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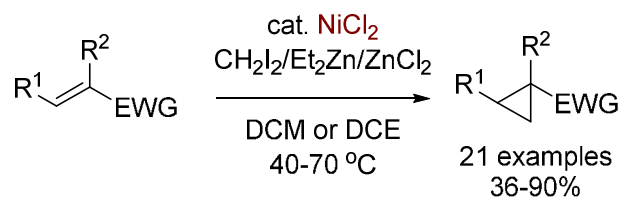


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An inexpensive nickel catalyst enables cyclopropanation of electron-deficient olefins under a modified Furukawa's procedure in moderate to good yields.



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Nickel-Catalysed Cyclopropanation of Electron-Deficient Alkenes with Diiodomethane and Diethylzinc

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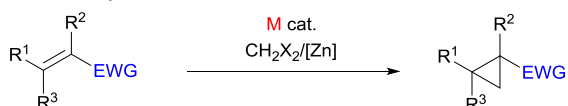
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In the presence of a nickel catalyst, the cyclopropanation of electron-deficient alkenes with diiodomethane and diethylzinc is drastically accelerated. A wide range of cyclopropyl ketones, esters and amides can be accessed under these conditions.

Cyclopropane is a structural element found in a wide range of natural and unnatural compounds that display important biological activities.¹ Due to its unique ring strain, cyclopropane can also serve as a versatile synthetic handle.² Simmons-Smith cyclopropanation is amongst the most widely used methods to access this valuable moiety from alkenes due to its excellent chemoselectivity and stereospecificity.^{3,4} In this reaction, an iodomethylzinc species (IZnCH_2I) is generated *in situ* from a combination of CH_2I_2 and a Zn/Cu couple. To overcome the cumbersome preparation of Zn/Cu couple, a number of methods have been introduced, for instance, the Furukawa's procedure to replace activated Zn with Et_2Zn , resulting in a more reactive reagent and better reproducibility.⁵



- (a) Kanai (1979); EWG = MVK, MA, AN; M = Ni(COD)₂, CH₂Br₂/Zn
 (b) Sugimura (2014); EWG = ketone; M = Cu(OTf)₂, CH₂I₂/Et₂Zn
 (c) **This work**; EWG = ketone, ester, amide; M = NiCl₂, CH₂I₂/Et₂Zn

Scheme 1. Cyclopropanation of electron-deficient alkenes with Simmons-Smith type reagents.

Simmons-Smith reaction of electron-deficient alkenes is rather sluggish due to the electrophilic nature of zinc carbenoid species.³ Methods addressing this reactivity issue could considerably enhance the synthetic utilities of Simmons-

Smith type reagents.⁶ In an interesting report, Kanai et al. showed that a nickel(0) catalyst can facilitate the cyclopropanation of methyl vinyl ketone (MVK), methyl acrylate (MA) and acrylonitrile (AN) with $\text{CH}_2\text{Br}_2/\text{Zn}$ (Scheme 1a).⁷ Notably, CH_2I_2 was less effective than CH_2Br_2 . The scope of this reaction, however, could not be extended to substrates bearing additional substituent(s). Recently, Sugimura et al. discovered a $\text{Cu}(\text{OTf})_2$ -catalysed cyclopropanation of α,β -unsaturated ketones with $\text{CH}_2\text{I}_2/\text{Et}_2\text{Zn}$ (Scheme 1b).⁸ We report herein a nickel-catalysed cyclopropanation with $\text{CH}_2\text{I}_2/\text{Et}_2\text{Zn}$ that allows access to a broad range of cyclopropyl ketones, esters and amides (Scheme 1c). Our conditions comprise a simple modification of the widely used Furukawa's procedure with the aid of an inexpensive nickel catalyst, and offer an alternative to other cyclopropanation methods for Michael acceptors (i.e. Corey-Chaykovsky reaction and metal-catalysed decomposition of diazomethane).

