

oil.

We have briefly studied solvent effects using 3-benzylamino-2-methylpropanoic acid, 1.2 equivalent of FMS reagent and triethylamine at 80 °C for 24 hr. Among various solvents employed in this study, acetonitrile gave the best results, yielding 64% of 1-benzyl-3-methyl-2-azetidinone. N,N'-Dimethylformamide, dichloromethane, and tetrahydrofuran were much less effective, yielding the corresponding β -lactam in 25%, 22%, and 17% yield, respectively.

Some experimental results are summarized in Table 1. As can be realized, N-substituted β -amino acids were cyclized to the corresponding β -lactams in excellent yields but N-unsubstituted β -amino acids gave very poor results. Extension of the present study to include other coupling reagents for β -lactam formation is in progress.

Acknowledgement. This work was supported by the Basic Science Research Institute Program, Ministry of Education, 1988.

References

1. For recent reviews, see (a) K. Mukerjee and A. K. Singh, *Tetrahedron*, **34**, 1731 (1978); (b) K. Hirdi, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 97 (1980); (c) R. Labia and C. Morin, *J. Antibiotics*, **37**, 1103 (1984).
2. Y. Watanabe and T. Mukaiyama, *Chem. Lett.*, 443 (1981).
3. S. Kobayashi, T. Limori, T. Izawa, and M. Ohno, *J. Am. Chem. Soc.*, **103**, 2406 (1981).
4. H. Huang, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, 1465 (1984).
5. S. Kim and T. A. Lee, *Bull. Korean Chem. Soc.*, **9**, 189 (1988).
6. C. H. Lee, C. J. Moon, K. S. Kim, J. H. Kim, and D. W. Kim, *Bull. Korean Chem. Soc.*, **8**, 336 (1987).
7. Y. K. Shim, K. S. Kim, C. H. Lee, and W. J. Kim, *Bull. Korean Chem. Soc.*, **9**, 187 (1988).

Reductive Homocoupling of Benzal Bromides Catalyzed by Transition Metal Complex under Phase Transfer Catalysis

Sang Chul Shim*, Chil Hoon Doh, Woo Hyun Park, and Hyung Soo Lee†

Department of Industrial Chemistry, Kyungpook National University, Taegu 702-701

†Department of Chemical Education, Hyosung Women's University, Hayang 713-900

Received June 19, 1989

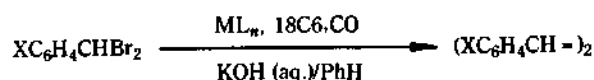
Recently, transition metals with a low oxidation state have been extensively used as reagents or catalysts for the reductive homocoupling reaction of benzal halides. For example, nickel¹, iron², cobalt³, palladium⁴, molybdenum⁵, tungsten⁶, copper⁷, and vanadium⁸ complexes have been employed for this purpose. Moreover, the reductive homocoupling reaction could occur under phase transfer catalysis in low selectivity⁹.

In the course of investigation for the carbonylation of benzal bromides¹⁰, ArCHBr₂, it was found that iron pentacarbonyl catalyzes the reductive homocoupling to give stilbenes with high selectivity under phase transfer catalysis¹¹. To our knowledge, there are no such reactions reported. The reaction is described in Scheme 1 and the results are summarized in Table 1.

Table 1 shows that various transition metal complexes in the presence of 18-crown-6-ether as a phase transfer cata-

lyst seem to be active catalysts for the reductive homocoupling of *p*-chlorobenzal bromide. In the cases of iron pentacarbonyl and diiron nonacarbonyl, the corresponding stilbenes were obtained in 78% and 74% yields in high selectivity, respectively. However, *p*-chlorophenylacetic acid was always produced less than 10% yield (runs 1 and 3). However, no product was obtained when molybdenum hexacarbonyl and dirhenium decacarbonyl were used (runs 4 and 6). Nevertheless, *trans*-4,4'-dichlorostilbene was obtained in 48% yield when 10M KOH¹²-molybdenum hexacarbonyl was used (run 5). In the case of dicobalt octacarbonyl, *trans*-4,4'-dichlorostilbene was obtained in 39% and carbonylated product, *p*-chlorophenylacetic acid, was obtained in 32% yields (run 7). When tetrakis(triphenylphosphine)-palladium(O) was used, *trans*-4,4'-dichlorostilbene was afforded in 60% yield (run 8). Other phase transfer agents such as tetrabutylammonium hydrogensulfate, benzyltriethylammonium chloride, and cetyltrimethylammonium chloride showed low selectivity toward stilbene formation. By these results, it was concluded that the combination of iron pentacarbonyl with 18-crown-6-ether was the most efficient catalytic system to the reductive homocoupling.

To confirm this observation, we attempted to investigate substituent effect of benzal bromides using iron pentacarbonyl in the presence of 18-crown-6-ether as a phase transfer catalyst. All of benzal bromides showed similar yields from 81% to 84%. This results indicated a small contribution of



X = H, *o*-Cl, *p*-Cl, *o*-CH₃, and *p*-CH₃

ML_n = Mo(CO)₆, Fe(CO)₅, Fe₂(CO)₉, Co₂(CO)₈,
and Pd(PPh₃)₄

Scheme 1

Table 1. Transition Metal Complexes Catalyzed Reductive Homocoupling of *p*-Chlorobenzal Bromide Under Phase Transfer Catalysis^a

