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Communication

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Carboxylation of Benzylic and Aliphatic C–H Bonds with CO_2 Induced by Light/Ketone/Nickel

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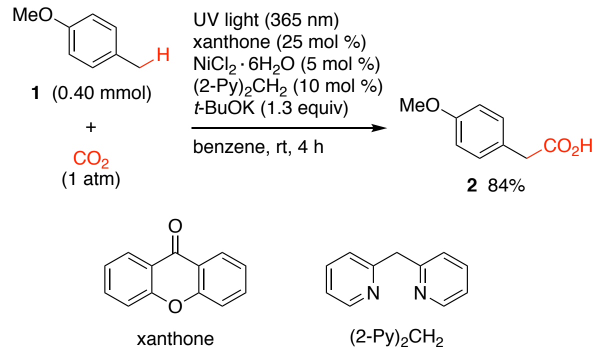
Supporting Information Placeholder

ABSTRACT: A photoinduced carboxylation reaction of benzylic and aliphatic C–H bonds with CO_2 is developed. Toluene derivatives capture gaseous CO_2 at the benzylic position to produce phenylacetic acid derivatives when irradiated with UV light in the presence of an aromatic ketone, a nickel complex, and potassium *t*-butoxide. Cyclohexane reacts with CO_2 to furnish cyclohexanecarboxylic acid under analogous reaction conditions. The present photoinduced carboxylation reaction provides a direct access from readily available hydrocarbons to the corresponding carboxylic acids with one-carbon extension.

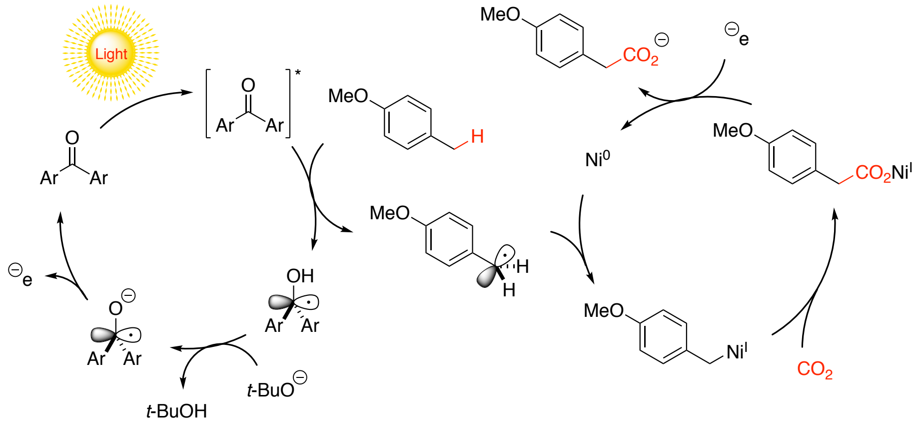
It presents a challenge of primary importance to exploit carbon dioxide (CO_2) as the C1 resource. In the field of organic synthesis, it is highly desired to develop reactions in which CO_2 is captured into organic skeletons through C–C bond formation.[1] Whereas various functional groups such as carbon–halogen and C–C double bonds have been successfully subjected to reactions fixing CO_2, examples of reactions directly fixing CO_2 into hydrocarbons remained limited to those of allylic,[2] aromatic,[3] and vinylic C–H bonds.[4,5] There have been no report for direct carboxylation of benzylic methyl C–H bonds of methylbenzenes and $C(sp^3)$–H bonds of saturated hydrocarbons promoted by homogeneous catalysts.[6] We now report a new photoinduced reaction fixing CO_2 into benzylic and aliphatic $C(sp^3)$–H bonds, which presents a direct access from readily available hydrocarbon molecules to carboxylic acids with one-carbon extension.

