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[4+1]/[2+1] Cycloaddition Reactions of Fischer Carbene Complexes with α,β-Unsaturated Ketones and Aldehydes**

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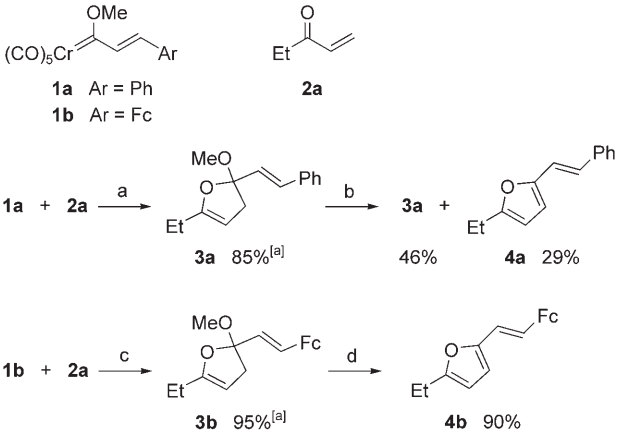
The cyclopropanation reaction of electron-deficient olefins with Group 6 Fischer carbene complexes is a rather general and well-established process[1] that was first reported in 1970.[2] Alkoxycarbene complexes are able to transfer their carbene ligand to the C=C bond of alkenes, which are substituted by various electron-withdrawing groups (EWG).[3] α,β-Unsaturated esters, amides, or nitriles,[4] alkenyl phosphonates,[4a,c–e,g,i] alkenyl sulfones,[4a,c] alkenyl oxazolines,[5] and alkenyl imines[6] are known to combine with different types of Group 6 alkoxycarbene complexes to give the corresponding [2+1] cycloadduct.[7] However, the cyclopropanation reaction of α,β-unsaturated carbonyl compounds (enones and enals) with Fischer carbene complexes (FCCs) has not been described thus far. Attempts to achieve this reaction were reported by Wienand and Reissig,[4a,c] and by Herndon and Tumer.[4b,f] They observed that the reaction of FCCs with enones produced a complex mixture of products, while in the analogous experiments with enals, the polymerization of these olefins seemed to be the major reaction pathway. Nevertheless, the ^{1}H NMR spectrum of the complex crude reaction mixture obtained from pentacarbonyl-(1-methoxybenzylidene)chromium and methyl vinyl ketone suggested the presence of a 2,3-dihydrofuran derivative; after treatment with acid, an approximately 1:1 mixture of 1-phenyl-1,4-pentanedione and 2-methyl-5-phenylfuran was produced in low yield.[4a,c] In addition, 2,7-octanedione was isolated in low yield from the reaction of pentacarbonyl-(1-cyclopropyl-1-methoxymethylene)chromium and methyl vinyl ketone.[4b,f]

In the context of our studies on the intermolecular cyclopropanation of electronically neutral olefins with alkoxy(alkenyl)carbene complexes,[8] we observed that the outcome of the reaction of this type of carbene complexes with electronically neutral 1,3-dienes is highly dependent on the type of solvent and on the reaction temperature.[9] Thus, reactions in toluene at 80 °C led exclusively to the corresponding $[3_{\mathrm{C}}+2_{\mathrm{D}}]$[10] cycloadduct, whereas reactions in THF at 120 °C gave only the $[4_{\mathrm{D}}+1_{\mathrm{C}}]$ cycloadduct. As an extension of this study, we decided to explore the reactivity of 1-oxa-1,3-dienes (α,β-enones and α,β-enals) under the reaction conditions that were used with the 1,3-carbodienes.[11]

Herein we report the preliminary results of the thermal reaction of FCCs with enones and enals that affords 2,3-dihydrofurans ($[4_{\mathrm{E}}+1_{\mathrm{C}}]$ adducts) from the corresponding acyl/formyl cyclopropane derivatives ($[2_{\mathrm{E}}+1_{\mathrm{C}}]$ adducts) independent of the solvent used.

