. For compounds **15**−**17**, addition of methanol (20 mL) followed by concentration resulted in the formation of solid material, which was filtered, washed with *n*-hexane and dried under reduced pressure.

Diethyl Maleate (10): Yield: 84%. − ^1H NMR ($CDCl_3$, 293 K): δ = 1.24 (t, 6 H, CH_3), 4.18 (q, 4 H, CH_2) 6.17 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 14.6 (CH_3), 61.8 (CH_2), 130.4 (=CH), 165.8 (CO). − MS (GCMS); *m*/*z* (%): 143 (10), 128 (22), 127 (78), 126 (47), 100 (27), 99 (100), 82 (15), 55 (10), 54 (16) 45 (13). − IR (neat): $\tilde{\nu}$ = 1733 cm^{-1} (C=O), 1645 (C=C).

(*Z*)-3-Hexene-2,5-dione (11): Yield: 81%. − ^1H NMR ($CDCl_3$, 293 K): δ = 2.31 (t, 6 H, CH_3), 6.31 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 29.7 (CH_3), 135.7 (=CH), 200.4 (CO). − MS (GCMS); *m*/*z* (%): 112 (29) [M^+], 98 (4), 97 (75), 69 (19), 43 (100). − IR (neat): $\tilde{\nu}$ = 1697 cm^{-1} (C=O), 1614 (C=C).

(*Z*)-4-Octene-3,6-dione (12): Yield: 73%. − ^1H NMR ($CDCl_3$, 293 K): δ = 1.12 (t, 6 H, CH_3), 2.57 (q, 4 H, CH_2), 6.33 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 7.4 (CH_3), 35.7 (CH_2), 135.5 (=CH), 203.3 (CO). − MS (GCMS); *m*/*z* (%): 140

(13) [M$^+$], 125 (16), 122 (74), 121 (33), 111 (100), 107 (74), 83 (62), 57 (34), 55 (46). − IR (neat): $\tilde{\nu}$ = 1717 cm^{-1} (C=O), 1618 (C=C).

(*Z*)-5-Decene-4,7-dione (13): Yield: 74%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.88 (t, 6 H, CH_3), 1.60 (tq, 4 H, CH_2) 2.44 (t, 4 H, CH_2) 6.40 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 14.2 (CH_3), 17.6 (CH_2), 45.0 (CH_2), 136.3 (=CH), 203.6 (CO). − MS (GCMS); *m*/*z* (%): 168 (1.5) [M$^+$], 150 (4), 139 (16), 126 (28), 125 (98), 97 (100), 83 (87), 71 (35), 69 (17), 55 (79), 54 (17), 43 (73), 41 (58). − IR (neat): $\tilde{\nu}$ = 1714 cm^{-1} (C=O), 1603 (C=C).

(*Z*)-2,7-Dimethyl-4-octene-3,6-dione (14): Yield: 70%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 1.08 (d, 12 H, CH_3), 2.67 (sept, 2 H, CH) 6.40 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 18.4 (CH_3), 41.1 (CH), 136.2 (=CH), 207.1 (CO). − MS (GCMS); *m*/*z* (%):168 (1.3) [M$^+$], 153 (5), 150 (10), 135 (33), 126 (95), 125 (31), 111 (100), 97 (51), 83 (13), 55 (16), 43 (75), 41 (57). − IR (neat): $\tilde{\nu}$ = 1712 cm^{-1} (C=O), 1587 (C=C).

(*Z*)-1,4-Diphenyl-2-butene-1,4-dione (15): Yield: 76%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 7.15 (s, 2 H, =CH), 7.3−8.0 (m, 10 H, C_6H_5). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 136.0 (=CH), 128.5, 128.7, 133.5, 136.3 (C_6H_5), 192.4 (CO). − MS (GCMS); *m*/*z* (%): 236 (86) [M$^+$], 208 (23), 207 (13), 159 (27), 131 (28), 105 (100), 103 (12), 77 (74), 51 (14). − $C_{16}H_{12}O_2$ (236.27): calcd. C 81.35, H 5.10; found C 80.80, H 5.05. − IR (KBr disk): $\tilde{\nu}$ = 1663 cm^{-1} (C=O), 1599 (C=C).

(*Z*)-13-Hexacosene-12,15-dione (16): Yield: 85%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.88 (t, 6 H, CH_3), 1.1−1.7 (m, 16 H, CH_2), 2.53 (t, 4 H, CH_2), 6.30 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 14.1 (CH_3), 22.6, 23.5, 29.1, 29.3, 29.4, 29.5, 29.6, 31.9, 42.6 (CH_2), 135.6 (=CH), 203.0 (CO). − $C_{26}H_{48}O_2$ (392.67): calcd. C 79.55, H 12.30; found C 79.25, H 12.45. − IR (KBr disk): $\tilde{\nu}$ = 1694 cm^{-1} (C=O), 1622 (C=C).

