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THE IRON CARBONYL INDUCED DEOXYGENATION OF ALCOHOLS

Howard Alper* and Marta Sališová
Department of Chemistry, University of Ottawa
Ottawa, Ontario, Canada K1N 9B4

Summary: Alcohols, able to form stable carbanions, are deoxygenated to hydrocarbons by treatment with potassium, iron pentacarbonyl, and then hydrochloric acid. Use of an alkyl halide in place of HCl results in reductive alkylation.

Iron pentacarbonyl is a useful reagent for deoxygenating epoxides[1], sulfoxides[2], and a variety of compounds containing a nitrogen-oxygen bond[2]. Much more challenging than any of these transformations, however, is the deoxygenation of alcohols to hydrocarbons. The latter process, which is of considerable importance in synthetic organic chemistry, is usually effected by initial derivatization of the alcohol (e.g., as a methanesulfonate ester)[3]. We now wish to report the iron carbonyl induced, direct deoxygenation of alcohols which are capable of forming relatively stable carbanions.

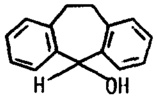
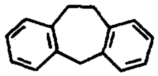
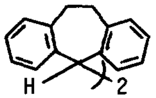
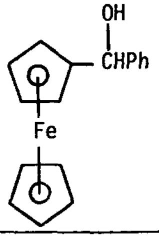
Treatment of triphenylmethanol with potassium in toluene results in *in situ* generation of the alkoxide ion, which is then reacted with $Fe(CO)_5$ in toluene. Acidic work-up of the reaction mixture affords triphenylmethane in 90% yields (Table 1). By-products of the reaction are hexaphenylethane (4%) and 1,1,1,2-tetraphenylethane (4%). The latter compound was not, of course, formed when p-xylene was used as the solvent; rather, 1,1,1-triphenyl-2-p-tolylethane was isolated in 5% yield [90% triphenylmethane and 2% hexaphenylethane].

Hydrocarbons were obtained in reasonable yields from the reaction of various primary, secondary, and tertiary benzylic alcohols with $Fe(CO)_5$ (Table 1). When 1,1-diphenyl-1-ethanol was reacted with potassium in the absence of $Fe(CO)_5$, only a trace of 1,1-diphenylethane was formed (in addition to recovered starting material). Phase transfer catalyzed generation of the alkoxide ion,[4] followed by reaction with the metal carbonyl, proved to be less useful since the product yields were appreciably lower than when potassium in toluene was used. This is because $Fe(CO)_5$ is converted to $HFe(CO)_4^-$ under the phase transfer conditions[5].

A proposed mechanism for the deoxygenation reaction is outlined in Scheme 1. The alkoxide ion (1), generated by exposure of an alcohol to potassium, can add in a nucleophilic manner to one of the carbonyl groups of $Fe(CO)_5$ to give 2. Loss of carbon dioxide and iron tetracarbonyl

TABLE 1

DEOXYGENATION OF ALCOHOLS BY $Fe(CO)_5$ IN TOLUENE

Alcohol	Product	Yield,[a] %	M.p. (b.p.) °C	Lit. m.p. (b.p.) °C
Triphenylmethanol	triphenylmethane	90	94-95	94[b]
	hexaphenylethane	4	148-149	145-147[b]
	1,1,1,2-tetraphenylethane	4	143-145	143-144[b]
2-Methylbenzhydrol	phenyl-o-tolylmethane	53	(151-154,10mm.)	(165-172,14mm.)[c]
	1,2-diphenyl-1,2-di-o-tolylethane	31	180-182	182[d]
1,1-Diphenyl-1-ethanol	1,1-diphenylethane	54	(283-285)	(286)[b]
	1,1-diphenylethylene	26	(127,6mm.)	(277)[b]
2-Naphthalenemethanol	2-methylnaphthalene	58	40-41	37-38[b]
	di-2-naphthylmethyl ether	25	122-123	121-123[b]
		43	74-75	76-77[e]
		36	275-276	271.5-272.5[e]
	Benzylferrocene	67	73-75	73-74[f]
	1,2-diferrocenyl-1,2-diphenylethane	19	261-263	258-261[g]