The initial experiments were performed with chromium methoxycarbene complexes **1a**,**b** and enone **2a** (Scheme 1). Thermal treatment of phenylalkenylcarbene complex **1a** with ethyl vinyl ketone (**2a**) in THF at 120 °C furnished the 2,2,5-trisubstituted 2,3-dihydrofuran **3a** in relatively high purity. In a similar way, the reaction of the ferrocenylalkenylcarbene complex **1b** with the same enone **2a** conducted in toluene at 80 °C gave the analogous 2,3-dihydrofuran **3b**. The subsequent purification of these 2-methoxy-2,3-dihydrofurans **3a**,**b** by column chromatography on silica gel promoted their total or partial aromatization depending on the experimental conditions. The 2,5-disubstituted furan **4b** was collected from the column when commercial silica gel was used directly, while a mixture of dihydrofuran **3a** and the corresponding furan **4a** was recovered when silica gel which was previously treated with triethylamine (hexane/Et$_3$N 9:1 was used as the solvent to pack the column) was employed. Dihydrofurans **3a**,**b** are the products derived from a formal



Scheme 1. Thermal reaction of carbene complexes **1a**,**b** with enone **2a**. Reagents and conditions: a) **2a** (5 equiv), THF, 120 °C, sealed flask, 0.5 h; b) Pretreated silica gel (hexane/Et$_3$N 9:1); c) **2a** (5 equiv), toluene, 80 °C, sealed flask, 5 h; d) Silica gel. [a] Yield of clean product without purification. Fc = ferrocenyl.

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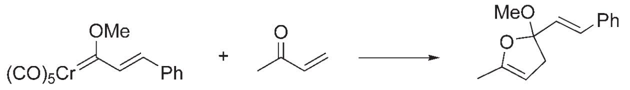
Supporting information for this article (experimental procedures and spectroscopic and analytical data for all products) is available on the WWW under http://www.angewandte.org or from the author.

$[4_E{+}1_C]$ cycloaddition process, in which the carbene carbon atom connects to the 1,4-positions of the 1-oxa-1,3-diene.[12]

The reaction of complex **1a** with methyl vinyl ketone (**2b**) was evaluated under various reaction conditions (Table 1). The experiments carried out in THF at 100 °C or 80 °C using either three or five equivalents of the enone all led to the 2,3-dihydrofuran **3c** in almost identical yields (Table 1, entries 1–3). The reaction carried out at 80 °C required a longer reaction time (Table 1, entry 2 vs 1). The use of only three equivalents of **2b** provided compound **3c** with the same efficiency as using five equivalents (Table 1, entry 3 vs 1). This product **3c** was also formed when toluene, hexane, or acetonitrile was used as the solvent (Table 1, entries 4–6), but the yield of the reaction in hexane was significantly lower. In addition, we observed a very fast and clean reaction under microwave conditions (Table 1, entry 7). Dihydrofuran **3c** was purified by column chromatography using silica gel that previously had been dried in an oven and treated with triethylamine. When commercial silica gel was employed directly, we observed partial conversion of **3c** into both the corresponding furan and 1,4-dicarbonyl derivatives.

Table 1: [4+1] Cycloaddition of carbene complex **1a** with **2b**. Optimization of reaction conditions for the synthesis of **3c**.[a]



1a **2b** **3c**

Entry	**2b** (equiv)	Solvent	*T* [°C][b]	*t* [min][c]	Yield [%][d]
1	5	THF	100	20	83
2	5	THF	80	85	84
3	3	THF	100	30	80
4	5	toluene	100	17	74
5	5	hexane	100	27	57
6	5	CH_3CN	100	18	79
7	3	THF	–[e]	1	95[f]