(*Z*)-17-Tetratriacontene-16,19-dione (17): Yield: 78%. − ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.88 (t, 6 H, CH_3), 1.1−1.4 (m, 20 H, CH_2), 1.62 (m, 4 H, CH_2), 2.53 (t, 4 H, CH_2), 6.30 (s, 2 H, =CH). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 14.1 (CH_3), 22.7, 23.5, 29.1, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 29.7, 31.9, 42.6 (CH_2), 135.6 (=CH), 203.0 (CO). − $C_{34}H_{64}O_2$ (504.88): calcd. C 80.90, H 12.80; found C 80.70, H 12.65. − IR (KBr disk): $\tilde{\nu}$ = 1694 cm^{-1} (C=O), 1621 (C=C).

Synthesis of (*Z*)-Ethyl 4-Oxo-2-nonadecenoate (33): Ethyl diazoacetate (456 mg, 4 mmol) and 1-diazo-2-heptadecanone (1.122 g, 4 mmol) in chloroform (20 mL) were slowly added, under argon, to a chloroform solution (10 mL) of catalyst **1** (31 mg; ca. 43 μmol), heated at 60 °C. The solvent was evaporated under reduced pressure, the residue was treated with ethyl ether (20 mL) and the orange solid removed by filtration. The product was purified by silica gel chromatography (diethyl ether), and obtained pure as a pale-yellow oily liquid in 49% yield (0.664 g). − ^{1}H NMR ($CDCl_3$, 293 K): δ = 0.88 (t, 3 H, CH_3), 1.1−1.4 (m, 27 H, CH_2/CH_3), 1.61 (m, 2 H, CH_2), 2.58 (t, 2 H, CH_2), 6.00 (s, 1 H, =CH, *J* = 12.1 Hz), 6.47 (s, 1 H, =CH, *J* = 12.1 Hz). − $^{13}C\{^1H\}$ NMR ($CDCl_3$, 293 K): δ = 14.1 (CH_3), 22.6, 23.3, 29.1, 29.2, 29.3, 29.4, 29.4, 29.6, 29.9, 31.9, 42.7 (CH_2), 61.2 (CH_2), 129.7 (=CH), 141.5 (=CH), 165.3 (CO), 203.7 (CO). − IR (neat): $\tilde{\nu}$ = 1727 cm^{-1} ν(C=O), 1708 cm^{-1} ν(C=O), 1630 cm^{-1} ν(C=C).

Synthesis of (*Z*)-Ethyl 3-(Trimethylsilyl)propenoate (34): Ethyl diazoacetate (456 mg, 4 mmol) and trimethylsilyl diazomethane (2 mL of 2 M hexane solution, 4 mmol) in chloroform (20 mL) were slowly added, under argon, to a chloroform solution (10 mL) of catalyst **1** (31 mg; ca. 43 μmol), heated at 60 °C. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography (diethyl ether). The product was obtained pure as a colourless liquid in 67% yield (0.465 g). − ^{1}H NMR ($CDCl_3$): δ = 0.19 (9 H, s, CH_3Si), 1.31 (3 H, t, CH_3), 4.20 (2 H, q, CH_2), 6.48 (1 H, d, =CH, *J* = 14 Hz), 6.53 (1 H, d, =CH, *J* = 14 Hz). − $^{13}C\{^1H\}$ ($CDCl_3$): δ = −0.7 (CH_3Si), 14.2 (CH_3), 65.8 (CH_2), 135.3 (=CH), 151.9 (=CH), 166.6 (CO). − IR (neat): $\tilde{\nu}$ = 1726 cm^{-1} ν(C=O), 1598 cm^{-1} ν(C=C). − MS (70 eV); *m*/*z* (%): 157 (40) [M$^+$], 130 (13), 129 (100), 127 (24), 111 (12), 101 (11), 75 (35), 73 (11).

Formation of Unsymmetrical *cis*-Enediones 18−32: In a typical experiment, a 5-mm NMR tube was charged with 0.1 mmol of two different α-diazo carbonyl compounds, 0.5 mL of $CDCl_3$ and 1 mg of **1**. The mixture was then warmed at 60 °C until evolution of N_2 ended. The vigorous bubbling of N_2 assured an oxygen-free ambient, enough to preserve the activity of the catalyst. The sample was then examined by ^{1}H and $^{13}C\{^1H\}$NMR spectroscopy (Table 1).

