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Structural Requirements for Decarbonylative α,α-Diarylation Reaction of 2-Methoxyalkanoic Acids in Phosphorus Pentoxide-Methanesulfonic Acid Mixture Yielding 1,1-Diarylalkane Homologs

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Abstract: 2-Methoxyalkanoic acids were found to undergo consecutive decarbonylative α,α-diarylation in P_2O_5-MsOH instead of Friedel-Crafts type arylation on the carbonyl carbon. The influence of the substituents of the arenes and the carboxylic acids in this reaction was elucidated based on the reaction yields. The reaction behavior was found to be primarily governed by the electron-withdrawing/releasing property of the α-substituents on the carboxylic acids as well as the positive species-accepting ability of the arenes. The steric hindrance was shown to participate in determining the reaction feasibility as a secondary factor.
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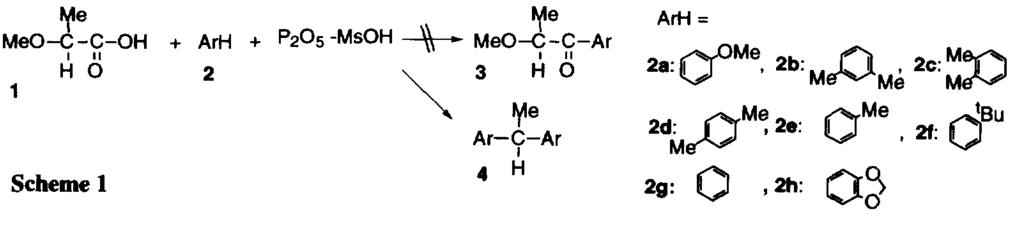
Introduction

Electrophilic aromatic substitution reaction still remains one of the important subjects in organic chemistry. For example, Shudo and his co-workers[1] and Olah and his co-workers[2] independently reported the hydroxyarylation of benzaldehyde and dehydroxylation of the products in super acids. In the reactions of benzaldehydes with arenes in trifluoromethanesulfonic acid, diarylmethanes were formed by reductive Friedel-Crafts alkylation reaction together with triphenylmethane and triarylcarbinol. Reductive Friedel-Crafts alkylation reaction has been studied as a current subject in this area, e.g., Saigo, Hashimoto, and the co-workers reported gallium dichloride-mediated reductive Friedel-Crafts reaction,[3] and super acid-catalyzed reductive Friedel-Crafts reaction was examined closely by Fukuzawa, Hiyama, and the co-workers.[4]

Recently we found that the reaction of 2-methoxypropanoic acid (**1**) with anisole (**2a**), *p*-xylene (**2d**), and toluene (**2e**) in phosphorus pentoxide-methanesulfonic acid mixture (P_2O_5-MsOH)[5] yielded diarylethanes (**4**) instead of the Friedel-Crafts acylation type products of α-methoxyphenones (**3**).[6] In this reaction, two aryl groups were introduced in the places of the carboxyl group and the methoxy one on 2-methoxypropanoic acid (**1**) as shown in Scheme 1.



Scheme 1

Some of the distinct features of this reaction were reported:[6] 1) P_2O_5-MsOH or PPA (polyphosphoric acid) effectively promotes the reaction, 2) an alkoxy group or a hydroxy one on the α-carbon of the carboxylic acid is indispensable, 3) the reaction does not proceed when the free carboxylic acid structure is converted to ester one, and 4) a large excess amount of arenes is essential.

P_2O_5-MsOH is an effective acidic condensing reagent having a better dissolving ability for various organic compounds than that of PPA. Utilizing this good solvent property, it has been used for several cation-initiated reactions[5,7] and in the synthesis of aromatic condensation polymers as a direct condensing reagent.[8] It is explained that in P_2O_5-MsOH a mixed anhydride should be formed directly from a phosphoric anhydride moiety and a free carboxylic acid which should act as an acyl cation equivalent to give a phenone skeleton via an electrophilic aromatic substitution reaction.

Quite recently, DeHaan and the co-workers reported the decarbonylative mono- and diarylation reactions of methoxyacetyl chloride in the presence of Lewis acids.[9] They investigated the utility of methoxyacetyl chloride as a selective chloromethylating reagent as well as chloromethyl methyl ether. Diarylmethane was explained to be formed from benzyl chloride which is the primary product between benzene and methoxyacetyl chloride with decarbonylation.

Contrary, the present reaction we report here characteristically proceeded from *the free carboxylic acid form*. However, the structural governing factors still remain to be solved for specification of the reaction that arylation on the α-carbon of the carboxylic acid predominantly occurs instead of phenone formation. In addition to the mechanistic aspects, neither the scope nor the limitation of this reaction has been sufficiently cleared yet. To clarify the general features of this reaction, we planned to elucidate the relationship between the reactivity and the structures of the substrates.

