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Catalytic Deallylation of Allyl- and Diallylmalonates

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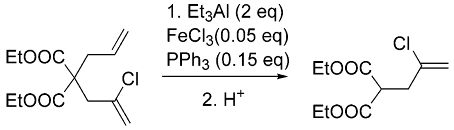
A transition-metal complex-catalyzed carbon−carbon bond cleavage under mild reaction conditions has been a long-pursued process of considerable theoretical and practical interest. It can be facilitated by the presence of an activating group and driven by decrease of steric strain.[1] Nevertheless, the ultimate goal in this area is the cleavage of unstrained and unactivated carbon−carbon bonds under mild reaction conditions. Typical examples may serve β-alkyl elimination in organometallics,[2] skeletal rearrangements,[3] and cleavage of tertiary homoallyl alcohols to ketones and propene.[4] Recently, we have reported that during attempts of Fe-catalyzed alkylative cyclization of allyl(2-chloroallyl)malonate **1a**, clean deallylation to (2-chloroallyl)malonate **2a** in 47% yield was observed (Scheme 1).[5] It is noteworthy that during the course of the reaction the unactivated γ,δ-carbon−carbon bond was cleaved and presumably the more reactive C−Cl bond remained intact. Although deallylation of malonates was reported for titanium-mediated process[6] and was observed during some Pd-catalyzed reactions,[7] its scope and generality has not been studied in detail. The lack of information on this reaction provided necessary impetus to study this reaction, and herein we would like to report the *first catalytic* deallylation of malonates and related compounds by various transition-metal complexes.

We began our study exploring the scope of the deallylation with respect to transition-metal complexes. Critical reaction parameters previously identified, including the amount of the catalyst (5 mol %), the amount of triethylaluminum, solvent (toluene), and temperature, remained the same. The deallylation of the allylbutylmalonate **1b** (Scheme 2) in the presence of several group VIII transition-metal phosphine complexes was chosen as a model reaction. As summarized in Scheme 2, all the complexes, with the exception of the iron one, showed catalytic activity. The activity of the complexes was decreasing in the following order Rh ≈ Ni > Ru > Co > Pd. It is worth mentioning that all deallylations proceeded very cleanly and only deallylation products and unreacted starting material were detected in the reaction mixtures. Except Et_3Al, other organoaluminums were tested as well; however, the yields of the deallylated product **2b** were rather low (Me_3Al: 15%, MAO: 15%, Et_2AlCl: 32%, i-Bu_3Al: 33%).

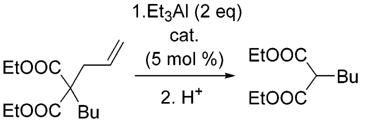
In the next step, we decided to compare the catalytic activity and selectivity of $RuCl_2(PPh_3)_3$ and $NiBr_2(PPh_3)_2$ to better assess the scope of the reaction. The first study focused on deallylation of substituted monoallylmalonates bearing functional groups on the double bond.[8] As summarized in Table 1, the use of $NiBr_2(PPh_3)_2$ proved to be more effective than $RuCl_2(PPh_3)_3$. The yields of the deallylation were higher (73−99%), and it proceeded regardless of the substitution on the double bond. The activity of the ruthenium catalyst was comparable only in the deallylation of the phenyl, **1c**, and the benzylallylmalonate, **1d**. The crotyl, **1e**, methallyl, **1f**, and cinnamylbutylmalonate, **1g**, did not react. Only partial success was achieved in the deallylation of **1h**.

