ORGANOCOPPER CHEMISTRY.   REACTION OF α,β-ETHYLENIC SULFONES
WITH LITHIUM DIALKYLCUPRATES

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The carbonyl group is one of the most versatile functionalities in organic synthesis.[2]
Although modification of an aldehyde or ketone carbonyl group can lead to a variety of functional
units, conversion to a gem-dialkyl group is not easily accomplished by currently available
methods.[3] We recently reported a partially successful sequence of steps for such a conversion
which involved replacing benzoyl oxygen first by the gem-dichloride functionality and then
replacing each chlorine by a methyl group using lithium dimethylcuprate(I) (Eq. 1).[4] Most
aliphatic gem-dichlorides, however, are unreactive toward organocuprate(I) reagents. An alter-
nate scheme for transformation of the oxo to the gem-dialkyl functionality involves formation
of an α,β-ethylenic aryl sulfone, reaction of this vinyl aryl sulfone with lithium dialkyl-
cuprates(I), and hydrogenolysis of the alkyl-sulfur bond in the alkyl aryl sulfone product
(Eq. 2). We now report successful execution of this scheme which involves two new transforma-
tions: methyl and n-butyl addition specifically to the β-carbon of α,β-unsaturated sulfones
using lithium dialkylcuprate(I) reagents and selective sodium-amalgam hydrogenolysis of the
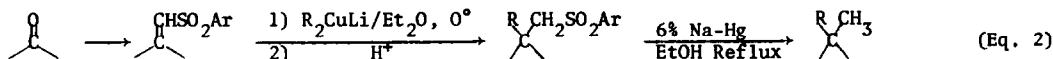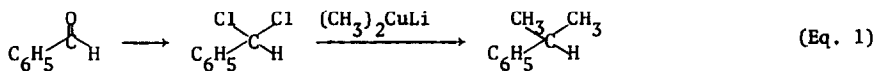alkyl-sulfur bond in alkyl p-chlorophenyl sulfones (Eq. 2, Ar = p-ClC$_6$H$_4$).

Table I summarizes the transformations of aldehydes and ketones to gem-dialkylalkanes.

α,β-Ethylenic methyl sulfones were prepared easily from aldehydes and ketones and sulfono-
methylphosphonate anions using a modification of the Horner-Wittig reaction.[5] These vinyl methyl
sulfones were found to be unsatisfactory for our purposes, however, since reaction with organo-
cuprate(I) reagents caused metalation of the methyl group as shown by deuterium incorporation
upon D$_2$O workup. α,β-Ethylenic aryl sulfones were prepared in high yield from aldehydes, even
from 3-ethoxycarbonylcyclohexane carboxaldehyde, but in poor yield from most ketones even under
forcing conditions and use of special solvents (e.g. hexamethylphosphoramide.)[6] Since acetone
and cyclohexanone can be converted to the corresponding alkylidene aryl sulfones in good yields,
the main difficulty with other ketones (e.g. 2-heptanone, 5-nonanone) presumably is steric

Table I. Conversion of Aldehyde and Ketone Carbonyl Groups to Tertiary and Quaternary Carbon Atoms Via Eq. 2.