It is known that, when excited by a photon, the oxygen of a carbonyl group abstracts a hydrogen atom from a $C(sp^3)$–H bond to furnish a pair of ketyl radical and alkyl radical.[7] Such an activation process has been exploited for direct functionalization of $C(sp^3)$–H bonds.[2a,8] We previously reported a carboxylation reaction of allylic C–H bonds with CO_2, in which light, a benzophenone derivative, and a copper(I) complex cooperate.[2a] Mechanistically, the resulting pair of ketyl radical and allyl radical couples to give a homoallyl alcohol, which generates a nucleophilic allylcopper species through copper-induced retro-allylation extruding the benzophenone derivative. The allylcopper intermediate adds onto CO_2 to furnish a carboxylic acid. We have tried to expand the scope to include substrates that potentially generate benzylic radicals, and thus, examined a carboxylation reaction of *p*-methoxytoluene (**1**). Initial attempts to apply the previous conditions for allylic carboxylation failed to prompt carboxylation of **1**. Detailed examination of other metals[9] disclosed that nickel(II) complexes, which have been employed for various carboxylation reactions,[10] were effective. Representative conditions are shown in Scheme 1. A solution containing *p*-methoxytoluene (**1**, 0.40 mmol), xanthone (25 mol %), $NiCl_2 \cdot 6H_2O$ (5 mol %), di(2-pyridyl)methane (10 mol %), and *t*-BuOK (1.3 equiv) in benzene (4 mL) was irradiated with UV LED lamps (λ_{max} = 365 nm) under an atmospheric pressure of CO_2 at an ambient temperature. After 4 h, 2N aq. HCl was added to quench the reaction. Carboxylic acid **2** was formed together with a trace amount of 1,2-di(*p*-anisyl)ethane. Purification by acid/base extraction followed by column chromatography on silica gel (ethyl acetate/methanol = 10/1) to give carboxylic acid **2** in 84% yield. Thus, the carboxylation reaction occurred site-selectively at the benzylic C–H bond with the methoxy C–H bonds remaining unreacted.

Scheme 1. Carboxylation of *p*-Methoxytoluene (1)



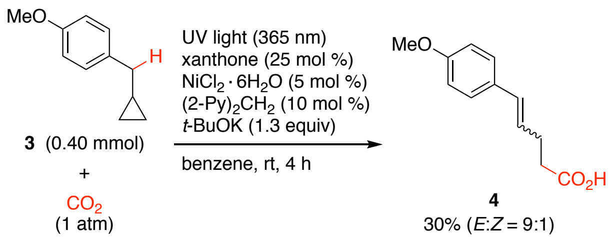
Scheme 2. Possible Mechanistic Pathway



A possible mechanistic pathway for the production of the carboxylic acid **2** from CO_2 and *p*-methoxytoluene (**1**) is depicted in Scheme 2. Initially, xanthone absorbs UV light to get excited. The carbonyl oxygen of the excited ketone abstracts hydrogen from the benzylic C–H bond of **1** to generate a pair of ketyl radical and benzylic radical, both of which are electronically neutral. The ketyl radical is deprotonated by *t*-BuOK[11] to give a ketyl radical anion, which transfers a single electron to the nickel(II) salt that is employed as the catalyst precursor. Ultimately, a nickel(0) species results[12] to initiate the catalytic cycle of nickel (right cycle). It combines with the benzylic radical (*vide supra*), giving rise to benzylnickel(I) species. Carbon dioxide inserts into the C–Ni(I) bond to give a nickel(I) carboxylate,[10g,h] which accepts a single electron from the ketyl radical anion to release the carboxylate anion of **2** with regeneration of the Ni(0) species. The 1,2-di(*p*-anisyl)ethane byproduct would be generated by homodimerization of the benzylic radical intermediate.

The result of the carboxylation reaction of cyclopropylmethylanisole **3** (Scheme 3) is consistent with the proposed mechanism shown in Scheme 2. When **3** was subjected to the reaction conditions, the cyclopropane ring was opened and the acyclic carboxylic acid **4** was produced as the major product (30% yield, E:Z = 9:1). A carboxylated product keeping the cyclopropyl ring was not formed.[13,14] This result indicates that the formation of a benzylic radical species is involved in the mechanistic pathway.