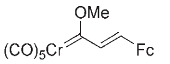
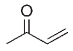
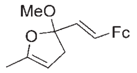
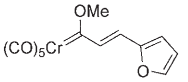
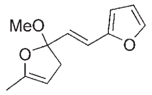
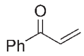
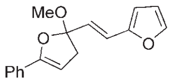
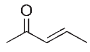
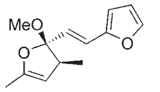
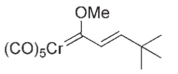
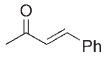
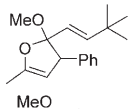
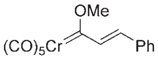
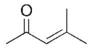
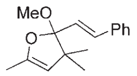
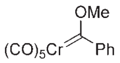
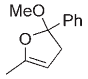
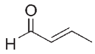
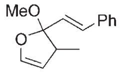
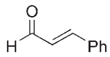
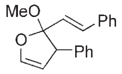
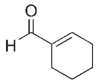
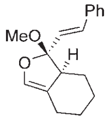
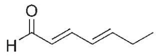
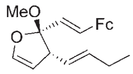
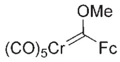
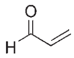
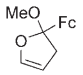
[a] All experiments were carried out in a sealed flask. [b] Bath temperature. [c] Reaction time required for complete disappearance of starting carbene complex **1a**. [d] Yield of isolated analytically pure product **3c** based on carbene complex **1a**. [e] Microwave irradiation at 600 W in a domestic microwave oven. [f] Yield of unpurified product (purification unnecessary).

The behavior of various chromium carbene complexes **1** and enones and enals **2** was subsequently investigated using as the standard reaction conditions: three equivalents of **2**, THF as the solvent, and heating the reaction mixture with an oil bath at 100 °C. The results are summarized in Table 2. Alkenylcarbene complexes **1a–d** reacted with enones **2b–f** with different degrees of substitution at the C=C bond to give the corresponding 2,3-dihydrofurans **3d–i** (Table 2, entries 1–6). Phenylcarbene complex **1e** was also able to transfer its carbene ligand to enone **2b** to give the dihydrofuran **3j** (Table 2, entry 7). Remarkably we found that alkenyl aldehydes **2g–k** also underwent this formal $[4_E{+}1_C]$ cycloaddition reaction with alkenylcarbene and heteroarylcarbene complexes **1a**,**b**,**f** to provide the corresponding 5-unsubstituted dihydrofurans **3k–o** (Table 2, entries 8–12). In general, the reactions with enals were slower than those with enones. Dienyl aldehyde **2j** was chosen to test the feasibility of the formation of a seven-membered ring (2,3-dihydrooxepine), but only the 3-vinyldihydrofuran **3n** was isolated as a 1.5:1 mixture of diastereoisomers (Table 2, entry 11). The diastereomeric excesses attained in these cycloaddition reactions were low (Table 2, entries 4, 5, and 8–11). Nevertheless, the bicyclic dihydrofuran **3m** was isolated as a 10:1 mixture of diastereoisomers when the reaction was heated for only 1.2 h, and some starting carbene complex **1a** was still present. When the reaction was heated for longer times (3 h) until the consumption of the carbene complex **1a** was complete, compound **3m** was obtained in a slightly higher yield, but a much lower diastereoselectivity (4:1; Table 2, entry 10). Chromatographic purification of the dihydrofurans **3d–h** and **3j–n** was effected as before (oven-dried silica gel, treated with Et_3N), which allowed the isolation of the major diastereoisomers **3g** and **3m**. The dihydrofurans **3**, particularly those derived from enals and those that contain a furyl group, were found to be somewhat unstable compounds and were stored under nitrogen and protected from light; on standing in air and light, the compounds slowly converted into polymeric material. The lower yields found in the reactions with some enals could be a result of this instability. The structure and relative configuration of the dihydrofurans **3g**,**n** and the bicyclic product **3m** were determined by one- and two-dimensional NMR spectroscopy.[13]

