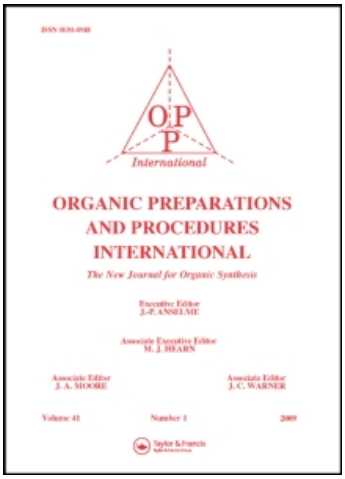


Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

2,3,5,6-TETRACHLORO-4-PYRIDYLCOPPER AND SOME DERIVATIVES

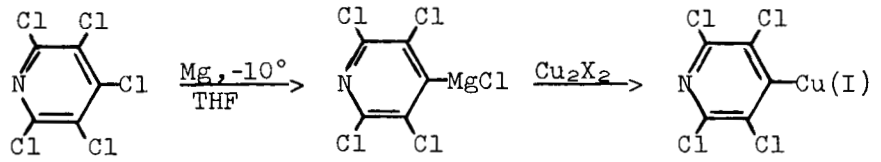
S. S. Dua[a]; A. E. Jukes[a]; H. Gilman[a]
[a] Department of Chemistry, Iowa State University, Ames, Iowa

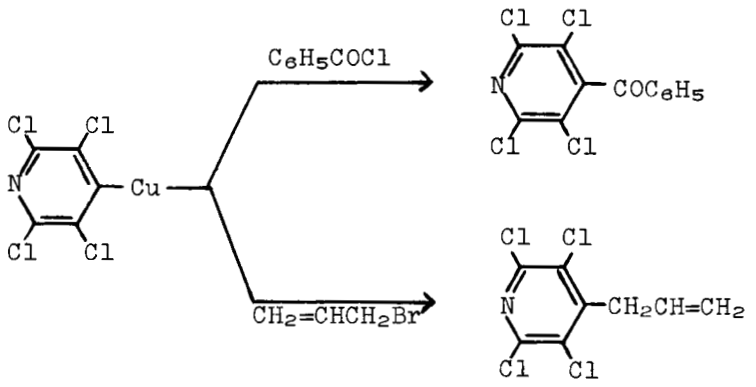
To cite this Article Dua, S. S. , Jukes, A. E. and Gilman, H.(1969) '2,3,5,6-TETRACHLORO-4-PYRIDYLCOPPER AND SOME DERIVATIVES', Organic Preparations and Procedures International, 1: 3, 187 — 191
To link to this Article: DOI: 10.1080/00304946909458378
URL: http://dx.doi.org/10.1080/00304946909458378

ORGANIC PREPARATIONS AND PROCEDURES 1(3), 187-191 (1969)

2,3,5,6-TETRACHLORO-4-PYRIDYLCOPPER AND SOME DERIVATIVES

S. S. Dua, A. E. Jukes and H. Gilman
Department of Chemistry, Iowa State University, Ames, Iowa





We have previously reported[1] the preparation of polyhaloarylcopper compounds or their complexes by two basic procedures: (i) addition of a copper(I) halide to a polyhaloaryl-Grignard reagent or lithium compound; and (ii) addition of a polyhaloarene to lithium dimethylcopper. All methods have been used to prepare 2,3,5,6-tetrachloro-4-pyridylcopper but, generally, preparation via the Grignard reagent gave the highest yields of

the various products. The easiest and least expensive method of preparing the pyridylcopper compound is also via the Grignard reagent[2], 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride. The copper compound is very stable, even at elevated temperatures and, for example, on heating at 100° with iodobenzene in the absence of other solvents afforded 4-phenyltetrachloropyridine in 55.5% yield. We have found that the copper compound reacts exothermally with acid chlorides to give 2,3,5,6-tetrachloro-4-pyridyl ketones in 60-70% yields and provides a useful route to such compounds. 2,3,5,6-Tetrachloro-4-pyridylcopper also reacts easily with allyl bromide at the ambient temperature to give 4-allyltetrachloropyridine.

Some typical details are given for the preparation of the copper compound, and from this compounds containing the 2,3,5,6-tetrachloro-4-pyridinoid nucleus.

Experimental

2,3,5,6-Tetrachloro-4-pyridylcopper.

