

Ruthenium complex-catalyzed novel transformation of alkyl formates

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Abstract

The following ruthenium-catalyzed novel transformations of alkyl formates have been developed: (1) selective decarbonylation of alkyl formates to the corresponding alcohols; (2) alkylation of arenes and alkenes using alkyl formates as an alkylating reagent via decarboxylation. Also the ruthenium-catalyzed addition of alcohols to alkenes has been developed as an appendant reaction, providing an effective method for the protection of alcohols.

Keywords: Ruthenium; Catalysis; Alkyl; Arene; Alkene; Alcohol

1. Introduction

Recently, considerable interest in the chemistry of formate esters has been stimulated by their importance as versatile industrial intermediates and functionalized C₁ units which can be easily prepared from carbon monoxide [1]. Representative utilization of alkyl formates in organic synthesis catalyzed by transition-metal complexes may be classified into (1) isomerization of methyl formate to acetic acid [2], (2) decarbonylation of alkyl formates to alcohols [3,4], (3) hydroesterification of alkenes [5] and alkynes [6] with alkyl formates, (4) carbonylation of organic halides with alkyl formates [7] and miscellaneous reactions [8].

The simplest transformation of alkyl formates is decarbonylation reaction which can produce high purity carbon monoxide as well as the corresponding alcohols [1b]. Both heterogeneous [3] and homogeneous [4] transition-metal catalyzed decarbonylations of alkyl formates have already been reported. However, the catalysts employed in these reactions were limited to iridium and rhodium complexes, and the catalytic activities were rather low and high pressures were sometimes necessary.

In the course of our studies on the ruthenium-catalyzed activation of formyl compounds [5e,9], we re-

ported the first ruthenium-catalyzed decarbonylation of alkyl formates to alcohol [10]¹. In this paper, we first describe in full detail the ruthenium-catalyzed decarbonylation of alkyl formates to alcohols, and secondly, effective ruthenium-catalyzed alkylation reactions of arenes and alkenes using alkyl formates as effective alkylating reagents via decarboxylation. Generally, Friedel–Crafts alkylation of arenes has been carried out in the presence of AlCl₃ using alkyl halides as alkylating reagents [12]. When alcohols instead of alkyl halides were employed as alkylating reagents, severe acidic reaction conditions were required [12]. In contrast, the present alkylation reaction using alkyl formates proceeds smoothly under neutral reaction conditions. Finally, we have explored the appendant reaction, i.e., the addition of alcohols to alkenes affording the corresponding ethers in high yields, which provides an effective method for the protection of alcohols.

2. Results and discussion

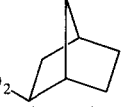
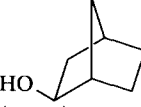
2.1. Decarbonylation of alkyl formates to alcohols

Alkyl formates have been decarbonylated smoothly using the Ru₃(CO)₁₂(CH₃)₃NO · 2H₂O catalyst system

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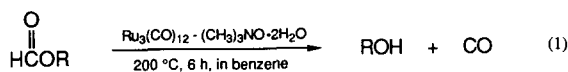
¹ Jenner et al. independently reported Ru₃(CO)₁₂/PR₃-catalyzed decarbonylation of alkyl formates simultaneously [11].

Table 1
Ruthenium-catalyzed decarbonylation of alkyl formates to alcohols ^a

Run	Formate	Catalyst	Conv. (%) ^b	Product (%) ^b
1	HCO ₂ CH ₂ Ph	Ru ₃ (CO) ₁₂	100	PhCH ₂ OH 74
2 ^c	HCO ₂ CH ₂ Ph	Ru(acac) ₃	0	— 0
3	HCO ₂ (CH ₂) ₂ Ph	Ru ₃ (CO) ₁₂	100	Ph(CH ₂) ₂ OH 82
4 ^d	HCO ₂ (CH ₂) ₂ Ph	Ru ₃ (CO) ₁₂	64	Ph(CH ₂) ₂ OH 11
5	HCO ₂ 	Ru ₃ (CO) ₁₂	96	 OH 74
6	HCO ₂ 	Ru ₃ (CO) ₁₂	62	 OH 50
7	HCO ₂ 	Ru ₃ (CO) ₁₂	100	 HO trace ^c
8	HCO ₂ C(C ₂ H ₅) ₃	Ru ₃ (CO) ₁₂	5	(C ₂ H ₅) ₃ COH 2

^a Alkyl formate (5.0 mmol) in benzene (4.0 ml) at 200°C for 6 h under an argon atmosphere. ^b Determined by GLC. ^c Ru(acac)₃ (0.30 mmol) was used. ^d (CH₃)₃NO · 2H₂O was not added. ^e Norcamphor was obtained in ~90% yield as a major product.

under an argon atmosphere to give the corresponding alcohols in good yield [Eq. (1)].



