PALLADIUM-CATALYZED PHENYLATION OF ALLYLIC ACETATES
BY TETRAPHENYLBORATE ANION

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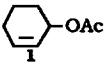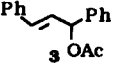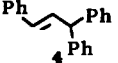91405 Orsay Cedex, France
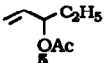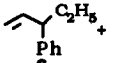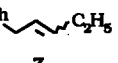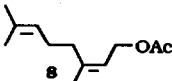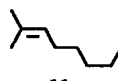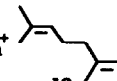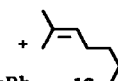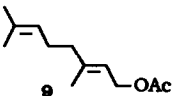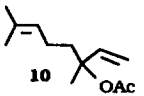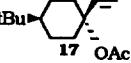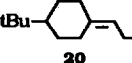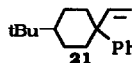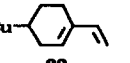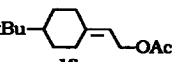
Abstract: Commercial sodium tetraphenylborate is a convenient phenylating reagent in the palladium(0)-catalyzed substitution of allylic acetates. Two phenyl groups of $NaBPh_4$ are available for transfer. Triphenylboron is also a phenylating agent in this reaction.

We report here the use of sodium tetraphenylborate as a convenient carbo-nucleophile for the palladium-catalyzed phenylation of allylic acetates. Sodium tetraphenylborate is commercially available, easier to handle than phenylzinc chloride or bromide which are commonly used as phenylating agents in the palladium-catalyzed substitution of allylic acetates.[1-8] Moreover, $NaBPh_4$ is chemically well defined, in contrast to arylzinc or cadmium reagents which are usually prepared in situ by exchange from Grignard reagents.

Sodium tetraphenylborate has been shown to be a phenylating agent and gave σ-phenyl complexes of transition metals.[9-14] Phenyl transfer from $NaBPh_4$ to norbornadiene,[15] cyclobutadiene[16] and allyl[17] ligands in palladium complexes has also been reported. Recently, $NaBPh_4$ has been used as a phenylating agent in palladium-catalyzed processes, such as substitution of allylic chlorides[18] and in anion-capture processes.[19,20]

Reaction of $NaBPh_4$ (1.5 equivalent) with cyclohexenyl acetate does not proceed in the absence of the palladium catalyst at 60°C, nor with 2% catalyst [$Pd(dba)_2$ + 2 PPh_3] at room temperature. With such a reagent: substrate ratio (1.5:1), biphenyl (≈20%) was detected as a by product. Use of 0.5 equivalent of $NaBPh_4$ lowered production of biphenyl (<5%) and gave a 69% yield of **2**, indicating that at least two phenyl groups were available for transfer to the allylic frame. Indeed triphenylboron BPh_3 (1 equivalent) was a phenylating agent under these reaction conditions, whereby **2** was obtained in 52% yield.

Table. Palladium-catalyzed phenylation of allylic acetates by NaBPh$_4$.[a]

Substrate	eq. of NaBPh$_4$	T (°C)	Product(s)[b]	Yield[c] (%)
(cyclohexenyl)–OAc **1**	1.5	60	(cyclohexenyl)–Ph **2**	80[d]
1	0.5	60	**2**	69
1	0.25	60	**2**	47
1	1.5	20	no reaction	e
Ph⌒⌒(OAc)Ph **3**	0.5	60	Ph⌒⌒(Ph)Ph **4**	85
⌇⌒(OAc)C$_2$H$_5$ **5**	0.5	60	**6** (C$_2$H$_5$, Ph) + **7** (Ph⌒⌒C$_2$H$_5$) 29 66:5	70
8 ⌁⌁⌁–OAc	0.5	60	**11** ⌁⌁–Ph + **12** ⌁⌁(–Ph) + **13** ⌁⌁(Ph) 70 17 13	87
9 ⌁⌁⌁–OAc	0.5	60	12 72 16	82
10 ⌁⌁(OAc)	0.5	60	25 56 19	81
14 (bicyclic)–CH$_2$OAc	0.5	60	**15** (–CH$_2$Ph) + **16** (=CH$_2$, Ph) 76 24[g]	50
tBu–(cyclohexyl)–(OAc) **17**	0.5	60	**20** tBu–⌁=⌁Ph + **21** tBu–(Ph) + **22** tBu–⌁⌁ 44 44[g] 12	73
tBu–(cyclohexyl)–⌁OAc **18**	0.5	60	43 40[g] 17	74

[a]The reaction was carried out following the procedure described in the text [b]Isomers ratios were determined by GLC and confirmed by ^{1}H NMR. [c]Isolated yield. [d]Biphenyl was also produced (20%). [e]Only recovered **1** and biphenyl (in small amount) were detected. [f]The two isomers were produced, but no assignement was possible. [g]A single diastereoisomer was detected.

