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Cyclocarbonylative Sonogashira Reactions of 1-Ethynylbenzyl Alcohols: Synthesis of 1-Carbonylmethylene-1,3-Dihydroisobenzofurans

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In this work, we present a carbonylative Sonogashira reaction of *o*-ethynyl benzyl alcohols and aryl iodides, followed by a cyclization process to selectively give carbonylmethylene isobenzofurans in high yields and in an atom-economic fashion. The reaction can be carried out in the absence of CuI, with a small amount of $PdCl_2(PPh_3)_2$ (0.2–0.5 mol-%), using aryl iodides bearing both electron-withdrawing and electron-donating groups. Of the two possible stereoisomeric products, *Z*-isobenzofuran derivatives were obtained as major products. But, when the reaction was extended to a secondary alcohol, an interesting switch in stereoselectivity was observed.

Introduction

The 1,3-dihydroisobenzofuran (phthalan) nucleus (Figure 1) is found in a vast number of natural and synthetic compounds that show antimycotic, antibacterial,[1] antioxidant,[2] antihistamine,[3] and antitumor[4] activities. Moreover, some synthetic analogues, such as 3-alkylidene-1,3-dihydroisobenzofurans, have recently been tested as free-radical scavengers.[5] They have also been evaluated as antidepressants,[6] and were shown to be more active than citalopram,[7] the reference drug commonly used to treat depression. Alkylidenephthalans are also endowed with a rich reactivity that makes them versatile building blocks for the synthesis of functionalized phenanthrofurans,[8] isoquinolinones,[9] and spiroketals.[10]

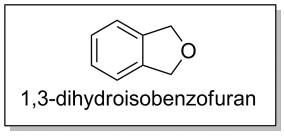
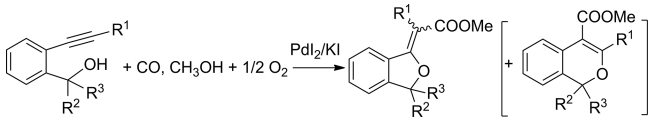


Figure 1. 1,3-Dihydroisobenzofuran structure.

Several methods for the preparation of 3-alkylidene-1,3-dihydroisobenzofurans are described in the literature. They are generally based on the cyclization of functionalized substrates such as alkynyloxiranes,[11] *o*-alkynylbenzaldehydes,[12] and *o*-alkynylbenzyl alcohols, which are often prepared by Sonogashira coupling of iodobenzyl alcohol with terminal acetylenes. The intramolecular cyclization of alkynyl alcohols can be promoted by a base (NaH,[13] KOH,[14] or *t*BuOK[15]) or mediated by lanthanide,[16] copper,[17] or palladium[18] catalysts. In this field, Gabriele and coworkers[19] have developed an interesting approach based on the use of a PdI_2/KI system. Using a palladium-catalysed oxidative carbonylation reaction, they obtained[20] alkoxycarbonylmethylene phthalans in good yields, together with small amounts of the corresponding benzopyran compounds (Scheme 1).



Scheme 1. Synthesis of alkoxycarbonylmethylene-1,3-dihydroisobenzofurans by oxidative carbonylation of alkynyl alcohols.

Intrigued by this data, and prompted by our recent results[21] on the cyclocarbonylative Sonogashira reaction of 2-(2-ethynylphenyl)ethanol, which generated 2-alkylidene-substituted isochromans in high yields and with high stereoselectivities (Scheme 2, $n = 1$), we decided to investigate the application of this protocol to ethynylbenzyl alcohol (Scheme 2, $n = 0$) to find out whether the synthesis of carbonylmethylene-1,3-dihydroisobenzofurans could be achieved.

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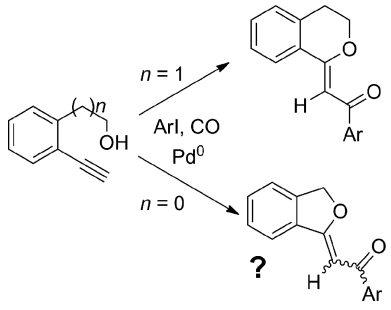
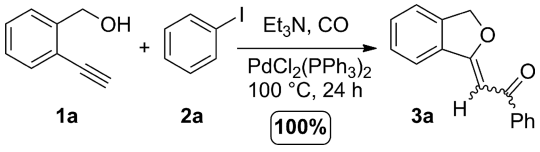


Scheme 2. Cyclocarbonylative Sonogashira reaction of ethynyl alcohols.