The results obtained are summarized in Table 1. The present catalyst system is extremely efficient for the decarbonylation of benzyl formate. Using the catalyst systems reported to date [4], decarbonylation of benzyl formate gave mainly toluene and/or sometimes benzaldehyde, and the selective decarbonylation of benzyl formate to benzyl alcohol has been found to be quite difficult. In the present reaction, however, benzyl formate was selectively decarbonylated to afford benzyl alcohol in 74% yield (Run 1). Even though the reactivity of secondary alkyl formates is less than that of benzyl formate, they were also decarbonylated without elimination occurring (Run 6) [4]. However, when *exo*-2-norbornyl formate was employed in the present reaction, the main product was norcamphor which was obtained by further dehydrogenation of the *exo*-norborneol generated (Run 7). Tertiary alkyl formates were only slightly decarbonylated, probably due to steric hindrance (Run 8). As for the catalysts, the present reaction is characteristic of Ru₃(CO)₁₂. Other ruthenium [Ru(acac)₃ (Run 2), RuCl₂(PPh₃)₃ and RuH₂(PPh₃)₄] and Group VII [Mn₂(CO)₁₀] and Group VIII metal carbonyls [Fe(CO)₅, Fe₃(CO)₁₂ and Co₂(CO)₈] were totally ineffective.

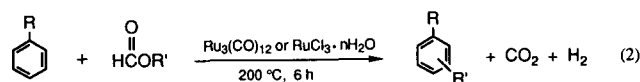
Although the present decarbonylation proceeded at 150°C, the catalytic activity was drastically decreased at 120°C (Table 2). Furthermore, addition of (CH₃)₃NO · 2H₂O as a cocatalyst considerably increased both the conversion of alkyl formates and the selectivity of the

corresponding alcohols (Runs 3 and 4 in Table 1). The same phenomenon was observed in our previous study [5e]. It has been reported that (CH₃)₃NO can be employed to displace or remove the carbonyl ligand from ruthenium [13] and osmium carbonyls [14] under mild conditions by oxidizing the carbonyl ligand to carbon dioxide. Thus, in the present reaction, (CH₃)₃NO · 2H₂O could also operate to remove the carbonyl ligand from Ru₃(CO)₁₂ to produce a catalytically active and coordinatively unsaturated ruthenium species (probably monomeric).

Accordingly, the most plausible catalytic cycle is as follows. Oxidative addition of the formyl C–H bond in alkyl formates to an active ruthenium centre occurs first, and subsequent migration of CO and reductive elimination gives the corresponding alcohols with regeneration of the active ruthenium species. A similar mechanism could also occur in the rhodium-catalyzed formyl C–H bond cleavage in ethyl formate [4f] and in our previous studies [5e,9].

2.2. Alkylation of arenes with alkyl formates

On further study, we found that it is possible to effect the decarbonylation or decarboxylation of alkyl formates selectively through the respective addition or exclusion of (CH₃)₃NO₂ · 2H₂O to the ruthenium catalyst system. Thus, when alkyl formates were treated with Ru₃(CO)₁₂ catalyst alone (i.e., in the absence of (CH₃)₃NO · 2H₂O) in the presence of arenes, decarboxylation of the alkyl formates proceeded selectively and subsequent alkylation of the arenes occurred [Eq. (2)]. Although the use of alkyl formates as an alkoxylating reagent is well known [5–7], this is the first example of the effective utilization of alkyl formates as an alkylating reagent.



As can be readily seen from Table 3, the alkylation of arenes with benzyl formate or secondary alkyl formates proceeded smoothly to give the alkylated products in 22%–77% yield. Toluene and xylene were more

Table 2
Effects of reaction temperature ^a

Run	Formate	Temp. (°C)	Conv. (%) ^b	Product (%) ^b
1	HCO ₂ CH ₂ Ph	200	100	PhCH ₂ OH 74
9	HCO ₂ CH ₂ Ph	150	92	PhCH ₂ OH 72
10	HCO ₂ CH ₂ Ph	120	5	— 0

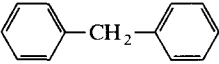
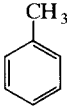
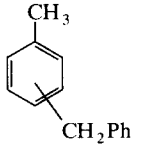
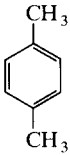
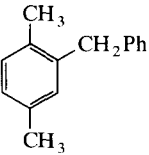
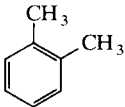
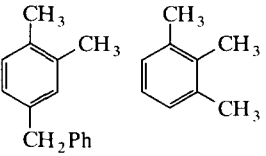
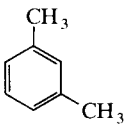
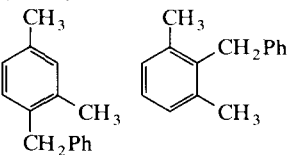
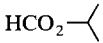
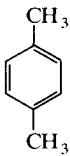
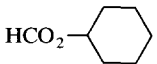
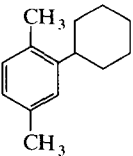
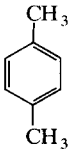
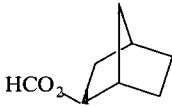
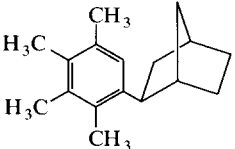
^a Alkyl formate (5.0 mmol) in benzene for 6 h under an argon atmosphere.

