Nucleophilic Addition of Lanthanoid Metal Umpoled Diaryl Ketones to Electrophiles

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Ytterbium metal promoted cross-coupling reactions of diaryl ketones with a variety of electrophiles are described. Diaryl ketones treated with 1–2 equiv of Yb metal react smoothly with other ketones, nitriles, epoxides, CO_2, etc., to give the corresponding unsymmetrical pinacols, α-hydroxy ketones, 1,3-diols, α-hydroxy carboxylic acids, etc., in good yields repectively. These reactions occur via nucleophilic addition of the intermediates **4a–c** to electrophiles. Reaction of benzophenone (**1a**) with Yb metal is discussed in detail and some information on the composition of the intermediates of the reaction of diaryl ketones with Yb metal are also given.

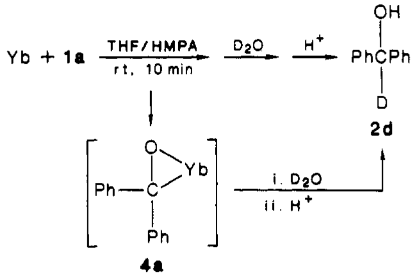
Rapid development in application of lanthanoids, especially lanthanoid salts, to organic synthesis has been recently achieved.[1] However, relatively few reports on the direct use of lanthanoid metals, the simplest lanthanoid reagents, could be found.[2,3] Since zerovalent lanthanoid elements have large absolute redox potential values[4] ($Yb^0/Yb^{3+} = -2.27$, $Sm^0/Sm^{3+} = -2.41$ V), they should behave as strong reducing agents. It was reported that in the presence of lanthanoid metals, reactions of β-bromopropionate and ketones gave γ-lactones.[2c] The Sm/CH_2I_2 system is effective in cyclopropanation and iodomethylation reactions.[2a,b] We have reported some lanthanoid metal mediated reactions such as reduction of C–C multiple bonds,[3a] reductive coupling of carbonyl compounds,[3b] and selective formation of azoxy compounds.[3c] We report here the lanthanoid metal mediated novel cross-coupling reactions of diaryl ketones with a wide variety of electrophiles, in which the carbonyl groups in diaryl ketones are umpoled by lanthanoid metals from electrophilic to nucleophilic.

Table I. Reaction of Diaryl Ketones with Lanthanoid Metals[a]

run	Ln	ketone	Ln:ketone	reaction time, min	product (% yield)[b]	
1	Yb	**1a**	1:2	<5	**2a** (—)	**3a** (97)
2	Yb	**1a**	1:1	10	**2a** (98)	**3a** (—)
3	Sm	**1a**	1:1	30	**2a** (31)	**3a** (62)
4	Yb	**1b**	2:1[c]	20	**2b** (95)	**3b** (—)
5	Yb	**1c**	1:1	20	**2c** (95)	**3c** (—)

[a] Room temperature in THF/HMPA. [b] Isolated yield based on the ketones. [c] 1 equiv of Yb metal gave a lower yield of **2b**.

Scheme I



Umpolung of a functional group (to change its polarity to the opposite) is very important in synthetic chemistry and much effort has been made in this field.[5] However, few examples concerning umpolung of a carbonyl group and its use in organic synthesis could be found. It was reported that reaction of diaryl ketones with an excess of alkali metals in dimethoxyethane or liquid ammonia gave diaryl ketone dianions that showed nucleophilicity toward some electrophiles.[6] However, the strong alkalinity limited their use in organic synthesis. Active titanium metal promoted cross-coupling reactions of diaryl ketones with other carbonyl compounds, which was considered to take place via nucleophilic addition of the in situ formed diaryl ketone dianions.[7] Electrochemical reduction of diaryl ketones was also reported to generate the corresponding dianions and attempts to use them in organic synthesis were made.[8] In our studies on application of lanthanoid elements to organic reaction,[3,9] we have found that when treated with 1–2 equiv of lanthanoid metals, the carbonyl groups in diaryl ketones are umpoled from electrophilic to nucleophilic and the reaction intermediates of diaryl ketones and lanthanoid metals can be used as efficient nucleophiles toward a variety of electrophiles. We now report these results. Preliminary communications on part of this work have already appeared.[3b,10]

Results and Discussion

Reactions of Diaryl Ketones with Lanthanoid Metals. Reactions of diaryl ketones **1** with ytterbium (Yb)

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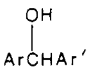
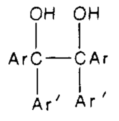
and samarium (Sm) metals proceeded rapidly at room temperature (Table I). It is worthy to note that the re-


$ArC(O)Ar'$

1a: Ar = Ar' = Ph
b: Ar = Ph, Ar' = 2-naphthyl
c: Ar, Ar' = biphenyl-2,2'-diyl


$ArCH(OH)Ar'$

2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action of 0.5 equiv of Yb metal with benzophenone (**1a**) gives the corresponding coupling product, benzopinacol (**3a**) selectively (run 1, Table I) whereas 1 equiv of Yb results in the sole formation of benzhydrol (**2a**) (run 2, Table I). Under the same conditions the reaction of Sm metal with benzophenone (**1a**) gives a mixture of **2** and **3a** (run 3, Table I). Reactions of phenyl 2-naphthyl ketone (**1b**) and fluoren-9-one (**1c**) with 1–2 equiv of Yb metal gives the corresponding reduction products, **2b** and **2c**, in excellent yields respectively (runs 4 and 5, Table I). Moreover, treating the reaction mixture of benzophenone (**1a**) and 1 equiv of Yb metal with D_2O gives the corresponding C-deuteriated reduction product (**2d**) in 98% (100% D) yield (Scheme I). This result indicates that a metallacycle intermediate like **4a**, which has a C–Yb bond, should remain until hydrolysis.

The present reactions of diaryl ketones with Yb metal are in striking contrast with those in the case of divalent lanthanoid reagents.[11] Ce/I_2 or cerium metal was reported to be unreactive toward benzophenone.[11b] Reaction of YbR_2 (R = PhC≡C or C_6F_6) with benzophenone gave benzopinacol (**3a**) as a main product.[11a] No C-deuteriated product was obtained when the reaction mixture of SmI_2 and ketones was treated with D_2O.[11c]

Reactions of WCl_2L_4 complex with acetone was reported to give the corresponding addition product, which has the three-membered metallacycle structure $[W(\eta^2\text{-O=CMe}_2)]$.[12] The reactivity of the intermediates **4a–c** was further studied as follows.

Reactions with Ketones. At room temperature addition of ketones **5a–d** to the diaryl ketone–ytterbium mixture gives the corresponding cross-coupling products **6a–j** in high yields (Table II). Reaction of **1a** with 4-*tert*-butylcyclohexanone (**5d**) gives a mixture of the corresponding axial alcohol and equatorial alcohol (66:44). Under the same conditions Sm metal shows lower reactivity than Yb.[13] In the Sm-promoted reaction of **1a** with **5a**, only 38% yield of cross-coupling product (**6a**) was obtained and the homocoupling product of **1a**, benzopinacol (**3a**), was also formed in 40% yield.

Few reports on the cross-coupling reaction between different carbonyl compounds could be found.[6b,c,7,14] Since a statistical product mixture was usually formed,[14] it was thought to be difficult to obtain the corresponding unsymmetrical pinacols selectively from the reactions between two different carbonyl compounds. It was reported that in the presence of active titanium metal the selective cross-coupling reaction between diaryl ketones and other ketones occurred, but the products were the corresponding deoxygenation products, unsymmetrical olefins, rather than pinacols, which means that the resulted pinacolate intermediates could not tolerate the reaction conditions.[7a,b] The reaction of disodiobenzophenones with benzaldehydes was reported to afford the corresponding unsymmetrical pinacols,[6b,c] however the results in the case of aliphatic carbonyl compounds were not given. Since disodiobenzophenones are very basic reagents, α-proton abstraction might occur in the reactions with aliphatic carbonyl compounds and give complex products.