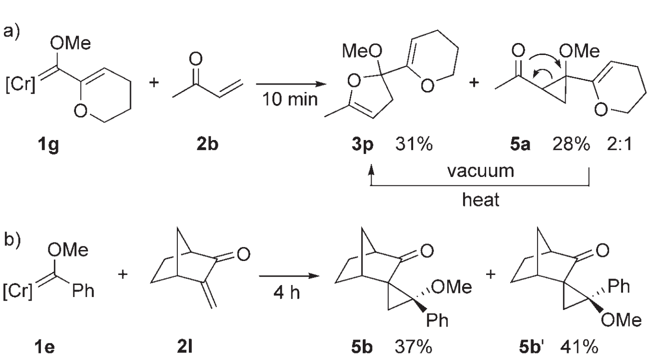
When the cyclic alkenylcarbene complex **1g** and enone **2b** were subjected to the reaction conditions indicated in Scheme 2a, gratifyingly a mixture of 2,3-dihydrofuran **3p** and cyclopropyl ketone **5a** was obtained. These products were separated by column chromatography, but unfortunately during removal of the solvents (carried out under vacuum and with some heating) from the column fractions that contained **5a**, the cyclopropyl ketone **5a** was completely converted into dihydrofuran **3p**, thus preventing the complete characterization of **5a**. In contrast, the reaction of the carbene complex **1e** and 3-methylene-2-norbornanone (**2l**) under the standard reaction conditions furnished exclusively the tricyclic ketone **5b** as an approximately 1:1 mixture of diastereoisomers that could be separated by column chromatography (Scheme 2b). A single-crystal X-ray analysis of **5b**[14] confirmed its structural assignment and allowed the relative stereochemistry of the benzylic stereogenic center to be ascertained. The relative configuration of **5b′**, initially assigned from the assumption that a selective transfer of the carbene ligand from the *exo* face of the alkene had occurred, was later confirmed by 2D NMR spectroscopy. These results provide evidence that the dihydrofuran formation involves an initial cyclopropanation of the electron-deficient C=C bond of an enone or enal, followed by a spontaneous rearrangement of the acyl- or formylcyclopropane to the corresponding dihydrofuran.[15] In addition, the reaction in Scheme 2b represents the first example of a successful cyclopropanation of an α,β-unsaturated ketone with a FCC to give a stable cyclopropyl ketone.[16]

Given the tendency of dihydrofurans **3** to undergo aromatization of the heterocyclic ring and as well a ring-opening reaction as a result of the cleavage of the acetal moiety, we decided to develop conditions to selectively

Table 2: [4+1] Cycloaddition of FCCs **1** with α,β-unsaturated carbonyl compounds **2**.[a]

Entry	Carbene complex 1		Enone/enal 2		t[b]	Product 3		Yield [%][c]	d.r.[d]
1		**1b**		**2b**[e]	20 min		**3d**	94	–
2		**1c**		**2b**	20 min		**3e**	77	–
3	**1c**			**2c**[f]	3.5 h		**3f**	75	–
4	**1c**			**2d**	2.5 h		**3g**[g]	46	2:1
5		**1d**		**2e**[f]	15 h		**3h**	46	2:1
6		**1a**		**2f**[e]	1 h[h]		**3i**	75[i]	–
7		**1e**		**2b**[e]	13 min		**3j**	82	–
8	**1a**			**2g**	11 h		**3k**	55[j]	2:1
9	**1a**			**2h**[e]	24 h		**3l**	37	1:1
10	**1a**			**2i**	1.2 h 3 h		**3m**[g]	50 56	10:1 4:1
11	**1b**			**2j**	15 h		**3n**[g]	38	1.5:1
12		**1f**		**2k**	1 h[k]		**3o**	87[i]	–

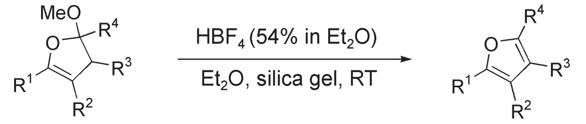
[a] All reactions were performed in THF at 100 °C (bath temperature) in a sealed flask using 3 equiv of the corresponding enone or enal **2**, unless otherwise noted. [b] Reaction time required for complete disappearance of **1**. [c] Yield of isolated analytically pure product **3** based on the corresponding **1**. [d] d.r. determined by ^{1}H NMR spectroscopy (300 or 400 MHz) of the crude products. [e] Reaction carried out with 5 equiv of the corresponding enone/enal **2**. [f] Reaction carried out with 2 equiv of enone. [g] The major diastereoisomer is shown. [h] Reaction heated at 120 °C (bath temperature). [i] Yield of crude product. [j] Yield of a clean unpurified product: 89%. [k] Reaction heated at 80 °C (bath temperature).