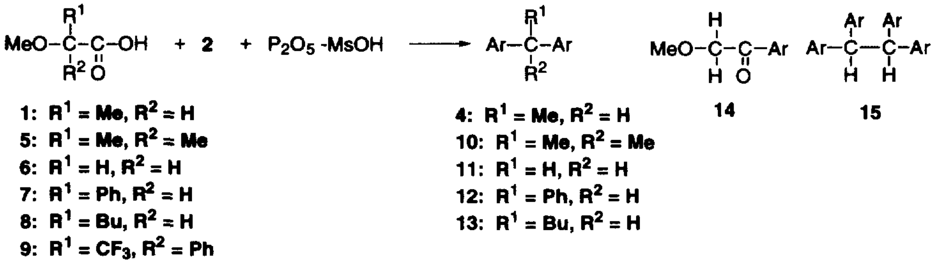
In this paper, we report the structural requirements of 2-methoxyalkanoic acid homologs and arenes for this decarbonylative α,α-diarylation reaction and discuss the influence of the substituents on the substrates in the reactivity estimated on the basis of the reaction yield.

Results

The α,α-diarylation reaction of a series of the 2-methoxyalkanoic acids was found to proceed intrinsically in P_2O_5-MsOH. At the same time, evolution of carbon monoxide occurred just after the reaction started. No generation of carbon dioxide was observed. Table 1 shows the results of the reaction of 2-methoxyalkanoic acids (**1** and **5-9**) with arenes **2**.

When the reaction of 2-methoxypropanoic acid (**1**) with arenes **2** was carried out at rt, anisole (**2a**) and *m*-xylene (**2b**) showed almost equal reactivities (runs 1 and 3). Xylene isomers (**2b-d**) exhibited distinct differences in reactivity (runs 3-8). *o*-Xylene (**2c**) showed somewhat lower reactivity than those of anisole (**2a**) and *m*-xylene (**2b**). *p*-Xylene (**2d**) was found to be the least reactive isomer in three xylenes. The reaction with toluene (**2e**) proceeded more smoothly than that with *p*-xylene (**2d**), and less than that with *o*-xylene (**2c**). *tert*-Butylbenzene (**2f**) gave the diarylated product (**4f**) in moderate yields (runs 11 and 12). Benzene (**2g**) did not react at all (runs 13 and 14). Acid **1** explosively reacted with 1,2-methylenedioxybenzene (**2h**) in P_2O_5-MsOH even when the reaction temperature was gradually raised from 0°C to rt, and the obtained tarry products were unidentified (runs 15 and 16). The order of the reactivities of arenes **2** at rt was as follows: anisole (**2a**) ~ *m*-xylene (**2b**) > *o*-xylene (**2c**) > toluene (**2e**) > *p*-xylene (**2d**) >> *tert*-butylbenzene (**2f**) > benzene (**2g**) (runs 1, 3, 5, 7, 9, 11, and 13).

Table 1 Reaction of 2-Methoxyalkanoic Acids (**1**, **5**, **6**, **7**, **8**, and **9**) with Arenes **2** in P_2O_5-MsOH[a]



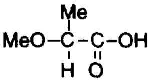
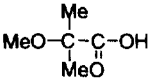
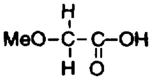
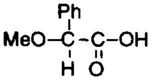
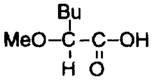
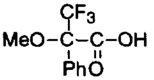
Run	2-Methoxyalkanoic Acid	Arene	Product	% Yield[b] rt, 24 h	 rt, 48 h	 60°C, 2 h
1	**1**	**2a**	**4a**		85[c]	
2	 $\mathrm{MeO-}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{\mathrm{C}}}\mathrm{-}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{-OH}$					90[c]
3		**2b**	**4b**		84	
4						56
5		**2c**	**4c**		74	
6						68
7		**2d**	**4d**		32[c]	
8						31[c]
9		**2e**	**4e**		47[c]	
10						25[c]
11		**2f**	**4f**		6	
12						10
13		**2g**	-		0	
14						0[c,f]
15		**2h**	-		-[d,e]	
16						-[d]
17	**5**	**2a**	**10a**	71		
18	 $\mathrm{MeO-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{\mathrm{C}}}\mathrm{-}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{-OH}$				84	
19						81
20		**2b**	-	0		
21						0
22		**2c**	-	0		
23						0
24		**2d**	-	0		
25						0
26		**2e**	-	0		
27					0	
28						0
29		**2h**	-	-[g]		

Table 1. Continued.