^b Determined by GLC.

reactive than benzene. The reaction of toluene with benzyl formate afforded a 40:8:52 (*o*/*m*/*p*) mixture of phenyltolylmethane in 77% total yield, together with the generation of CO₂ (2.36 mmol) (Run 12). *p*-Xylene also reacted with benzyl formate to give only one benzylated product (Run 13). In contrast, *o*- and *m*-xylene gave two isomers, respectively (Runs 14 and 15).

In the reaction of *m*-xylene with benzyl formate, the 2- and 4-positions of *m*-xylene were benzylated, but the 5-position, which was *meta* relative to both methyl substituents on *m*-xylene, was not benzylated at all (Run 15). This result clearly indicates that orientation of the present reaction is controlled by *ortho* and *para*, but not *meta*, substituents alkyl formates, secondary

Table 3
Ruthenium-catalyzed alkylation of arenes with alkyl formates ^a

Run	Arene	Formate	Products ^b	Yield (%) ^b
11		HCO ₂ CH ₂ Ph		(22)
12 ^c		HCO ₂ CH ₂ Ph	 (<i>o</i> / <i>m</i> / <i>p</i> = 40:8:52) ^d	77
13		HCO ₂ CH ₂ Ph		(51)
14		HCO ₂ CH ₂ Ph	 (64:36) ^d	(48)
15		HCO ₂ CH ₂ Ph	 (80:20) ^d	(59)
16 ^e		HCO ₂ - 		24
17 ^e		HCO ₂ - 		(23)
18		HCO ₂ - 		(34)

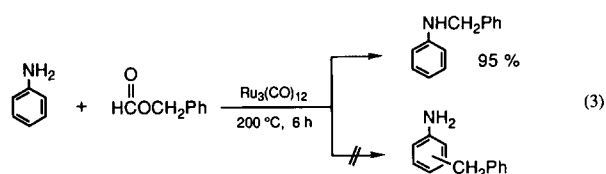
^a Formate (5.0 mmol), arene (4.0 ml), Ru₃(CO)₁₂ (0.10 mmol) at 200°C for 6 h under an argon atmosphere. ^b Determined by GLC; figures in parentheses were isolated yields. ^c RuCl₃ · nH₂O (0.30 mmol) was used. ^d Determined by ¹³C NMR. ^e HCOOH (5.0 mmol) was added.

alkyl formates such as isopropyl, cyclohexyl and *exo*-2-norbornyl formate also reacted with arenes to give the corresponding products in moderate to good yield (Runs 16–19). However, with the exception of *exo*-2-norbornyl formate, in those reactions involving secondary alkyl formates further addition of an equimolar amount of HCOOH with the alkyl formate enhanced the yields of alkylated products, probably due to regeneration of alkyl formates from the alcohols generated and added HCOOH. On the other hand, except for benzyl formate, primary alkyl formates and tertiary alkyl formates did not react with arenes under the present reaction conditions.

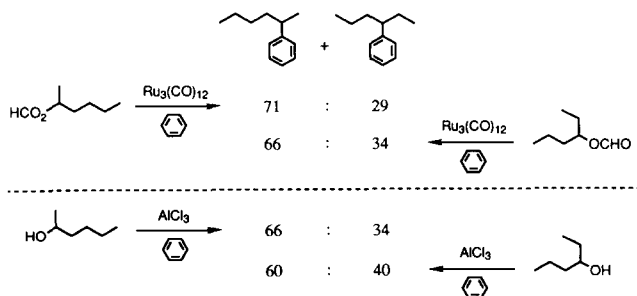
When 2-hexyl and/or 3-hexyl formate were employed in the reaction with benzene, a mixture of 2-phenyl- and 3-phenylhexane was obtained in the ratio of ca. 7:3. This ratio of the products accords with that obtained in Friedel–Crafts alkylation using AlCl_3 (Scheme 1).

The catalytic activities of several ruthenium complexes were examined in the benzylation of toluene with benzyl formate (Table 4). Of the ruthenium complexes investigated, only $\text{Ru}_3(\text{CO})_{12}$ and $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ showed high catalytic activities (Runs 12 and 20), other ruthenium complexes and ruthenium metal (as a heterogeneous catalyst) being totally ineffective.

Unfortunately, when benzyl formate was treated in anisole or *N,N*-dimethylaniline, only decarbonylation of benzyl formate to benzyl alcohol occurred. On the other hand, in aniline, benzylation of amino group occurred to give *N*-benzylaniline, almost quantitatively [Eq. (3)].



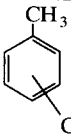
The importance of the formyl functionality is explicitly demonstrated by the use of benzyl alcohol in place of benzyl formate. Under the same reaction conditions



Scheme 1. Alkylation of benzene with 2- and 3-hexyl formates.