Scheme 1. Fe-Catalyzed Deallylation of **1a**



1a **2a**

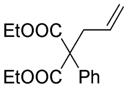
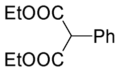
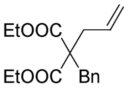
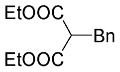
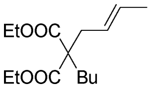
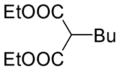
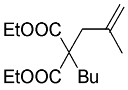
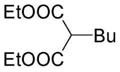
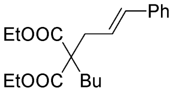
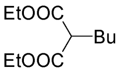
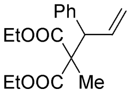
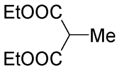
Scheme 2. Catalytic Deallylation of Allylbutylmalonate **1b**



1b **2b**

$FeCl_3$/3PPh_3	0%
$RuCl_2(PPh_3)_3$	81%
$CoBr(PPh_3)_3$	68%
$RhCl(PPh_3)_3$	97%
$NiBr_2(PPh_3)_2$	92%
$PdCl_2(PPh_3)_2$	36%

Table 1. Ru- and Ni-Catalyzed Deallylation of Monoallyl Malonates

Reactant		Product		Yield (%)[a] Ru-cat.[b]	Yield (%)[a] Ni-cat.[c]
	(**1c**)		(**2c**)	88	99
	(**1d**)		(**2d**)	79	99
	(**1e**)		(**2b**)	0	86
	(**1f**)		(**2b**)	0	73
	(**1g**)		(**2b**)	0	98
	(**1h**)		(**2e**)	39	96

[a] ^{1}H NMR yields. [b] $RuCl_2(PPh_3)_3$. [c] $NiBr_2(PPh_3)_2$.

Further attention focused on the deallylation of various substrates **1i**−**p** to **2f**−**m** (Table 2). As indicated, a considerable difference in reactivity was again observed for both complexes. The nickel complex was again more effective and afforded deallylated products in high yields (60−99%). (Partial hydrogenation of **2f** to the propylmalonate in 22% yield was observed during the deallylation of **1i**.) A comparable activity of the Ru catalyst was observed for the deallylation of the diallylmalonate **1i**, the allylmethallylmalonate **1j**, the allylcrotylmalonate **1k**, and the diallylcyanoacetate **1p**. The

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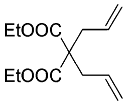
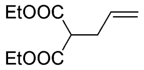
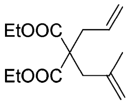
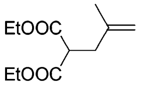
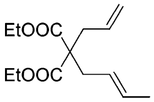
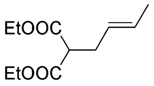
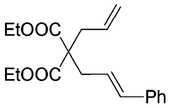
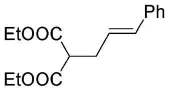
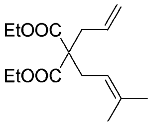
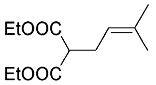
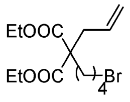
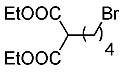
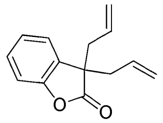
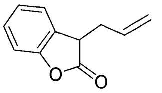
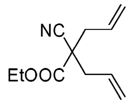
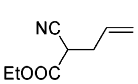
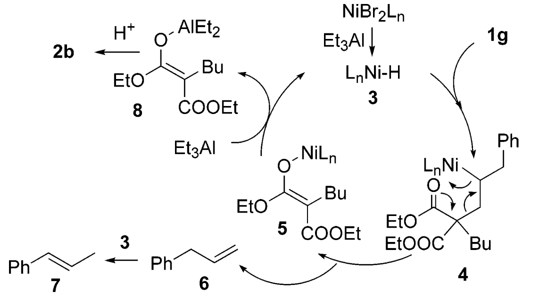
Table 2. Ru- and Ni-Catalyzed Deallylation of Diallyl Malonates

Reactant		Product		Yield (%)[a] Ru-cat.[b]	Yield (%)[a] Ni-cat.[c]
	(**1i**)		(**2f**)	91	75
	(**1j**)		(**2g**)	99	99
	(**1k**)		(**2h**)	89	98
	(**1l**)		(**2i**)	34	85
	(**1m**)		(**2j**)	46	99
	(**1n**)		(**2k**)	35	68
	(**1o**)		(**2l**)	16	94
	(**1p**)		(**2m**)	59	60

[a] ^{1}H NMR yields. [b] $RuCl_2(PPh_3)_3$. [c] $NiBr_2(PPh_3)_2$.

