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$TiCl_4$-Zn INDUCED REDUCTIVE COUPLING REACTIONS IN THE ABSENCE OF SOLVENT

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OPPI BRIEFS

$TiCl_4$-Zn INDUCED REDUCTIVE COUPLING REACTIONS IN THE ABSENCE OF SOLVENT

Submitted by (07/15/96)

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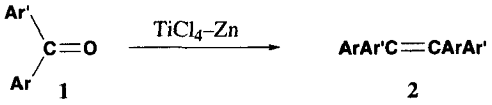
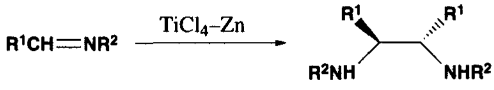
The reductive coupling of carbonyl compounds induced by low valent titanium reagent is one of the most conventional methods to prepare olefins[1] and has been extensively studied in solvent, generally THF.[2] We now report two types of coupling reactions carried out in the absence of solvent.

We found the coupling of diarylketones with $TiCl_4$-Zn to tetrasubstituted ethylenes in the absence of solvent proceeds simply and easily. We investigated the coupling of benzophenone at different temperatures. At temperatures higher than 120°, the main product was 2,2,2-triphenylacetophenone; tetraphenylethylene was produced only as by-product. If aliphatic ketones are used, the products are complex and the yields of olefins are low. Symmetrical *vic* (R,R)-diamines are versatile starting materials in asymmetric synthesis and have been obtained from imines using the low-valent titanium in tetrahydrofuran.[3,4] For example, treatment of mines in tetrahydroftiran by low valent titanium generated by the reaction of titanium tetrachloride and magnesium amalgam, yields three products: the *(R,R)-d,l-diamine, (R,S)-meso-diamine* and an amine resulting from reduction ofthe starting imine. But in the absence of solvent the reductive coupling of mines leads only to the symmetrical vicinal (R,R)-diamines, which are purified readily. If R^1 and R^2 are aliphatic, only low yields of products were obtained.



a) Ar = Ar' = C_6H_5 b) Ar = p-$CH_3C_6H_4$, Ar' = C_6H_5 c) Ar = Ar' = p-$CH_3C_6H_4$
d) Ar = Ar' = p-ClC_6H_4 e) Ar = Ar' = 2.2'-biphenylyl



(R, R)

3 4

a) $R^1 = R^2 = C_6H_5$ b) $R^1 = C_6H_5$, $R^2 = p$-$CH_3C_6H_4$ c) $R^1 = p$-$Cl_3C_6H_4$, $R^2 = C_6H_5$
d) $R^1 = C_6H_5$, $R^2 = p$-ClC_6H_4 e) $R^1 = p$-$CH_3C_6H_4$, $R^2 = p$-C_6H_5
f) $R^1 = C_6H_5$, $R^2 = m$-ClC_6H_4 g) $R^1 = C_6H_5$, $R^2 = p$-FC_6H_4

TABLE 1. Yields, mps and ^{1}H NMR Spectral Data of Compounds **2**

Cmpd	Yield (%)	mp. (°C) (solvent)[a]	lit. mp. (°C)	^{1}H NMR (δ, $CDCl_3$)
2a	87	220-222	221-222[b]	7.04 (s, 20H)
2b	25	121-123	120[c]	6.70 (m, 18H), 2.09 (s, 6H)
2c	21	149-150	151[d]	6.88 (s, 16H), 2.24 (s, 12H)
2d	52	212-214	216-217[e]	7.15-6.84 (q, 16H)
2e	54	182-1 83[f]	187-188[g]	8.31 (d, 4H), 7.61 (d, 4H), 7.12 (m, 8H)

a) From petroleum ether (60-90°) except where noted. b) J. E. McMurry, M. G. Silvestri, M. P. Fleming, Tova Hoz and M. W. Grayston, *J. Org. Chem.*, **43**, 3249 (1978). c) F. A. Bottino, P. Finocchiaro, E. Libertini, A. Reale and A. Recca, *J. Chem. Soc. Perkin Trans II*, 77 (**1982**). d) S. Goldstein, *Ber.*, **49**, 1923, (1916). e) T. B. Norris, *ibid.*, **43**, 2946 (1910). f) From EtOH. g) N. P. Buu-Hoi and G. Saint Ruf, *Bull. Soc. Chim. Fr.*, **10**, 3738 (1967).

TABLE 2. Yields, mps. and ^{1}H NMR Spectral Data of Compounds **4**

Cmpd	Yield (%)	mp. (°C)	lit. mp. (°C)	^{1}H NMR (δ, $CDCl_3$)
4a	26	144-146	146-149[a]	7.15-6.44 (m, 20H), 4.55(s, 4H)
4b	35	140-142	140-142[a]	7.13-6.33 (m, 18H), 4.53 (s, 2H), 4.17 (br, 2H), 2.22 (s, 6H)
4c	28	194-196	194-195[c]	7.30-6.42 (m, 18H), 4.93 (s, 2H), 4.27 (s, 2H)
4d	27	112-114	131.5-114.5[a]	7.25-6.33 (m, 18H), 4.87 (5, 2H), 4.50 (br, 2H)
4e	48	131-132	131.5-132[b]	7.20-6.40 (m, 18H), 4.55 (s, 2H), 4.22 (br,2H), 2.33 (s, 6H)
4f	46	138-140	140-141[a]	7.17-6.30 (m, 18H), 5.03 (br, 2H), 4.77 (s, 2H)
4g	60	141-143	140-142[d]	7.10-6.27 (m, 18H), 4.47 (s, 4H)

a) R. Jaunin and P. Courbat, *Helv. Chim. Acta*, **43**, 2029 (1960). b) G. James and H. Isaac, *J. Org. Chem.*, **37**, 653 (1972). c) H. Thies and H. Schonenberger, *Arch. Pharm.*, **291**, 620 (1958). d) D. Schulz and R. Pohloudek, *ibid.*, **297**, 757 (1964).

EXPERIMENTAL SECTION

Mps were determined using a capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained on a JEOL-PMX 6051. IR spectra were recorded on a Nicolet FT-5DX spectrometer.

General Procedure for Compounds 2.- To a dry 100mL flask charged with a well ground up mixture of the aromatic ketone **1** (10 minol) and zinc dust 2.60g (40 mmol),was added $TiCl_4$ 2.2 mL (20 mmol) dropwise *via* a syringe at 80° under an argon atmosphere. When the addition was complete, the mixture was heated to 120° for 10 h. After cooling naturally to room temperature, the solid mixture was hydrolyzed with 5% aqueous HCl solution and extracted with $CHCl_3$ (100 mLx3). The combined $CHCl_3$ extract was washed with water (30mLx3), dried over anhydrous Na_2SO_4, and the solvent was removed *in vacuo.* The resulting material was purified by column chromatography on silica gel [chloroform: petroleum ether (60-90°)]. In the low yield reactions, the formation of tarry mixture was extensive and no starting materials could be recovered.

General Procedure for Compounds 4.- A procedure similar to the above was used except that the temperature differences (at 80° for 20 h), because higher temperatures led only to black oily mixture. When the reaction was completed, 100 mL of 30% aqueous K_2CO_3 solution was poured into the flask to hydrolyze the mixture.

meso- and *d,l-vic*-1,2-Diamines are easily distinguished by their melting points and ^{1}H NMR[5].

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