We initially investigated the cyclopropanation of chalcone

Table 1. Cyclopropanation of chalcone **1a**.^a

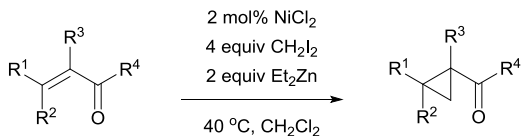
Entry	Ni catalyst	CH ₂ I ₂ (equiv)	Et ₂ Zn (equiv)	T (°C)	Conv. (%) ^b	Yield of 2a (%) ^b
1	20 mol% NiCl ₂	4	2	0	79	58
2	None	4	2	0	25	7
3	20 mol% NiCl ₂	4	2	rt	84	71
4	20 mol% NiCl ₂	4	2	40	>99	96
5	20% Ni(COD) ₂	4	2	40	67	41
6 ^c	20 mol% NiCl ₂	4	2	40	100	0 (98) ^d
7	20 mol% NiCl ₂	4	1.2	40	56	38
8	20 mol% NiCl ₂	2	2	40	91	71 (9) ^d
9	10 mol% NiCl ₂	4	2	40	94	94
10	2 mol% NiCl ₂	4	2	40	98	96
11	None	4	2	40	30	7

^a A solution of Et_2Zn in hexane was added slowly to a mixture of **1a**, CH_2I_2 and Ni catalyst in CH_2Cl_2 . ^b Determined by GC analysis using dodecane as an internal standard. ^c CH_2Br_2 was used instead of CH_2I_2 . ^d Yield of **2a'**.

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[†] Electronic Supplementary Information (ESI) available: Full experimental procedures, compound characterisation and copies of NMR spectra. See DOI: 10.1039/x0xx00000x

1a with CH₂I₂/Et₂Zn under nickel catalysis. To minimize the potential competitive conjugate addition of Et₂Zn to **1a**,⁹ a solution of Et₂Zn (2 equiv.) in hexane was added slowly to a mixture of **1a**, NiCl₂ (20 mol%) and CH₂I₂ (4 equiv.) in CH₂Cl₂ at 0 °C. 58% of **2a** was formed as determined by GC analysis (Table 1, entry 1). No change in the conversion and yield could be observed beyond 1h. Only 7% of **2a** was obtained in the absence of the nickel catalyst (entry 2). An increase in the reaction temperature to 40 °C led to 96% yield of **2a** (entries 3 and 4). The reaction was completed within 10 min after the addition of Et₂Zn. Other nickel halides exhibited reactivity similar to NiCl₂ (see ESI† for more details) while Ni(COD)₂ only led to 41% of the product (entry 5). Reaction with CH₂Br₂ instead of CH₂I₂ resulted in exclusive formation of **2a'** (entry 6). While attempts to reduce the amount of CH₂I₂ or Et₂Zn was detrimental to the reaction yields (entries 7 and 8), the catalyst loading could be lowered to 2 mol% (entries 9-11).

Table 2. Ni-catalysed cyclopropanation of α,β -unsaturated ketones.


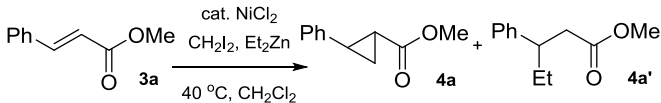
Alkenes	Product, (%) ^a
	2a , 86
	2b , 74
	2c , 84
	2d , 77
	2e , 57 (74) ^c
	2f , 47 (61) ^d
	2g , 51
	2h , 65
	2i , 53
	2j , 59
	2k , 44
	2l , (21) ^f
	2m , (18) ^f
	2n , (9) ^f

^a Isolated yields. ^b Reaction was run with 3 equiv. of Et₂Zn. ^c Reaction was run with 20 mol% of NiCl₂. ^d Reaction was run with 10 mol% of NiCl₂. ^e Reaction was run with 20 mol% NiCl₂ in DCE at 70 °C. ^f Determined by GC analysis using dodecane as an internal standard.