Run	2-Methoxyalkanoic Acid	Arene	Product	% Yield[b]		
				rt, 24 h	rt, 48 h	60°C, 2 h
30	**6**  $\mathrm{MeO{-}\overset{H}{\underset{H}{C}}{-}\underset{O}{C}{-}OH}$	**2a**	**11a**[h]	49[h](*p,p-*: *o,p-*: *o,o-* = 28: 12: 9)		
31		**2b**	**11b**	50 (85[i]) (*p,p-*: *o,p-*: *o,o-* = 43: 7: -)		
32		**2c**	**11c**	84 (*p,p-*: *o,p-*: *o,o-* = 61: 23: -)		
33		**2d**	**11d**	84		
34		**2e**	**11e**	76 (*p,p-*: *o,p-*: *o,o-* = 43: 33: -)		
35		**2f**	**11f**	73 (*p,p-*: *o,p-*: *o,o-* = 73: -: -)		
36		**2g**	**11g**	55		
37	**7**  $\mathrm{MeO{-}\overset{Ph}{\underset{H}{C}}{-}\underset{O}{C}{-}OH}$	**2a**	**12a**	94 (*p,p-*: *o,p-*: *o,o-* = 64: 30: -)		
38		**2a**[j]	**12a**	100 (*p,p-*: *o,p-*: *o,o-* = 69: 31: -)		
39		**2b**	**12b**	95		
40		**2c**	**12c**	91		
41		**2d**	**12d**	99		
42		**2e**	**12e**	100 (*p,p-*: *o,p-*: *o,o-* = 67: 33: -)		
43		**2g**	**12g**	22		
44	**8**  $\mathrm{MeO{-}\overset{Bu}{\underset{H}{C}}{-}\underset{O}{C}{-}OH}$	**2a**	**13a**	87		
45		**2a**	**13a**			87
46		**2d**	-	-[k]		
47		**2e**	-	-[k]		
48	**9**  $\mathrm{MeO{-}\overset{CF_3}{\underset{PhO}{C}}{-}\underset{O}{C}{-}OH}$	**2a**	-[l]	-[l]		

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[a] Reaction conditions: to 1 mmol of 2-methoxyalkanoic acid, 4 mL of P_2O_5-MsOH and 40 mmol of arene were used. [b] Isolated yield. [c] Published data, ref. 6. [d] Explosively reacted. [e] Reaction temperature was raised from 0°C to rt in an ice-water bath. [f] Reaction time is 3 h. [g] Reaction was carried out at 0-20°C for 1.5 h. Unidentified tarry products were obtained. [h] Phenone **14** (38%) and tetraarylethane **15** (1%) were also formed. [i] Before column chromatographical separation, almost ^{1}H NMR spectroscopically pure product was obtained in an 85% yield. [j] Amounts of anisole (**2a**) to acid **7** is 20 mmol/mmol. [k] A complex mixture was obtained. [l] The products were unidentified.

When the reaction was carried out at 60°C, the yields for *m*-xylene (**2b**) and toluene (**2e**) largely decreased. The order of the reactivities partially changed as follows: anisole (**2a**) > *o*-xylene (**2c**) > *m*-xylene (**2b**) > *p*-xylene (**2d**) > toluene (**2e**) >> *tert*-butylbenzene (**2f**) > benzene (**2g**) (runs 2, 4, 6, 8, 10, 12, and 14).

As alternate carboxylic acid substrates, 2-methoxy-2-methylpropanoic acid (**5**) and methoxyacetic acid (**6**) were allowed to react with arenes **2** in P_2O_5-MsOH. Acid **5** has an additional methyl group on the α-carbon, and acid **6** has no α-alkyl groups.

Acid **5** only reacted with anisole (**2a**) to give the diarylated product (**10a**) (runs 17-19). To *m*-xylene (**2b**), *o*-xylene (**2c**), *p*-xylene (**2d**) and toluene (**2e**) acid **5** was completely inactive (runs 20-28). The tarry product obtained by the reaction of acid **5** with 1,2-methylenedioxybenzene (**2h**) in P_2O_5-MsOH could not be identified (run 29).

The reaction of methoxyacetic acid (**6**) with anisole (**2a**) gave the dianisylmethane (**11a**) together with α-methoxy-4-methoxyacetophenone (**14**) and tetraarylethane (**15**) were obtained (run 30). Phenone (**14**) is the Friedel-Crafts acylation product and tetraarylethane (**15**) is its prolonged reaction product. Except for the rather low yield for anisole (**2a**), the reactivity of methoxyacetic acid (**6**) was ascertained to be very high. It gave diphenylmethane (**11g**) by the reaction in a good yield with benzene (**2g**) (run 36) and the corresponding diarylmethanes (**11**) were obtained in high yields with other arenes (**2b-f**) (runs 31-35).