Table 4

Catalytic activities of several transition metal complexes in the benzylation of toluene with benzyl formate ^a

Run	Catalyst	Conv. (%) ^b	Product (%) ^b			
			PhCH ₂ OH	PhCHO		CH ₂ Ph
20	$\text{Ru}_3(\text{CO})_{12}$	100	0	0	68	
21 ^c	$\text{Ru}_3(\text{CO})_{12}$	100	0	0	55	
12	$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	100	0	0	77	
22	$\text{Ru}(\text{COD})(\text{COT})$	57	15	12	0	
23	$\text{Ru}(\text{acac})_3$	0	0	0	0	
24	Ru metal	0	0	0	0	
25	RhCl_3	64	0	0	29	
26	AlCl_3	16	0	0	9	

^a Benzyl formate (5.0 mmol), catalyst (0.30 mmol as metal), toluene (4.0 ml) at 200°C for 6 h under an argon atmosphere. ^b Determined by GLC. ^c 2,6-Di-*t*-butylphenol (0.50 mmol) was added as a radical scavenger.

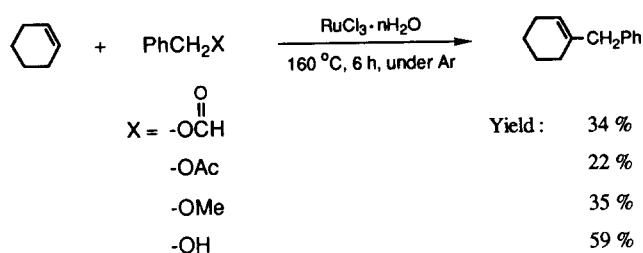
as Run 20 (benzylation of toluene), the yield of phenyltolymethane decreased drastically to 23%.

Although the possibility of tightly ‘caged’ radical could not be eliminated completely, a radical scavenger such as 2,6-di-*t*-butylphenol did not affect the present reaction (Run 21). Hence, we consider that the present reaction proceeds via an alkyl cation intermediate, not a free-radical intermediate. Thus, we consider that the present alkylation reaction proceeds via electrophilic substitution of arenes [12] ², i.e., ruthenium-catalyzed decarboxylation of alkyl formate occurs first and the generated alkyl cation subsequently reacts electrophilically with arenes to give the alkylated product together with molecular hydrogen.

2.3. Alkylation of alkenes with alkyl formates or alcohols

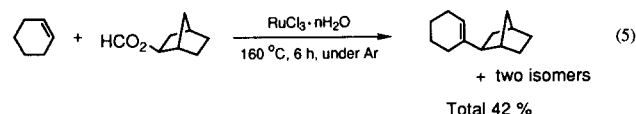
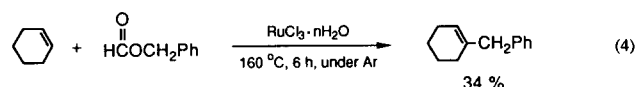
The coupling reaction of vinyl halides with activated alkenes such as methyl acrylate catalyzed by palladium complex is well known as the Heck reaction [16], and we recently reported that this type of reaction was also promoted by a ruthenium catalyst [17]. To our knowledge, however, this type of reaction, i.e. the alkylation reaction of vinyl carbon in alkenes using alkyl formates or alcohols as an alkylating reagent, has not yet been reported. We have now established that the alkylation of vinyl carbon in non-activated cyclic alkenes such as cyclohexene and trisubstituted alkenes with benzyl formate and *exo*-2-norbornyl formate proceeded in the

² Dixneuf et al. have reported ruthenium-catalyzed alkylation of furan and thiophene in which they suggest a mechanism involving C–H bond activation [15].



Scheme 2.

presence of a catalytic amount of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ [Eqs. (4) and (5)].



We first investigated the effect of the leaving groups (Scheme 2). Surprisingly, the hydroxy functionality gave the best results, i.e. benzylation of cyclohexene with benzyl alcohol afforded 1-benzylcyclohexene in 59%

yield. For this reason, we examined the following alkylation of alkenes catalyzed by $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ employing alcohols as alkylating reagents (Scheme 2).

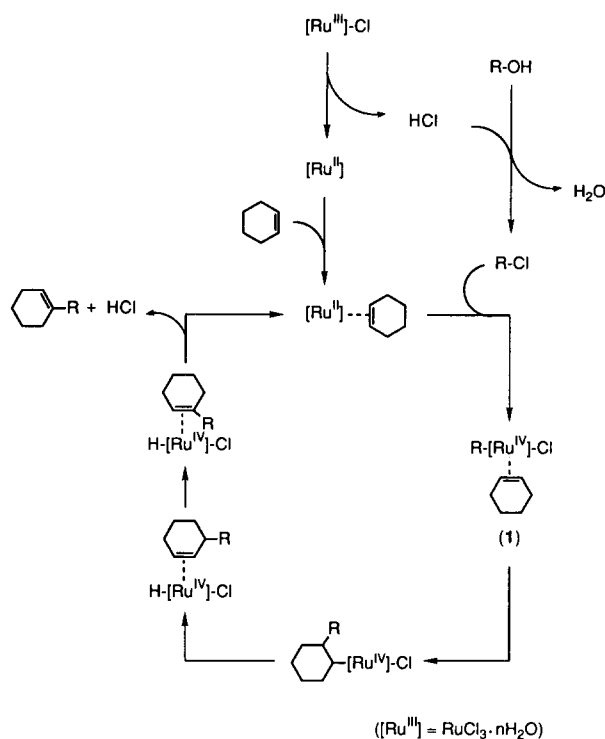
The results obtained are summarized in Table 5. In the reaction of cyclohexene with benzyl alcohol, 1-benzylcyclohexene was obtained in 59% yield (Run 27) at 120°C. However at 100°C, the yield of 1-benzylcyclohexene decreased considerably (Runs 28 and 29). When $\text{Ru}_3(\text{CO})_{12}$ or $\text{Ru}(\text{acac})_3$ were employed as catalyst, the corresponding benzylated product was not obtained at all (Runs 31 and 32). Palladium complex, which is a well-known catalyst for Heck reaction, was totally ineffective (Run 33). On the other hand, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ or $\text{SnCl}_4 \cdot n\text{H}_2\text{O}$ showed some catalytic activity (Runs 34 and 35), suggesting that the catalyst precursor employable in the present reaction should have labile halogen ligands vide infra. Alkenes other than cyclohexene also reacted with benzylic alcohols to afford products (Runs 36 and 37). *p*-Methylbenzyl alcohol also reacted with cyclohexene to give the corresponding alkylated product in 31% yield (Run 38). However, benzylation of less-substituted acyclic alkenes such as 1-pentene and 2-pentene did not proceed at all under the present reaction conditions.