Scheme 3. Carboxylation of Cyclopropylmethylbenzene 3



The results of carboxylation reactions of other methylbenzene derivatives with the catalysts shown in Scheme 1 were summarized in Table 1. *m*-Methoxytoluene (**5**) was carboxylated site-selectively at the benzylic C–H bond with the methoxy C–H bonds remaining unreacted (entry 1), as with the case of *p*-methoxytoluene (**1**). *p*-Xylene (**7**) selectively underwent mono-carboxylation to afford the arylacetic acid **8** in 75% yield (entry 2). No dicarboxylated product was formed, probably because of the low solubility of the resulting carboxylate salt in benzene. *m*-Xylene (**9**, entry 3), *o*-xylene (**11**, entry 4), and mesitylene (**13**, entry 5) also afforded the corresponding mono-carboxylated products **10**, **12**, and **14**, respectively. 3,4-Dimethylanisole (**15**) underwent carboxylation site-selectively at the 4-methyl group (entry 6). Since the excited carbonyl oxygen is electrophilic rather than nucleophilic, it abstracted hydrogen from the most electron-rich C–H bond. 4-Methylveratrole (**17**) underwent an efficient carboxylation reaction to produce homoveratric acid **18** in 81% yield (entry 7). 4-Fluoro- (**19**, entry 8), 4-chloro- (**21**, entry 9), and 4-methoxy-3-cyanotoluene (**23**, entry 10) were carboxylated with the functional groups being retained. On the other hand, no carboxylic acid products were produced in case of 4-dimethylamino-, 4-methylthio-, 4-cyano-, and 3-benzoyltoluenes.

The carboxylation reaction of ethylbenzene (**25**) afforded carboxylic acid **26** in 15% yield along with the formation of 2,3-diphenylbutane (17% yield, 1:1 dr,

Scheme 4. Carboxylation of Ethylbenzene (23)

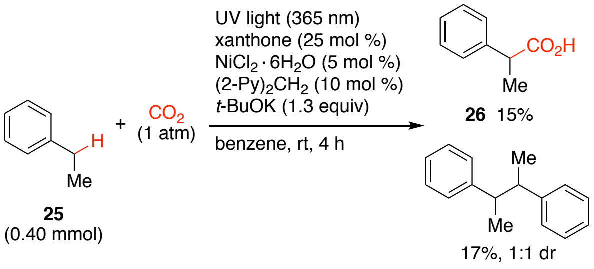
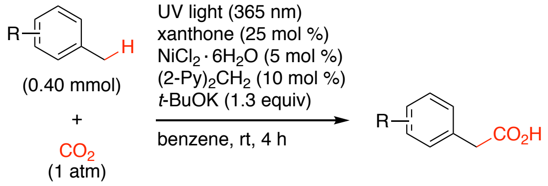
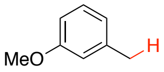
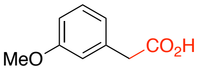
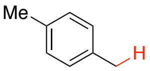
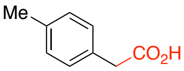
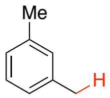
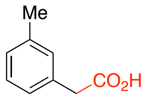
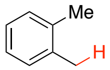
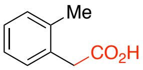
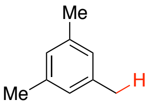
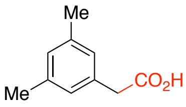
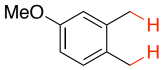
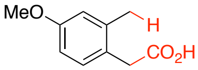
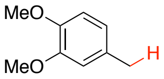
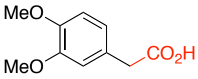
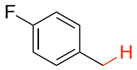
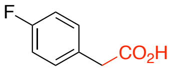
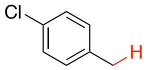
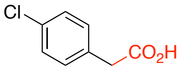
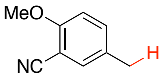
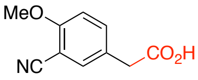


Table 1. Carboxylation of Methylbenzene Derivatives[a]