The Grignard reagent, 2,3,5,6-tetrachloro-4-pyridylmagnesium chloride, was prepared as reported[2]. Pentachloropyridine (12.62 g., 0.05 mole) in dry THF (100 ml.) was added to magnesium turnings (1.32 g., 0.055 g. at.) in a small volume of THF over 30 minutes while cooling at -10° (ice-salt bath). The mixture was stirred at -10° for 2 hr. and then filtered. By titration[3] of 3 ml. aliquots the dark red solution was found to be 0.28 N and the yield of the Grignard reagent was 90.5%. This solution gave Color Test I[4]. The Grignard reagent could be detected when the solution was 0.08 N although the Malachite Green color developed

slowly and was easily masked by excess iodine. However, any excess iodine can be removed by dropwise addition of a dilute solution of sodium thiosulphate. To the solution of the Grignard reagent at 0° was added copper(I) iodide[5] (10.0 g., 0.05 mole). Color Test I on the mixture was negative within 1 hour. However, the mixture was usually stirred at 0° for a few more hours to ensure complete formation of the copper compound. Freshly prepared[6] copper(I) chloride can also be used.

Reaction with benzoyl chloride.

To the copper compound [prepared as above from pentachloropyridine (10.0 g., 0.04 mole), magnesium (1.07 g., 0.044 g. at.) and copper(I) iodide (7.7 g., 0.04 mole)] in THF at 0° was added benzoyl chloride (6 ml., 7.3 g., 0.052 mole) and the mixture stirred for several hours. Copper salts were removed by addition of aqueous ammonium chloride and ammonium hydroxide. The mixture was extracted with ether (2 x 100 ml.). After drying ($MgSO_4$), the ether-THF solution was evaporated to dryness and the residue chromatographed on a column of silica gel in carbon tetrachloride. Removal of the solvent from the eluate and crystallization of the solid so obtained from ethanol afforded 4-benzoyltetrachloropyridine (8.1 g., 63%), m.p. 134-135°. The compound was identical to that obtained by oxidation of 4-benzyltetrachloropyridine[7].

In a similar preparation on the same scale but employing copper(I) chloride (4.0 g., 0.04 mole) the yield of 4-benzoyltetrachloropyridine was 7.8 g., 61%. IR (CCl_4): 1685 (C=O), 1316, 1103 cm^{-1} (C_5Cl_4N). UV (cyclohexane) λ_{max} (ϵ): 233 mμ (15900), 260 (16000), 292.5 (6700). ^1H NMR (CCl_4): singlet 2.7τ.

Reaction with allyl bromide.

2,3,5,6-Tetrachloro-4-pyridylcopper was prepared as above from pentachloropyridine (12.62 g., 0.05 mole), magnesium (1.32 g., 0.055 g. at.) and copper(I) chloride (5.0 g., 0.05 mole) in THF. To the copper compound at the ambient temperature was added allyl bromide (6.7 g., 0.055 mole) and the mixture stirred for six hours. The reaction was slightly exothermic Copper salts were removed by addition of ammonium chloride solution and the mixture extracted with ether (2 x 100 ml.). The dry ($MgSO_4$) ether-THF solution was fractionally distilled to yield 4-allyltetrachloropyridine(8.44 g., 76.4%), b.p. 99-101°/0.1 mm. IR (liq. film): 1637 (C=C), 1530, 1330 cm^{-1} (C_5Cl_4N). The ^1H NMR spectrum was typical of allyl compounds[8]. [Found: C, 37.01; H, 2.02. Calc. for $C_8H_5Cl_4N$: C, 37.40; H, 1.96].

In a similar preparation on a smaller scale (0.03 mole) and employing copper(I) iodide the yield of 4-allyltetrachloropyridine was 5.55 g., 72%.

Acknowledgements

We are grateful to the Olin Mathieson Chemical Corporation for a gift of pentachloropyridine. This research was supported by the United States Air Force under Contract AF 33(613)-2368 monitored by Materials Laboratory, Wright Air Development Center, Wright-Patterson AFB, Dayton, Ohio.

References

1. S. S. Dua, A. E. Jukes and H. Gilman, J. Organometal. Chem., 12, P24 (1968); A. E. Jukes, S. S. Dua, and H. Gilman, J. Organometal. Chem., 12, P44 (1968). See also A. Cairncross and W. A. Sheppard, J. Amer. Chem. Soc., 90, 2186 (1968); R. J. DePasquale and C. Tamborski, J. Organometal. Chem., 15, 494 (1968).

2. S. S. Dua and H. Gilman, J. Organometal. Chem., 12, 234 (1968).

3. H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, J. Amer. Chem. Soc., 45, 150 (1923). See also M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances", p. 94, Prentice-Hall, Inc., New York, N.Y., 1954.

4. H. Gilman and F. Schulze, J. Amer. Chem. Soc., 47, 2002 (1925).

5. Purchased from Alfa Inorganics, Inc.

6. R. N. Keller and H. D. Wycoff, "Inorganic Syntheses", Vol. 2, p. 1, McGraw-Hill, 1946.

7. S. S. Dua and H. Gilman, J. Organometal. Chem., 12, 299 (1968).

8. "NMR Spectra Catalog", Varian Associates, 1963.

(Received April 29, 1969)