2-Methoxy-2-phenylacetic acid (*O*-methylmandelic acid, **7**) reacted with anisole (**2a**), *p*-xylene (**2d**), and toluene (**2e**) to give the corresponding triarylmethanes (**12e**) quantitatively (runs 37-42). The reaction of acid **7** with benzene (**2g**) also underwent to give the triphenylmethane (**12g**) in a moderate yield (run 43). The quantitative formation of the diarylated product (**12a**) was confirmed even when the amount of anisole (**2a**) used was reduced to one-half its initial value of 40 times.

The reaction of 2-methoxyhexanoic acid (2-methoxycapric acid, **8**) with anisole (**2a**) proceeded smoothly to give 1,1-diarylpentane (**13a**) in 87% yields both at rt and at 60°C (runs 44 and 45). However, acid **8** afforded complex mixtures in the reactions with *p*-xylene (**2d**) and toluene (**2e**). Separation of the products was not successful (runs 46 and 47).

3,3,3-Trifluoro-2-methoxy-2-phenylpropanoic acid (**9**) yielded no corresponding diarylated adducts.

The reaction of 3-methoxypropanoic acid (**16**) with anisole (**2a**) under the same conditions gave solely the corresponding phenone ($H_2C(OMe)CH_2(C{=}O)Ar$, **17**), the Friedel-Crafts acylation type product, in an 85% yield.

Discussion

The results of the reaction of 2-methoxypropanoic acid (**1**) with arenes **2** demonstrate that the arenes should be essentially required to be electronically activated to the level of anisole (**2a**) or *m*-xylene (**2b**) for the reaction to proceed to a considerable extent.

The inversion of the reactivity orders between *m*-xylene (**2b**) and *o*-xylene (**2c**) and between *p*-xylene (**2d**) and toluene (**2e**) at rt (runs 3, 5, 7, and 9) and 60°C (runs 4, 6, 8, and 10) are not yet clarified well. However, the steric hindrance of acid **1** to these arenes (**2b-e**) is supposed to function differently in this temperature range. Among the three isomers of xylenes (**2b-d**), *m*-xylene (**2b**) is most activated electronically. Electronic activation for *o*- and *p*-xylenes (**2c, d**) should be almost the same. In terms of steric hindrance, *p*-xylene (**2d**) has the largest hindrance and *o*-xylene (**2c**) has the smallest one. Toluene (**2e**) is less activated electronically than xylenes (**2b-d**), and has smaller steric hindrance. Then, the relative reaction feasibility among these arenes should be sensitively perturbed by the reaction temperature.

The inertness of benzene (**2g**) suggested that the electron density on the aromatic ring is insufficient for the reaction with acid **1** (runs 13 and 14). In the case of *tert*-butylbenzene (**2f**) (runs 11 and 12), the yields could be lowered by the decomposition of *tert*-butylbenzene (**2f**) or its primary product under such an acidic circumstance. The acetal moiety in 1,2-methylenedioxybenzene (**2h**) is also considered to decompose under such acidic conditions (runs 15 and 16).

The presence of the distinct border of reactivity between anisole (**2a**) and other arenes (**2b-h**) in the reaction of 2-methoxy-2-methylpropanoic acid (**5**) (runs 17-29) is explained as follows: as 2-methoxy-2-methylpropanoic acid (**5**) is very inactive for the decarbonylative α,α-diarylation, the high activation of the arenes (**2**) should be required for the first arylation to proceed. Once this stage is attained, the second arylation reaction might complete spontaneously under these conditions. Anisole (**2a**) is supposed to be electronically activated sufficiently without considerable steric hindrance to initiate the reaction with acid **5** achieving a high conversion. Presumably because of less electronical activation and/or more steric hindrance other arenes (**2b-h**) should not be able to overcome the barrier of the first arylation reaction resulting in the complete depression of the total reaction.