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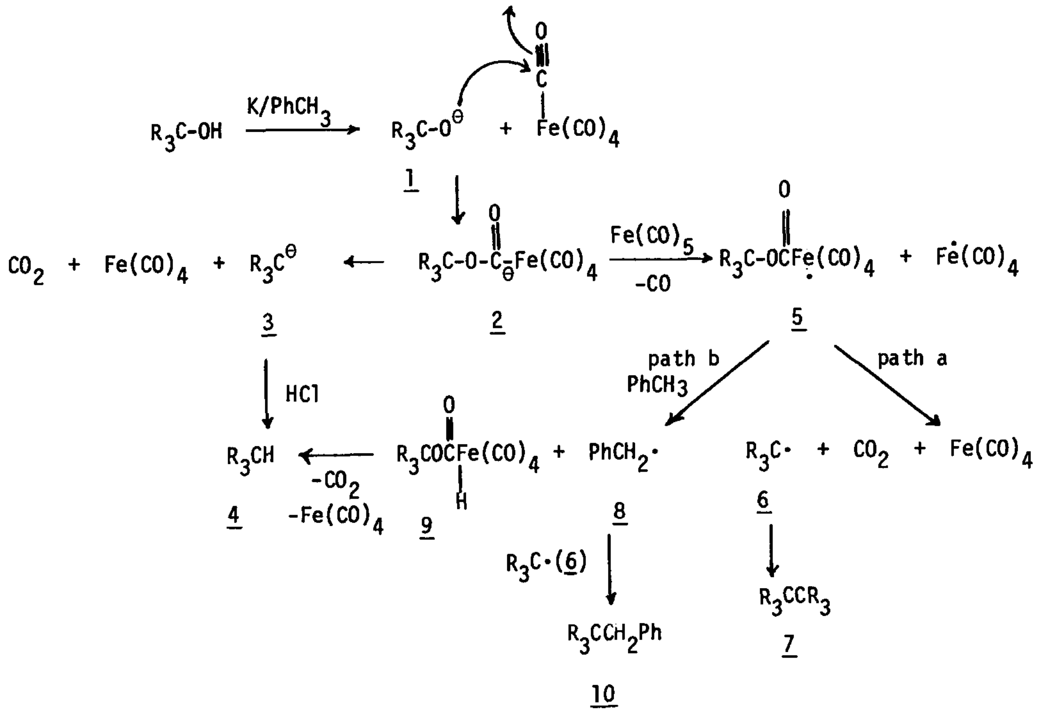
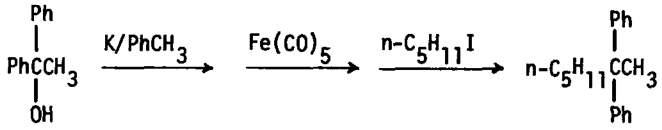
[a] Products were identified by comparison of m.p. or b.p. and spectral data [ir,nmr(^1H,^{13}C),ms] with that for authentic materials. [b] Handbook of Chemistry and Physics, 50th edition, 1969-70, The Chemical Rubber Publishing Co., Cleveland, Ohio. [c] G. Wittig, G. Closs and F. Mindemann, Ann., 594, 89 (1955). [d] J. de Pascual Teresa and H. Sanchez Bellido, Anales Real Soc. Españ. Fis. y. Quim., 52B, 557 (1956); Chem. Abstr., 51, 6537c (1957). [e] I. Moritani, S.I. Murahashi, K. Yoshinaga, and H. Ashitaka, Bull Chem. Soc. Japan, 40, 1506 (1967). [f] M. Rausch, M. Vogel and H. Rosenberg, J. Org. Chem., 22, 903 (1957). [g] R. Reimschneider and D. Helm, Chem. Ber., 89, 155 (1956).

Scheme 1



from $\underline{2}$ would afford the carbanion $\underline{3}$, which on protonation gives $\underline{4}$. It is also conceivable that $\underline{2}$ undergoes electron-transfer with another molecule of $Fe(CO)_5$ to give the radical $\underline{5}$. This species can then either lose CO_2 to give the carbon radical $\underline{6}$ which on coupling affords the ethane $\underline{7}$ (e.g., hexaphenylethane - path a), or abstract hydrogen from toluene affording the benzyl radical $\underline{8}$ and the iron hydride $\underline{9}$ (path b). Coupling of $\underline{8}$ with $\underline{6}$ would give $\underline{10}$ (e.g., 1,1,1,2-tetraphenylethane), while $\underline{9}$ is convertible to the hydrocarbon $\underline{4}$ on decomplexation.

If, as postulated, the deoxygenation proceeds via carbanionic (and radical) species (i.e., $\underline{3}$) then it should be possible to effect reductive alkylation of alcohols by work-up of the reaction using an alkyl halide in place of HCl. Indeed, treatment of triphenylmethanol with potassium, $Fe(CO)_5$, and then α-bromo-p-xylene in toluene affords 1,1,1-triphenyl-2-p-tolylethane. Similarly, 2,2-diphenylheptane was formed by reaction of 1,1-diphenyl-1-ethanol with potassium, $Fe(CO)_5$ and 1- iodopentane.



$$\mathrm{Ph}\overset{\mathrm{Ph}}{\underset{\mathrm{OH}}{\mathrm{C}}}\mathrm{CH_3} \xrightarrow{K/PhCH_3} \xrightarrow{Fe(CO)_5} \xrightarrow{n\text{-}C_5H_{11}I} n\text{-}C_5H_{11}\overset{\mathrm{Ph}}{\underset{\mathrm{Ph}}{\mathrm{C}}}\mathrm{CH_3}$$

The following deoxygenation procedure is representative: Potassium [0.50 g., .0125 g-atom] in dry toluene [50 ml.] was heated to reflux. Triphenylmethanol [3.90 g., 15.0 mmol] in toluene [50 ml.] was added, the reaction mixture was vigorously stirred at reflux for 1-2 hours, and then $Fe(CO)_5$ [5.0 ml., 35.0 mmol] in toluene [10 ml.] was added dropwise. After heating for 12 hours, 6M HCl [20 ml.] was added to the hot reaction mixture and the solution was cooled to room temperature, poured into water, and extracted with ether. The ether extract was concentrated and then chromatographed on silica gel. Elution with hexane gave 3.3 g. (90%) of triphenylmethane. Elution with 3:1 hexane-benzene gave 0.20 g. (4%) of 1,1,1,2-tetraphenylethane, followed by 0.15 g. (4%) of hexaphenylethane.

ACKNOWLEDGEMENT

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