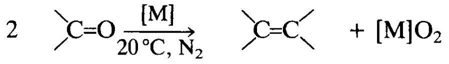
Reductive Dimerization of Carbonyl Compounds using Reduced and Electroreduced Tungsten Species

Michele Petit, Andre Mortreux, and Francis Petit*

Laboratoire de Chimie Organique Appliquée, ERA CNRS 458, B.P. 108, E.N.S.C. Lille 59652 — Villeneuve d'Ascq, France

Carbonyl compounds are easily transformed into olefins by chemically or electrochemically reduced tungsten species; the best results are obtained by means of a controlled potential electroreduction of WCl_6 at a platinum electrode: benzaldehyde gives stilbene quantitatively when anhydrous tetrahydrofuran is used as the solvent and aluminium as the anode; in CH_2Cl_2, styrene can also be produced with lower yields.

Much work relating to the use of transition metals in the reduction of organic compounds such as *geminal* and *vicinal* dihalides,[1] epoxides,[2] 1,2-diols,[3,4] and carbonyl compounds has been reported. With a low valent metal reagent these substrates are often converted into the corresponding alkenes; low valent titanium and tungsten[4,5] have been successfully employed for carbon–carbon bond formation and particularly for the reductive dimerization of carbonyl compounds, equation (1).



(1)

However, with a W^{II} solution [tetrahydrofuran (THF)] produced from a stoicheiometric 'WCl_6–reducer' combination and benzaldehyde as substrate, the coupling is never quantitative and not totally selective when the Fujiwara procedure is used.[6] Among the tested reducing reagents [Ni(0), $AlEt_3$, $LiBEt_3H$, $LiAlH_4$] the best reducer is found to be $LiAlH_4$, but the reaction is often unpredictable since the yields are variable (50—75%) and the final products, mainly stilbenes, are difficult to recover and isolate because of the high viscosity of the medium.

We now report results related to the electrogeneration of reduced tungsten species active for the stoicheiometric synthesis of unsaturated hydrocarbons from carbonyl compounds. In solvents usually used in electrochemical reactions such

Table 1. Electroreduction of WCl_6 in THF with PhCHO.[a]

Time/h	Q/mF	% Conversion[c]	% Selectivity PhCH=CHPh	 $PhCH_2$–CH_2Ph	 $PhCH_2OH$
0.5	1.1	26.5	98.5	0.5	1
1	2.2	54	98.5	0.5	1
2	2.8	72	98	1	1
3	3.6	92	97.5	1	1.5
4	3.9[b]	99	97	1.5	1.5

[a] [PhCHO] = 2 mmol, [WCl_6] = 1 mmol, −1900 mV/SCE, 6 h. [b] Analogous results are obtained with a Zn or Fe anode. [c] Conversions (based on benzaldehyde) and selectivities were determined by g.l.c. (Carbowax 20 M 10% 3 m × 0.32 mm, 180 °C, N_2 : 20 ml min^{-1}) using biphenyl as an internal standard.

Table 2. Coupling of carbonyl compounds by electroreduced WCl_6 in THF.[a]

			% Yield[c]		
Substrate	Product	V_c[b]/mV	*E*		*Z*
Benzaldehyde	Stilbene	−1900	87.5		8.5
Benzophenone	Tetraphenylethylene	−1850		50.8	
Acetophenone	1,2-Dimethylstilbene	−1800	30		16
Propionaldehyde	3-Hexene	−1950		8	
Acetone	Tetramethylethylene	−1975		6	

[a] Conditions are as in Table 1. [b] Fixed cathodic potential *vs.* SCE was determined for each substrate. [c] Based on olefins formed.

as THF, dimethyl sulphoxide (DMSO), *N,N*-dimethylformamide (DMF), but not CH_2Cl_2, the polarogram obtained with a 2 mM solution of WCl_6 (rotating platinum electrode, 0.2 M $NBu_4^+ClO_4^-$ as supporting electrolyte) exhibits three reversible steps characterized by three half wave potentials [−150, −950, and −1800 mV *vs.* standard calomel electrode (SCE) in THF]. Constant potential coulometry on the third level of the reduction, with or without PhCHO, in all aforementioned solvents yielded an '*n*' value of 4.0 ± 0.1 equiv. of electrons passed per mole of salt. Most of the preparative experiments were conducted in anhydrous THF on the third plateau ($V \leqslant -1900$ mV/SCE) in an undivided cell with a platinum cylindrical grid cathode and an aluminium foil anode.

When PhCHO (2 mmol) was added after the electroreduction of WCl_6 (1 mmol) in THF at −1900 mV/SCE over 6 h, stilbene was always obtained in surprisingly low yields (10%). In contrast, when the electrolysis was effected in the presence of PhCHO the reductive coupling of this substrate was quantitative and the products were easily recovered (Table 1).

Mechanistic proposals remain speculative but as no diols have been detected during the coupling, the reduction of the carbonyl compound to the corresponding diols may not be involved. The high yields obtained when the benzaldehyde is added before electrolysis can be explained by the easy reducibility of the 18 electron complex $WCl_6(PhCHO)_2$, which may be formed initially. However as can be seen from Table 2, the electroreduced tungsten is not capable of coupling aliphatic compounds in good yields.

In CH_2Cl_2, reduction of an excess of WCl_6 (*ca.* 10 mmol) at a platinum cathode (V_c = +900 mV *vs.* SCE) with an aluminium anode gave *in situ* carbenic species[7] which transformed benzaldehyde (1 mmol) into styrene at room temperature in THF, equation (2).

$$[\mathrm{W}{\ddagger}\mathrm{CH_2} + \mathrm{PhCHO} \longrightarrow [\mathrm{W}{\ddagger}\mathrm{O} + \mathrm{PhCH{=}CH_2} \qquad (2)$$

Received, 5th October 1983; Com. 1322

References

1 C. E. Coffey, *J. Am. Chem. Soc.*, 1961, **83**, 1623.

2 K. B. Sharpless, M. A. Unbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, 1972, **94**, 6538.

3 K. B. Sharpless, R. P. Hanzlik, and E. E. Van Tamelen, *J. Am. Chem. Soc.*, 1968, **90**, 209.

4 J. E. McMurry and M. P. Fleming, *J. Am. Chem. Soc.*, 1974, **96**, 4708.

5 T. Mukaiyame, T. Sato, and J. Hanna, *Chem. Lett.*, 1973, 1041; S. Tyrlik and I. Wolochowicz, *Bull. Soc. Chim. Fr.*, 1973, 2147; E. J. Corey, R. L. Danheiser, and S. Chandrasekaran, *J. Org. Chem.*, 1976, **41**, 260; J. E. McMurry and R. L. Krepski, *ibid.*, p. 3929; J. E. McMurry and K. L. Kees, *ibid.*, 1977, **42**, 2656; H. Ledon, I. Tkatchenko, and D. Young, *Tetrahedron Lett.*, 1979, 173; J. E. McMurry and M. P. Fleming, *J. Org. Chem.*, 1975, **41**, 896.

6 Y. Fujiwara, R. Ishikawa, F. Akiyama, and S. Teranishi, 1978, **43**, 2477.

7 M. Gilet, A. Mortreux, J. C. Folest, and F. Petit, *J. Am. Chem. Soc.*, 1983, **105**, 3876.