Table II. Cross-Coupling Reaction of Diaryl Ketones with Other Ketones[a]

diaryl ketone	ketone	product (% yield)[b]	
1a	5a	6a (60)	2a (18)
1a	5a	6a (38)[c]	2a (4)
1a	5b	6b (90)	2a (8)
1a	5c	6c (91)	2a (9)
1a	5d	6d (83)[d]	2a (10)
1b[e]	5a	6e (72)	2b (8)
1b[e]	5b	6f (80)	2b (8)
1b[e]	5c	6g (90)	2b (5)
1c	5a	6h (91)	2c (5)
1c	5b	6j (88)	2c (8)
1c	5c	6j (81)	2c (3)

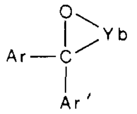
[a] Yb:diaryl ketone:ketone = 1:1:1, room temperature, 10–20 min. [b] Isolated yields based on diaryl ketones. [c] Sm metal (2 equiv) was used instead of Yb. **3a** was also formed in 40% yield. [d] Ratio of axial alcohol to equatorial alcohol = 66:44. [e] 2 mmol of Yb metal was used.

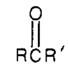
Table III. Reaction of Diaryl Ketones with Nitriles[a]

diaryl ketone	nitrile	product (% yield)[b]		
1a	7a	8a (76)	9a (—)	2a (2)
1a	7b	8b (65)	9b (6)	2a (25)
1a	7c	8c (72)	9c (5)	2a (6)
1a	7d	8d (82)	9d (—)	2a (5)
1b[c]	7a	8e (92)	9e (—)	2b (2)
1b[c]	7b	8f (60)	9f (15)	2b (23)
1b[c]	7c	8g (76)	9g (11)	2b (6)
1c	7a	8h (55)	9h (—)	2c (33)
1c	7b	8i (83)	9i (—)	2c (10)
1c	7c	8j (53)	9j (—)	2c (46)

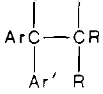
[a] Yb:diaryl ketone:nitrile = 1:1:1, room temperature, 4 h. [b] Isolated yields based on diaryl ketones. [c] 2 equiv of Yb used.

In contrast, none of these side reactions was observed in the present lanthanoid mediated cross-coupling reactions. Furthermore, because of their high yield, mild conditions, and simplicity, the present reactions constitute a useful method for the synthesis of unsymmetrical pinacols.


4a: Ar = Ar' = Ph
b: Ar = Ph, Ar' = 2-naphthyl
c: Ar, Ar' = biphenyl-2-2'-diyl


$RC(O)R'$

5a: R = R' = Me
b: R = Me, R' = n-C_6H_{13}
c: R,R' = $-(CH_2)_5-$
d: R,R' = $-(CH_2)_2CH(t\text{-Bu})(CH_2)_2-$
e: R = Me, R' = H


6a: Ar = Ar' = Ph, R = R' = Me
b: Ar = Ar' = Ph, R = Me, R' = n-C_6H_{13}
c: Ar = Ar' = Ph, R,R' = $-(CH_2)_5-$
d: Ar = Ar' = Ph, R,R' = $-(CH_2)_2CH(t\text{-Bu})(CH_2)_2-$
e: Ar = Ph, Ar' = 2-naphthyl, R = R' = Me
f: Ar = Ph, Ar' = 2-naphthyl, R = Me, R' = n-C_6H_{13}
g: Ar = Ph, Ar' = 2-naphthyl, R,R' = $-(CH_2)_5-$
h: Ar, Ar' = biphenyl-2, 2'-diyl, R = R' = Me
i: Ar, Ar' = biphenyl-2, 2'-diyl, R = Me, R' = n-C_6H_{13}
j: Ar, Ar' = biphenyl-2, 2'-diyl, R = R' = $-(CH_2)_5-$
k: Ar = Ar' = Ph, R = Me, R' = H

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[13] The Yb and Sm metals used here were activated just by treatment with 1–2 drops of methyl iodide or alkyl iodide. Since the Sm metal surface is more inactivated, more effective activation methods are required for higher reactivity.

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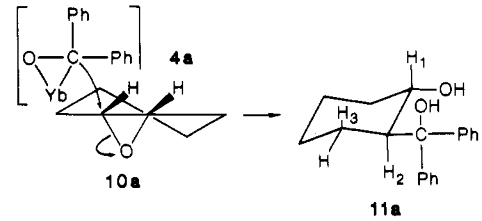
Table IV. Reaction of Diaryl Ketones with Epoxides[a]

diaryl ketone	epoxide	product (% yield)[b]		
1a	**10a**	**11a** (67)	**2a** (33)	
1a	**10b**	**11b** (64)	**12b** (–)	**2a** (12)
1a	**10c**	**11c** (56)	**12c** (tr)[c]	**2a** (28)
1a	**10d**	**11d** (38)	**12d** (37)	**2a** (15)
1b[d]	**10a**	**11e** (77)	**2b** (19)	
1b[d]	**10b**	**11f** (77)	**12f** (–)	**2b** (5)
1b[d]	**10c**	**11g** (65)	**12g** (tr)	**2b** (19)
1b[d]	**10d**	**11h** (42)	**12h** (26)	**2b** (17)
1c	**10a**	**11i** (58)	**2c** (24)	
1c	**10b**	**11j** (61)	**12j** (–)	**2c** (39)
1c	**10c**	**11k** (47)	**12k** (tr)	**2c** (39)
1c	**10d**	**11l** (54)	**12l** (20)	**2c** (18)

[a] Yb:**1**:**10** = 1:1:2, room temperature, 2 h. [b] Isolated yields based on diaryl ketones. [c] tr = trace. [d] 2 equiv of Yb used.

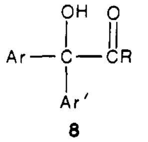
Scheme II



Reactions with Nitriles. These results are summarized in Table III. Both aromatic and aliphatic nitriles react well with diaryl ketones to give the corresponding addition product, α-hydroxy ketones **8a–j**. In some cases compounds **9** were also formed, which might be derived from the reduction of **8** by the unchanged Yb metal or divalent ytterbium species.[15] It seems that the intermediates **4a–c** derived from reaction of **1a–c** with Yb metal possess higher reactivity toward nitriles even than Grignard reagents and lithium reagents.[16] Addition of Grignard reagents to nitriles requires higher temperatures and low yields of the addition products are usually obtained because of α-proton abstraction by Grignard reagents. In the reactions of lithium reagents with acetonitrile and phenylacetonitrile, α-proton removal is faster than the normal addition. Reaction of disodiobenzophenone with benzonitriles in liquid ammonia was reported to give α-arylbenzoins; however, results in the case of nitriles bearing α-protons were not given.[6c] The present Yb metal promoted reactions of diaryl ketones with nitriles should be a convenient method for synthesis of α-hydroxy ketones.

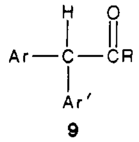
RCN

7a: R = Ph
b: R = $PhCH_2$
c: R = Me
d: R = Me_2CH



$\mathrm{Ar{-}\overset{OH}{\underset{Ar'}{C}}{-}\overset{O}{\overset{\|}{C}}R}$

8



$\mathrm{Ar{-}\overset{H}{\underset{Ar'}{C}}{-}\overset{O}{\overset{\|}{C}}R}$

9

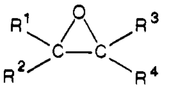
a: Ar = Ar′ = Ph, R = Ph
b: Ar = Ar′ = Ph, R = $PhCH_2$
c: Ar = Ar′ = Ph, R = Me
d: Ar = Ar′ = Ph, R = Me_2CH
e: Ar = Ph, Ar′ = 2-naphthyl, R = Ph
f: Ar = Ph, Ar′ = 2-naphthyl, R = $PhCH_2$
g: Ar = Ph, Ar′ = 2-naphthyl, R = Me
h: Ar, Ar′ = biphenyl-2,2′-diyl, R = Ph
i: Ar, Ar′ = biphenyl-2,2′-diyl, R = $PhCH_2$
j: Ar, Ar′ = biphenyl-2,2′-diyl, R = Me

Reactions with Epoxides. In this case, since epoxides can react with Yb metal to give complex products (one of them is the corresponding alcohol), the diaryl ketone–ytterbium mixture was first transferred by a cannula to another vessel to obviate the influence of the unchanged Yb metal, and the epoxides were then added. As shown in Table IV, the corresponding cross-coupling products, 1,3-diols (**11** and **12a–l**), are formed in good yields. In the reaction of benzophenone (**1a**) with cyclohexene oxide (**10a**) only one stereoisomer (**11a**) is obtained. ^{1}H NMR (400 MHz) spectra show that **11a** has a trans structure (J_{12} = 9.7, J_{23} = 12.5, J_{24} = 2.7 Hz),[17] which means that back-side attack of **4a** to the epoxide is here operative (Scheme II). Stereochemistry of other products was not determined. In the case of styrene oxide (**10b**), C–C bond formation occurs predominantly on the more substituted carbon atom, whereas in the case of isobutylene oxide (**10c**), on the less hindered one. A product mixture derived from attack at both carbon atoms was obtained in the reactions of 1,2-butylene oxide. In some cases the reduction products **2a–c** of diaryl ketones **1a–c** were obtained in considerable yields; however, prolonged reaction time and increased temperature scarcely changed the product distribution. The present reactions constitute the first example of the cross-coupling reaction between ketones and epoxides and should be a good method for synthesis of 1,3-diols although their regioselectivity depends on epoxide. Stereochemistry of the reactions also seems interesting.

