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ORGANOCOPPER SPECIES III.[1,2] THE REACTION OF COPPER (I) CARBOXYLATES WITH ORGANYL HALIDES

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Cuprous carboxylates (acetate, benzoate, pivalate) react with primary, secondary, tertiary, allylic and vinylic halides and tosylates to give the corresponding carboxylate esters. The reaction is executed in refluxing pyridine, under an inert atmosphere and under rigorously anhydrous conditions. The cuprous carboxylate is either generated *in situ*[1b] or preformed[1b]. A similar reaction with aryl halides has been reported.[1b]

Neopentyl and neophyl bromides and tosylates react without rearrangement to give neopentyl and neophyl esters. Optically active neopentyl tosylate-1-d[4] reacts with cuprous benzoate to give benzoate (α_D= +0.337) with 49.2% net inversion. When the reaction of neophyl bromide with cuprous pivalate is carried out in the presence of pivalic acid-O-d *t*-butylbenzene-ω-d is produced. No neopentane is formed, however, when pivalic acid is present in the reaction of neopentyl bromide under the same conditions.

These results are incompatible with the intermediacy of either a free radical or a carbonium ion since both these species would be expected to rearrange and lose optical activity, neither of which is observed. A nucleophilic displacement by carboxylate anion as the nucleophile is ruled out since neither lithium nor ammonium carboxylate react with primary halides and tosylates under the reaction conditions[6].

Our results are compatible with nucleophilic attack by the d-electrons of copper (I)[8] to give a transient organocopper (III) intermediate with inverted configuration at carbon and subsequent collapse of this species by expulsion of copper (I) with retention of configuration to yield ester. Stabilization of the organocopper (III)intermediate by the vicinal phenyl group could account for its capture by protonation[9] by pivalic acid in the neophyl system, but not in the neopentyl case.

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   b) Part II. T. Cohen and A.H.Lewin, J.Amer.Chem.Soc., 88, 4521 (1966).
2. a) This work was supported in part by a grant from the Research Corporation.
   b) Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, for partial support of this research.
3. Taken from the dissertation of N. L. Goldberg to be submitted to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry (1972).
4. Prepared from neopentyl alcohol-1-d, which was synthesized by asymmetric reduction of trimethylacetaldehyde by actively fermenting yeast[5]. The acid phthalate derivative had a rotation α_D= -1.07, corresponding to 93% optical activity.
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6. A"push-pull" mechanism analogous to that proposed for the reaction between alkyl halides and silver salts[7] does not account for reduction by protonation.
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8. Analogous to attack by Co(I); G.N.Schrauzer and E. Deutch, J. Amer. Chem. Soc., 91, 3341 (1969); F.R.Jensen, V.Madan and H. Buchanan, ibid., 92, 1414 (1970).
9. Stabilization of the organocopper intermediate to allow for its capture by protonation was required in the Ullmann Biaryl Synthesis.[1a]