

NEW MIXED ORGANOCUPRATES  
 DERIVED FROM  $\eta^4$ -(1,5-CYCLOOCTADIENATO)-COPPER<sup>I</sup> BROMIDE

François LEYENDECKER\* and Francis JESSER

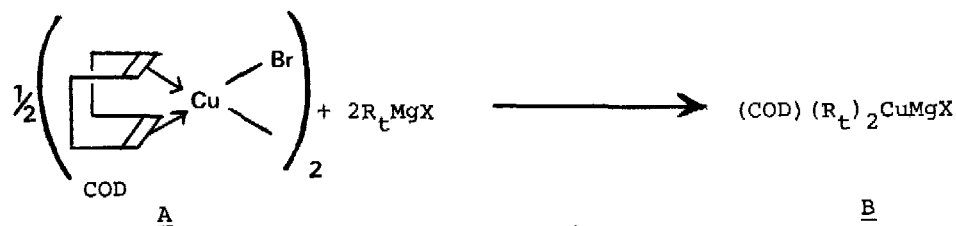
*Laboratoire de Chimie Organométallique de l'Ecole Nationale Supérieure de Chimie, associé au CNRS, Université Louis Pasteur, B.P. 296/R8 - 67008 STRASBOURG (France)*

$\eta^4$ -(1,5-Cyclooctadienato)-copper<sup>I</sup> bromide is shown to be a good precursor of highly reactive mixed organocuprates with a bidentate residual ligand.

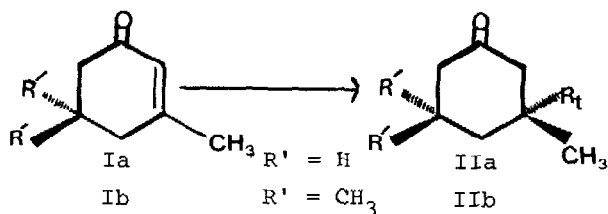
The main drawback of the symmetrical diorganocuprates commonly used in organic synthesis is that only one of the two alkyl groups is converted to product<sup>1</sup>. This feature has led to the development of mixed ate complexes  $R_r R_t CuZ$  ( $Z = Li, MgX$ ) with the intended outcome of the single transfer of the  $R_t$  group. Different models of monodentate residual  $R_r$  ligands have been studied<sup>2</sup>. The underlying reasons of the observed selectivities are still not clearly understood, but parameters like ligand basicity, steric bulk or bridging ability in the metal cluster have been mentioned to be operative<sup>3</sup>.

Beside their selectivity, mixed cuprates should also be as reactive as the corresponding homocuprates and until now both requirements are best fulfilled when the former are derived from the rather expensive copper  $\eta$ -propyl<sup>4</sup> or *ter*-butylacetylde<sup>5</sup>.

In the present communication, we wish to report on the mixed cuprates B prepared as outlined in Equation 1.



TABLE

0.65 equiv. B + 1 equiv.

<sup>f</sup> R <sub>t</sub>	Enone	Product Distribution <sup>c</sup>		Isolated <sup>c</sup>
		I%	II%	Yield of II %
	Ia	1,5	98,5	65
	Ib	0	100	73
	Ia	0	100	70
	Ib	100	0	0
	Ia	100	0	0
	Ib	0	100	0
	Ia	6	94	60
	Ib	6	94	58
	Ia	0	90 <sup>e</sup>	58
	Ib	6	94	60
	Ia	-	-	86 <sup>d</sup>
	Ib	-	-	63 <sup>d</sup>

Reactions were performed in Et<sub>2</sub>O, at -30° for 1 hr ; <sup>c</sup>Product distribution analysis and product isolation were realised by gas chromatography, unless other wise stated ; <sup>d</sup>Isolated by chromatography on SiO<sub>2</sub>. <sup>e</sup>1,2 addition amounted to 10%. <sup>f</sup>Grignard reagents have been titrated with *o*-phenanthroline<sup>11</sup> and are estimated accurate within ± 2%.

This new type of cuprate, with a potential residual bidentate ligand<sup>6</sup>, has proven to be interesting in many aspects :

- the precursor A of the reagent is easily available<sup>7</sup> from the commercially low cost ligand COD<sup>8</sup> and can be kept for months at room temperature in an exsiccator.
- neither a complexing agent nor a large excess of the mixed cuprates is required to bring the 1,4 addition to go to completion. (See Table, product distribution). This last feature points to the fact that both R<sub>t</sub> groups are transferred to the substrate, despite in some cases of the misleading yields (≤ 65%) due to the more important loss of product during isolation by VPC than by chromatography on silica gel.

Furthermore, it appears (see Table) that all primary ligands R<sub>t</sub> add conjugatively to both enones tested in good yields. A particularly attractive case is the last example shown in the Table, which involves a d<sub>3</sub> umpolung reagent<sup>9</sup>.

The bulky secondary isopropyl group adds to 3-methylcyclohexenone Ia, but not to isophorone Ib, whereas the t-butyl group fails to react with both. This trend fits well with the idea of a balance between steric bulk of the enone on the one side and of the ligand R<sub>t</sub> on the other. It is in agreement with the observation that the t-butyl group does add to cyclohexenone itself<sup>4</sup>. But on this sole basis, the easy addition of the isopropenyl group to isophorone is rather surprising.

Finally, the most interesting aspect of the new cuprates is their selectivity associated with their chemical reactivity in transferring various functionalised ligands. This arises from the double function of the ligand COD: it is a non-participating ligand in the 1,4 addition reaction and also an activating complexing agent like phosphines<sup>4</sup> or sulfides<sup>10</sup>.

#### References and Notes

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