Results and Discussion

We began our investigation using equimolar amounts of (2-ethynylphenyl)methanol (**1a**), a commercially available reactant, and iodobenzene (**2a**) as the coupling partner, using the experimental conditions already optimized for the formation of isochromans.[21] Thus, the reactions were carried out under CO pressure (2.0 MPa) in Et_3N as both the solvent and the base, at 100 °C and using $PdCl_2(PPh_3)_2$ (0.2 mol-%) as the catalyst. After 24 h, we observed quantitative consumption of the starting materials, and the formation of five-membered dihydroisobenzofuran **3a** as the sole product (Scheme 3).



Scheme 3. Preliminary cyclocarbonylative Sonogashira reaction between (2-ethynylphenyl)methanol and iodobenzene.

Even though Baldwin's rules[22] allow the formation of both 5-*exo*-*dig* and 6-*endo*-*dig* derivatives, no traces of the possible benzopyran derivative were detected (Scheme 3).

Both stereoisomers (i.e., *Z* and *E*) of phthalan **3a** were present in the crude product, but they could easily be distinguished by ^1H NMR spectroscopic analysis. Indeed, according to the literature,[12a] proton H_a of the *E* isomer is found at an unusually high chemical shift (δ = 9.43 ppm), due to its interaction with the carbonyl deshielding cone, whereas proton H_b appears at a higher field (δ = 7.75 ppm) (Figure 2).

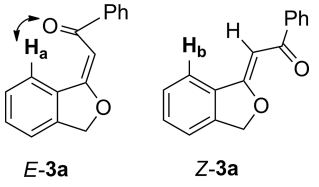
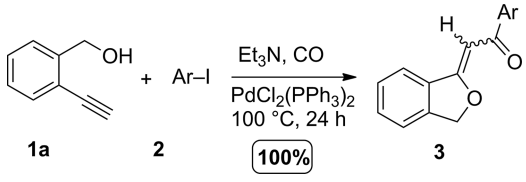


Figure 2. *E*/*Z* stereoisomers of 2-[isobenzofuran-1(3*H*)-ylidene]-1-phenylethanone.

The two stereoisomers could easily be separated and isolated in pure form by column chromatography. Unexpectedly the relative amount of the two isomers changed after separation: *Z*/*E* crude: 63:37; pure: 68:25. This suggests that an isomerization of *E*-**3a** into *Z*-**3a** took place under the purification conditions.

The same trend was observed when the reaction was extended to several iodoarenes with electron-donating and electron-withdrawing substituents in the *ortho* and *para* positions (Scheme 4). As shown in Table 1, in almost all cases (entries 1–7) the reactions yielded the dihydroisobenzofurans (i.e., **3**) quantitatively. The *E* derivative was always the minor product, and the relative amount of the *Z* compound generally increased after purification. To evaluate whether an interaction of the crude product with the stationary phase (SiO_2) or with the eluent ($CHCl_3$) could be the reason for the change in the ratio between the two isomers, 100 mg of pure *E*-**3f** was treated with SiO_2 in $CDCl_3$. After 24 h both steroisomers were present in reaction mixture, and a *Z*/*E* ratio of 92:8 was observed; this ratio remained constant even after five more days (Scheme 5).



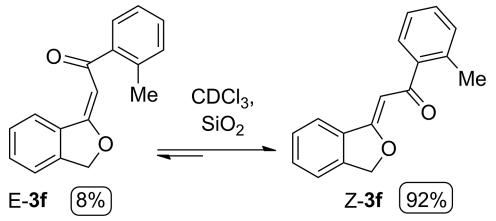
Scheme 4. Cyclocarbonylative Sonogashira reactions between (2-ethynylphenyl)methanol and aryl iodides.

