Tetrahedron Letters,Vol.29,No.29,pp 3533-3536,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

A NEW AND EFFICIENT REACTION FOR THE SYNTHESIS OF THE CARBON-CARBON BOND

Derek H. R. Barton, Nubar Ozbalik and Manian Ramesh

Department of Chemistry, Texas A&M University
College Station, Texas 77843

Summary. Palladium (O) converts tellurides of type R^1-Te-R^2 into coupled product R^1-R^2 and metallic tellurium (as a mirror) in high yield under mild conditions. There is little or no sign of β-elimination and no evidence for cross coupling.

We recently reported that palladium (O) converts aryl derivatives of Bi(III) and Bi(V) to diaryl compounds and metallic bismuth in high yield under mild conditions.[1] More interesting was the fact that tris-β-phenyl- ethylbismuth 1 afforded the coupled product 2 (74%) at room temperature. This coupling was unexpected as Pd(II) species such as 3 are supposed to β- eliminate and not give ligand coupling.[2] The product of the reaction should have been styrene.[3]

We decided to examine the effect of Pd(O) on symmetrical and unsymmetrical tellurides.[4] Bergman[5] noted that diaryl tellurides treated with degassed Raney nickel gave diaryls in good yield. Uemura and his colleagues[6] studied the arylation of olefins using Te(IV) compounds and Pd(II). Diaryls were formed in moderate yield in the absence of the olefin. Finally, Uemura[7] has also examined the carbonylation of aryl- and vinyl-tellurium compounds under the influence of Pd(II) species; Te(O) and Pd(O) are also formed. We have not found any record of a potentially β- eliminatable alkyl residue (with transfer from tellurium) being used in Pd(O) coupling.

Nevertheless a series of tellurides, including four with alkyl residues, have been smoothyl coupled (Table) using Pd(O) generated from $Pd(OAc)_2$ and triethylamine. In only one case was there some indication of β-elimination; there was no scrambling of ligands.

Table[a]

Entry	Substrate	Solvent	Reaction Time	Product[b]	Yield %
1	4	CH_3CN	8h	6	100
2	5	HMPA	7h[c]	6	82
3	7	CH_3CN	10h	2	85[d]
4	8	CH_3CN	5h	9	81
5	10	CH_3CN	7h	11	89
6	12	CH_3CN	7h	13	76

a) All reactions performed with Pd(O) catalyst, prepared in situ from $Pd(OAc)_2$ (1 mmole) and NEt_3 (2 mmole), and the telluride (1 mmole) at 65° under argon atmosphere.

b) All compounds were characterised by m.p. (where appropriate), N.M.R. and Mass Spectrometry.

c) An additional equivalent of Pd(O) catalyst was added 3 hrs. after the commencement of the reaction.

d) Some styrene was also formed.

$(PhCH_2CH_2)_3Bi$
1

$(PhCH_2CH_2)_2$
2

$(PhCH_2CH_2)_2Pd$
3

An_2Te
4

$(AnTe)_2$
5

AnAn
6

$(PhCH_2CH_2)_2Te$
7

$PhCH_2CH_2TeCH_2Ph$
8

$Ph(CH_2)_3Ph$
9

An-Te-t-Ad
10

An-t-Ad
11

$An\text{-}Te\text{-}C_{15}H_{31}$
12

$An\text{-}C_{15}H_{31}$
13

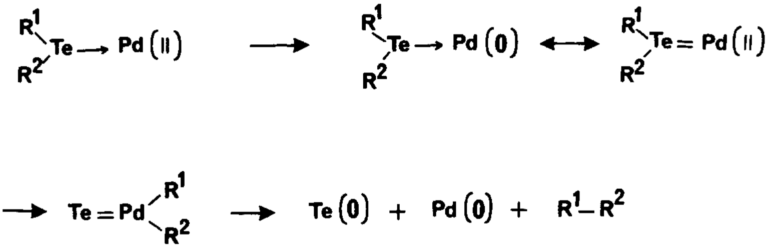
Whilst 4 gave dianisyl 6 in quantitative yield, the ditelluride was much less reactive. Only in HMPA was a good yield obtained. The telluride 7 gave the same coupled product 2 (85%) as had been obtained before from the bismuth derivative 1. There was some β-elimination to give styrene.

The telluride 8 gave the coupled product 9 (81%). The telluride 10 contained a weak t-adamantyl ligand as well as a stronger phenyl-tellurium bond. Again the yield was good (89%) and g.c. analysis of the total product showed no sign of dianisyl, the likely product of scrambling. The mass spectrum of the total reaction mixture did not show any scrambled product either. Finally telluride 12 gave the coupled product 13 without β-elimination.

The tellurides used in this work were prepared by standard methods.[4] The two tellurides 10 and 12 were obtained using the photochemical method already reported.[8] This works well with diaryl ditellurides, but is less efficient with dialkyl ditellurides.

It is relevant to our present findings that recent work[9] has shown that pyrolysis of (2,2′-bipyridine) diethylpalladium(II) without additive gave, as expected, ethane and ethylene. However, addition of certain olefins like methyl acrylate afforded n-butane with no β-elimination. It is clear that palladium-tellurium bonding of some kind is responsible for the success of our coupling reactions.

Although it would be premature to give an exact mechanism for our new reaction, the Scheme outlines a suitable working hypothesis. The other ligands involved remain to be determined.



Scheme

This coupling reaction should be useful in the chemistry of Natural Products.

Acknowledgements. We thank the Welch Foundation and the Schering-Plough Corporation for their generous support of this work.

References

1. D.H.R. Barton, N. Ozbalik and M. Ramesh, Tetrahedron, in press.

2. T. Hosokawa and P.M. Maitlis, J. Am. Chem. Soc., 95, 4924 (1973); D.J. Mabbot and P.M. Maitlis, J. Organomet. Chem., 102, C34 (1975); G.M. Whitesides, Pure and Appl. Chem., 53, 287 (1981); A. Yamamoto, T. Yamamoto, S. Komiya and F. Ozawa, ibid. 56, 1621 (1984).

3. R.H. Crabtree, "The Organometallic Chemistry of the Transition Metals", John Wiley and Sons, New York, 1988; R.F. Heck, "Palladium Reagents in Organic Syntheses", Academic Press, New York, 1985.

4. K.J. Irgolic, "The Organic Chemistry of Tellurium", Gordon and Breach Science Publishers Inc., New York, 1974.

5. J.Bergman, Tetrahedron, 28, 3323 (1972); see also L. Engman, Acc. Chem. Res., 18, 274 (1985); D.L.J. Clive, P.C. Anderson, N. Moss and A. Singh, J. Org. Chem., 47, 1641 (1982).

6. S. Uemura, M. Wakasugi and M. Okano, J. Organomet. Chem., 194, 277 (1980).

7. S. Uemura, K. Oke, J.-R. Kim, K. Kudo and N. Sugita, J. Chem. Soc. Chem. Commun., 271 (1985); K. Oke, H. Takahashi, S. Uemura and N. Sugita, J. Organomet. Chem., 326, 35 (1987); idem, J. Org. Chem., 52, 4859 (1987).

8. D.H.R. Barton, D. Bridon and S.Z. Zard, Heterocycles, 25, 449 (1987).

9. R. Sustmann and J. Lau, Chem. Ber., 119, 2531 (1986); Tetrahedron Letts., 26, 4907 (1985); see also T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93, 3350 (1971).

(Received in USA 26 April 1988)