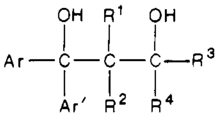
Table V. Reaction of Diaryl Ketones with CO_2[a]

diaryl ketone	product (% yield)[b]		
1a	**13a** (61)	**14a** (4)	**2a** (12)
1b[c]	**13b** (68)	**14b** (8)	**2b** (8)
1c	**13c** (61)	**14c** (15)	**2c** (5)

[a] Yb:diaryl ketone = 1:1, CO_2, 1 atm. room temperature, 30 min. [b] Isolated yields based on diaryl ketones. [c] Yb:**1b** = 2:1.

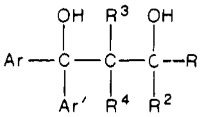


10a: $R^1 = R^3 = H$, $R^2, R^4 = -(CH_2)_4-$
b: $R^1 = R^3 = R^4 = H$, $R^2 = Ph$
c: $R^1 = R^2 = H$, $R^3 = R^4 = Me$
d: $R^1 = R^3 = R^4 = H$, $R^2 = Et$



$\mathrm{Ar{-}\overset{OH}{\underset{Ar'}{C}}{-}\overset{R^1}{\underset{R^2}{C}}{-}\overset{OH}{\underset{R^4}{C}}{-}R^3}$

11



$\mathrm{Ar{-}\overset{OH}{\underset{Ar'}{C}}{-}\overset{R^3}{\underset{R^4}{C}}{-}\overset{OH}{\underset{R^2}{C}}{-}R^1}$

12

a: Ar = Ar′ = Ph, $R^1 = R^3 = H$, $R^2, R^4 = -(CH_2)_4-$
b: Ar = Ar′ = Ph, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$
c: Ar = Ar′ = Ph, $R^1 = R^2 = H$, $R^3 = R^4 = Me$
d: Ar = Ar′ = Ph, $R^1 = R^3 = R^4 = H$, $R^2 = Et$
e: Ar = Ph, Ar′ = 2-naphthyl, $R^1 = R^3 = H$, $R^2, R^4 = -(CH_2)_4-$
f: Ar = Ph, Ar′ = 2-naphthyl, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$
g: Ar = Ph, Ar′ = 2-naphthyl, $R^1 = R^2 = H$, $R^3 = R^4 = Me$
h: Ar = Ph, Ar′ = 2-naphthyl, $R^1 = R^3 = R^4 = H$, $R^2 = Et$
i: Ar, Ar′ = biphenyl-2,2′-diyl, $R^1 = R^3 = H$, $R^2, R^4 = -(CH_2)_4-$
j: Ar, Ar′ = biphenyl-2,2′-diyl, $R^1 = R^3 = R^4 = H$, $R^2 = Ph$
k: Ar, Ar′ = biphenyl-2,2′-diyl, $R^1 = R^2 = H$, $R^3 = R^4 = Me$
l: Ar, Ar′ = biphenyl-2,2′-diyl, $R^1 = R^3 = R^4 = H$, $R^2 = Et$

Reactions with CO_2. Bubbling CO_2 through the reaction mixture of diaryl ketones **1a–c** and Yb metal gives the corresponding carboxylation products **13a–c** in good yields (Table V). Compounds **14a–c** were also obtained as byproducts in these reactions, which might result from reduction of **13a–c** by the unchanged Yb metal or divalent ytterbium species as in the reduction of α-heterosubstituted ketones by SmI_2.[15] Reaction of disodiobenzophenone

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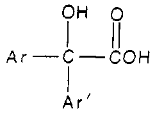
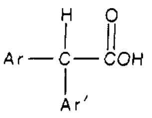
[15] Molander, G. A. Hahn, G. *J. Org. Chem.* **1986**, *51*, 1135.

[16] Stowell, J. C. *Carbanions in Organic Synthesis*; John Wiley and Sons: New York, 1987; pp 58–59.

[17] Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: Oxford, 1969; pp 195–290.



13

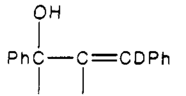


14

a: Ar = Ar′ = Ph
b: Ar = Ph, Ar′ = 2-naphthyl
c: Ar, Ar′ = biphenyl-2,2′-diyl

with CO_2 was reported to give similar carboxylation products.[6c]

Reactions with Other Electrophiles. In the presence of Yb metal, benzophenone (**1a**) also reacts with acetaldehyde, phenyl isocyanate, and ethyl acetate to give the corresponding addition products **6k**, **15**, and **8c** in fair to high yields, respectively (Scheme III). The similar addition reaction occurs even in the case of *N*,*N*-dimethylformatamide (DMF) and diphenylacetylene to give products **16** and **17**, respectively. Moreover, in the case of diphenylacetylene, D_2O treatment of the reaction mixture gave the corresponding deuteriated product **17a**.

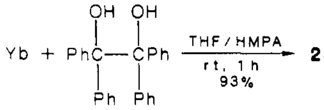


17a

In the case of CO, carbonylation reaction did not take place at room temperature under 1 atm. Reaction with CS_2 gave unidentified products.

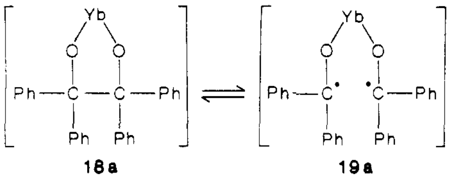
Mechanism of Formation of the Intermediates 4a–c and Some Information on Their Structures. As mentioned above, reaction of benzophenone (**1a**) with Yb metal depends very much on the ratio of the reactants: 0.5 equiv of Yb gaves selectively benzopinacol (**3a**) whose precursor is expected to be **18a**, whereas 1 equiv of Yb results in sole formation of benzhydrol (**2a**) whose precursor is **4a**. Consequently there should be some relationship between **4a** and **18a**. To check this point, we carried out some experiments and obtained the following results. Addition of benzophenone (**1a**, 0.5 mmol) to the benzophenone (0.5 mmol)/Yb (1 mmol) mixture gave benzhydrol (**2a**) in 90% yield and no coupling product (**3a**) was obtained (eq 1). Furthermore, reaction of benzopinacol (**3a**) (0.5 mmol) with Yb metal (1 mmol) gave benzhydrol (**2a**) in 93% yield (eq 2). These results show that **18a** can be reduced into **4a** by Yb metal under the present conditions. It was also found that on exposure to the air at room temperature both **4a** and **18a** were turned into the starting benzophenone (**1a**) in 93 and 95% yields, respectively, which shows that there might be an equilibrium between **18a** and the benzophenone ketyl radical (**19a**), and the latter was expected to give **1a** on air oxidation. Similar equilibrium has been confirmed by ESR in the case of sodium benzophenone ketyl.[18]

$$\mathrm{Yb} + \mathbf{1a} \longrightarrow \mathbf{4a} \xrightarrow[\substack{\text{rt,}\\ 10\ \text{min}\\ 90\%}]{\mathbf{1a}} \mathbf{2a} \qquad (1)$$