In order to examine the reaction mechanism, we investigated the effect of radical scavenger but found

Table 5
Alkylation of alkenes with alcohols ^a

Run	Alkene	Alcohol	Catalyst	Temp. (°C)	Product ^b	Yield (%) ^b
27			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	160		59
28			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	120		49
29			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	100		31
30 ^c			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	160		57
31			$\text{Ru}_3(\text{CO})_{12}$	120	—	0
32			$\text{Ru}(\text{acac})_3$	120	—	0
33			PdCl_2	120	—	0
34			$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	120		19
35			$\text{SnCl}_4 \cdot n\text{H}_2\text{O}$	120		18
36			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	160		(14)
37			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	160		(21)
38			$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$	160		31

^a Alcohol (5.0 mmol), catalyst (0.30 mmol as metal) and alkene (4.0 ml) for 6 h under an argon atmosphere. ^b Determined by GLC based on the amount of alcohol; figures in parentheses were isolated yields. ^c 2,6-Di-*t*-butylphenol (0.10 mmol) was added as radical scavenger.



Scheme 3.

that addition of a radical scavenger such as 2,6-di-*t*-butylphenol had no effect on the reaction (Run 30). Hence, the possibility that the mechanism of this alkylation reaction involves a radical process is unlikely.

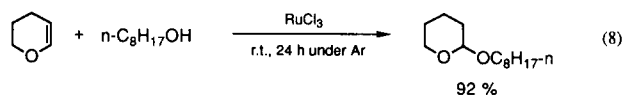
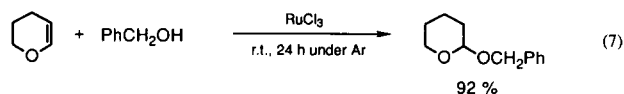
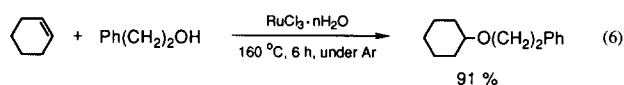
As shown previously in Scheme 2, benzyl bromide, benzyl methyl ether and benzyl acetate rather than benzyl alcohol could also be employed in the present reaction to afford 1-benzylcyclohexene. This suggests that bond cleavage of benzyl alcohol occurs at a C–O bond rather than an O–H bond.

On the basis of all the results mentioned above, a possible catalytic cycle is illustrated in Scheme 3. The initial step involves the dissociation of a Cl[−] ligand from RuCl₃ · *n*H₂O to give an active Ru^{II} species [18]. The Cl[−] generated nucleophilically substitutes the hydroxy group of an alcohol, affording the corresponding alkyl chloride. Oxidative addition of the alkyl chloride to an alkene-coordinated Ru^{II} species then occurs to give an Ru^{IV} intermediate (1). Further alkene insertion into the alkyl–Ru^{IV} bond and β-hydride elimination affords mainly 3-alkylcyclohexene. Isomerization of 3-alkylcyclohexene to 1-alkylcyclohexene then proceeds via addition–elimination of a H–[Ru] species to yield 1-alkylcyclohexene. That this isomerization requires a H–[Ru] species is based on the observation that the isomerization of 3-benzylcyclohexene to 1-benzylcyclohexene does not proceed in the presence of a catalytic amount of RuCl₃ · *n*H₂O under the reaction conditions employed.

For the present reaction to proceed, a low and steady-state concentration of Cl[−] is essential. If the concentration of halogen anion increases (for example, when benzyl bromide is used as a substrate), initial formation of an active Ru^{II} species must be suppressed. This mechanism provides a reasonable explanation for the result that only catalyst precursors bearing labile halogen ligands exhibit catalytic activity in the present reaction (*vide supra*).