Table 1. Cyclocarbonylative reactions of 2-(2-ethynylphenyl)ethanol and aryl iodides.

Entry[a]	**2**	Ar	**3**	*Z* [%][b]	*E* [%][b]
1	**2a**	Ph	**3a**	63 (68)	37 (25)
2	**2b**	1-naphthyl	**3b**	86 (87)	14 (10)
3	**2c**	4-$MeOC_6H_4$	**3c**	75 (83)	25 (14)
4	**2d**	2-$MeOC_6H_4$	**3d**	81 (81)	19 (14)
5	**2e**	4-MeC_6H_4	**3e**	59 (60)	41 (33)
6	**2f**	2-MeC_6H_4	**3f**	71 (72)	29 (27)
7	**2g**	4-Cl	**3g**	61 (51)	39 (11)
8[c]	**2h**	2-NCC_6H_4	**3h**	83 (69)	–
9[d]	**2i**	4-NCC_6H_4	**3i**	50 (33)	25 (13)

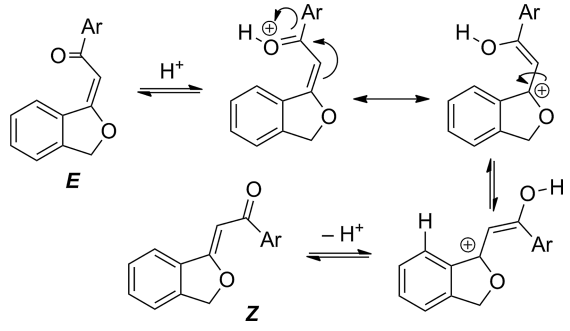
[a] The reactions were carried out with **1a** (2 mmol), **2** (2 mmol), $PdCl_2(PPh_3)_2$ (0.004 mmol; 0.2 mol-%), in Et_3N (5 mL) at 100 °C for 24 h under CO (2.0 MPa). Conversions (100% in all cases) were evaluated by GC and ^1H NMR spectroscopic analysis. [b] Selectivities were evaluated by ^1H NMR spectroscopy; isolated yields are reported in parentheses (the products were obtained chemically pure after column chromatography). [c] The reaction also yielded 17% of 2-{3-[2-(hydroxymethyl)phenyl]propioloyl}benzonitrile **4**. [d] The reaction was carried out in a mixture of Et_3N (5 mL) and toluene (4 mL) in order to dissolve **2**; 4-{3-[2-(hydroxymethyl)-phenyl]propioloyl}benzonitrile **5** (25%) was also formed.

This means that *Z*-**3f** is more stable than the *E* isomer by about 1.3 kcal/mol,[23] and this value is comparable with that reported for similar acylylidene isobenzofurans.[12]



Scheme 5. Interconversion of the two stereoisomers.

Probably, the presence of traces of acid during the purification step could cause the interconversion to take place, as already pointed out by Herndon and coworkers[12a] (Scheme 6).



Scheme 6. Mechanism of the stereoisomerization of *E*-**3a** into *Z*-**3a**.

When the cyclocarbonylative Sonogashira reaction was carried out using benzonitriles **2h** and **2i** (Table 1, entries 8 and 9), significant amounts of 2-{3-[2-(hydroxymethyl)-phenyl]propioloyl} benzonitrile (**4**; 17%) and 4-{3-[2-(hydroxymethyl)phenyl]propioloyl} benzonitrile (**5**; 25%) were generated (Figure 3).

