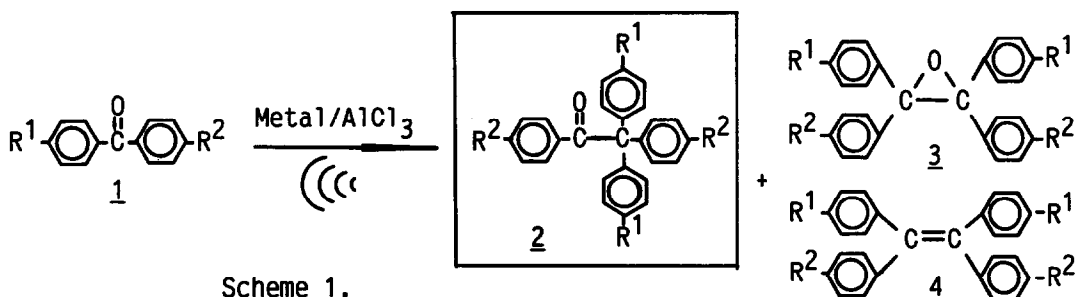


NOVEL REDUCTIVE COUPLING-REARRANGEMENT OF CARBONYL COMPOUNDS WITH METAL/LEWIS ACID UNDER IRRADIATION OF ULTRASONIC WAVE

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Abstract Novel reductive coupling-rearrangement of carbonyl compounds such as benzophenones with Al or Zn / AlCl₃ in CH₃CN under irradiation of ultrasonic wave gave benzopinacolones via epoxides in good yields.

Numerous reports concerning the reduction of organic compounds with chemically active metals such as sodium, potassium, and calcium have appeared hitherto.¹⁾ Recently much attention has been, however, centered on improvement of such reduction so as to overcome various difficulties: for example, problems in the handling of such metals, reactivity control, and increase of the selectivity.²⁾ We have recently reported the selective reduction of disulfides to the corresponding thiols by Al/NH₃/halide and the novel reductive coupling reaction of carbonyl compounds by Al/NH₃/halide under irradiation of ultrasonic wave respectively.³⁾ In the course of our study on the reduction using metal, it was found that the treatment of benzophenones with metallic (Zn or Al)/Lewis acid (AlCl₃) under irradiation ultrasonic wave gives benzopinacolones which are reductive coupling-rearrangement products (Scheme 1).



Scheme 1.

Typical procedure is as follows. A suspension of Zn (8 mg atom) in CH₃CN (10 ml) containing benzophenone (1 mmol) and AlCl₃ (4.0 mmol) was irradiated ultrasonically at 35 °C for 12 h under nitrogen atmosphere. The reaction was quenched with aq. NH₄Cl solution and the resulting Zn(OH)₂ was

filtered off. The filtrate was extracted with CH_2Cl_2 (20 ml x 3) and the combined extracts were evaporated in vacuo. The chromatography of the residue on silica gel with $\text{CHCl}_3/\text{CCl}_4$ (1/1, v/v) gave 2a (157 mg, 90%) and 4a (12 mg, 7%). The results are summarized in Table 1.

Benzophenone was easily reacted with metallic zinc and aluminum in the presence of AlCl_3 in CH_3CN under irradiation of ultrasonic wave to give benzopinacolone 2, epoxide 3, and ethylene 4.⁴⁾ Especially, the use of zinc effectively afforded rearrangement product 2 (Run 2, 12, 14, and 16) and epoxide 3 (Run 6, 8, and 10) but the employment of magnesium gave 2 in low yield (Run 3). The activation of metal was achieved by the irradiation of ultrasonic wave and the addition of Lewis acid to the system. Only

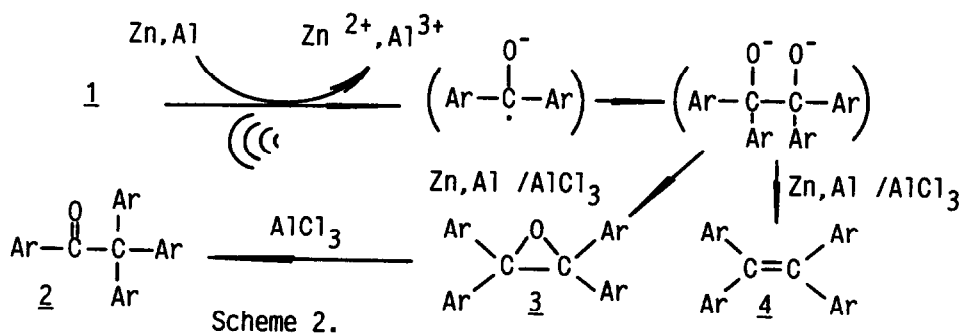
Table 1. Reaction of benzophenones with Metal/Lewis acid