MS (GCMS); *m*/*z* (%): **18**: 142 (7) [M$^+$], 127 (79), 125 (34), 99 (100), 97 (25), 82 (24), 43 (30); **19**: 156 (0.6) [M$^+$], 127 (54), 111 (20), 99 (100), 97 (25), 83 (9), 57 (8); **20**: 170 (0.1) [M$^+$], 127 (38), 125 (15), 99 (100), 97 (13), 83 (7), 55 (11), 54 (7), 43 (16); **21**: 170 (0.2) [M$^+$], 128 (27), 127 (90), 125 (22), 100 (23), 99 (100), 97 (15), 82 (17), 55 (13), 54 (13), 43 (38); **22**: 204 (9) [M$^+$], 175 (7), 159 (14), 131 (16), 105 (100), 99 (9), 77 (44); **23**: 126 (10) [M$^+$], 111 (6), 98 (16), 97 (100), 83 (25), 69 (11), 57 (12), 55 (9), 43 (41); **24**: 140 (0.7) [M$^+$], 112 (13), 98 (59), 97 (100), 83 (20), 71 (13), 69 (31), 55 (30), 43 (76), 41 (36); **25**: 140 (0.6) [M$^+$], 125 (4), 98 (100), 97 (72), 70 (14), 69 (15), 55 (20), 43 (77), 41 (33); **26**: 174 (6) [M$^+$], 159 (19), 131 (20), 105 (100), 77 (48), 51 (8); **27**: 154 (1.4) [M$^+$], 125 (49), 111 (58), 97 (89), 83 (100), 55 (35), 43 (23); **28**: 154 (12) [M$^+$], 139 (37), 136 (11), 125(14), 112(100), 111(22), 97 (83), 83 (18), 57 (13), 55 (15), 43 (34); **29**: 188 (4) [M$^+$], 173 (6), 170 (5), 159 (100), 131 (36), 105 (70), 103 (22), 77 (54), 51 (8); **30**: 168 (0.6) [M$^+$], 150 (4), 126 (50), 125 (28), 97 (100), 83 (21), 55 (23), 43 (48), 41 (27); **31**: 202 (0.8) [M$^+$], 184 (2), 159 (58), 131 (63), 105 (100), 103 (26), 97 (96), 77 (56), 51 (9); **32**: 202 (1.8) [M$^+$], 184 (10), 171 (17), 160 (100), 159 (56), 131 (47), 115 (14), 105 (73), 103 (23), 77 (69), 51 (12).

Formation of Unsymmetrical *cis*-Alkenes 35−41: In a typical experiment, a 5-mm NMR tube was charged with 0.1 mmol of α-diazo carbonyl compound, 50 μL of a hexane solution of Me_3SiCHN_2 (0.1 mmol), 0.5 mL of $CDCl_3$ and 1 mg of **1**. The mixture was then warmed at 60 °C until evolution of N_2 ended, and the sample was transferred into the probe of the NMR spectrometer for ^{1}H and $^{13}C\{^1H\}$NMR analysis.

MS (GCMS); *m*/*z* (%): **35**: 127 (100), 99 (22), 73 (8), 61 (5), 45 (6), 43 (7); **36**: 141 (100), 127 (14), 115 (10), 99 (11), 75 (19), 73 (15); **37**: 155 (100), 127 (22), 113 (21), 111 (12) 99 (10), 75 (18), 73 (17); **38**: 155 (100), 127 (47), 125 (11), 99 (17), 75 (24), 73 (22); **39**: 204 (1) [M$^+$], 190 (58), 189 (100), 161 (38), 135 (15), 115 (18), 105 (23), 77 (28), 73 (35); **40**: 267 (100), 139 (12), 127 (36), 113 (14), 111 (11), 75 (20), 73 (14); **41**: 323 (55), 142 (16), 139 (15), 127 (100), 124 (23), 99 (16), 94 (15), 75 (51), 73 (33).

Catalytic Decomposition of $N_2CHCO(CH_2)_nCOCHN_2$ Precursors 42−44

Method A: A 5-mm NMR tube was charged with 0.2 mmol of the diazo compound, 0.5 mL of $CDCl_3$ and 2 mg of **1** (3 μmol). The

mixture was then warmed at 60 °C until evolution of N_2 ended, and the sample was analysed by ^1H and $^{13}C\{^1H\}$ NMR.