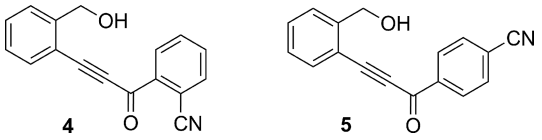
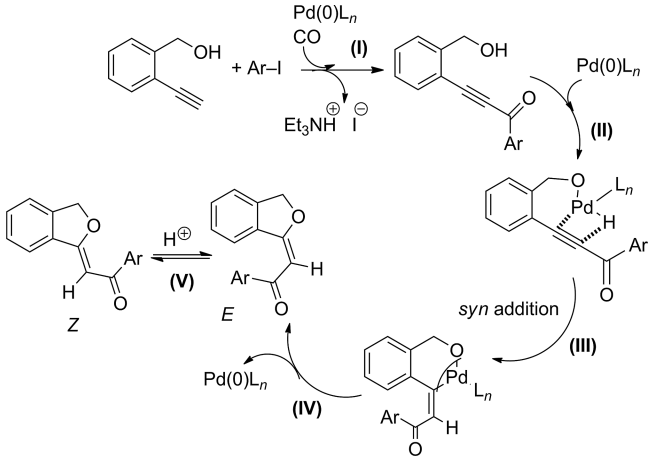


Figure 3. Carbonylative Sonogashira byproducts.

To rationalize all these outcomes, we propose the hypothetical mechanism shown in Scheme 7. It involves an initial carbonylative Sonogashira coupling between the iodo derivative and the alkynyl moiety (Scheme 7, I). Then a Pd^0 insertion into the O–H bond takes place (Scheme 7, II), and a palladium hydride species is obtained. This species then undergoes a *syn* hydropalladation step with the triple bond (Scheme 7, III). A subsequent reductive elimination (Scheme 7, IV) regenerates Pd^0, and gives isobenzofuran *E*-**3**, which equilibrates with the corresponding *Z*-**3** isomer (Scheme 7, V).

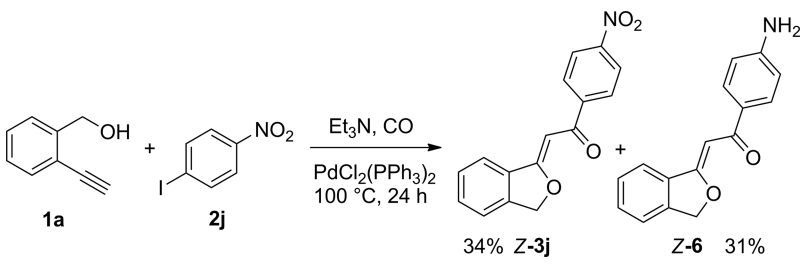


Scheme 7. Proposed mechanism.

The formation of the two *E* and *Z* stereoisomers is apparently in contrast with the data obtained in our previous work on the synthesis of isobenzopyrans through the Sonogashira cyclocarbonylation reaction of 2-(2-ethynylphenyl)-ethanol.[21] Indeed, in that case, not even traces of the *E* species were detected. In the light of these new results, our previous data could be explained with a *trans* hydropalladation step to the triple bond of the alkynyl ketone intermediate or, more probably, by a very fast conversion of the *E* isomer into the *Z* isomer as soon as it is formed in the reaction medium.

The proposed mechanism is also consistent with the presence of the uncyclized products that were obtained when iodobenzonitriles were used as the coupling partners (Table 1, entries 8 and 9). In these cases, the presence of a strongly electron-withdrawing group could reduce the electron density on the triple bond of the Sonogashira coupling product, thus slowing the hydropalladation step.

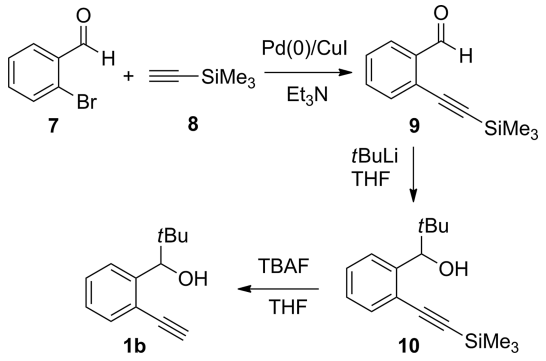
The presence of palladium–H species in the catalytic cycle could be the reason for the formation of (*Z*)-1-(4-aminophenyl)-2-[isobenzofuran-1(3*H*)-ylidene]ethanone (**6**) in the reaction between 1-iodo-4-nitrobenzene (**2j**) and **1a** (Scheme 8). Indeed, aminobenzofuran **6** could reasonably



Scheme 8. Cyclocarbonylative Sonogashira reactions between (2-ethynylphenyl)methanol and 1-iodo-4-nitrobenzene.