2.4. Addition of alcohols to alkenes

When 2-phenylethanol was used in the reaction with cyclohexene, the product was not 1-(2-phenylethyl)cyclohexene but cyclohexyl 2-phenylethyl ether which was generated from the direct addition of alcohols to alkenes [Eq. (6)]. Even when benzyl alcohol was used, if 3,4-dihydro-2*H*-pyran was also employed the product was again the ether [Eqs. (7) and (8)]. Anhydrous RuCl₃ showed higher catalytic activity than RuCl₃ · *n*H₂O in this reaction which proceeded smoothly at room temperature. Such reactions can be regarded as a means of protecting the hydroxy groups in alcohols. A large number of methods for hydroxy group protection have been devised with a view to maintaining the sensitivity of the molecule towards acidic and basic conditions [19]. Recently, palladium- [20] or cobalt-catalyzed [21] addition of alcohols to vinyl ethers has been shown to be an efficient method of protecting hydroxy groups under neutral reaction conditions. The present reaction also offers a novel means of protecting hydroxy groups using a ruthenium catalyst under neutral reaction conditions. It is noteworthy that all alkenes except vinyl ethers can be employed in the present reaction [Eq. (6)].



3. Experimental details

3.1. Materials

Arenes, alkenes and alcohols were commercial products and distilled before use. While tertiary alkyl formates were prepared via published methods [22], the primary and secondary alkyl formates were prepared as follows. A mixture of a primary or secondary

alcohol (50 mmol) and formic acid (two- or three-fold excess) was placed in a 50 ml Pyrex flask equipped with a reflux condenser and a magnetic stirring bar. The reaction mixture was stirred at ca. 100°C for 24–48 h. The system was then cooled and the reaction was quenched by the addition of saturated aqueous NaHCO_3 . The organic layer was extracted with ether and the product (formate) fractionally distilled. Secondary alkyl formates such as cyclohexyl formate and *exo*-2-norbornyl formate were prepared by addition of formic acid to alkenes (cyclohexene and norbornylene) according to the literature method [23].

The various reactants, i.e. $\text{Ru}_3(\text{CO})_{12}$, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, RuCl_3 (anhydrous), $\text{Ru}(\text{acac})_3$, Ru metal, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{SnCl}_4 \cdot n\text{H}_2\text{O}$ and AlCl_3 , were commercially available and used without further purification. $\text{Ru}(\text{COD})(\text{COT})$ was prepared according to the literature method [24]. The compound $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$ was dried under vacuum at room temperature for 24 h before use.

3.2. General procedures

3.2.1. Decarbonylation of alkyl formates

A mixture of alkyl formate (5.0 mmol), $\text{Ru}_3(\text{CO})_{12}$ (0.10 mmol), $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$ (0.50 mmol) and benzene (4.0 ml) was placed in a 50 ml stainless-steel autoclave (Yuasa Giken; SUS 316) equipped with a glass liner and a magnetic stirring bar. The unit was sealed and then purged three times using pressurization–depressurization cycles of argon at 10 kg cm^{-2} pressure. The reactor was heated to 200°C within 15 min with stirring and held at this temperature for 6 h. The reaction was terminated by rapid cooling. The gaseous products were collected in a gas burette and analyzed by directly GLC methods. The resulting brown solution were also analyzed by GLC and the products isolated by Kugelrohr distillation.

3.2.2. Alkylation of arenes with alkyl formates

Experiments were carried out using the same procedure as for the decarbonylation of alkyl formates but without the addition of $(\text{CH}_3)_3\text{NO} \cdot 2\text{H}_2\text{O}$. When alkyl formates other than benzyl formate and *exo*-2-norbornyl formate were used as the substrate, formic acid (5.0 mmol) was also added.

3.2.3. Alkylation of benzene with 2- or 3-hexanol using AlCl_3

A mixture of 2-hexanol (12.61 ml, 0.10 mol), benzene (44.68 ml, 0.50 mol) and AlCl_3 (13.334 g, 0.10 mol) was stirred at room temperature for 24 h under an argon atmosphere. The products were analyzed by GLC and GC–MS methods. The experiment involving 3-hexanol was carried out using the same procedure.

3.2.4. Alkylation of alkenes with alcohols

Experiments were carried out using the same procedure as for the decarbonylation of alkyl formates. A mixture of the alcohol (5.0 mmol), catalyst (0.30 mmol as metal) and alkenes (4.0 ml) was treated at 160°C for 6 h under an argon atmosphere.

3.3. Analytical procedures

The identity of all the products was confirmed by ^1H and ^{13}C NMR spectroscopy and GC–MS methods. ^1H NMR (90 MHz) and ^{13}C NMR (25.05 MHz) spectra were recorded on JEOL JNM FX-90 and JEOL JNM FX-100 spectrometers, respectively. Samples were dissolved in CDCl_3 and the chemical shift values are expressed relative to tetramethylsilane (TMS) as internal standard. Mass spectra were obtained using a Shimadzu GC–MS–QP-2000 instrument (for GC, Shimadzu GC-14A chromatograph equipped with a Shimadzu capillary column HiCap CBP10-M25-0.25). The GLC analyses were carried out on Shimadzu GC-8A and GC-12A chromatographs equipped with columns (3 mm i.d. $\times$ 3 m length) packed with PEG-HT (5% on Uniport HP, 60–80 mesh), silicone OV-17 (2% on Chromosorb W(AW-DMCS), 80–100 mesh) and active carbon (60–80 mesh).