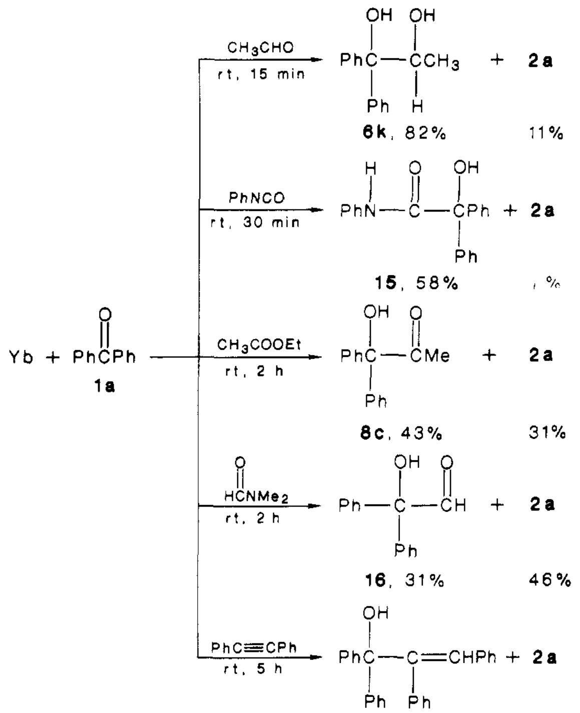
$$\mathrm{Yb} + \mathrm{PhC(OH)(Ph)}\!-\!\mathrm{C(OH)(Ph)Ph} \xrightarrow[\substack{\text{rt, 1 h}\\ 93\%}]{\text{THF / HMPA}} \mathbf{2a} \qquad (2)$$

3a



18a **19a**

Scheme III



On the basis of the above experimental results, we now propose a possible mechanism of reaction of diaryl ketones **1a–c** with Yb metal as depicted in Scheme IV. Electron transfer from Yb metal to diaryl ketones **1a–c** gives the univalent ytterbium intermediate **20**. There would be two paths from here. The highly reactive **20** would immediately react with another molecule of diaryl ketone to give **19**, which couples into **18** (path A). The latter turns into **3a–c** after hydrolysis. Or, **20** undergoes intramolecular reaction (cyclization) to give **4a–c**, which then add to another molecule of diaryl ketone to give **18** (path B). When 1 equiv or excess amount of Yb metal is used, **18** or **19** is further reduced by Yb metal into **4a–c**, which gives **2a–c** after hydrolysis.

4a and **18a** are different also in IR spectrum. Upon treatment of benzophenone (**1a**) with 1 equiv of Yb metal, the carbonyl peak of **1a** at 1664 cm^{-1} disappeared, and a new strong peak assignable to **4a** at 1566 cm^{-1} emerged, which then went out after hydrolysis (Figure 1, a–c).[19] Contrary to this, in the case of 0.5 equiv of Yb metal used, no obvious new peak was observed (Figure 2, a). It is also clear from the IR spectra that air oxidation of both intermediates results in formation of benzophenone (Figure 1, d and Figure 2, b).

We have used the three-membered metallacycle structure (**4a–c**) to represent the intermediates of the reaction of diaryl ketones and Yb metal, in which the ytterbium species behaves as divalent. However, the real structure

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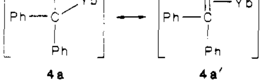
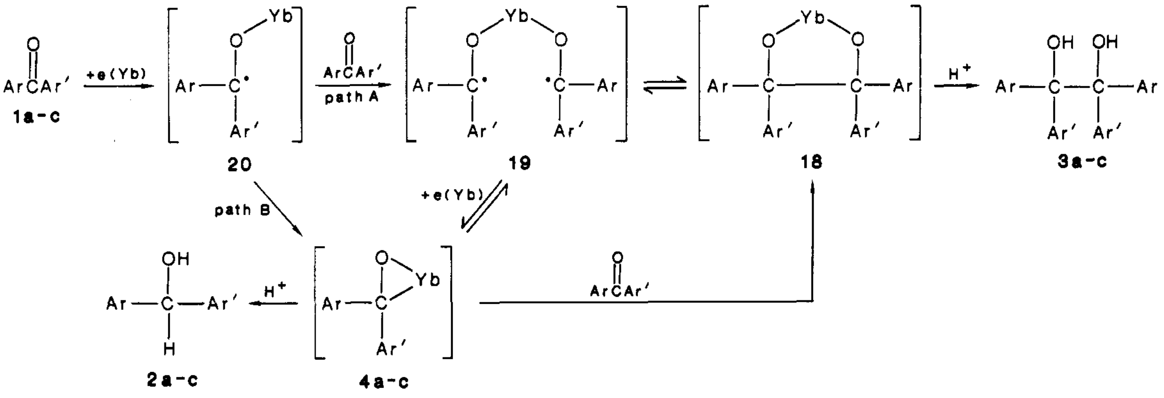
[18] Hirota, N.; Weissman, S. I. *J. Am. Chem. Soc.* **1964**, *86*, 2538.

[19] Since the peak at 1566 cm^{-1} for **4a** is rather strong and has a larger wave number than a C–O single bond,[12] there might be a resonance structure like **4a′**:



4a **4a′**

Scheme IV



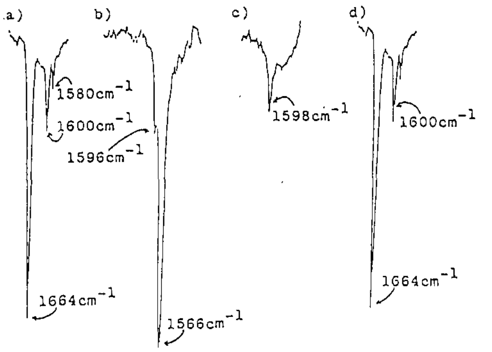


Figure 1. IR spectra of (a) PhCOPh (**1a**), (b) the intermediate of the reaction of Yb with **1a** (1:1) in THF/HMPA at room temperature for 20 min, assignable to **4a**, (c) the product after hydrolysis of **4a**, assignable to **2a**, and (d) the product on exposure of **4a** to air, assignable to **1a**.

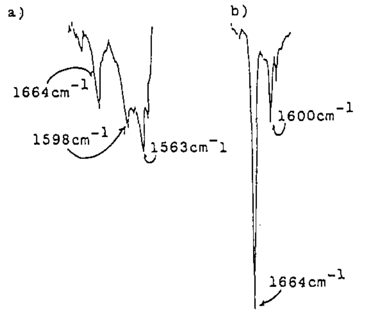


Figure 2. IR spectra of (a) the intermediate of the reaction of Yb with PhCOPh (**1a**) (1:2) in THF/HMPA at room temperature for 5 min, assignable to **18a** ⇌ **19a** and (b) the product on exposure of **18a** ⇌ **19a** to air, assignable to **1a**.

may be more complex. Analysis of the hydrolysis products of the reaction intermediate of benzophenone (1 mmol) and Yb metal (1 mmol) showed that the ratio of **2a** to ytterbium was 1.0 to 0.92.[20] And the unchanged Yb metal was also recovered in 7% (0.07 mmol). These results suggest that besides the divalent ytterbium species, there should be a small amount of trivalent species in the intermediate.[21-23] Quantitative determination of the divalent ytterbium species by iodometry failed since the end point was not distinguishable.[24]

Conclusions. We have demonstrated a novel class of ytterbium metal promoted cross-coupling reactions of diaryl ketones with a variety of electrophiles, which constitute a new example of carbonyl umpolung and its use in organic synthesis. These reactions could be explained by nucleophilic addition of the reaction intermediates **4a–c** to the electrophiles. Because of the experimental simplicity, mild reaction conditions, and high product yield, these intermediates could form a new type of useful nucleophiles. The results described here are important not only in synthetic chemistry but also in chemistry of lanthanoids.