For the reason of the high reactivity of methoxyacetic acid (**6**, runs 30-36), two ways of explanation are considered to be plausible: one is based on the electronic conditions of the acid (**6**) and the other is based on the steric effects. An α-alkyl group should cooperatively assist the partial positive charge of the α-carbon to decrease with donation of a lone electron pair from the oxygen atom of the methoxy group. The lack of α-alkyl groups means there exist no additional electron-donating inductive effects on the α-carbon. The less electronical stabilization of the partial positive charge at the α-carbon should result in rather low reaction rate in the attack of the arenes on the α-carbon leading to decarbonylation. The attack on the carbonyl carbon is considered to relatively accelerated to form a phenone compound. This assumption is supported by the fact that the reaction of the acid (**6**) with anisole (**2a**) gave a direct Friedel-Crafts acylation product prior to the decarbonylated adduct (run 30). Furthermore, the methoxy group remained unsubstituted. This result is interpreted as follows: as acid **6** has neither alkyl nor aryl groups on the α-carbon, the attack on the carbonyl carbon should occur more readily than that on the α-carbon. This selectivity should be brought about by the electronic factors rather than steric ones. Then, the methoxy group should remain for a longer time than those in other carboxylic acids. When attack on the α-carbon occurred first, it should lead to diarylmethane **11**, otherwise phenone **14** should form through direct condensation of the general manner. In contrast, decarbonylative α,α-diarylation reaction of acid **6** occurred with a lower activated arene, i.e., toluene (**2e**). Though a highly reactive arene such as anisole (**2a**) can react both on the acyl carbon and on the α-carbon, the reaction on the α-carbon with an arene of lower activation could not proceed. Instead that on the α-carbon should gradually take place specifically. The low yield for benzene (**2g**) despite of small steric hindrance is considered to be due to its relatively low charge density.

2-Methoxy-2-phenylacetic acid (**7**) is estimated to have a larger steric hindrance on the α-carbon than that of acid **1**. However, acid **7** smoothly reacted even with benzene (**2g**) to give triphenylmethane (**12g**) (run 43). It means that a phenyl group on the α-carbon of an α-methoxycarboxylic acid should promote the reaction more smoothly than a methyl group on the corresponding position. This tendency is considered to be caused by the resonance effect of the α-substituent which should effectively stabilize the intermediate or the transition state in this reaction. The lower yield of the reaction of benzene (**2g**) with acid **7** than that with acid **6** is speculated as follows: in the case of an arene of poor activated electrophile-accepting ability such as benzene (**2g**), the steric factor should affect more greatly. Then, the reaction feasibility about benzene (**2g**) perturbed (runs 36 and 43). Accordingly, the more crowded circumstance of the α-carbon of acid **7** than that of acid **6** should cause this difference.

The reaction behavior of 2-methoxyhexanoic acid (**8**) is not identified sufficiently. We assume that the decarbonylative α,α-diarylation might proceed to an appreciable content, however, some kind of prolonged reaction such as fragmentation or rearrangement of the long aliphatic chain should occur to give a complex mixture (runs 44-47).

The failure of this type of reaction of 3,3,3-trifluoro-2-methoxy-2-phenylpropanoic acid (**9**) might be due to too much electron deficiency on the α-carbon.

The specific formation of a Friedel-Crafts acylation product in the reaction of β-methoxypropanoic acid (**16**) and anisole (**2a**) manifests that an α-methoxy group in a carboxylic acid skeleton is essential for this decarbonylative α,α-diarylation reaction.

According to the discussion above, the structural determining factors in this reaction about the carboxylic acid substrate were elucidated as following two terms: primarily, the resonance electron-withdrawing ability of the substituents on the α-carbon of the carboxylic acid substrate is needed to realize the suitable conditions for accepting first aryl groups; secondarily, the steric hindrance on the α-carbon should refine the reaction feasibility in some cases.

The structural requirements for arenes **2** were elucidated according to the relative activation level of the individual carboxylic acid substrate. When the carboxylic acid has sufficiently high reactivity, even the arenes having relatively low electron density could undergo the decarbonylative substitution reaction. When xylenes (**2b-d**) were used in this reaction, the steric hindrance is suspected to affect the conversions to a considerable extent, which should occasionally reverse the order of the reactivity according to the reaction conditions.

There have been a few cases reported on the decarbonylation of α-hydroxycarboxylic acids.[10] The dehydration followed by decarbonylation of the protonated carboxyl group of malic acid and citric acid was explained to be driven by stability of the resulting carboxonium ions from the α-carbon and the hydroxy groups. In this reaction the α-alkoxyalkanoic acids are considered to decompose with evolution of carbon monoxide in the similar manner. However, it remains still unclarified whether these reactions proceeded stepwise or concertedly. If decarbonylation would occur stepwise from an α-ketoacylium ion to generate an α-alkoxycarbocation, i. e., an alkylcarboxonium, the generated cationoid in this stage is supposed to be stabilized or trapped by the other species involved in this reaction. An α-alkoxy group may decrease the positive charge on the adjacent carbon by donating the lone electron pair of the oxygen atom. It should participate in acceleration of generation and stabilization of the oxonium cation (acylium cation) via evolution of carbon monoxide. The resulting cationoid is considered to be very soft and poorly electrophilic, so the arene should need a highly activated structure to accomplish this reaction.

Even if the reaction proceeded through a concerted mechanism, the discussion about the electronic situation should be essentially the same.