Analytical data for the representative products are listed below. Some benzylated products were prepared separately by literature methods [25]; their spectral data were consistent with those of the reaction products.

Phenyl-*o*-tolylmethane: Kugelrohr distillation (90–95°C/1.0 mmHg), colorless liquid. ^{13}C NMR (CDCl_3) δ : 19.45 (q, $-\text{CH}_3$); 39.30 (t, $-\text{CH}_2-$); 125.52 (d, phenyl); 125.62 (d, phenyl); 126.06 (d, phenyl); 127.95 (d, phenyl); 128.29 (d, phenyl); 129.56 (d, phenyl); 129.89 (d, phenyl); 136.07 (s, phenyl); 138.45 (s, phenyl); 139.92 (s, phenyl) ppm. MS (m/z): 182 (M^+).

Phenyl-*m*-tolylmethane: Kugelrohr distillation (90–95°C/1.0 mmHg), colorless liquid. ^{13}C NMR (CDCl_3) δ : 21.20 (q, $-\text{CH}_3$); 41.73 (t, $-\text{CH}_2-$); 125.67 (d, phenyl); 126.45 (d, phenyl); 128.00 (d, phenyl); 128.53 (d, phenyl); 129.31 (d, phenyl); 137.39 (s, phenyl); 140.59 (s, phenyl); 140.79 (s, phenyl) ppm. MS (m/z): 182 (M^+).

Phenyl-*p*-tolylmethane: Kugelrohr distillation (90–95°C/1.0 mmHg), colorless liquid. ^{13}C NMR (CDCl_3) δ : 20.82 (q, $-\text{CH}_3$); 41.39 (t, $-\text{CH}_2-$); 125.57 (d, phenyl); 128.00 (d, phenyl); 128.49 (d, phenyl); 128.78 (d, phenyl); 134.91 (s, phenyl); 137.68 (s, phenyl); 140.98 (s, phenyl) ppm. MS (m/z): 182 (M^+).

1-Benzyl-2,5-dimethylbenzene: Kugelrohr distillation (115°C/4.0 mmHg), colorless liquid. ^1H NMR (CDCl_3) δ : 2.12 (s, 3H, $-\text{CH}_3$); 2.22 (s, 3H, $-\text{CH}_3$); 3.87 (s, 2H, $-\text{CH}_2-$); 6.80–7.16 (m, 8H, phenyl) ppm. ^{13}C NMR (CDCl_3) δ : 19.08 (q, $-\text{CH}_3$); 20.90 (q,

–CH₃); 39.39 (t, –CH₂–); 125.70 (d, phenyl); 127.05 (d, phenyl); 128.22 (d, phenyl); 128.58 (d, phenyl); 130.10 (d, phenyl); 130.69 (d, phenyl); 131.21 (s, phenyl); 135.09 (s, phenyl); 138.50 (s, phenyl); 140.31 (s, phenyl) ppm. MS (*m/z*): 196 (M⁺).

1-Benzyl-3,4-dimethylbenzene: Kugelrohr distillation (162°C/15 mmHg), colorless liquid. ¹H NMR (CDCl₃) δ: 2.16 (s, 6H, 2-CH₃); 3.85 (s, 2H, –CH₂–); 6.81–7.19 (m, 8H, phenyl) ppm. ¹³C NMR (CDCl₃) δ: 19.20 (q, –CH₃); 19.67 (q, –CH₃); 41.45 (t, –CH₂–); 125.81 (d, phenyl); 128.28 (d, phenyl); 128.75 (d, phenyl); 129.57 (d, phenyl); 130.10 (d, phenyl); 133.98 (s, phenyl); 136.33 (s, phenyl); 138.38 (s, phenyl); 141.38 (s, phenyl) ppm. MS (*m/z*): 196 (M⁺).

1-Benzyl-2,3-dimethylbenzene: Kugelrohr distillation (162°C/15 mmHg), colorless liquid. ¹³C NMR (CDCl₃) δ: 15.26 (q, –CH₃); 20.55 (q, –CH₃); 39.98 (t, –CH₂–); 125.29 (d, phenyl); 125.81 (d, phenyl); 126.23 (d, phenyl); 127.99 (d, phenyl); 128.28 (d, phenyl); 128.52 (d, phenyl); 134.97 (s, phenyl); 136.80 (s, phenyl); 138.56 (s, phenyl); 140.67 (s, phenyl) ppm. MS (*m/z*): 196 (M⁺).

1-Benzyl-2,4-dimethylbenzene: Kugelrohr distillation (117°C/4.0 mmHg), colorless liquid. ¹H NMR (CDCl₃) δ: 2.12 (s, 3H, –CH₃); 2.22 (s, 3H, –CH₃); 3.86 (s, 2H, –CH₂–); 6.82–7.22 (m, 8H, phenyl) ppm. ¹³C NMR (CDCl₃) δ: 19.73 (q, –CH₃); 21.08 (q, –CH₃); 39.22 (t, –CH₂–); 125.93 (d, phenyl); 126.75 (d, phenyl); 128.46 (d, phenyl); 128.75 (d, phenyl); 130.04 (d, phenyl); 131.22 (d, phenyl); 135.86 (s, phenyl); 135.92 (s, phenyl); 136.38 (s, phenyl); 140.79 (s, phenyl) ppm. MS (*m/z*): 196 (M⁺).