Experimental Section

General Methods. Infrared spectra were recorded on a Hitachi 270-30 IR spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-600 (FT, 60 MHz) or a JNM-GX 400 (FT, 400 MHz) spectrometer and are reported in ppm from internal tetramethylsilane (TMS) on the δ scale with splitting pattern and relative integrated area. The letter designates the multiplicity of the signal: s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. ^{13}C NMR spectra were recorded on a JNM-GX 400 (FT, 100 MHz) spectrometer and chemical shifts are reported relative to internal TMS. Mass spectra were obtained on a JEOL GC-MS JMS-GH-100 apparatus. Elemental analyses were performed by the Chemical Analysis Center of Kyushu University. Melting points were taken on a Yanaco micro melting point apparatus and are uncorrected. Ytterbium (40-mesh) and samarium (20-mesh) metals were obtained from Rare Metallic Co. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under N_2 prior to use. All starting organic compounds were commercial grades and purified by distillation or recrystallization. All reactions were carried out under N_2. The D_2O quenching experiments were carried out by treating the reaction mixtures first with 1 mL of D_2O and then with 2 N HCl.

Reaction of Ytterbium Metal with Diaryl Ketones. In a 50-mL centrifuge tube were placed a magnetic stirring bar and

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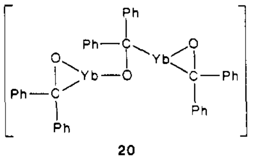
(20) A small amounts (ca. 3%) of deoxygenation product, diphenylmethane, was also formed,[12] which was also calculated here as **2a**. No benzophenone was recovered.

(21) Suppose one molecule of benzophenone accepts two electrons and all starting benzophenone reacts with Yb metal to give benzhydrol (**2a**) after hydrolysis, if there is only divalent ytterbium in the intermediate, the ratio of **2a** to ytterbium should be 1:1 and no Yb metal could be recovered; if there is only trivalent ytterbium, the ratio should be 1.0:0.67 and 0.33 mmol of unchanged Yb metal would be recovered.

(22) A plausible structure for the trivalent ytterbium species might be **20**, which is also expected to show nucleophilic reactivity.



20

(23) A mixed-valence ($Yb^{II,III}$) complex has been reported: Burns, C. J.; Berg, D. J.; Anderson, R. A. *J. Chem. Soc., Chem. Commun.* **1987**, 272.

(24) Magnetic susceptibility measurement by an NMR method may be useful for this determination. See: Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931.

a proper amount of Yb powder under the air, and the tube was sealed with a serum cap. Pure nitrogen was then passed through and the metal was dried by being heated under the stream of nitrogen. One drop of methyl iodide was added by a micro syringe and the metal was heated slightly by a heat gun to activate the Yb metal.[25] Addition of THF (2 mL) gave a pale yellow slurry to which HMPA (1 mL) was introduced.[26] A proper amount of diaryl ketones in THF (2 mL) was then added and the solution immediately turned dark blue (green in the case of **1c**). The mixture was then stirred at room temperature for a proper time (see Table I) and a purple solution (dark green in the case of **1c**) was finally obtained. In the reaction of 0.5 equiv of Yb with **1a** the solution remained dark blue (run 1, Table I). The products were treated with 2 N HCl and then extracted with diethyl ether (3 × 30 mL). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. After the solvent was evaporated, the products were isolated with medium-pressure liquid chromatography (silica gel) and identified by comparison of their NMR, IR, and mass spectra and melting points with those of authentic samples. In the case of Sm the metal was activated with allyl iodide and the reaction procedure was the same as in the case of Yb. Physical properties of the products are recorded below.

Benzhydrol (2a): mp 64–66 °C (lit.[27] mp 67 °C); ^{1}H NMR (CCl_4) δ 2.29 (br s, 1 H), 5.60 (s, 1 H), 7.18 (s, 10 H); IR (KBr) 3288 cm^{-1} (ν OH); MS, *m/e* 184 (M$^+$).

Diphenyl-*C*-deuteriocarbinol (2d): mp 64–65 °C; ^{1}H NMR (CCl_4) δ 2.30 (br s, 1 H), 7.18 (s, 10 H); IR (KBr) 3290 cm^{-1} (ν OH); MS, *m/e* 185 (M$^+$).

2-Naphthylphenylcarbinol (2b): mp 85–87 °C (lit.[28] mp 82–83 °C); ^{1}H NMR (CCl_4) δ 3.01 (br s, 1 H), 5.67 (s, 1 H), 7.15–7.81 (m, 12 H); IR (KBr) 3256 cm^{-1} (ν OH); MS, *m/e* 234 (M$^+$).

9-Fluorenol (2c): mp 156–158 °C (lit.[27] mp 154.5–155.5 °C); ^{1}H NMR ($CDCl_3$) δ 1.97 (d, J = 10.0 Hz, 1 H), 5.53 (d, J = 10.0 Hz, 1 H), 7.22–7.71 (m, 8 H); IR (KBr) 3280 cm^{-1} (ν OH); MS, *m/e* 182 (M$^+$).

Benzopinacol (3a): mp 185–187 °C (lit.[29] mp 188–190 °C); ^{1}H NMR ($CDCl_3$) δ 3.03 (br s, 2 H), 7.20 (s, 20 H); IR (KBr) 3400 cm^{-1} (ν OH); MS, *m/e* 348 (M$^+$ – 18).

Reaction of Diaryl Ketones with Electrophiles. To the diaryl ketone–ytterbium mixture prepared as above was added a proper amount of electrophiles (in THF, 2 mL), and the mixture was stirred at room temperature for the proper time (see the corresponding tables and text). In the case of epoxides, the diaryl ketone–ytterbium mixture was first transferred by cannula to another vessel and the epoxides were then added. The products were worked up and isolated as above. Physical properties of the products are as follows.

1,1-Diphenyl-2-methylpropane-1,2-diol (6a): mp 91–92 °C; ^{1}H NMR ($CDCl_3$) δ 1.25 (s, 6 H), 2.01 (br s, 1 H), 2.55 (br s, 1 H), 7.01–7.68 (m, 10 H); IR (Nujol) 3480, 3312 cm^{-1} (ν OH); MS, *m/e* 224 (M$^+$ – 18). Anal. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.44. Found: C, 79.21; H, 7.50.

1,1-Diphenyl-2-methyloctane-1,2-diol (6b): mp 65–68 °C; ^{1}H NMR ($CDCl_3$) δ 0.61–1.52 (m, 16 H), 2.11 (br s, 1 H), 2.83 (br s, 1 H), 6.88–7.68 (m, 10 H); IR (KBr) 3568, 3464 cm^{-1} (ν OH); MS, *m/e* 294 (M$^+$ – 18). Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.71; H, 9.04.

1-(Diphenylhydroxymethyl)cyclohexanol (6c): mp 133–135 °C; ^{1}H NMR ($CDCl_3$) δ 1.15–1.72 (m, 10 H), 1.82 (s, 1 H), 2.74 (s, 1 H), 7.06–7.84 (m, 10 H); IR (KBr) 3556, 3468 cm^{-1} (ν OH); MS, *m/e* 264 (M$^+$ – 18). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.75; H, 7.85.

4-*tert*-Butyl-1-(diphenylhydroxymethyl)cyclohexanol (6d):[30] trans isomer (axial alcohol) mp 120–122.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.83 (s, 9 H), 1.41–1.70 (m, 9 H), 1.75 (br s, 1 H), 2.70 (br s, 1 H), 7.05–7.75 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 144.43, 128.41, 127.58, 126.90, 96.15, 82.33, 47.31, 32.81, 32.37, 27.57, 22.39; IR (KBr) 3564, 3400 cm^{-1} (ν OH); MS, *m/e* 320 (M$^+$ – 18). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.35; H, 9.21. Cis isomer (equatorial alcohol): mp 115–118 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (s, 9 H), 1.21–1.61 (m, 9 H), 1.79 (br s, 1 H), 2.55 (br s, 1 H), 7.05–7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 144.91, 128.37, 127.67, 126.96, 96.16, 83.70, 43.02, 33.28, 33.03, 27.41, 21.89; IR (KBr) 3544, 3468 cm^{-1} (ν OH); MS, *m/e* 320 (M$^+$ – 18). Anal. Calcd for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.37; H, 9.00.

1-(2-Naphthyl)-1-phenyl-2-methylpropane-1,2-diol (6e): ^{1}H NMR ($CDCl_3$) δ 1.32 (s, 6 H), 2.36 (s, 1 H), 3.00 (s, 1 H), 7.05–8.20 (m, 12 H); IR (neat) 3460 cm^{-1} (ν OH); MS, *m/e* 274 (M$^+$ – 18). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.23; H, 7.03.