From the standpoint of the synthetic utility of this reaction, 2-methoxyalkanoic acid is considered to behave as an aldehyde or ketone equivalent in P_2O_5-MsOH. As the Baeyer reaction[11, 12] and Reichert-Nieuwland reaction,[12, 13] where aldehydes or acetylenes (as the precursors of aldehydes) afford diarylated products, in this reaction 2-methoxyalkanoic acid accepts two arenes to give the adduct with loss of a carboxyl group and a methoxy group. It means that 2-methoxyalkanoic acids are assumed to be a stable and highly activated specific synthetic equivalents for aldehyde or ketone compounds.

Study on the mechanism of this decarbonylative α,α-diarylation reaction is now in progress and will be reported elsewhere.

Conclusion

The carboxylic acids containing an α-alkoxy group were proved to have the potentiality to undergo decarbonylative α,α-diarylation reaction essentially. An α-alkyl substituent was ascertained to retard the reaction. Two α-alkyl groups were shown to depress the reaction critically. On the other hand, an α-phenyl group was revealed to accelerate the reaction.

For the arene substrates, a certain level of electron-donating ability of the substituents according to the reactivity of the carboxylic acid substrates is required in accordance with general Hamett rule.[14] In several cases steric factors could determine the feasibility of the reaction apparently.

Experimental Section

General. Purification of reagents was performed according to the literature[15] as occasion calls. NMR spectra were recorded at 200 or 500 MHz for ^1H and at 50 or 125 MHz for ^{13}C in $CDCl_3$ using TMS as an internal reference. P_2O_5-MsOH was prepared by stirring the 1:10 wt/wt mixture of P_2O_5 and MsOH at rt according to the method in literature.[5]

The syntheses of 2-methoxyalkanoic acids were performed according to the modified methods for 2-methoxypropanoic acid (**1**) in literature.[16]

Typical procedure for preparation of 2-methoxyalkanoic acids: Synthesis of 2-methoxypropanoic acid (1). On a three-necked flask (300 mL), 2 g of NaH dispersion (60%) was placed and washed with hexane (100 mL x 2) and dry THF (10 mL x 2) under N_2. After dry THF (20 mL) was added the mixture was cooled to -78°C. Then a mixture of ethyl L-lactate (11.81 g, 100 mmol) and 10 mL of dry THF was dropped for 2 h with vigorous stirring. The temperature was gradually raised to rt and the solution was vigorously stirred for 30 min at rt. The solution was cooled to -78°C again and a mixture of methyl iodide (15.5 g, 109 mmol) and dry THF (10 mL) was added dropwise for 30 min. The mixture was stirred at -78°C for 1 h and at rt for 2 h. Then, THF was evaporated under reduced pressure carefully. The residue was dissolved in water (50 mL) and extracted with ether (30 mL x 3). The combined organic layer was washed with aqueous 10% Na_2CO_3 solution (30 mL x 1) and brine (80 mL x 1), dried over $MgSO_4$ overnight, and concentrated under reduced pressure. The residue was distilled under diminished pressure to give ethyl 2-methoxypropanoate. The ester thus obtained (5.00 g, 37.83 mmol) was hydrolyzed in a mixture of KOH (3.00 g, 53.5 mmol) and 80% aqueous EtOH (30 mL) for 3 h at reflux temperature. After evaporation of EtOH, the aqueous solution was acidified by conc. hydrochloric acid to pH 1-2. Continuous extraction with ether for 24 h, drying over $MgSO_4$ for one night, evaporation of ether at 20-25°C, and distillation under reduced pressure (93-4°C/22 Torr) gave pure methoxy acid **1**. Yield 50%. ^1H NMR δ ($CDCl_3$) 1.45 (3H, d, J = 8 Hz), 3.45 (3H, s), 3.90 (1H, q, J = 8 Hz) ppm. ^1H NMR Data for ethyl 2-methoxypropanoate: δ ($CDCl_3$) 1.31 (3H, t, J = 8 Hz), 1.43 (3H, d, J = 8 Hz), 3.40 (3H, s), 3.88 (1H, q, J = 8 Hz), 4.24 (2H, q, J = 8 Hz) ppm.

2-Methoxy-2-methylpropanoic acid (5). Yield 45%. ot 85°C (6 Torr). ^1H NMR δ ($CDCl_3$) 1.43 (6H, s), 3.30 (3H, s) ppm.

2-Methoxyhexanoic Acid (8). Yield 40%. ot 110°C (9 Torr). ^1H NMR δ ($CDCl_3$) 0.91 (3H, br t, J = 7 Hz), 1.22-1.50 (4H, m) 1.71-1.83 (2H, m) 3.44 (3H, s) 3.82 (1H, t, J = 7 Hz) ppm.