With the optimized conditions in hand, we explored the scope of the nickel-catalysed reaction (Table 2). Chalcones **1a-1d** were cyclopropanated in good yields. The reaction of **1b** required 3 equiv. of Et₂Zn to achieve full conversion due to deactivation of the substrate by a strongly electron-donating methoxy group. Lower yields were obtained in the reactions of

less activated systems, including chalcone **1e** and enones **1f-1j**, due to decomposition of starting materials. An increase in NiCl₂ could help improve the reaction yield of **1e** from 57% (2 mol% NiCl₂) to 74% (20 mol% NiCl₂). Similarly, 61% of **2f** could be obtained at 10 mol% catalyst loading. Cyclohexenone **1k** also underwent the cyclopropanation in 44% isolated yield. Reactions of tri-substituted olefins **1l-1n** were sluggish. Even under forcing conditions (20 mol% NiCl₂, 70 °C), the reaction of **1l** only led to 21% of **2l** as determined by GC analysis, together with 30% of the starting material remaining. Reactions of **1m** and **1n** also gave poor yields of the desired products.

We further probed the possibility to cyclopropanate methyl cinnamate **3a** under nickel catalysis (Table 3). ZnCl₂ (1 equiv.) additive was found to considerably improve the reaction yield to give 90% of **4a** (entries 1-3). In this case, only 2 equiv. of CH₂I₂ was needed as the nickel-catalysed conjugate addition of Et₂Zn to **3a** was no longer competitive. No addition product was observed in the reaction of **3a** with Et₂Zn in the presence of NiCl₂ (entry 4).

Table 3. Cyclopropanation of methyl cinnamate **3a**.


Entry	NiCl ₂ (mol%)	Additive (mol%)	CH ₂ I ₂ (equiv)	Et ₂ Zn (equiv)	Conv. (%) ^a	4a (%) ^a
1	20	none	2	2	91	64
2	20	ZnCl ₂ (50)	2	2	96	83
3	20	ZnCl ₂ (100)	2	2	99	90
4	20	ZnCl ₂ (100)	0	2	7	0 (0) ^b
5	20	ZnBr ₂ (100)	2	2	94	76
6	20	ZnI ₂ (100)	2	2	97	88
7	20	Zn(OTf) ₂ (100)	2	2	76	50
8	20	AlCl ₃ (100)	2	2	89	63
9	20	Sc(OTf) ₃ (100)	2	2	41	17
10	0	ZnCl ₂ (100)	2	2	20	10
11	20	ZnCl ₂ (100)	1	2	79	62
12	20	ZnCl ₂ (100)	2	1	89	80
13	5	ZnCl ₂ (100)	2	2	98	89
14	2	ZnCl ₂ (100)	2	2	99	90

^a Determined by GC analysis using dodecane as an internal standard. ^b Yield of **4a'**.

The addition of zinc bromide or iodide was also advantageous to the reaction yields (entries 5 and 6). While zinc halides may serve as a Lewis acid to activate the electron-deficient alkene,¹⁰ Zn(OTf)₂, AlCl₃ and Sc(OTf)₃ were not as effective (entries 7-9). In the absence of a nickel catalyst, ZnCl₂ alone led to only 10% of the cyclopropane (entry 10). Attempts to reduce the amounts of CH₂I₂ or Et₂Zn led to reductions in yields (entries 11-12). The catalyst loading could be reduced to 2 mol% without affecting the reaction outcome to any noticeable extent (entries 13-14).

The conditions developed were applicable to the synthesis of a range of cyclopropyl esters (Table 4). **4a** was isolated in 90% yield from the reaction of **3a**. Cyclopropanation of cinnamate **3b** with a fluorine substituent on the phenyl ring

gave 76% yield of the desired product whereas a lower reactivity was observed with **3c** featuring a methoxy group. As expected, benzyl cinammate **3d** underwent cyclopropanation in 82% yield. The reaction of benzyl crotonate **3e** was sluggish due to deactivation of the olefin by a methyl substituent. Even running the reaction in DCE at 70 °C only resulted in 37% of **4e**. For the more reactive terminal alkene **3f**, a good yield (76%) of the cyclopropane could be obtained with only 1 equiv. of CH_2I_2 and 1.1 equiv. of Et_2Zn .¹¹

Table 4. Ni-catalysed cyclopropanation of α,β -unsaturated esters and amides.