1-(2-Naphthyl)-1-phenyl-2-methyloctane-1,2-diol (6f): ^{1}H NMR ($CDCl_3$) δ 0.60–1.65 (m, 16 H), 2.12 (br s, 1 H), 2.88 (br s, 1 H), 6.91–8.21 (m, 12 H); IR (neat) 3540 cm^{-1} (ν OH); MS, *m/e* 344 (M$^+$ – 18). Anal. Calcd for $C_{25}H_{30}O_2$: C, 82.83; H, 8.34. Found: C, 82.56; H, 8.62.

1-[(2-Naphthyl)phenylhydroxymethyl]cyclohexanol (6g): mp 173–175 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 1 H), 2.14–2.84 (m, 10 H), 2.89 (s, 1 H), 7.17–8.20 (m, 12 H); IR (KBr) 3560, 3490 cm^{-1} (ν OH); MS, *m/e* 314 (M$^+$ – 18). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.02; H, 7.28.

2-(9-Hydroxy-9-fluorenyl)-2-propanol (6h): mp 100–101 °C; ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 6 H), 2.61 (s, 1 H), 2.71 (s, 1 H), 7.15–7.79 (m, 8 H); IR (KBr) 3464 cm^{-1} (ν OH); MS, *m/e* 222 (M$^+$ – 18). Anal. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.72; H, 6.89.

2-(9-Hydroxy-9-fluorenyl)-2-octanol (6i): mp 147–150 °C; ^{1}H NMR ($CDCl_3$) δ 0.50–1.61 (m, 16 H), 2.70 (br s, 1 H), 3.30 (br s, 1 H), 6.90–7.80 (m, 8 H); IR (KBr) 3424 cm^{-1} (ν OH); MS, *m/e* 292 (M$^+$ – 18). Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.44; H, 8.14.

1-(9-Hydroxy-9-fluorenyl)cyclohexanol (6j): mp 168–169 °C; ^{1}H NMR ($CDCl_3$) δ 0.50–1.65 (m, 10 H), 2.36 (s, 1 H), 3.17 (s, 1 H), 7.05–7.65 (m, 8 H); IR (KBr) 3560, 3496 cm^{-1} (ν OH); MS, *m/e* 262 (M$^+$ – 18). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.35; H, 7.19.

1,1-Diphenylpropane-1,2-diol (6k): mp 89–91 °C; ^{1}H NMR ($CDCl_3$) δ 1.05 (d, J = 6.0 Hz, 3 H), 1.99 (br s, 1 H), 3.01 (br s, 1 H), 4.75 (q, J = 6.0 Hz, 1 H), 7.06–7.92 (m, 10 H); IR (KBr) 3468 cm^{-1} (ν OH); MS, *m/e* 210 (M$^+$ – 18). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.08. Found: C, 78.81; H, 7.10.

α-Phenylbenzoin (8a): mp 86–88 °C; ^{1}H NMR (CCl_4) δ 4.95 (s, 1 H), 7.06–7.88 (m, 15 H); IR (KBr) 3496 (ν OH), 1670 cm^{-1} (ν CO); MS, *m/e* 288 (M$^+$). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.31; H, 5.60.

2-Oxo-1,1,3-triphenylpropan-1-ol (8b): ^{1}H NMR (CCl_4) δ 3.74 (s, 2 H), 4.32 (s, 1 H), 6.75–7.40 (m, 15 H); IR (neat) 3468 (ν OH), 1714 cm^{-1} (ν CO); MS, *m/e* 285 (M$^+$ – 17). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.32; H, 6.21.

2-Oxo-1,1-diphenylpropan-1-ol (8c): oil crystallized on cooling; mp 66.5–67.5 °C (lit.[31] mp 64–65 °C); ^{1}H NMR ($CDCl_4$) δ 2.10 (s, 3 H), 4.58 (s, 1 H), 7.22 (s, 10 H); IR (neat) 3456 cm^{-1} (ν OH), 1712 cm^{-1} (ν CO); MS, *m/e* 226 (M$^+$). Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.52; H, 6.26.

2-Oxo-1,1-diphenyl-3-methylbutan-1-ol (8d): mp 72–73 °C; ^{1}H NMR (CCl_4) δ 0.81 (d, J = 7.2 Hz, 6 H), 3.07 (sep, J = 7.2 Hz, 1 H), 4.53 (s, 1 H), 7.25 (s, 10 H); IR (KBr) 3440 (ν OH), 1706 cm^{-1} (ν CO); MS, *m/e* 254 (M$^+$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.24; H, 7.03.

α-(β-Naphthyl)benzoin (8e): ^{1}H NMR (CCl_4) δ 4.85 (s, 1 H), 6.89–7.80 (m, 17 H); IR (neat) 3452 (ν OH), 1680 cm^{-1} (ν CO); MS, *m/e* 321 (M$^+$ – 17). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 84.90; H, 5.65.

2-Oxo-1,3-diphenyl-1-(2-naphthyl)propan-1-ol (8f): ^{1}H NMR (CCl_4) δ 3.78 (s, 2 H), 4.44 (s, 1 H), 6.80–7.82 (m, 17 H); IR (neat) 3460 (ν OH), 1714 cm^{-1} (ν CO); MS, *m/e* 352 (M$^+$). Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.95; H, 5.85.

2-Oxo-1-phenyl-1-(2-naphthyl)propan-1-ol (8g): mp 105–107 °C; ^{1}H NMR (CCl_4) δ 2.18 (s, 3 H), 4.64 (s, 1 H), 7.16–7.83

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(25) The metal must be activated for high reactivity. See also ref 3a–c.

(26) The reaction was much slower without using HMPA as a cosolvent. See also ref 3b.

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(m, 12 H); IR (KBr) 3504 (ν OH), 1704 cm^{-1} (ν CO); MS, m/e 276 (M$^+$). Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.54; H, 5.81.

9-Benzoyl-9-fluorenol (8h): mp 132–134 °C; ^{1}H NMR (CCl_4) δ 5.37 (s, 1 H), 6.85–7.75 (m, 13 H); IR (KBr) 3476 (ν OH), 1676 cm^{-1} (ν CO); MS, m/e 286 (M$^+$). Anal. Calcd for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93. Found: C, 83.95; H, 5.16.

9-(Phenylacetyl)-9-fluorenol (8i): mp 108–110 °C; ^{1}H NMR (CCl_4) δ 3.00 (s, 2 H), 4.82 (s, 1 H), 6.40–7.77 (m, 13 H); IR (KBr) 3472 (ν OH), 1714 cm^{-1} (ν CO); MS, m/e 300 (M$^+$). Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.00; H, 5.47.

9-Acetyl-9-fluorenol (8j): mp 109–111 °C; ^{1}H NMR (CCl_4) δ 1.53 (s, 3 H), 4.88 (s, 1 H), 7.10–7.85 (m, 8 H), IR (KBr) 3464 (ν OH), 1712 cm^{-1} (ν CO); MS, m/e 224 (M$^+$). Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.30; H, 5.39. Found: C, 80.19; H, 5.33.

α,α,α'-Triphenylacetone (9b): ^{1}H NMR (CCl_4) δ 3.67 (s, 2 H), 5.08 (s, 1 H), 6.85–7.86 (m, 15 H); IR (neat) 1720 cm^{-1} (ν CO); MS, m/e 286 (M$^+$). Anal. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34. Found: C, 87.90; H, 6.06.

α,α-Diphenylacetone (9c): mp 59–61 °C; ^{1}H NMR (CCl_4) δ 2.12 (s, 3 H), 4.96 (s, 1 H), 7.17 (s, 10 H); IR (neat) 1716 cm^{-1} (ν CO); MS, m/e 210 (M$^+$). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.52; H, 6.93.

α,α'-Diphenyl-α-(β-naphthyl)acetone (9f): ^{1}H NMR (CCl_4) δ 3.71 (s, 2 H), 5.24 (s, 1 H), 6.90–7.80 (m, 17 H); IR (neat) 1720 cm^{-1} (ν CO); MS, m/e 336 (M$^+$). Anal. Calcd for $C_{25}H_{20}O$: C, 89.25; H, 5.99. Found: C, 89.16; H, 6.08.