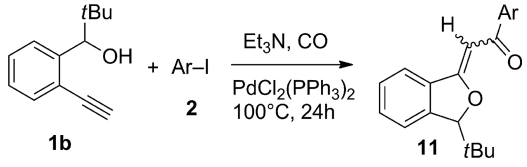
be derived from the reduction of the NO_2 moiety into an NH_2 group, as already observed in our previous work on the synthesis of isochromans.[21]

Finally, the cyclocarbonylative Sonogashira reaction was extended to a sterically hindered secondary alcohol. We chose *tert*-butyl alcohol (**1b**) as a representative example. Since it is not commercially available, **1b** was synthesized from aldehyde **7** according to the procedure (not optimized) shown in Scheme 9.[14] 2-Bromobenzaldehyde was initially coupled with trimethylsilylacetylene to give product **9** (87%). *t*BuLi was then added to 2-(trimethylsilylethynyl)-benzaldehyde, generating 2,2-dimethyl-1-{2-[(trimethylsilyl)ethynyl]phenyl}propan-1-ol (**10**; 28%). Finally, the $SiMe_3$ group was easily removed by treatment of **10** with an excess of tetrabutylammonium fluoride (TBAF; 77%).



Scheme 9. Preparation of 1-(2-ethynylphenyl)-2,2-dimethylpropan-1-ol.

A preliminary study on the carbocyclization reactions (Scheme 10, Table 2) again showed a quantitative conversion of the reagents, but a slightly higher catalyst loading (0.5 mol-%) was necessary to obtain the desired products (Table 2, entries 1 vs. 2). To our surprise, we observed that, at least in the few cases examined, when hindered alcohol **1b** was used with iodoarenes **2a** and **2d**, the stereoselectivity of the process was switched in favour of the *E* isomer (Table 2, entries 2 and 3).



Scheme 10. Cyclocarbonylative Sonogashira reactions of 1-(2-ethynylphenyl)-2,2-dimethylpropan-1-ol.

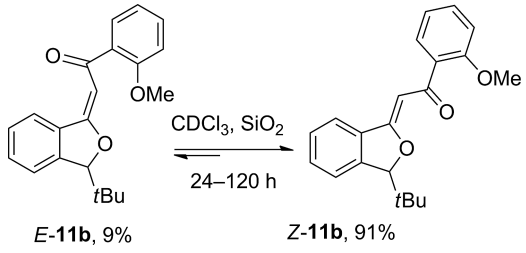
These results could tentatively be ascribed to a reduced overall rate of the catalytic cycle due to the higher steric hindrance of substrate **1b** relative to **1a**; thus a lower conversion of isomer *E* into *Z* (Scheme 7, step V) resulted. Indeed, a greater amount of the catalyst had to be used in order to obtain complete conversion of the reactants (Table 2, entries 1 and 2).

Table 2. Cyclocarbonylative reactions of 1-(2-ethynylphenyl)-2,2-dimethylpropan-1-ol and aryl iodides.

Entry[a]	2	Ar	Cat. [mol-%]	Conv.[b] [%]	11	*Z* [%][b]	*E* [%][b]
1	**2a**	Ph	0.2	28	**11a**	26	74
2	**2a**	Ph	0.5	100	**11a**	22 (15)	78 (57)
3	**2d**	2-$MeOC_6H_4$	0.5	100	**11b**	44 (32)	56 (35)

[a] The reactions were carried out with **1a** (2 mmol), **2** (2 mmol), in Et_3N (5 mL) at 100 °C for 24 h, under CO (2.0 MPa). [b] Conversions were evaluated through ^1H NMR spectroscopic analysis; isolated yields are reported in parentheses.