Run	ML _n	Product	Yield(%) ^b
1	Fe(CO) ₅	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	78
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	10
2	None	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	0
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	0
3	Fe ₂ (CO) ₉	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	74
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	10
4	Mo(CO) ₆	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	0
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	0
5 ^c	Mo(CO) ₆	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	48
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	0
6 ^d	Re ₂ (CO) ₁₀	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	0
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	0
7	Co ₂ (CO) ₈	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	39
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	32
8	Pd(PPh ₃) ₄	<i>t</i> -(<i>p</i> -ClC ₆ H ₄ CH=) ₂	68
		<i>p</i> -ClC ₆ H ₄ CH ₂ COOH	0

^aA mixture of 5M KOH (10 ml), benzene (10 ml), 18-crown-6-ether (0.3 mmole, 0.07 g), *p*-chlorobenzal bromide (3 mmole, 0.86 g), and metal complex (0.75 mmole) was stirred at room temperature for 12 h under atmospheric pressure of carbon monoxide. ^bIsolated yield based on halide charged. ^c10M KOH aqueous phase was used. ^dFor 5M or 10M KOH aqueous phase.

Table 2. Iron Pentacarbonyl-18C6 Catalyzed Reductive Homocoupling of Benzal Bromides^a

Run	Reactant XC ₆ H ₄ CHBr ₂	Product (XC ₆ H ₄ CH=) ₂	Yield ^b (%)	Trans/Cis ^c
1	X = H	X = H	84	9
2	<i>o</i> -Cl	<i>o</i> -Cl	83	15
3	<i>p</i> -Cl	<i>p</i> -Cl	86	19
4	<i>o</i> -CH ₃	<i>o</i> -CH ₃	81	12
5	<i>p</i> -CH ₃	<i>p</i> -CH ₃	82	16
6	(C ₆ H ₅ CH-) ₂ Br	H	96	17

^aA mixture of 5M KOH (10 ml), benzene (10 ml), 18-crown-6-ether (0.3 mmole, 0.07 g), substituted benzal bromide (3 mmole), and iron pentacarbonyl (0.75 mmole, 0.15 g) was stirred at room temperature for 12 h under atmospheric pressure of carbon monoxide. ^bIsolated yield. ^cBased on isolated yield.

electronic and steric effect. The reaction was further carried out in the presence of an excess of alkene such as cyclohexene, styrene, and benzalaniline in order to trap the carbene intermediate. However, the formation of cycloadducts was

not seen. When meso-1,2-dibromo-1,2-diphenylethane, supposed as an intermediate, was employed in this reaction, corresponding stilbene was obtained in 96% yield.

A typical procedure for the reaction is as follows; A mixture of *p*-chlorobenzal bromide (3 mmole, 0.86 g), 5M KOH (10 ml), benzene (10 ml), 18-crown-6-ether (0.3 mmole, 0.07 g), and iron pentacarbonyl (0.75 mmole, 0.15 g) was stirred at room temperature for 12 hours under atmospheric pressure of carbon monoxide. After purging of carbon monoxide, organic phase was carefully separated and dried with anhydrous magnesium sulfate. Solvent was evaporated to give the crude product. It was further purified by preparative thin layer chromatography on silica gel to give *trans*-4,4'-dichlorostilbene (0.29 g, 78%) and *cis*-4,4'-dichlorostilbene (0.02 g, 5%). The products were identified by IR, ¹H-NMR, and M.P., respectively.

Acknowledgement. This work was supported by the Korea Science and Engineering Foundation (881-0306-025-2) in 1988-1989.

References

- (a) J. Yamashita, Y. Inoue, T. Kondo and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **58**, 2709 (1985); (b) K. Takagi, H. Mimura and S. Inokawa, *ibid.*, **57**, 3517 (1984); (c) S. I. Inabe, H. Matsumoto and R. D. Ricke, *J. Org. Chem.*, **49**, 2093 (1984); (d) I. Hashimoto, N. Tsuruta, M. Ryang and S. Tsutsumi, *ibid.*, **35**, 3748 (1970); (e) E. Hashisato and S. Tsutsumi, *ibid.*, **33**, 869 (1968).
- H. Alper and D. D. Roches, *ibid.*, **41**, 80f (1976).
- Y. Fugiwara, R. Ishikawa and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **51**, 589 (1978).
- (a) H. Nozaki, T. Shirafushi and Y. Yamamoto, *Tetrahedron*, **25**, 3461 (1969); (b) R. E. Buckles and G. M. Metlack, *Org. Synth., Coll.* **4**, 914 (1964).
- (a) C. E. Coffey, *J. Am. Chem. Soc.*, **83**, 1623 (1961); (b) H. Alper and E. C. Keung, *J. Org. Chem.*, **37**, 2566 (1972).
- T. Nakano, M. Takahashi, T. Ashizawa, T. Arai, S. Seki, H. Matsumoto and Y. Nagai, *Chem Lett.*, 613 (1982).
- Y. Yamada and D. I. Momose, *ibid.*, 1277 (1981).
- T. A. Cooper, *J. Am. Chem. Soc.*, **95**, 4158 (1973).
- (a) S. Gambarotta and H. Alper, *J. Organomet. Chem.*, **212**, C23 (1981); (b) H. Alper, K. Hashem and J. Heveling, *Organometallics*, **1**, 775 (1982).
- S. C. Shim, C. H. Doh, W. H. Park, Y. G. Kwon, and H. S. Lee, *J. Organomet. Chem.*, in press (1989).
- E. V. Dehmlow and S. S. Dehmlow, "Phase Transfer Catalysis", Verlag Chemie Publishers, Weinheim, 1983.
- R. B. King, C. C. Frazier, R. M. Hanes and A. D. King, Jr., *J. Am. Chem. Soc.*, **100**, 2925 (1978).