Scheme 3. Proposed Reaction Mechanism of Catalytic Deallylation



deallylation of substrates bearing substituents exerting bigger steric hindrance on the double bond such as the allylcinnamylmalonate **1l** and the allyl(3-methyl-2-buten-1-yl)malonate **1m** proceeded in moderate yields of 34 and 46%, respectively. Surprisingly, the Ru-catalyzed deallylation of the allyl(2-(4′-bromobutyl))malonate **1n** and diallylcoumaranone **1o** afforded **2k** and **2l** only in 35 and 16% yields, respectively. In addition, the deallylation of **1i** with the nickel catalyst proceeded also in the presence of Et_2Zn in 99% yield.

On the basis of the experimental results, we propose the following reaction mechanism (Scheme 3): (i) alkylation of the Ni complex with Et_3Al followed by β-hydrogen elimination to give the nickel-hydride species **3**, (ii) hydronickelation of the double bond to the alkylnickel species **4**, (iii) the double bond shifts with the cleavage of the C−C bond to the nickel enolate **5** and the alkene **6** (it further isomerizes to the internal alkene **7**),[9] and (iv) transmetalation of **5** with Et_3Al to the enolate **8** and release of the nickel species back into the catalytic cycle. Finally, hydrolysis of **8** will afford **2b**. Quenching of the reaction mixture with DCl resulted in the formation of diethyl 2-[^{2}H]-butylmalonate *D*-**2b**, which confirms that the deallylation stops with the formation of the enolate **8**.

In summary, we have developed the first and practical catalytic method for smooth deallylation of 2-substituted-2-allylmalonates to 2-substituted malonates via selective cleavage of the C−C bond under mild reaction conditions. The reaction seems to be general with respect to the transition-metal complexes; however, the comparison of Ru and Ni catalysts indicates considerable differences in their specific activity and selectivity. Last but not least, the smooth deallylation offers an opportunity to use the allyl group as an effective protective group for acidic hydrogen of malonic esters. The scope of deallylation and mechanistic aspects of this reaction with the respect to other substrates and transition-metal catalysts are currently under investigation.

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Supporting Information Available: Characteristics and spectral data for all starting material and products as well as the reaction condition details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(3) For Ni-catalyzed rearrangement of 1,4-dienes, see: (a) Miller, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 2785−2787. (b) Miller, R. G.; Pinke, P. A.; Baker, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 4490−4492. (c) Gosser, L. W.; Parshall, G. W. *Tetrahedron Lett.* **1971**, 2555−2558. (d) Miller, R. G.; Golden, H. J.; Baker, D. J.; Stauffer, R. D. *J. Am. Chem. Soc.* **1971**, *93*, 6308−6304. (e) Miller, R. G.; Pinke, P. A.; Stauffer, R. D.; Golden, H. J.; Baker, D. J. *J. Am. Chem. Soc.* **1974**, *96*, 4211−4220. For Pd-catalyzed Cope rearrangement of 1,5-dienes, see: (f) Overman, L. E.; Renaldo, A. F. *J. Am. Chem. Soc.* **1990**, *112*, 3945−3949. (g) Hill R. K. in *Comprehensive Organic synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5; pp 799−802.

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(7) Oppolzer, W.; Schröder, F. *Tetrahedron Lett.* **1994**, *35*, 7939−7942.

(8) A typical experimental procedure was carried out as follows: Into a solution of diethyl allylbutylmalonate **1b** (128 mg, 0.5 mmol), $NiBr_2(PPh_3)_2$ (19 mg, 0.025 mmol) in toluene (3 mL) was added a 2 M toluene solution of Et_3Al (0.5 mL, 1 mmol), and the reaction mixture was stirred at 20 °C for 24h. Then the reaction mixture was quenched with 3 M HCl (2 mL) and analyzed by ^{1}H NMR spectroscopy.

(9) (*E*)-1-Propenylbenzene was found as the side product of the deallylation of **1g** and **1h**.). An independent experiment showed that allylbenzene **6**, the side product of the deallylation of **1g**, is quickly isomerized into (*E*)-1-propenylbenzene under the reaction conditions.

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