1-Benzyl-2,6-dimethylbenzene: Kugelrohr distillation (117°C/4.0 mmHg), colorless liquid. ¹³C NMR (CDCl₃) δ: 20.02 (q, 2-CH₃); 34.93 (t, –CH₂–); 125.58 (d, phenyl); 126.17 (d, phenyl); 127.64 (d, phenyl); 128.05 (d, phenyl); 128.22 (d, phenyl); 136.62 (s, phenyl); 136.80 (s, phenyl); 139.55 (s, phenyl) ppm. MS (*m/z*): 196 (M⁺).

2,5-Dimethyl-1-*exo*-(2-norbornyl)benzene: Kugelrohr distillation (120°C/1.0 mmHg), colorless liquid. ¹H NMR (CDCl₃) δ: 1.17–1.79 (m, 8H, –CH₂–); 2.22 (s, 3H, –CH₃); 2.28 (s, 3H, –CH₃); 2.32 (br, 1H, –CH–); 2.34 (br, 1H, –CH–); 2.75 (dd, 1H, –CH–, *J* = 5.94 and 8.41 Hz); 6.84 (d, 1H, phenyl, *J* = 7.91 Hz); 6.98 (d, 1H, phenyl, *J* = 7.91 Hz); 7.02 (s, 1H, phenyl) ppm. ¹³C NMR (CDCl₃) δ: 19.58 (q, –CH₃); 21.31 (q, –CH₃); 29.17 (t, –CH₂–); 30.58 (t, –CH₂–); 36.38 (t, –CH₂–); 36.93 (d, –CH–); 38.69 (t, –CH₂–); 41.51 (d, –CH–); 43.84 (d, –CH–); 125.58 (d, phenyl); 125.82 (d, phenyl); 130.15 (d, phenyl); 132.92 (s, phenyl); 134.81 (s, phenyl); 145.22 (s, phenyl) ppm. MS (*m/z*): 200 (M⁺).

1-Benzylcyclohexene: Kugelrohr distillation (70°C/4.0 mmHg), colorless liquid. ¹³C NMR (CDCl₃) δ: 22.46 (t, –CH₂–); 22.95 (t, –CH₂–); 25.34 (t, –CH₂–); 28.07 (t, –CH₂–); 44.69 (t, –CH₂–); 122.90

(d, =CH–); 125.72 (d, phenyl); 128.06 (d, phenyl); 128.84 (d, phenyl); 137.62 (s, phenyl); 140.34 (s, =C–) ppm. MS (*m/z*): 172 (M⁺).

4-(1-Cyclohexenylmethyl)toluene: Kugelrohr distillation (90°C/2.0 mmHg), colorless liquid. ¹³C NMR (CDCl₃) δ: 21.11 (q, –CH₃); 22.57 (t, –CH₂–); 23.10 (t, –CH₂–); 25.48 (t, –CH₂–); 28.16 (t, –CH₂–); 44.31 (t, –CH₂–); 122.56 (d, =CH–); 128.68 (d, phenyl); 128.87 (d, phenyl); 131.31 (s, phenyl); 135.01 (s, phenyl); 137.24 (s, =C–) ppm.

Benzyl 2-tetrahydropyranyl ether: Kugelrohr distillation (95°C/6.0 mmHg), colorless liquid. ¹H NMR (CDCl₃) δ: 1.34–2.00 (m, 6H, –CH₂–); 3.42–3.50 (m, 1H, –OCHH–); 3.79–3.90 (m, 1H, –OCHH–); 4.42 (d, 1H, *J* = 11.87 Hz, –OCHHPh); 4.63 (t, –OCHO–); 4.71 (d, 1H, *J* = 11.87 Hz, –OCHHPh) 7.16–7.31 (m, 5H, phenyl) ppm. ¹³C NMR (CDCl₃) δ: 19.32 (t, –CH₂–); 25.54 (t, –CH₂–); 30.59 (t, –CH₂–); 61.70 (t, –CH₂–); 68.63 (t, –CH₂–); 97.46 (d, –CH–); 127.28 (d, phenyl); 127.63 (d, phenyl); 128.16 (d, phenyl); 138.38 (s, phenyl) ppm.

Cyclohexyl 2-phenylethyl ether: Kugelrohr distillation (110°C/3.0 mmHg), colorless liquid. ¹³C NMR (CDCl₃) δ: 24.08 (t, –CH₂–); 25.84 (t, –CH₂–); 32.23 (t, –CH₂–); 36.86 (t, –CH₂–); 68.79 (t, –OCH₂–); 77.40 (d, –OCH–); 125.74 (d, phenyl); 127.91 (d, phenyl); 128.61 (d, phenyl); 138.92 (s, phenyl) ppm.

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