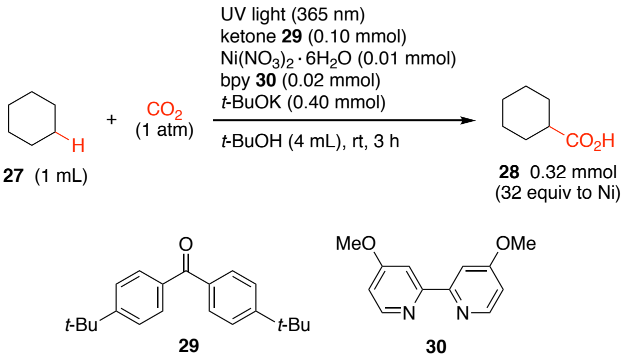
entry	substrates	products
1[b]	 **5**	 **6** 30%
2	 **7**	 **8** 75%
3	 **9**	 **10** 69%
4	 **11**	 **12** 55%
5	 **13**	 **14** 43%
6[b]	 **15**	 **16** 58%
7	 **17**	 **18** 81%
8	 **19**	 **20** 34%
9	 **21**	 **22** 33%
10	 **23**	 **24** 33%

[a] Reaction conditions: methylbenzenes (0.40 mmol), xanthone (0.10 mmol, 25 mol %), $NiCl_2 \cdot 6H_2O$ (0.02 mmol, 5 mol %), di(2-pyridyl)methane (0.04 mmol, 10 mol %), *t*-BuOK (0.50 mmol, 1.3 equiv), benzene (4 mL), CO_2 (1 atm), UV LED lamps (λ_{max} = 365 nm), ambient temperature, 4 h. [b] Xanthone (50 mol %), $NiCl_2 \cdot 6H_2O$ (10 mol %), di(2-pyridyl)methane (20 mol %).

Scheme 4). The additional methyl group at the benzylic radical center makes the radical species more stable, i.e., less reactive, and also, sterically encumbers its coupling with a nickel(0) species. Thus, the direct homodimerization of the radical species is allowed. Cyclohexene failed to incorporate CO_2, under the present reaction conditions. The C–C double bond might coordinate to nickel, retarding coupling of the cyclohexenyl radical species with nickel.

Next, we tackled a challenge to carboxylate saturated hydrocarbons. When reaction conditions similar to those shown in Scheme 1 were applied to a solvent amount of cyclohexane (**27**), only a trace amount of cyclohexanecarboxylic acid (**28**) was formed. After extensive screening of the reaction parameters,[9] we found slightly modified reaction conditions that were suitable for carboxylation of **27** (Scheme 5). When a mixture of **27** (1 mL), ketone **29** (0.10 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.01 mmol), bipyridine **30** (0.02 mmol), and *t*-BuOK (0.40 mmol) in *t*-BuOH (4 mL) was irradiated with UV LED lamps, 0.32 mmol of carboxylic acid **28** was produced. It is 32 times equivalent of the employed nickel. The yield of **28** based on *t*-BuOK (0.40 mmol) is 80%. A similar mechanism is expected to operate for the carboxylation of **27**.

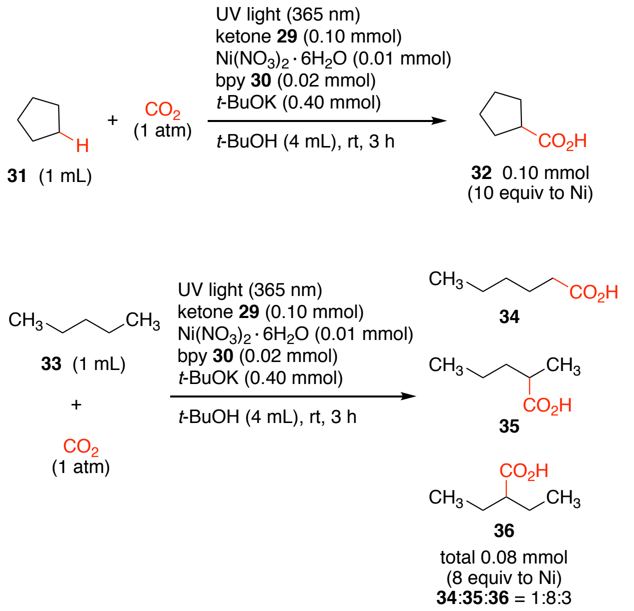
Scheme 5. Carboxylation of Cyclohexane (27)