α-Phenyl-α-(β-naphthyl)acetone (9g): ^{1}H NMR (CCl_4) δ 2.19 (s, 3 H), 5.13 (s, 1 H), 7.15–7.85 (m, 12 H); IR (neat) 1714 cm^{-1} (ν CO); MS, m/e 260 (M$^+$). Anal. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.20. Found: C, 87.64; H, 6.16.

2-(Diphenylhydroxymethyl)cyclohexanol (11a): mp 164.5–165.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (qd, J = 12.9, 3.4 Hz, 1 H), 1.09 (qt, J = 13.2, 3.7 Hz, 1 H), 1.25 (qt, J = 12.9, 3.4 Hz, 1 H), 1.43 (m, 1 H), 1.58–1.76 (m, 3 H), 1.89–1.92 (m, 1 H), 2.50 (qd, J = 12.5, 9.7, 2.7 Hz, 1 H), 3.35 (unsymmetrical td, J = 10.2, 4.4 Hz, 2 H), 4.28 (br s, 1 H), 7.24–7.48 (m, 10 H); IR (KBr) 3200 cm^{-1} (ν OH); MS, m/e 264 (M$^+$ – 18). Anal. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 7.85. Found: C, 80.63; H, 7.81.

1,1,2-Triphenylpropane-1,3-diol (11b): mp 140.5–142.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.93 (br s, 1 H), 3.6–4.0 (m, 3 H), 4.31 (br s, 1 H), 6.90–7.81 (m, 15 H); IR (KBr) 3496, 3416 cm^{-1} (ν OH); MS, m/e 286 (M$^+$ – 18). Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 83.06; H, 6.71.

1,1-Diphenyl-3-methylbutane-1,3-diol (11c): mp 118–120 °C; ^{1}H NMR ($CDCl_3$) δ 0.98 (s, 6 H), 2.61 (s, 2 H), 3.12 (br s, 1 H), 5.20 (br s, 1 H), 6.90–7.61 (m, 10 H); IR (KBr) 3490 cm^{-1} (ν OH); MS, m/e 238 (M$^+$ – 18). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.59; H, 7.74.

1,1-Diphenyl-2-ethylpropane-1,3-diol (11d): mp 94.5–97 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.2 Hz, 3 H), 1.20–1.71 (m, 2 H), 2.10–2.51 (m, 1 H), 2.65 (br s, 1 H), 3.31–3.80 (m, 2 H), 4.49 (br s, 1 H), 7.01–7.62 (m, 10 H); IR (KBr) 3340 cm^{-1} (ν OH); MS, m/e 238 (M$^+$ – 18). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.73; H, 8.01.

1,1-Diphenylpentane-1,3-diol (12d): mp 74.0–74.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.2 Hz, 3 H), 1.35 (qu, J = 7.2 Hz, 2 H), 1.90–2.70 (m, 2 H), 2.98 (br s, 1 H), 3.28–3.80 (m, 1 H), 4.88 (br s, 1 H), 7.01–7.50 (m, 10 H); IR (KBr) 3280 cm^{-1} (ν OH); MS, m/e 256 (M$^+$). Anal. Calcd for $C_{17}H_{20}O_2$: C, 79.65; H, 7.86. Found: C, 79.63; H, 7.96.

2-[(2-Naphthyl)phenylhydroxymethyl]cyclohexanol (11e): mp 160–163 °C; ^{1}H NMR ($CDCl_3$) δ 0.70–2.01 (m, 8 H), 2.20–2.71 (m, 1 H), 3.24 (m, 1 H), 3.83 (br s, 1 H), 4.96 (br s, 1 H), 7.10–8.01 (m, 12 H); IR (KBr) 3236 cm^{-1} (ν OH); MS, m/e 314 (M$^+$ – 18). Anal. Calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 82.94; H, 7.28.

1,2-Diphenyl-1-(2-naphthyl)propane-1,3-diol (11f): mp 52–53 °C; ^{1}H NMR ($CDCl_3$) δ 1.94 (br s, 1 H), 3.60–4.20 (m, 3 H), 4.35 (br s, 1 H), 6.80–7.82 (m, 17 H); IR (KBr) 3392 cm^{-1} (ν OH); MS, m/e 336 (M$^+$ – 18). Anal. Calcd for $C_{25}H_{22}O_2$: C, 84.72; H, 6.26. Found: C, 84.44; H, 6.49.

1-Phenyl-1-(2-naphthyl)-3-methylbutane-1,3-diol (11g): mp 127.5–128.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.97 (s, 6 H), 2.68 (s, 2 H), 3.14 (br s, 1 H), 5.53 (br s, 1 H), 7.00–8.02 (m, 12 H); IR (KBr) 3492 cm^{-1} (ν OH); MS, m/e 306 (M$^+$). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.60; H, 7.13.

1-Phenyl-1-(2-naphthyl)-2-ethylpropane-1,3-diol (11h): ^{1}H NMR ($CDCl_3$) δ 0.70–1.70 (m, 5 H), 2.20–2.50 (m, 1 H), 2.65 (br s, 1 H), 3.73 (m, 2 H), 4.56 (br s, 1 H), 7.00–8.10 (m, 12 H); IR (neat) 3282 cm^{-1} (ν OH); MS, m/e 288 (M$^+$ – 18). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.10; H, 7.32.

1-Phenyl-1-(2-naphthyl)pentane-1,3-diol (12h): mp 110–117 °C; ^{1}H NMR ($CDCl_3$) δ 0.80 (t, J = 7.2 Hz, 3 H), 1.45 (qu, J = 7.2 Hz, 2 H), 2.01–2.62 (m, 1 H), 2.84 (br s, 1 H), 3.22–3.82 (m, 1 H), 4.98 (br s, 1 H), 7.00–8.10 (m, 12 H); IR (KBr) 3284 cm^{-1} (ν OH); MS, m/e 306 (M$^+$). Anal. Calcd for $C_{21}H_{22}O_2$: C, 82.32; H, 7.24. Found: C, 82.09; H, 7.22.

2-(9-Hydroxy-9-fluorenyl)cyclohexanol (11i): mp 166–167.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.60–2.40 (m, 9 H), 3.91 (m, 1 H), 4.25 (br s, 1 H), 4.71 (br s, 1 H), 7.10–7.72 (m, 8 H); IR (KBr) 3320 cm^{-1} (ν OH); MS, m/e 280 (M$^+$). Anal. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19. Found: C, 81.70; H, 7.14.

2-(9-Hydroxy-9-fluorenyl)-2-phenylethanol (11j): mp 163–165 °C; ^{1}H NMR ($CDCl_3$) δ 3.20–4.50 (m, 5 H), 6.20–7.71 (m, 13 H); IR (KBr) 3272 cm^{-1} (ν OH); MS, m/e 284 (M$^+$ – 18). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00. Found: C, 83.34; H, 5.97.

1-(9-Hydroxy-9-fluorenyl)-2-methyl-2-propanol (11k): mp 157–160 °C; ^{1}H NMR ($CDCl_3$) δ 0.93 (s, 6 H), 2.22 (br s, 2 H), 2.49 (s, 2 H), IR (KBr) 3400 cm^{-1} (ν OH); MS, m/e 254 (M$^+$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.31; H, 7.28.

2-(9-Hydroxy-9-fluorenyl)-1-butanol (11l): mp 91–92.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.35–1.70 (m, 5 H), 1.98–2.51 (m, 1 H), 3.50–4.20 (m, 3 H), 5.76 (br s, 1 H), 7.10–7.70 (m, 8 H); IR (KBr) 3210 cm^{-1} (ν OH); MS, m/e 254 (M$^+$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.27; H, 7.12.

1-(9-Hydroxy-9-fluorenyl)-2-butanol (12l): mp 95–96.5 °C; ^{1}H NMR ($CDCl_3$) δ 0.79 (t, J = 7.2 Hz, 3 H), 1.15–1.55 (m, 2 H), 1.60–2.60 (m, 2 H), 3.31–4.10 (m, 3 H), 7.10–7.70 (m, 8 H); IR (KBr) 3200 cm^{-1} (ν OH); MS, m/e 254 (M$^+$). Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.11; H, 7.19.