Scheme 2. [4+1] and [2+1] cycloaddition processes between FCCs **1g,e** and enones **2b,l**. Reagents and conditions: **2b,l** (3 equiv), THF, 100 °C, sealed flask. [Cr] = {(CO)$_5$Cr}.

accomplish both of these transformations. Aromatization of dihydrofurans **3** was observed under several reaction conditions such as treatment with silica gel, use of a non-aqueous acid (HBF$_4$, CF$_3$COOH), or simply by heating; various solvents (diethyl ether, ethyl acetate, or mixtures of hexane/ethyl acetate) were equally effective for this process. The reaction conditions that we consider to be more convenient to perform the elimination of methanol are presented in Table 3, and involve the treatment of a solution of the appropriate dihydrofuran **3** in diethyl ether with tetrafluoroboric acid (54% solution in diethyl ether) in the presence of silica gel at room temperature. Thus, the furans **4** with various degrees of substitution and functionalization were cleanly isolated (Table 3).[17,18] Conversion of dihydrofurans **3** into the corresponding 1,4-dicarbonyl compounds **6** was smoothly achieved

Table 3: Furans **4** obtained from 1,2-dihydrofurans **3**.

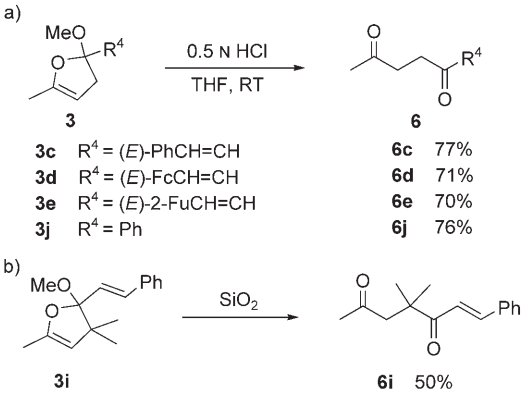


3 **4**

Entry	3	R^1	R^2	R^3	R^4	4	Yield [%][a]
1	**3c**	Me	H	H	(*E*)-PhCH=CH	**4c**[b]	94
2	**3d**	Me	H	H	(*E*)-FcCH=CH	**4d**[d]	87
3	**3e**	Me	H	H	(*E*)-2-FuCH=CH[c]	**4e**	85
4	**3j**	Me	H	H	Ph	**4j**[e]	69
5	**3k**	H	H	Me	(*E*)-PhCH=CH	**4k**[f]	55
6	**3l**	H	H	Ph	(*E*)-PhCH=CH	**4l**	62
7	**3m**	H	−(CH$_2$)$_4$−		(*E*)-PhCH=CH	**4m**	80
8	**3o**	H	H	H	Fc	**4o**	71

[a] Yield of isolated analytically pure product **4** based on the corresponding **3**. [b] Hexane/EtOAc (20:1) was used as solvent instead of Et$_2$O. [c] Fu = furyl. [d] Reaction carried out by treatment with silica gel in hexane/EtOAc (20:1) at RT. [e] Reaction carried out in the absence of silica gel. [f] Solvent: EtOAc instead of Et$_2$O.

by exposure of a solution of **3** in THF at room temperature to a catalytic amount of hydrochloric acid (0.5 N aqueous solution; Scheme 3a). Moreover, the 1,4-diketone **6i** was formed when the 3,3-disubstituted dihydrofuran **3i** (for which elimination of methanol is not possible) was subjected to purification by column chromatography with normal silica gel (Scheme 3b). While furans **4** are the products from the formal aromatic $[4_E+1_C]$ cycloaddition reaction between an FCC and an enone or enal, the 1,4-dicarbonyl compounds **6** (with an umpolung pattern of reactivity)[19] represent the formal Michael adduct of an acyl anion equivalent to an enone/enal, the synthetically equivalent reagent being the chromium carbene complex (the electrophilic carbene carbon atom).[20] This synthetic equivalence has been previously recognized.[4c]



Scheme 3. 1,4-Dicarbonyl compounds **6** generated from 1,2-dihydrofurans **3**.

In summary, we have developed the first successful thermal reaction between Fischer carbene complexes and enones or enals. This process leads to 2-methoxy-2,3-dihydrofurans by ring enlargement of the corresponding formyl- or acylcyclopropanes. A stable tricyclic cyclopropyl ketone also has been isolated. Further studies are underway to determine the scope, mechanism, and synthetic applications of these novel cyclization reactions.

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