Tetrahedron Letters,Vol.23,No.12,pp 1239-1240,1982 0040-4039/82/121239-02$03.00/0
Printed in Great Britain

THE OXIDATION OF (ARENE)CHROMIUMTRICARBONYL ALCOHOLS BY ACETIC ANHYDRIDE - DMSO

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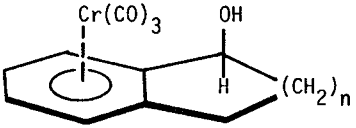
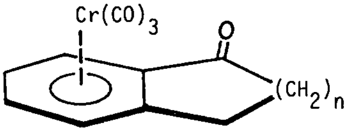
Summary. A mixture of acetic anhydride and dimethyl sulfoxide is a useful reagent for the oxidation of (arene)chromiumtricarbonyl alcohols without loss of the $Cr(CO)_3$ group. Yields are dependent on the nature of the starting alcohol.

The increasing importance of (arene)chromiumtricarbonyl (CT) complexes as intermediates in organic synthesis[1] may be attributed to their remarkable chemical and stereochemical properties, and to the ease of eventual removal of the $Cr(CO)_3$ grouping under mild oxidative conditions. In fact, a serious limitation to the wider exploitation of (arene)CT complexes in synthesis is the lack of an efficient reagent for the oxidation of alcohols to carbonyl compounds without concomitant decomplexation. Until now, only MnO_2 oxidation conditions are known to be compatible with maintenance of a CT complex. This reagent was used[2] for the oxidation of optically active (1-indanol)CT (1a) and (1-tetralol)CT (1b) to the corresponding optically active ketones 2a and 2b but conversions of only about 20% were achieved. Since these products are of proven value as chiral synthons[3], we were motivated to seek a more efficient reagent for the oxidation of their alcohol precursors as well as other CT alcohols. We have found that a mixture of acetic anhydride and DMSO, a known[4] oxidizing agent of the "activated dimethyl sulfoxide" type[5], is suitable for this purpose. However, two other oxidizing systems in this category: oxalyl chloride-DMSO[6] and tosyl chloride-HMPA-SMSO[7], led to decomplexation. Our results with AC_2O-DMSO are given in table 1.

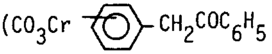


1a n = 1
1b n = 2



2a n = 1
2b n = 2

Table 1. Acetic Anhydride-DMSO Oxidation Reactions

Product	Reaction Time(hr)	Yield (%)	m.p.	m.p. (lit.)
1. (benzaldehyde)CT	1½	57	46-6°	46.5-47.5 (5)
2. (benzophenone)CT	2	65	88-9°	88° (6)
3. 	2	60	155-6°	158° (6)
4. ±(1-indanone)CT	2	76	124-5°	124° (6)
5. ±(1-tetralone)CT	2½	77	126-7°	128° (6)
6. (3-(4-methoxyphenyl)-propanal)CT	2	26	oil	
7. (4-phenyl-2-butanone)CT	5	29	oil	
8. (estrone-3-methyl ether)CT	5½	32	oil	

The reactions were carried out by dissolving 0.4 mmole of complexed alcohol in 6 ml of DMSO and 4 ml of Ac_2O. The clear solution was stored in the dark at room temperature until disappearance of starting alcohol was determined by TLC. The reaction solution was then diluted with benzene and washed once with 20% aq. NaOH and several times with water. The yields for entries 1-5 (Table 1) refer to crystallized (from Et_2O-hexane) products having the given melting point. The non-crystalline products of entries 6-8 were obtained as pure (TLC) fractions after dry-column chromatography on silica gell (column wrapped with aluminum foil to exclude light).

The highest yields were obtained with benzylic alcohols (entries 1-5). The non-benzylic alcohols gave only modest yields of carbonyl products (entries 6-8) due largely to their lower rates of oxidation which allowed methylthiomethyl ether formation[4] to become competitive. In these three cases, side-products of the type $ROCH_2SCH_3$ were isolated in yields up to 45%.

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(Received in USA 3 November 1981)