

Reactions of Mixed Homocuprates containing Sulphonyl-stabilized Carbanions as Non-transferable Ligands

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Treatment of α -lithiosulphones with copper(I) iodide in tetrahydrofuran followed by 1 mol. equiv. of an alkyl-lithium or Grignard reagent produces mixed homocuprates $[\text{R}'\text{SO}_2\text{CH}_2\text{CuR}]^- \text{M}^+$ ($\text{M} = \text{Li}$ or MgX) which are effective reagents for the conjugate addition of R to enones and substitution of chloride in acid chlorides to produce ketones (>90% yields).

Unfavourable stoichiometry necessary in the preparation of symmetrical homocuprates (LiR_2Cu) led to the early development of mixed cuprates in which only one copper ligand was transferable.^{1,2} Mixed heterocuprates (LiRZCu , $\text{Z} = \text{OR}'$,

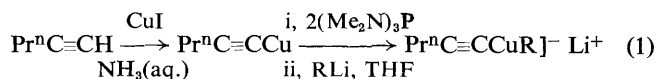
SR' , CN)³ and mixed homocuprates ($\text{LiRR}'\text{Cu}$) have been found useful in this way, and we report here our results on the latter class. Corey first introduced acetylides as operationally non-transferable carbon ligands in his early studies of

Table 1. Yields^a/ % of ketone (2) from reactions of (1)^b with cyclohex-2-enone (equation 3).

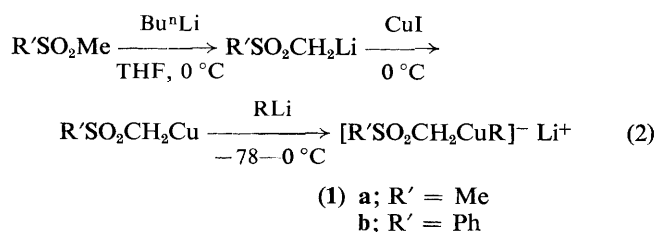
R	Me	Bu ⁿ	Bu ^s	Bu ^t	CH=CH ₂	Ph
Cuprate (1a)	95	90	90	96		95 ^c
(1b)	96	92	91	97	95 ^c	97 ^c

^a Isolated. ^b 1.2 mol. equiv. of cuprate used. ^c MgBr cuprates.

pent-1-yne (equation 1).⁴ From a cost viewpoint, the MeOC(Me₂)C≡C⁻ ligand provided significant improvement.⁵ Favourable reactivity and solubility of the Bu^tC≡C⁻ ligand has been noted.⁶ Koosha and co-workers have examined a series of mixed homocuprates in which the stoichiometry was consistent with the production of various combinations of Me, Buⁿ, Prⁱ, Bu^t, and Ph ligands.⁷ Their study, which involved the examination of additions to sulphur- and phosphorus-substituted allenes, led to the conclusion that the propensity to transfer followed the order of the ligands as listed above. Marino and Floyd have examined the reactions of the cuprate mixture, obtained by the addition of lithium dimethylcuprate and methyl α-bromoacrylate, with a vinyl epoxide; only methyl transfer was observed.⁸

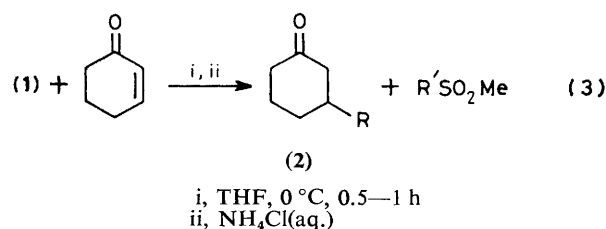


We now report a new class of mixed homocuprates containing α-sulphonyl-stabilized carbanions as non-transferable ligands. These new cuprates are easily and economically prepared (equation 2) and can be utilized without special precautions. Dimethyl sulphone or methyl phenyl sulphone (3 mmol) in tetrahydrofuran (THF) (10–15 ml) was treated with 1 mol. equiv. of butyl-lithium in hexane at room temperature for 15 min or less. A crystal of triphenylmethane was occasionally added as an indicator; butyl-lithium was added until a slight pink colouration persisted. The resulting slurry of methylsulphonylmethyl-lithium or clear solution of phenylsulphonylmethyl-lithium was drawn into a syringe and slowly added to a slurry of copper(I) iodide (3.1 mmol) in THF (3 ml) and stirred at 0 °C until a dark brown-green solution was obtained (5–15 min). The methylsulphonylmethylcopper or phenylsulphonylmethylcopper solution was cooled to -78 °C, 1 mol. equiv. of alkyl-lithium (or Grignard reagent) was added, and the mixture was allowed to warm to 0 °C with stirring to produce a light brown solution of the mixed homocuprate (1). The cuprates (1) underwent smooth conjugate addition to cyclohex-2-enones at 0 °C (Table 1 and equation 3). Halide substitution on benzoyl chloride occurred cleanly at -78 °C (Table 2 and equation 4). The by-products, dimethyl sulphone and methyl phenyl sulphone, have very low mobility on silica gel and are readily separated from the ketones by percolation of the reaction mixture (after workup with aqueous ammonium chloride, then extraction, and concentration) through a short plug of silica gel with 5% ethyl acetate in hexanes. If desired, the sulphones can be recovered and recycled.

**Table 2.** Yields^a/ % of ketone (3) from reactions of (1)^b with benzoyl chloride (equation 4).

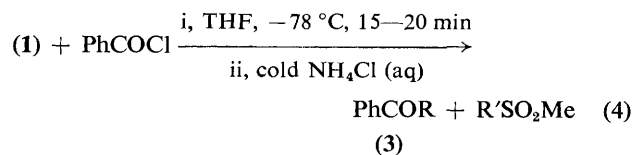
R	Me	Bu ⁿ	Bu ^s	Bu ^t	Ph
Cuprate (1a)	90	90			97 ^c
(1b)	90	91	95	95	98 ^c

^a Isolated. ^b 1.2 mol. equiv. of cuprate used. ^c MgBr cuprate.



The reactivity of this new class of mixed cuprates is somewhat moderated in comparison with simple dialkyl cuprates. Treatment of cyclopropyl phenyl ketone with (1b) for 50 h at room temperature resulted in recovery of the ketone whereas lithium dimethylcuprate converted the ketone into 1-phenylpentan-1-one in 65% yield overnight.

The cuprates described herein are the first reported involving α-heteroatom-stabilized carbanions as ligands.⁹



This new class of cuprates is based on readily available and inexpensive sulphones as the source of the non-transferable ligand. The reactions are manipulatively simple. The yields of the conjugate addition products are superior to those of the heterocuprates and comparable with those with alkynylcuprates which are more difficult to prepare and often expensive.

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