***N*-Phenyldiphenylhydroxyacetamide (15)**: mp 179–181 °C; ^{1}H NMR ($CDCl_3$) δ 3.66 (s, 1 H), 7.10–7.65 (m, 15 H), 8.45 (br s, 1 H); IR (KBr) 3356 (ν OH, NH), 1672 cm^{-1} (ν CO); MS, m/e 303 (M$^+$). Anal. Calcd for $C_{20}H_{17}NO_2$: C, 79.19; H, 5.62; N, 4.62. Found: C, 78.89; H, 5.67; N, 4.63.

Diphenylhydroxyacetaldehyde (16): mp 51–53 °C; ^{1}H NMR ($CDCl_3$) δ 4.38 (br s, 1 H), 7.35 (s, 10 H), 9.94 (s, 1 H); IR (KBr) 3468 (ν OH), 1720 cm^{-1} (ν CO); MS, m/e 212 (M$^+$). Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.31; H, 5.79.

1,1,2,3-Tetraphenylprop-2-en-1-ol (17): mp 67–69 °C; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 1 H), 6.13 (s, 1 H), 6.52–7.71 (m, 20 H); IR (Nujol) 3500 cm^{-1} (ν OH); MS, m/e 362 (M$^+$). Anal. Calcd for $C_{27}H_{22}O$: C, 89.47; H, 6.12. Found: C, 89.20; H, 6.21.

1,1,2,3-Tetraphenyl-3-deuterioprop-2-en-1-ol (17a): mp 66–68 °C; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 1 H), 6.52–7.71 (m, 20 H); IR (Nujol) 3500 cm^{-1} (ν OH); MS, m/e 363 (M$^+$).

Reaction of Diaryl Ketones with CO_2. Carbon dioxide was passed through the diaryl ketone–ytterbium mixture and the color of the solution turned to brown within 5 min. The brown mixture was stirred for 30 min at room temperature under a CO_2 atmosphere. Products were worked up as above and identified by comparison of their NMR, IR, and mass spectra and melting point with those of authentic samples. Physical properties of the products are recorded below.

Diphenylhydroxyacetic acid (13a): mp 151–153 °C (lit.[32] mp 148–150 °C); ^{1}H NMR ($CDCl_3$) δ 6.65 (br s, 2 H), 7.10–7.70 (m, 10 H); IR (KBr) 3412 (ν OH), 3290–2500 (ν OH), 1720 cm^{-1} (ν CO); MS, m/e 228 (M$^+$).

Diphenylacetic acid (14a): mp 147.5–148.5 °C (lit.[33] mp 147–148 °C); ^{1}H NMR ($CDCl_3$) δ 5.03 (s, 1 H), 5.96 (br s, 1 H), 7.31 (s, 10 H); IR (KBr) 2400–3250 (ν OH), 1708 (ν CO); MS, m/e 212 (M$^+$).

(2-Naphthyl)phenylhydroxyacetic acid (13b): mp 145–146 °C (lit.[34] mp 145–146 °C); ^{1}H NMR ($CDCl_3$) δ 6.10 (br s, 2 H), 7.12–8.10 (m, 12 H); IR (KBr) 3428 (ν OH), 3300–2400 (ν OH), 1718 cm^{-1} (ν CO); MS, m/e 278 (M$^+$).

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Phenyl(2-naphthyl)acetic acid (14b): mp 141–142 °C (lit.[35] mp 141 °C); ^{1}H NMR ($CDCl_3$) δ 5.11 (s, 1 H), 6.00 (br s, 1 H), 7.12–7.80 (m, 12 H); IR (KBr) 3400–2400 (ν OH), 1712 cm^{-1} (ν CO); MS, *m/e* 262 (M^+).

9-Hydroxy-9-fluorenecarboxylic acid (13c): mp 170–172 °C (lit.[36] mp 167 °C); ^{1}H NMR ($CDCl_3$) δ 5.48 (br s, 2 H), 7.20–7.75 (m, 8 H); IR (KBr) 3452 (ν OH), 3300–2500 (ν OH), 1724 cm^{-1} (ν CO); MS, *m/e* 226 (M^+).

9-Fluorenecarboxylic acid (14c): mp 222–224 °C (lit.[33] mp 225–227 °C); ^{1}H NMR ($CDCl_3$) δ 4.87 (s, 1 H), 6.01 (br s, 1 H), 7.10–7.85 (m, 8 H); IR (KBr) 3300–2500 (ν OH), 1700 cm^{-1} (ν CO); MS, *m/e* 210 (M^+).

IR Measurement of the Intermediates. These experiments were carried out in THF/HMPA solution with a liquid cell under N_2. Samples were transferred by a syringe and their spectra were obtained as difference spectra of the samples and the solvents. The results are shown in Figures 1 and 2.

Titration Analysis. A reaction mixture of benzophenone (1 mmol) and Yb (1 mmol) was prepared as described above. The solution was transferred to another vessel by a syringe and the unchanged Yb metal was left. The unchanged metal was dissolved in concentrated HCl and then the amount determined by EDTA (ethylenediaminetetraacetic acid disodium salt) titration with XO (xylenol orange) as an indicator.[37,38] It was 0.07 mmol. The solution was hydrolyzed and the organic products were extracted with ether (3 × 30 mL) and isolated by medium pressure liquid chromatography (silica gel). The products were benzhydrol (**2a**) (174.8 mg, 0.95 mmol) and diphenylmethane (5.0 mg, 0.03 mmol). EDTA titration of the aqueous solution gave Yb^{3+} = 0.90 mmol.

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Synthesis and Photochemistry of Some New Pentacycloundecan-8-ones. Probes for Hydrogen Abstraction in the π-Plane

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A new series of pentacycloundecan-8-ones was prepared to evaluate the reactivity of hydrogen abstraction reactions by excited states of cycloalkanones in the realm perpendicular to the carbonyl plane. Compounds of types 1 and 2 were inert to irradiation at 300 nm (ϕ [−K] < 10^{-3}) despite close proximity of oxygen and hydrogen atoms in the ground states (ca. 2.5–2.6 Å). A transition-state model for 2 did not reveal any barriers attributable to unusual steric strain. Estimates of the reactivity of 2 relative to 2-hexanone indicate a decrease in hydrogen abstraction rate of at least 10^3. These studies confirm the importance of stereoelectronic barriers toward hydrogen abstraction in this realm that have been predicted by diverse theoretical models.

Introduction

Hydrogen atom abstraction reactions by photoexcited carbonyl groups are among the most widely studied photoreactions from both experimental as well as theoretical standpoints.[2] A comprehensive body of experimental data exemplifies the dependency of reactivity on a wide variety of parameters, for example: spin multiplicity, electronic configuration, C–H bond strength, physical state, solvent, steric effects, inductive effects, and stereoelectronic factors.

Recent studies of the solid phase have reopened the question of the definition of the optimum transition-state geometry for hydrogen atom abstraction reactions.[3] Earlier workers concluded that hydrogen atom abstraction reactions occur preferentially in the region of space near the n orbital of n,π* states of simple ketones.[4] Wagner proposed a $\cos^2 \phi$ dependency where ϕ is the C—C=O···H torsion angle.[2] Certain polycyclic ketones were claimed to be "unreactive" because proximate hydrogen did not lie in the plane of the carbonyl group.[5] Scheffer, Trotter, et al.[6] proposed that the ideal stereoelectronic arrangement involves an in-plane interaction of a half-filled n orbital with the abstracted hydrogen at an angle normal to the C=O bond at H···O distances between 2.3 and 2.6 Å. Studies of Norrish type II reactions in the solid state were rationalized in terms of a looser transition state that permitted O···H contacts as long as 3.10 Å and out-of-plane angles as large 62.3°.

Photochemical studies of solid complexes of desoxycholic acid and acetophenone derivatives have provided examples of intermolecular hydrogen abstractions from the perpendicular direction of the carbonyl plane, but it was concluded that molecular motions within the crystal lattice permitted approach of the reactive hydrogen to the locus of the n orbital of the excited ketone.[7]

Several recent theoretical studies have also dealt with the problem of the critical stereoelectronic parameters in hydrogen abstraction reactions.[8] In an ab initio computational analysis of the hydrogen abstraction reaction between methane and the triplet state of formaldehyde, Morrison et al.[9] calculated the following angles for the optimized transition-state geometry: C=O···H = 108.9°;

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