Aldehyde or Ketone	Vinyl Aryl[a] Sulfone (% Yield)[b]	Alkyl Aryl Sulfone (% Yield)	Hydrocarbon (% Yield)	Overall % Yield of Hydrocarbon from Aldehyde or Ketone
$n\text{-}C_6H_{13}CHO$	$n\text{-}C_6H_{13}CH{=}CHSO_2Ar$ (80)	$n\text{-}C_6H_{13}CH(CH_3)CH_2SO_2Ar$ (97)	$n\text{-}C_6H_{13}CH(CH_3)_2$ (85)	66 (82)[c]
		$n\text{-}C_6H_{13}CH(n\text{-}C_4H_9)CH_2SO_2Ar$ (93)	$n\text{-}C_6H_{13}CH(n\text{-}C_4H_9)CH_3$ (72)	53 (69)[c]
C_6H_5CHO	$C_6H_5CH{=}CHSO_2Ar$ (90)	$C_6H_5CH(CH_3)CH_2SO_2Ar$ (100)	$C_6H_5CH(CH_3)_2$ (99)	89
		$C_6H_5CH(n\text{-}C_4H_9)CH_2SO_2Ar$ (75)	$C_6H_5CH(n\text{-}C_4H_9)CH_3$ (92)	62
$C_6H_5CH(CH_3)CHO$	$C_6H_5CH(CH_3)CH{=}CHSO_2Ar$ (~80)	$C_6H_5CH(CH_3)CH(CH_3)CH_2SO_2Ar$ (97)	$C_6H_5CH(CH_3)CH(CH_3)_2$ (100)	~78
		$C_6H_5CH(CH_3)CH(n\text{-}C_4H_9)CH_2SO_2Ar$ (~90)[d]	$C_6H_5CH(CH_3)CH(n\text{-}C_4H_9)CH_3$ (~80)	55-60
cyclohexane ($CO_2C_2H_5$, CHO)	cyclohexane ($CO_2C_2H_5$, $CH{=}CHSO_2Ar$) (55)	cyclohexane ($CO_2C_2H_5$, $CH(CH_3)CH_2SO_2Ar$) (55)	e	
		cyclohexane ($CO_2C_2H_5$, $CH_2(C_4H_9)CH_2SO_2Ar$) (97)	e	
			f	
$(CH_3)_2CO$	$(CH_3)_2C{=}CHSO_2Ar$ (97)	$(CH_3)_3CCH_2SO_2Ar$ (72)	$(CH_3)_3CC_4H_9\text{-}n$ (70)	65
		$(CH_3)_2C(n\text{-}C_4H_9)CH_2SO_2Ar$ (96)		
cyclohexanone	cyclohexane${=}CHSO_2Ar$ (72)	cyclohexane (CH_3, CH_2SO_2Ar) (30)	cyclohexane (CH_3, CH_3) (~70)	~15
		cyclohexane ($C_4H_9\text{-}n$, CH_2SO_2Ar) (95)[d]	cyclohexane ($C_4H_9\text{-}n$, CH_3) (55)	38

[a]Ar = p-ClC₆H₄. [b]Of distilled or recrystallized material. [c]This is overall yield of hydrocarbon formed from aldehyde without purification of vinyl sulfone or of alkyl aryl sulfone. [d]Yield based on ~50% recovered starting material. [e]Na-Hg apparently caused reduction of ester as well as alkyl sulfone groups. [f]No Na-Hg hydrogenolysis was attempted due to the volatility of the expected product, neopentane.

hindrance to approach of the bulky diethyl arylsulfonomethylphosphonate anion.

Addition of hydrocarbon groups specifically to the β-carbon of α,β-unsaturated carbonyl compounds using organocopper reagents is a widely used reaction.[7] Because the mechanism of this organocopper conjugate addition apparently is not cyclic and does not involve initial complexation of organocopper reagent with substrate, it is reasonable to assume that the carbonyl group serves mainly to polarize the α,β multiple bond and to stabilize the developing negative charge on the α carbon atom as conjugate addition proceeds. That the carbonyl group is not necessary for organocopper addition to certain carbon-carbon multiple bonds has been shown recently by organocopper addition to the β carbon of α,β-unsaturated epoxides,[8a] of α,β-unsaturated phosphine oxides and sulfides,[8b] and of allylic[8c] and propargylic acetates.[8d] It was expected, therefore, that the sulfonyl group might be used in place of the carbonyl group: 5 equiv of lithium dimethyl or di-n-butylcuprates(I) in diethyl ether at 0° for several hrs do indeed cause addition of a methyl or an n-butyl group in high yield to the β-carbon of α,β-ethylenic p-chlorophenyl sulfones (see Table I). Furthermore, lithium dimethyl and di-n-butylcuprates(I) react selectively with the vinyl sulfone unit even in the presence of an ester group.[9] It should be noted that methyllithium, methyllithium-tetramethylethylenediamine complex, and the new tert-butoxyalkylcuprate(I)[10] reagents fail to react with p-chlorophenyl styrylsulfone.

The last step in the reaction scheme involves alkyl-sulfur bond hydrogenolysis in various alkyl aryl sulfones. No general method has been reported for such a transformation, and indeed treating alkyl aryl sulfones with lithium in methylamine causes cleavage of the aryl-sulfur bond.[11] Nevertheless, we have found that 6% sodium amalgam in boiling ethanol[12] for about 12 hrs causes the desired hydrogenolysis to form alkane (and p-chlorobenzenesulfinic acid) consistently in high yields.

The overall sequence (Eq. 2) described herein allows effective conversion of aldehyde carbonyls to tertiary alkyl carbon atoms in which each of the alkyl groups may be different and permits transformation of certain ketone carbonyl groups to quaternary carbon units. The maximum efficienty of this sequence is exemplified by the conversion of heptanal to 2-methyloctane in 82% overall yield and benzaldehyde to isopropylbenzene in 89% overall yield.

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