The photoinduced carboxylation reaction was examined using other cyclic and acyclic saturated hydrocarbons under the same reaction conditions (Scheme 6). Cyclopentane (**31**) also underwent the carboxylation reaction to give cyclopentanecarboxylic acid (**32**), although the yield was lower than that of cyclohexane (0.10 mmol, 10 equiv to Ni).[15] An isomeric mixture of carboxylic acids (0.08 mmol, 8 equiv to Ni) was produced when pentane (**33**) was used as the substrate. The ratio of **34**:**35**:**36** was 1:8:3, which reflected the stability of the alkyl radical intermediates as well as the numbers of the parent C–H bonds.

In conclusion, we have developed a carboxylation reaction of C(sp^3)–H bonds with CO_2 which is induced by light/ketone/nickel. Substituted benzene derivatives were effectively carboxylated at the benzylic position under an atmospheric pressure of CO_2 at ambient temperature. The carboxylation reaction was successfully extended to saturated hydrocarbons such as cyclohexane and pentane. The present carboxylation reaction provides a direct access from readily available hydrocarbons to the corresponding carboxylic acids with one-carbon extension.

Scheme 6. Carboxylation of Hydrocarbons 31 and 33



ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Results of optimization and details of experimental procedures including spectroscopic data of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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(11) Since there is an equilibrium between *t*-BuO^- and *t*-$BuOCO_2^-$ under a CO_2 atmosphere, it might be *t*-$BuOCO_2^-$ that deprotonates the neutral ketyl radical. For generation of *t*-$BuOCO_2^-$ from *t*-BuO^- onto CO_2, see: (a) Song, L.; Zhu, L.; Zhang, Z.; Ye, J.-H.; Yan, S.-S.; Han, J.-L.; Yin, Z.-B.; Lan, Y.; Yu, D.-G. Catalytic Lactonization of Unactivated Aryl C–H Bonds with CO_2: Experimental and Computational Investigation. *Org. Lett.* **2018**, *20*, 3776-3779. (b) Shigeno, M.; Hanasaka, K.; Sasaki, K.; Nozawa-Kumada, K.; Kondo, Y. Direct Carboxylation of Electron-Rich Heteroarenes Promoted by LiO*t*-Bu with CsF and [18]Crown-6. *Chem. Eur. J.* **2019**, *25*, 3235-3239.

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(13) ^{1}H NMR analysis of the crude reaction mixture showed that 25% of **26** remained intact and a complex mixture of other unidentified non-carboxylated products was produced.

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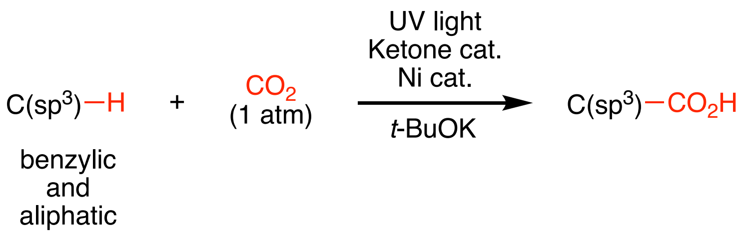
(15) The lower yield with cyclopentane can be ascribed to the stabilities of the cycloalkylnickel(I) intermediate. The nickel(I) moiety with the ligand is sterically bulky. A cyclohexylnickel(I) would accommodate the bulky nickel substituent in its staggered conformation. A cyclopentylnickel(I) would be less stable due to torsional strain. Acyclic pent-2-ylnickel(I) and pent-3-ylnickel(I) would be less reactive than cyclohexylnickel(I) because they are more sterically congested owing to the lack of the cyclic constraint.

TOC graphic


C(sp3)—H
benzylic and aliphatic
+
CO2 (1 atm)
UV light
Ketone cat.
Ni cat.
t-BuOK
C(sp3)—CO2H