

THE NEUTRAL DEOXYGENATION (REDUCTION) OF ARYL CARBONYL COMPOUNDS WITH RANEY-NICKEL.  
 AN ALTERNATIVE TO THE CLEMMENSON, WOLF-KISHNER OR MOZINGO (THIOKETAL) REDUCTIONS.

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**Summary:** W-7 Raney-Nickel reduces mono or diaryl carbonyl compounds in 50% aqueous ethanol in excellent yields to the aryl methanes.

Because Friedel-Crafts alkylation is difficult to control, the sequence Friedel-Crafts acylation<sup>1</sup> followed by deoxygenation of the resultant carbonyl compound is one of the best known in chemistry to prepare an alkyl substituted aromatic. Although both the Clemmenson<sup>2d</sup> and Wolf-Kishner<sup>2e</sup> conversions of  $>C=O$  to  $>CH_2$  work well,<sup>2</sup> they are used under strongly acidic and basic conditions respectively. The Mozingo reduction<sup>3</sup> of dithioketals using Raney-Nickel has partially overcome this problem. We have however accidentally discovered a much simpler alternative. In the course of attempting to remove the -SMe groups of the [2.1.2.1] cyclophane described in the preceding communication we observed that W-7 Raney Nickel also reduced the carbonyl group to a methylene. The Raney-Nickel reduction of aryl carbonyl compounds was in fact reported<sup>4</sup> in 1942, however the reduction was carried out by dissolving the compound together with Ni-Al alloy in strong NaOH solution. The harshness of these conditions possibly accounts for the fact that except for an early review<sup>5</sup> the reaction appears to have been forgotten.<sup>6</sup>

We have found that a number of aryl ketones and aldehydes can be reduced to the aryl methane both conveniently and efficiently<sup>8</sup> under *neutral* conditions by refluxing with *ca.* 5 fold excess of W-7 Raney-Nickel<sup>10</sup> in 50% aqueous ethanol as indicated in Table 1. The reaction proceeds considerably more slowly in the absence of water as a hydrogen donor.<sup>11</sup> These conditions

TABLE 1

REACTANT	PRODUCT	REACTION TIME <sup>a</sup>	YIELD <sup>b</sup>	ALDRICH LIBRARY	
				NMR	IR
$\phi$ -CO- $\phi$	$\phi$ -CH <sub>2</sub> - $\phi$	3h	97%	4:7A	501G
Fluorenone	Fluorene	3h	94%	4:31D	515E
$\phi$ -CO-CH <sub>3</sub>	$\phi$ -CH <sub>2</sub> CH <sub>3</sub>	5h	94%	5:1C	499C
$\alpha$ -Tetralone	Tetralin	6h	95%	4:6D	502H
4-HO- $\phi$ -COCH <sub>3</sub>	4-HO- $\phi$ -CH <sub>2</sub> CH <sub>3</sub>	5h	99%	4:114C	577D
4-CH <sub>3</sub> O- $\phi$ -COCH <sub>3</sub>	4-CH <sub>3</sub> O- $\phi$ -CH <sub>2</sub> CH <sub>3</sub>	6h	92%	c	-
1-Naphthaldehyde	1-Me-naphthalene	2h <sup>d</sup>	89%	4:26B	513E
4-HO <sub>2</sub> C- $\phi$ -CHO	4-HO <sub>2</sub> C- $\phi$ -CH <sub>3</sub>	5h	89%	6:148C	840G
4-(CH <sub>3</sub> ) <sub>2</sub> N- $\phi$ -CHO	4-(CH <sub>3</sub> ) <sub>2</sub> N- $\phi$ -CH <sub>3</sub>	5h	95%	5:59A	639H
$\phi$ -CO-CO- $\phi$	$\phi$ -CH <sub>2</sub> -CH <sub>2</sub> - $\phi$	5h	99%	4:7B	501H
2-Cl- $\phi$ -CO- $\phi$	$\phi$ -CH <sub>2</sub> - $\phi$	6h	91%	4:7A	501G
2-CH <sub>3</sub> O <sub>2</sub> C- $\phi$ -CO- $\phi$	2-CH <sub>3</sub> O <sub>2</sub> C- $\phi$ -CH <sub>2</sub> - $\phi$	25h <sup>e</sup>	40%	f	-
3-O <sub>2</sub> N- $\phi$ -COCH <sub>3</sub>	3-H <sub>2</sub> N- $\phi$ -COCH <sub>3</sub>	5h	80%	6:38D	767B
4-O <sub>2</sub> N- $\phi$ -CHO	Mixture	5h	-	-	-

do not affect methoxyl, hydroxyl, carboxyl, carbomethoxy, or dimethylamino groups which have been reported<sup>12</sup> to be problematic on occasion. However, nitro, cyano and halo groups suffer reduction. The latter are removed cleanly under what seem superior conditions to those reported<sup>13</sup> previously and we will be studying this further. Overall the method seems an attractive alternative to the recently reported method of Gribble<sup>14</sup> which uses  $\text{NaBH}_4 - \text{CF}_3\text{COOH}$  and seems to be successful only for diaryl compounds.

We thank the University of Victoria and the Natural Sciences and Engineering Research Council of Canada for financial support.

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#### NOTES FOR TABLE 1

- (a) The compound was refluxed with ca. 5 fold excess\* of W-7 RaNi in 50% aq. EtOH for the time shown. The product was then extracted into ether. If very old alloy samples are used to prepare W-7 RaNi reaction times appear to increase. (b) Product identification and purity was by comparison of <sup>1</sup>Hmr and ir spectra to those reported in the Aldrich Library of NMR (and IR spectra (published by Aldrich Chemical Company, Wisconsin, USA) and in every case identical spectra were observed to the numbers given in the table. (c) <sup>1</sup>Hmr (CDCl<sub>3</sub>-90MHz) δ 7.4-6.7 (4H, m, ArH), 3.73 (3H, s, -OCH<sub>3</sub>), 2.55(2H, q, -CH<sub>2</sub>-) and 1.18 (3H, t, -CH<sub>3</sub>). (d) Prolonged heating causes reduction of the aryl ring. (e) The reduction appears slow, but the ester function is not hydrolysed. (f) <sup>1</sup>Hmr (CDCl<sub>3</sub>-90MHz): δ 8.2-7.1 (9H, m, ArH), 4.45 (2H, s, -CH<sub>2</sub>-) and 3.60 (3H, s, -OCH<sub>3</sub>).

(Received in USA 12 March 1980)

\*This amount may be reduced to about 2 fold excess if convenient on larger scale (eg. ~1 mole) reactions.