Method B: 0.1 mmol of the α,ω-bis(diazo) ketone was dissolved in 20 mL of $CHCl_3$, and the solution was added dropwise within 30 min to a flask, kept at 60 °C, containing **1** (2 mg, 3 μmol) in 5 mL of $CHCl_3$. When nitrogen evolution ended, the solvent was removed in vacuo. The residue was dissolved in 0.5 mL of $CDCl_3$ and the solution transferred into a 5-mm NMR tube for the ^1H and $^{13}C\{^1H\}$ NMR analysis.

2-Cyclooctene-1,4-dione (45): ^1H NMR ($CDCl_3$): δ = 1.88 (m, 4 H, CH_2), 2.55 (m, 4 H, CH_2), 6.38 (2 H, =CH). − $^{13}C\{^1H\}$ NMR: 23.3 (CH_2), 40.3 (CH_2), 136.8 (=CH), 204.7 (CO). − MS (GCMS); *m*/*z* (%): 138 (81) [M^+], 110 (86), 95 (52), 82 (85), 81 (61), 55 (100), 54 (72).

2-Cyclododecene-1,4-dione (46): ^1H NMR ($CDCl_3$): δ = 1.30 (m, 8 H, CH_2), 1.64 (m, 4 H, CH_2), 2.54 (m, 4 H, CH_2), 6.32 (2 H, = CH). − $^{13}C\{^1H\}$ NMR: 23.2 (CH_2), 28.5 (CH_2), 29. 0 (CH_2), 42.5 (CH_2), 135.8 (=CH), 202.9 (CO). − MS (GCMS); *m*/*z* (%): 194 (3) [M^+], 109 (31), 97 (100), 82 (39), 81 (33), 55 (54), 41 (42).

2-Cyclotetradecene-1,4-dione (47): ^1H NMR ($CDCl_3$): δ = 1.28 (m, 12 H, CH_2), 1.62 (m, 4 H, CH_2), 2.54 (m, 4 H, CH_2), 6.38 (2 H, = CH). − $^{13}C\{^1H\}$ NMR: 23.3 (CH_2), 28.8 (CH_2), 28. 9 (CH_2), 29. 2 (CH_2), 42.2 (CH_2), 136.4 (=CH), 203.5 (CO). − MS (GCMS); *m*/*z* (%): 222 (3) [M^+], 138 (24), 112 (29), 109 (36), 97 (100), 82 (30), 81 (25), 55 (48), 41 (36).

2,10-Cyclohexadecadiene-1,4,9,11-tetraone (48): ^1H NMR ($CDCl_3$): δ = 1.72 (m, 8 H, CH_2), 2. 94 (m, 8 H, CH_2), 6.31 (4 H, =CH). − $^{13}C\{^1H\}$ NMR: 22.3 (CH_2), 41.1 (CH_2), 135.3 (=CH), 202.1 (CO). − MS (GCMS); *m*/*z* (%): 276 (84) [M^+], 258 (9), 164 (28), 147 (30), 136 (29), 124 (31), 120 (33), 107 (39), 97 (54), 95 (32), 91 (32), 84 (37), 79 (44), 68 (39), 55 (100), 41 (32).

Synthesis of 2-Cyclooctene-1,4-dione (45): Under argon, 194 mg (1 mmol) of 1,8-bis(diazo)octane-2,7-dione (**42**) in 200 mL of chloroform was added dropwise to 20 mg (30 μmol) of **1** in chloroform (30 mL) at 60 °C. After removal of the solvent, the residue was extracted with boiling heptane (2 × 10 mL), which was then pumped off to give an analytically pure sample of the product. Yield: 89 mg (64%).

NMR Study of the Reaction between $N_2CHSiMe_3$ and $N_2CHCOOEt$: 0.5 mL of a 2.0 M hexanes solution of $N_2CHSiMe_3$ (1 mmol), 0.114 g of $N_2CHCOOEt$ (1 mmol), 10 mg of $[RuCl(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ (14 μmol), and 4 mL of $CDCl_3$ was mixed and gently warmed (30 °C) until the catalyst completely dissolved. The solution was then transferred into eight 5-mm NMR tubes, which were placed in a thermostatted bath at 60 °C. After the formation of the first N_2 bubbles, the first sample was removed from the bath and cooled at 0 °C. The other tubes were removed and immediately cooled after 30, 60, 90, 120, 150, 180, and 210 s. Each sample was then analysed by ^1H NMR spectroscopy at room-temperature.

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[18] Each test-tube was charged with 0.5 mmol of the diazo compound, 1 mg of **1** and 5 mL of $CHCl_3$. The samples were then transferred to a bath at 60 °C, and N_2 evolution was followed. The formation of bubbles from the test-tube containing EDA was observed within a few seconds, while the other two samples required about 3 min.
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