Alkenes	Product, (%) ^a
Reaction conditions: 2 mol% NiCl2, 1 equiv ZnCl2, 2 equiv CH2I2, 2 equiv Et2Zn, 40 °C, CH2Cl2	
	4a , 90%
	4b , 76%
	4c , 59%
	4d , 82%
	4e , 37%
	4f , 82% (76%) ^c
	4g , 68% ^{c,d}
	4h , 60%
	4i , 36%
	4j , 72%

^a Isolated yields. ^b Reaction was run in DCE at 70 °C. ^c 1 equiv. of CH_2I_2 and 1.1 equiv. of Et_2Zn were employed. ^d 20 mol% of NiCl_2 . ^e 10 mol% of NiCl_2 was employed.

Remarkably, the nickel catalyst can reverse the chemoselectivity normally observed in Simmons-Smith reaction. A 2:1 ratio of the mono- and bis-cyclopropanation products was obtained in the reaction of diene **3g**, favouring cyclopropanation at the electron-deficient alkene. An increase in the catalyst loading to 20 mol% helped improve the selectivity to 7:1, and 68% of the mono-cyclopropanation product was isolated.

α,β -unsaturated amides can also be cyclopropanated under nickel catalysis, albeit requiring more forcing conditions to achieve reasonable conversions (10 mol% of NiCl_2 , 70 °C) (Table 4). The reactions of cinnamoylamides **3h** and **3j** afforded the corresponding cyclopropanes in 60% and 72% yields, respectively, while cyclopropanation of crotonamide **3i** produced **4i** in 36% yield.¹²

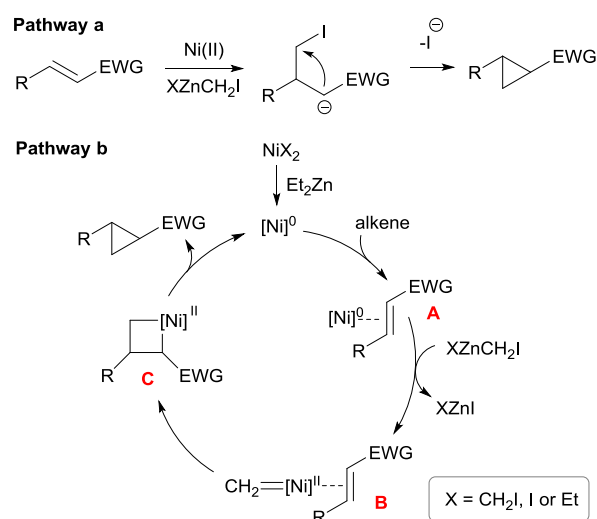
The nickel-catalysed cyclopropanation is compatible with a wide range of functional groups, including ketones, esters, amides, ethers and aryl bromides (Tables 2 and 4).

Alkenes:	Z-1f	Z-1o	Z-1p	Z-3a
Cyclopropanes:	<i>cis</i> - 2f (0%) <i>trans</i> - 2f (52%) ^a	complex	<i>cis</i> - 2p (20%) ^b <i>trans</i> - 2p (41%) ^b	complex

^a Isolated yield. ^b Determined by GCMS and ¹H NMR analysis.

Scheme 2. Cyclopropanation of Z-olefins.