Typical procedure for reaction of 2-methoxyalkanoic acid and arenes (2): reaction of acid 1 and anisole (2a). P_2O_5-MsOH (6 mL) was added to an ice-cooled mixture of acid **1** (156 mg, 1.5 mmol) and anisole (**2a**, 6.48 g, 60 mmol) under vigorous stirring. The mixture was stirred at the prescribed temperature for the prescribed time interval. Then the mixture was poured into ice-water. The aqueous solution was extracted with ether (40 mL x 2). The combined organic layer was washed with aqueous 1 M NaOH solution and saturated aqueous NaCl solution, dried over $MgSO_4$ overnight, and concentrated under reduced pressure. Dianisylethane (**4a**) was obtained as an isomeric mixture. The products were separated by silica–gel column chromatography (eluent: benzene/hexane = 1/1 v/v).

Identification of the evolved carbon monoxide gas. The reactions of α–methoxy acid (**1**) with arenes (**2**) were undertaken under nitrogen atmosphere in the reaction vessel which was evacuated and filled with N_2 for three times. The evolution gas from the reaction mixture was collected into the rubber balloon equipped to the three way ground joint on the top of the Dimroth condenser. The gas in the balloon was introduced into the GASTEC^R gas detector tube (No. 1H for CO and No. 2L for CO_2, GASTEC Co. Ltd.), and from the change of the color of the reagent the presence of CO was confirmed.

The reactions of the acids (**5**, **6**, **7**, **8**, **9**, and **16**) were undertaken in essentially the same manner. The products were isolated or separated by silica-gel column chromatography. Benzene was used as the eluent of silica-gel column chromatography for the separation of the isomeric products (**4b**, **4c**, and **4e**) except for 1,1-bis(4-*tert*-butylphenyl)ethane (**4f**) (eluent: benzene/hexane = 2/1 v/v).

The structures of 1,1-diarylethanes (**4**),[12, 17] 2,2-dianisylpropane (**10a**),[18] diarylmethanes (**11**), and triarylmethanes (**12**)[19] were identified by ^{1}H and ^{13}C NMR spectroscopy and/or literature data.

The NMR spectral and related physical data are as follows.

1,1-Bis(2,4-dimethylphenyl)ethane (4b). ^{1}H NMR δ ($CDCl_3$) 1.53 (3H, d, J = 8 Hz), 2.19 (6H, s), 2.28 (6H, s), 4.30 (1H, q, J = 8 Hz), 6.93-6.98 (6H, m); ^{13}C NMR δ ($CDCl_3$) 19.04, 20.70, 20.86, 36.62, 126.60, 126.73, 131.21, 135.33, 135.70, 141.52 ppm. ot 180°C (20 Torr).

1,1-Bis(3,4-dimethylphenyl)ethane (4c). ^{1}H NMR δ ($CDCl_3$) 1.58 (3H, d, J = 8 Hz), 2.21 (12H, br s), 4.01 (1H, q, J = 8 Hz), 6.92-7.15 (6H, m); ^{13}C NMR δ ($CDCl_3$) 19.00, 19.12 (overlapped), 43.87, 124.90, 129.06, 129.70, 131.16, 136.51, 144.36 ppm.

1,1-Bis(2,5-dimethylphenyl)ethane (4d). ^{1}H NMR δ ($CDCl_3$) 1.51 (3H, d, J = 8 Hz), 2.19 (6H, s), 2.28 (6H, s), 4.31 (1H, q, J = 8 Hz), 6.89-7.09 (6H, m) ppm.

1,1-Bis(4-methylphenyl)ethane (4e). ^{1}H NMR δ ($CDCl_3$) 1.59 (3H, d, J = 8 Hz), 2.30 (6H, s), 4.08 (1H, q, J = 8 Hz), 7.09 (8H, pseudo s) ppm.

1,1-Bis(4-*tert*-butylphenyl)ethane (4f). ^{1}H NMR δ ($CDCl_3$) 1.29 (18H, s), 1.63 (3H, d, J = 8 Hz), 4.10 (1H, q, J = 8 Hz), 7.17 (4H, d, J = 8 Hz), 7.30 (2H, d, J = 8 Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 21.96, 31.59, 34.31, 43.86, 125.16, 127.16, 143.46, 148.59 ppm.

2,2-Bis(4-methoxyphenyl)propane (10a). ^{1}H NMR δ ($CDCl_3$) 1.64 (6H, s), 3.78 (6H, s), 6.80 (4H, dd, J = 8 and 2 Hz), 7.15 (4H, dd, J = 8 and 2 Hz) ppm.

Bis(4-methoxyphenyl)methane (11a). ^{1}H NMR δ ($CDCl_3$) 3.78 (6H,s), 3.82 (2H,s), 6.81 (4H, dd, J = 8 and 2 Hz), 7.04 (4H, dd, J = 8 and 2 Hz) ppm. *o,p*-isomer: 3.86(2H, s), *o,o*-isomer: 3.91 (2H, s) ppm.