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According to this stoichiometry, the phenylation scheme can be described by the set of consecutive reactions:

$$\text{1} \quad \text{(cyclohexenyl)}-OAc \ + \ NaBPh_4 \ \xrightarrow{\text{Pd(0) cat.}} \ \text{2} \quad \text{(cyclohexenyl)}-Ph \ + \ BPh_3$$

$$\text{1} \quad \text{(cyclohexenyl)}-OAc \ + \ BPh_3 \ \xrightarrow{\text{Pd(0) cat.}} \ \text{2} \quad \text{(cyclohexenyl)}-Ph \ + \ \text{"}AcOBPh_2\text{"}$$
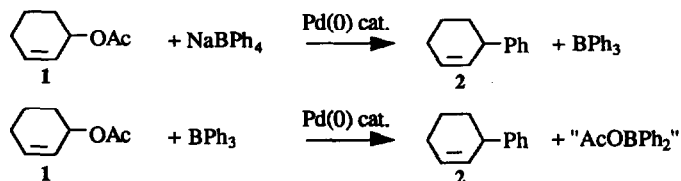
All subsequent reactions were thus conducted with a reagent: substrate ratio of 0.5:1. Representative results are summarized in the Table.

In a typical experiment, cyclohexenyl acetate 1 (140 mg, 1 mmol) in 0.5 mL of THF was added under argon to a mixture of palladium bis(dibenzylideneacetone) Pd(dba)$_2$ (11.5 mg, 0.02 mmol) and triphenylphosphine PPh$_3$ (10.5 mg, 0.04 mmol) in 0.5 mL of THF. After 0.25 h stirring, this solution was transferred onto a solution of sodium tetraphenylborate NaBPh$_4$ (188 mg, 0.55 mmol) in 0.5 mL of THF. The reaction mixture was stirred at 60°C during 12 h, then diluted with pentane and filtered through celite. After evaporation of the solvent, the residue was purified by flash chromatography on silica (eluent hexane) followed by Kugelrohr distillation to give 2 (109 mg, 0.69 mmol, 69% yield).

The ratio of regio- and stereoisomers in the products reflects the average of the regio- and stereoselectivities of the reactions of the two nucleophilic agents NaBPh$_4$ and BPh$_3$.

In all cases, the major regioisomer arose from attack of the nucleophile to the less hindered terminus of the allylic intermediate: neryl 8, geranyl 9 and linalyl 10 acetates afforded mixtures of isomers in which branched 13 was always the minor product. Acetates 17 and 18 gave substantial amounts of diene 22, an elimination product. In these cases, the regioselectivity was somewhat lower (~1:1 mixture of 20 and 21) arising from attack at the primary and tertiary allylic terminii of the intermediate, respectively.

Reactions with the E,Z isomers geranyl and neryl acetates indicate a retention of the olefinic double bond stereochemistry to some extent: neryl acetate 8 afforded (Z)-olefinic product 11 as the major diastereomer and geranyl acetate 9 the (E)-olefinic product 12.

Where geometric (cis/trans) stereoisomers could have been produced, as from 14, 17 or 18, only one of them (16 or 21 respectively) was detected; the relative configuration of which could not be assigned however.

The phenylation could be readily scaled up and carried out without solvent. Allyl acetate (40 mmol) was stirred at 60°C with 0.5 equivalent (20 mmol) NaBPh$_4$ in the presence of 0.1% catalyst [0.04 mmol Pd(dba)$_2$ + 0.08 mmol PPh$_3$]. After 24 h stirring,

allylbenzene was isolated in 60% yield after flash chromatography (eluent pentane) and Kugelrohr distillation.

Thus, commercial sodium tetraphenylborate $NaBPh_4$ is a smooth, efficient phenylating reagent in palladium-catalyzed substitution of allylic acetates, in THF at 60°C. Up to two phenyl groups from one mole of $NaBPh_4$ can be transferred. Triphenylborane acts also as a phenylating agent in the above reaction under the same conditions.

Work is in progress for comparison of the relative reactivities and enantio-selectivities of $NaBPh_4$ and BPh_3 as reagents in the palladium-catalyzed substitution of allylic acetates, and will be reported in due course.

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