

## Preliminary communication

## A novel deoxygenation of a carbonyl group of iron pentacarbonyl

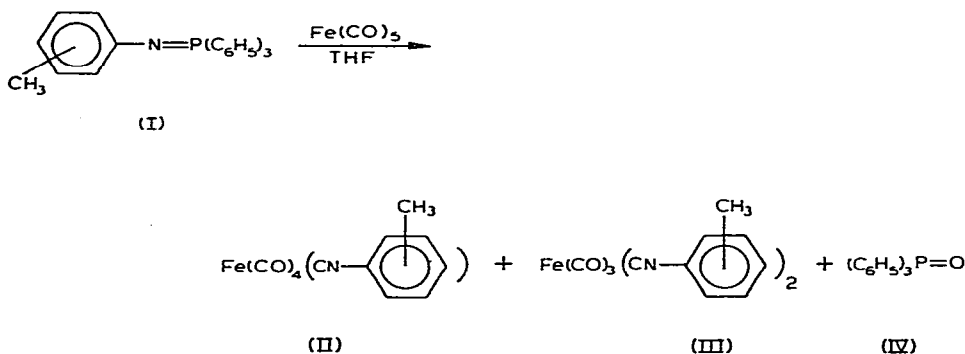
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Iron pentacarbonyl is a useful reagent for effecting deoxygenation of sulfoxides<sup>1</sup> and various organic compounds containing the N—O linkage<sup>2</sup>. This communication reports a rare example of the reverse reaction: deoxygenation of a carbonyl group of  $\text{Fe}(\text{CO})_5$  without cleavage of the metal—carbon bond<sup>\*</sup>.

Reaction of each of the three *N*-tolyltriphenylphosphine imines (I, *o*-, *m*-, or *p*- $\text{CH}_3$ -) and  $\text{Fe}(\text{CO})_5$  (1.15/1.00 mole ratio of  $\text{Fe}(\text{CO})_5$  to I) in refluxing dry tetrahydrofuran (THF) for 19–22 h affords the corresponding tolylisocyanideiron



tetracarbonyl (II), bis(tolylisocyanide)iron tricarbonyl (III) (60–94% total yield of II and III) as well as triphenylphosphine oxide (IV, 97%)<sup>★★</sup>. Pertinent IR and <sup>1</sup>H NMR data for II and III are listed in Table 1.

<sup>\*</sup>To our knowledge, the only other case of deoxygenation of  $\text{Fe}(\text{CO})_5$  without Fe—C cleavage results from treatment of the sodium salt of 1,1,1,3,3,3-hexamethyldisilazane with the metal carbonyl<sup>3</sup>.

<sup>★★</sup>Satisfactory elemental analyses were obtained for new compounds.

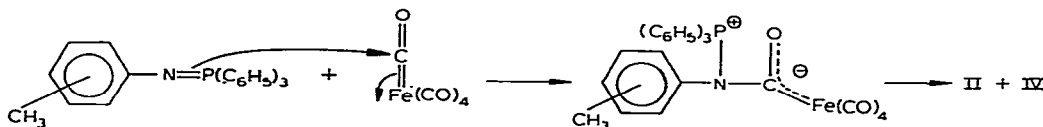
TABLE 1

IR AND  $^1\text{H}$  NMR DATA FOR II AND III

Complex	IR <sup>a</sup>		$^1\text{H}$ NMR <sup>b</sup>	
	$\nu(\text{CN})$	$\nu(\text{CO})$	$\text{CH}_3(\text{singlet})$	Aromatic
II, <i>o</i> -CH <sub>3</sub> -	2163	2055, 1992, 1963	1.90	6.50–6.85m
II, <i>m</i> -CH <sub>3</sub> - <sup>c</sup>	2169 <sup>d</sup>	2058, 1994, 1965	1.85	6.30–6.70m
II, <i>p</i> -CH <sub>3</sub> - <sup>c,e</sup>	2175	2060, 1995, 1965	1.89	6.54s
III, <i>o</i> -CH <sub>3</sub> -	2105	1998, 1934	2.07	6.69s
III, <i>m</i> -CH <sub>3</sub> - <sup>f,g</sup>	2106	1993, 1937	1.83	6.50–6.67m
III, <i>p</i> -CH <sub>3</sub> - <sup>e</sup>	2115	2000, 1955	1.86	6.62s

<sup>a</sup>Measured in methylene chloride solution. <sup>b</sup>ppm downfield of TMS, measured in C<sub>6</sub>D<sub>6</sub>. <sup>c</sup>Mass spectrum gave a molecular ion peak at *m/e* 285, followed by successive loss of four carbonyls. <sup>d</sup>A weak shoulder was also observed at 2153 cm<sup>-1</sup>. <sup>e</sup>Taylor and Horrocks<sup>4</sup> have reported the preparation of II (*p*-CH<sub>3</sub>-) and III (*p*-CH<sub>3</sub>-) but no IR data was given. IR results for some related complexes have been published by Cotton and Parish<sup>5</sup>. <sup>f</sup>Molecular weight determined by vapor-phase osmometry (benzene) was 375 (calcd. 374). <sup>g</sup>IR shows weak bands due to II (*m*-CH<sub>3</sub>-).

Complexes of type II probably result from initial attack of I at a metal carbonyl carbon to give the dipolar intermediate V. The latter can then collapse to II and the very stable IV, the formation of which is a driving force for this reaction. Complex (III) may arise from disproportionation of (II) at room temperature or under the reaction conditions.



Complexes II (*p*-CH<sub>3</sub>-) and III (*p*-CH<sub>3</sub>-) are also obtained by reaction of *N-p*-tolyltriphenylphosphine imine (I, *p*-CH<sub>3</sub>-) with diiron enneacarbonyl [Fe<sub>2</sub>(CO)<sub>9</sub>] in benzene at room temperature. In addition, *N,N'*-di-*p*-tolylurea (44%), 4,4'-dimethyloxanilide (8%), and 4,4'-dimethylhydrazobenzene (5%) are organic products of the reaction. It should be noted that the same or analogous organic products were produced in lower yields in the Fe(CO)<sub>5</sub> reactions but we have not, as yet, attempted to optimize yields.

We are currently investigating the generality of this novel metal carbonyl deoxygenation reaction. For example, molybdenum hexacarbonyl reacts with I (*m*-CH<sub>3</sub>-) in 1,2-dimethoxyethane to form *m*-tolylisocyanidemolybdenum pentacarbonyl and triphenylphosphine oxide.

#### ACKNOWLEDGMENT

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## REFERENCES

- 1 H. Alper and E.C.H. Keung, *Tetrahedron Letters*, (1970) 53.
- 2 H. Alper and J.T. Edward, *Canad. J. Chem.*, 48 (1970) 1543.
- 3 U. Wannagat and H. Seyffert, *Angew. Chem. Int. Ed.*, 4 (1965) 438.
- 4 R.P. Taylor and W.D. Horrocks, *Inorg. Chem.*, 3 (1964) 584.
- 5 F.A. Cotton and R.V. Parish, *J. Chem. Soc.*, (1960) 1440.

*J. Organometal. Chem.*, 35 (1972)