Run	Substrate ^{a)}		1	Metal	Lewis acid	Time ^{b)} h	Yield of Product		
	R ¹	R ²					2/%	3/%	4/%
1	H	H	<u>1a</u>	Al	AlCl_3	12	87 <u>2a</u>	3 <u>3a</u>	4 <u>4a</u>
2	H	H	<u>1a</u>	Zn	AlCl_3	12	90 <u>2a</u>	0 <u>3a</u>	7 <u>4a</u>
3	H	H	<u>1a</u>	Mg	AlCl_3	30	20 <u>2a</u>	57 <u>3a</u>	7 <u>4a</u>
4	H	H	<u>1a</u>	Zn	AlBr_3	12	12 <u>2a</u>	trace <u>3a</u>	57 <u>4a</u>
5 ^{c)}	H	H	<u>1a</u>	Zn	AlI_3	48	2 <u>2a</u>	14 <u>3a</u>	1 <u>4a</u>
6	H	H	<u>1a</u>	Zn	EtAlCl_2 ^{d)}	3	12 <u>2a</u>	72 <u>3a</u>	0 <u>4a</u>
7	H	Cl	<u>1b</u>	Al	AlCl_3	24	22 <u>2b</u>	72 <u>3b</u>	0 <u>4b</u>
8 ^{c)}	H	Cl	<u>1b</u>	Zn	AlCl_3	20(min)	7 <u>2b</u>	70 <u>3b</u>	0 <u>4b</u>
9	Cl	Cl	<u>1c</u>	Al	AlCl_3	15	8 <u>2c</u>	70 <u>3c</u>	0 <u>4c</u>
10 ^{c)}	Cl	Cl	<u>1c</u>	Zn	AlCl_3	20(min)	2 <u>2c</u>	55 <u>3c</u>	0 <u>4c</u>
11	CH_3	H	<u>1d</u>	Al	AlCl_3	6	87 <u>2d</u>	trace <u>3d</u>	0 <u>4d</u>
12	CH_3	H	<u>1d</u>	Zn	AlCl_3	20(min)	92 <u>2d</u>	0 <u>3d</u>	2 <u>4d</u>
13	CH_3	CH_3	<u>1e</u>	Al	AlCl_3	6	79 <u>2e</u>	0 <u>3e</u>	0 <u>4e</u>
14	CH_3	CH_3	<u>1e</u>	Zn	AlCl_3	20(min)	97 <u>2e</u>	0 <u>3e</u>	3 <u>4e</u>
15	CH_3O	CH_3O	<u>1f</u>	Al	AlCl_3	12	92 <u>2f</u>	0 <u>3f</u>	0 <u>4f</u>
16	CH_3O	CH_3O	<u>1f</u>	Zn	AlCl_3	20(min)	97 <u>2f</u>	0 <u>3f</u>	3 <u>4f</u>

a) Substrate, 1.0 mmol; solvent, CH_3CN (10 ml); Lewis acid, 4.0 mmol.

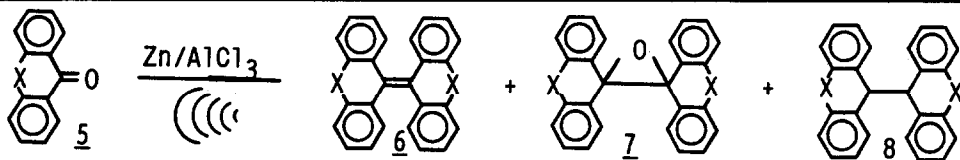
b) Irradiation time of ultrasonic wave. c) Simple coupling product pinacol was also obtained. d) EtAlCl_2 , 1.0 mmol.

AlCl₃ as a Lewis acid in this reaction gave favorable results in the yield of pinacolone (Run 1-6). Usual solvent such as CH₂Cl₂, CHCl₃, and CH₃CN was employed for this reaction. It is noteworthy that epoxide 3 was isolated in satisfactory yields under such acidic condition, since in the Pinacol-pinacolone rearrangement no epoxide has ever been isolated.⁵⁾ Furthermore, the intermediacy of the epoxide 3 was confirmed by conversion to 2 under the same condition.⁶⁾ Some benzophenones bearing substituents were explored in the reaction to give the same products (Run 7-16). In the reaction of unsymmetrical benzophenones, 1b and 1d, we could observe a migration of the benzene ring bearing an electron-donating group, to yield 2b and 2d.⁷⁾ Since the reaction of 1b and 1c resulted in increased yield of epoxide 3 (Run 7-10), such introduction of an electron-withdrawing group may stabilize epoxide 3 and retard the rearrangement to pinacolone 2. Whereas, introduction of an electron-donating group lead the reaction to exclusive formation of pinacolones (Run 11-16). Although McMurry has reported the exclusive olefination of carbonyl compounds by reductive coupling-deoxygenation with low valent titanium, Ti(0),⁸⁾ the yields of ethylenes 4 in the present reaction were always low except when AlBr₃ was used as a Lewis acid. Since, to our knowledge, there has been only one report on such rearrangement using titanium,⁹⁾ the present method is the first example using metallic zinc and aluminum. The plausible reaction pathway is depicted as shown in Scheme 2 based on the above results.



In the reaction of some bridged benzophenones such as xanthone 5a and the related compounds 5b-d, under the same condition, the rearrangement products were not obtained but reductive coupling products, 6, 7, and 8, were formed (Table 2).¹⁰⁾ It should be noted that treatment of xanthone with aluminum gave 8a in 19% yield, since this type of compound has not been obtained by the reaction of benzophenones 1a-f. The methylene-linked benzophenones, 5c and 5d, yielded epoxides, 7c and 7d, in considerable amounts.

Although other carbonyl compounds such as acetophenone and cyclohexa-

Table 2. Reduction of Bridged Benzophenones with Zn/AlCl₃

Run	Substrate/X	Yield of Product/%					
1	-O- <u>5a</u>	51 (50)* <u>6a</u>	0 (0)* <u>7a</u>	0 (19)* <u>8a</u>			
2	-S- <u>5b</u>	36 (48) <u>6b</u>	40 (0) <u>7b</u>	0 (0) <u>8b</u>			
3	-CH ₂ - <u>5c</u>	trace (75) <u>6c</u>	52 (25) <u>7c</u>	0 (0) <u>8c</u>			
4	-CH ₂ CH ₂ - <u>5d</u>	34 (17) <u>6d</u>	48 (54) <u>7d</u>	0 (0) <u>8d</u>			

* () is the yields by employment of aluminum

none were also treated with metallic zinc, only aldol-condensation products were obtained. Further investigations on the application of this method are now in progress in our laboratory.

References and Notes

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