Bis(2,4-dimethylphenyl)methane (11b). ^{1}H NMR δ ($CDCl_3$) 2.23 (6H,s), 2.30 (6H, s), 3.83 (2H, s), 6.76 (2H, d, J = 8 Hz), 6.91 (2H, d, J = 8 Hz), 7.01 (2H, s) ppm; ^{13}C NMR δ ($CDCl_3$) 19.30, 20.74, 35.73, 126.73, 129.19, 131.01, 135.67, 135.70, 136.50 ppm. *o,p*-isomer: 3.86(2H, s) ppm.

Bis(3,4-dimethylphenyl)methane (11c). ^{1}H NMR δ ($CDCl_3$) 2.22 (12H,s), 3.83 (2H, s), 6.92 (2H, d, J = 8 Hz), 6.96 (2H, s), 7.04 (2H, d, J = 8 Hz) ppm. *o,p*-isomer: 3.94(2H, s) ppm.

Bis(2,5-dimethylphenyl)methane (11d). ^{1}H NMR δ ($CDCl_3$) 2.22 (6H,s), 2.34 (6H, s), 3.84 (2H, s), 6.71 (2H, s), 6.95 (2H, d, J = 8 Hz), 7.08 (2H, d, J = 8 Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 18.96, 20.86, 36.46, 126.92, 130.03 (overlapped), 133.52, 135.52, 138.45 ppm.

Bis(4-methylphenyl)methane (11e). ^{1}H NMR δ ($CDCl_3$) 2.31 (6H, s), 3.90 (2H, s), 7.08 (8H, s) ppm. *o,p*-isomer: 3.94(2H, s) ppm.

Bis(4-*tert*-butylphenyl)methane (11f). ^{1}H NMR δ ($CDCl_3$) 1.31 (18H, s), 3.94 (2H, s), 7.15 (4H, dd, J = 8 and 2 Hz), 7.32 (4H, dd, J = 8 and 2 Hz) ppm. *o,p*-isomer: 3.87 (2H, s) ppm.

Diphenylmethane (11g). ^{1}H NMR δ ($CDCl_3$) 3.98 (2H, s), 7.10-7.32 (10H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 41.82, 126.19, 128.58, 129.07, 141.29 ppm.

Bis(4-methoxyphenyl)phenylmethane (12a). ^{1}H NMR δ (CDCl$_3$) 3.78 (6H, s), 5.46 (1H, s), 6.81 (4H, dd, J = 8 and 2 Hz), 7.01 (4H, dd, J = 8 and 2 Hz), 7.13 (2H, dd, J = 8 and 2 Hz), 7.20-7.32 (3H, m) ppm.

Bis(2,5-dimethyphenyl)phenylmethane (12d). ^{1}H NMR δ (CDCl$_3$) 2.11 (6H, s), 2.20 (6H, s), 5.62 (1H, s), 6.52 (2H, s), 6.93 (2H, dd, J = 8 and 2 Hz), 6.99-7.07 (4H, m), 7.18-7.32 (3H, m) ppm.

Bis(4-methylphenyl)phenylmethane (12e). ^{1}H NMR δ (CDCl$_3$) 2.21 (6H, s), 5.46 (1H, s), 6.95-7.13 (8H, AA'BB' pattern), 7.17-7.29 (5H, m) ppm.

1,1-Bis(4-methoxyphenyl)pentane (13a). ^{1}H NMR δ (CDCl$_3$) 0.88 (3H, br t, J = 7 Hz), 1.13-1.42 (4H, m), 1.90-2.03 (2H,m), 3.78 (6H,s), 3.79 (1H, t, J = 8 Hz), 6.81 (4H, dd, J = 8 and 2 Hz), 7.13 (4H, dd, J = 8 and 2 Hz) ppm.

Anisyl 2-methoxymethyl ketone (14). ^{1}H NMR δ (CDCl$_3$) 3.51 (3H, s), 3.88 (s, 3H), 4.67 (s, 2H), 6.95 (dd, 2H, J = 9 and 2 Hz), 7.94 (dd, 2H, J = 9 and 2 Hz) ppm.

1,1-2,2-Tetraanisylethane (15). ^{1}H NMR δ (CDCl$_3$) 3.70 (12H, s), 4.60 (2H, s), 6.67 (dd, 8H, J = 8 and 2 Hz), 7.05 (dd, 8H, J = 8 and 2 Hz) ppm. ^{13}C NMR δ (CDCl$_3$) 56.76, 56.90, 115.5, 131.34, 138.40, 159.50 ppm.

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