For reactions of **1a-1h**, **3a-3e** and **3h-3j**, the *trans*-products were obtained exclusively. We further investigated the cyclopropanation of ketones **Z-1f**, **Z-1o**, **Z-1p** and ester **Z-3a** (Scheme 2). Reaction of **Z-1f** led to exclusive formation of *trans*-**2f** in 52% isolated yield. Both the *E*- and *Z*-olefins could be observed by ¹H NMR in the reaction mixtures of **Z-1f**, **Z-1o** and **Z-3a**, suggestive of isomerization of the starting material to the *trans*-isomer during the course of the reaction. The reaction mixtures of **Z-1o** and of **Z-3a** were rather complex, indicating extensive side reactions occurring. Cyclopropanation of **Z-1p** resulted in a 1:2 mixture of the *cis*- and *trans*-products as determined by ¹H NMR analysis. Overall, it was not possible to obtain *cis*-cyclopropanes selectively from (*Z*)- α,β -unsaturated carbonyls.

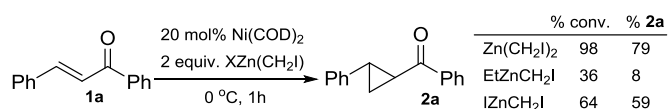


Scheme 3. Plausible pathways for the nickel-catalysed cyclopropanation with $\text{CH}_2\text{I}_2/\text{Et}_2\text{Zn}$.

Two plausible pathways for the nickel-catalysed cyclopropanation could be considered. The first proceeds via a Michael-initiated ring closure process whereby a nickel-catalysed conjugate addition of an iodomethylzinc species to an α,β -unsaturated carbonyl is followed by an intramolecular cyclisation (Scheme 3, pathway a).⁹ Alternatively, a mechanism similar to that proposed by Kanai et al. could involve a reaction of a nickel-carbene with an electron-deficient olefin to form a nickelacyclobutane **C** (Scheme 3, pathway b).^{7b} Milstein et al. previously showed that $\text{Zn}(\text{CH}_2\text{I})_2$ ¹³ can serve as an effective reagent for the formation of ruthenium and iridium carbenes.¹⁴ Thus, it is possible that a nickel-carbene intermediate could be generated from the reaction of $\text{Ni}(0)$

with an iodomethylzinc species.¹⁵ Reactions of metal-carbenes and electron-deficient olefins are known to afford cyclopropanes.¹⁶ Furthermore, Grubbs et al. and by Hillhouse et al. showed that isolated nickelacyclobutanes can undergo reductive elimination.¹⁷ The intermediacy of nickel-carbene in cyclopropanation has also been invoked in some cases.^{7b,18}

While further studies are needed to evaluate these possibilities, some initial observations deserve attention. Ester **3a** failed to undergo conjugate addition with Et₂Zn under nickel catalysis, and yet, can be cyclopropanated efficiently (Table 3). The result seems to cast doubt on pathway a. Notably, Ni(COD)₂ was not as effective as nickel halides in the cyclopropanation of **1a** with CH₂I₂/Et₂Zn (Table 1, entry 5). The difference in the catalytic efficiencies of Ni(0) and Ni(II) salts in reactions involving dialkylzinc is well-documented.^{15,19} Interestingly, Ni(COD)₂ catalysed the cyclopropanation of **1a** with pre-formed Zn(CH₂I)₂ in 79% yield (Scheme 4) whereas the corresponding reaction employing NiCl₂ afforded 30% of **2a**. Compared to Zn(CH₂I)₂, other iodomethylzinc (i.e. EtZnCH₂I and IZnCH₂I), which could also be present in the reaction mixture,¹⁰ resulted in lower yields of **2a** under similar conditions. While these experiments do not provide a direct evidence for a nickel-carbene mechanism, they indicate that a Ni(0)-catalysed pathway could be possible.



Scheme 4. Ni(COD)₂-catalysed cyclopropanation of **1a** with iodomethylzinc.

Conclusions

In conclusion, a nickel-catalysed cyclopropanation of α,β -unsaturated carbonyls with CH₂I₂/Et₂Zn has been developed. Under our conditions, a variety of cyclopropyl ketones, esters and amides can be prepared in moderate to good yields. Further studies are needed to gain a better understanding of the reaction mechanism.

Acknowledgements

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