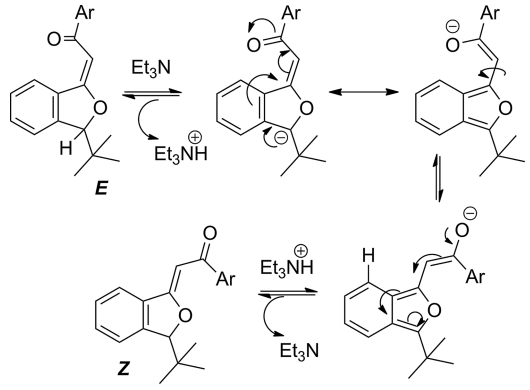
When a sample of pure *E*-**11b** was allowed to equilibrate in $CDCl_3$, and the content of the mixture was monitored, after 24 h a *Z*/*E* ratio of 91:9 was determined; this ratio remained constant after several days (Scheme 11), clearly confirming that the *Z* isomer is the thermodynamically more stable isomer.



Scheme 11. Stereoisomerization of *E*-**11b** and *Z*-**11c**.

The difference in the stereoisomeric ratio observed at the end of the reaction (Table 2, entry 3, 44:56) compared to the ratio detected after the stereoisomerization test (Scheme 11, 91:1) could be due to the experimental conditions used in the two cases. Indeed, while the interconversion of the pure *E* isomer into the *E*/*Z* mixture was carried out under acidic conditions, the cyclocarbonylation reactions were carried out in Et_3N. As shown in Scheme 12, in the second case, the isomerization requires the removal of a proton from the substituted carbon atom by triethylamine. In the case of alcohol **1b**, the very hindered *tert*-butyl moiety would interfere with the approach of the base, slowing down the overall isomerization process (Scheme 12).

Finally, two reactions were carried out using benzoyl chloride instead of iodobenzene under the usual experimental conditions [i.e., **1a** (2 mmol), PhCOCl (2 mmol), in Et_3N (5 mL) at 100 °C for 4–24 h, under N_2] in order to verify whether the cyclization could be carried out without carbon monoxide. In fact, Sonogashira reactions of acyl chlorides are well known in the literature.[25] Unfortunately, already after 4 h, almost a complete consumption of the alcohol was observed in the ^1H NMR spectrum of the crude product, together with the formation of polymeric material. These results can probably be ascribed to the interaction between the OH moiety of **1a** and the benzoyl chloride, which can generate ester derivatives that can undergo polycondensation processes.



Scheme 12. Possible mechanism of the stereoisomerization under basic reaction conditions.

Conclusions

In conclusion, we have developed an atom-efficient reaction to obtain acylylidene phthalans through a Pd-catalysed carbonylative Sonogashira reaction,[24] followed by an in situ cyclization process. The reaction proceeds smoothly with both electron-rich and electron-deficient aryl iodides, with almost complete chemoselectivity for isobenzofuran products. The stereoselectivity of the cyclization step depends mainly on the structure of the benzyl alcohol used. Indeed, when 2-(ethynylphenyl)methanol (**1a**) was treated with iodoarenes, carbonylmethylene isobenzofurans *Z*-**3** were obtained as the major products, together with small amounts of the corresponding *E* isomers. In contrast, the reactions carried out with *tert*-butyl functionalized alcohol **1b** gave preferentially the *E* stereoisomers, which could easily be converted into the corresponding *Z* compounds by simple treatment with $CHCl_3/SiO_2$.

Experimental Section

Typical Procedure for the Synthesis of Acylylidene Isobenzofurans 3: Alcohol **1a** or **1b** (2–4 mmol), aryl iodide **2** (2–4 mmol), and Et_3N (5 mL) were put into a Schlenk tube. $PdCl_2(PPh_3)_2$ (0.2–0.5 mol-%) was put into an autoclave, and then the solution prepared as described above was introduced into the autoclave by a steel siphon. The autoclave was then put under vacuum. The reactor was pressurized with CO (2.0 MPa), and the mixture was stirred for 24 h at 100 °C. After removing the excess CO (fume hood), the mixture was diluted with CH_2Cl_2, and filtered through Celite, and the solvent was removed under vacuum. The crude product was purified by column chromatography (SiO_2, $CHCl_3$).

Supporting Information (see footnote on the first page of this article): Detailed experimental procedures, spectroscopic data, copies of the ^1H and ^{13}C NMR spectra

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