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Graphical Abstract

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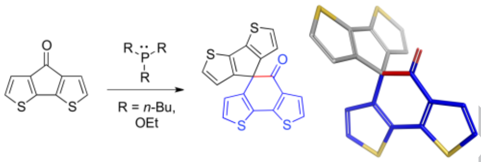

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Trivalent organophosphorus reagent induced pinacol rearrangement of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one

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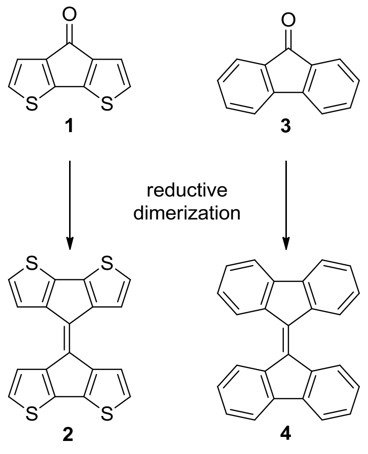
ABSTRACT

In this paper we report on the reaction of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one with various trivalent organophosphorus derivatives, with an emphasis on the final products depending on the applied reagents. No reaction occurred upon treatment with either triphenyl- or tricyclohexylphosphine, whereas addition of triethyl phosphite or tri(*n*-butyl)phosphine resulted in pinacol rearrangement. Structure elucidation of the isolated 5*H*-spiro(benzo[1,2-*b*:6,5-*b'*]dithiophene-4,4'-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen)-5-one was achieved by combined NMR experiments, theoretical chemical shift and geometry calculations and single crystal X-ray analysis.

The growing need for highly efficient light harvesting materials for organic optoelectronic applications, *e.g.* light emitting diodes and photovoltaics, has led to the development of a broad variety of novel π-conjugated building blocks.[1] The combination of heterocyclic donor and acceptor units in an alternate fashion into small molecules and/or semiconducting polymers affords low band gap materials, able to absorb light into the near-IR region of the visible spectrum, where the incident photon flux is most abundant. 4*H*-Cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) was among the first and most successful donor building blocks to be incorporated in low band gap polymers for bulk heterojunction (BHJ) organic solar cell applications.[2] Due to their versatility and ease of functionalization, CPDT derivatives are currently also further explored as active materials for molecular photovoltaics and dye sensitized solar cells.[3] The presence of a keto function on the bridging carbon atom, as in the common CPDT precursor **1** (4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one, Scheme 1), allows to perform (at both the monomer and polymer stage) a variety of synthetic transformations. For instance, the synthesis of (mixed) heterocyclic fulvalenes, starting from aromatic ketones such as CPDT-one **1**, fluorenones and/or a combination of the two, is well known (Scheme 1).[4] The resulting π-bridged two-dimensionally conjugated materials show promising electron accepting features and are potential substitutes for the commonly used fullerene derivatives in BHJ organic solar cells.[5] Having this in mind – and as we have been exploring novel synthetic pathways toward (a)symmetrically substituted CPDTs and their integration in small molecules and low band gap copolymers for organic photovoltaics[6,7] – we were interested to analyze the reactivity of CPDT-4-one **1**[8] (and a series of 2*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-2,6(4*H*)-diones[9]) toward similar reductive



Scheme 1. Synthesis of bicyclidene derivatives by reductive dimerization.

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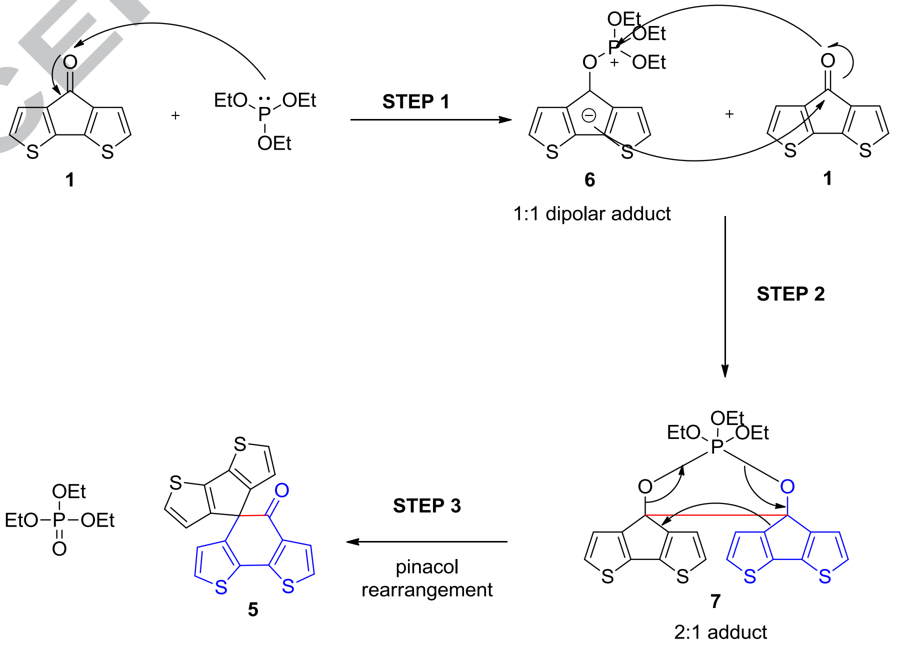
dimerization transformations. These reactions are known to occur in the presence of Lawesson's reagent,[10] various trivalent organophosphorus reagents such as phosphites and phosphines,[11] or low-valent titanium compounds (McMurry reactions).[12] In this paper, we report on the reactivity of CPDT-4-one **1** toward a series of trivalent organophosphorus reagents, with an emphasis on the isolated reaction products depending on the employed reagents.

$\Delta^{4,4'}$-Dicyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**2**) (Scheme 1) has previously been obtained, in low to moderate yields (23-51%), by reductive coupling of ketone **1** upon application of Lawesson's reagent in refluxing benzene or toluene.[10] Similar transformations in the presence of trivalent organophosphorus reagents have not yet been explored for the CPDT family, but were successfully implemented for fluorenone and other diones.[11,13] A strong dependence of the isolated reaction product(s) on the nature of the substituents on the phosphorus atom and the solvent (to a lesser extent) was noticed. Starting from 9-fluorenone (**3**), the corresponding bicyclic derivative **4** (Scheme 1) could be obtained as the sole reaction product upon treatment with tri(*n*-butyl)phosphine. On the other hand, the use of triethyl phosphite afforded a pinacol rearrangement product. The different outcome was explained by the relatively different nucleophilic character of the employed reagents. Based on the structural resemblance between CPDT-4-one **1** and 9-fluorenone (**3**), one would expect a rather similar behavior toward these types of transformations.[13]

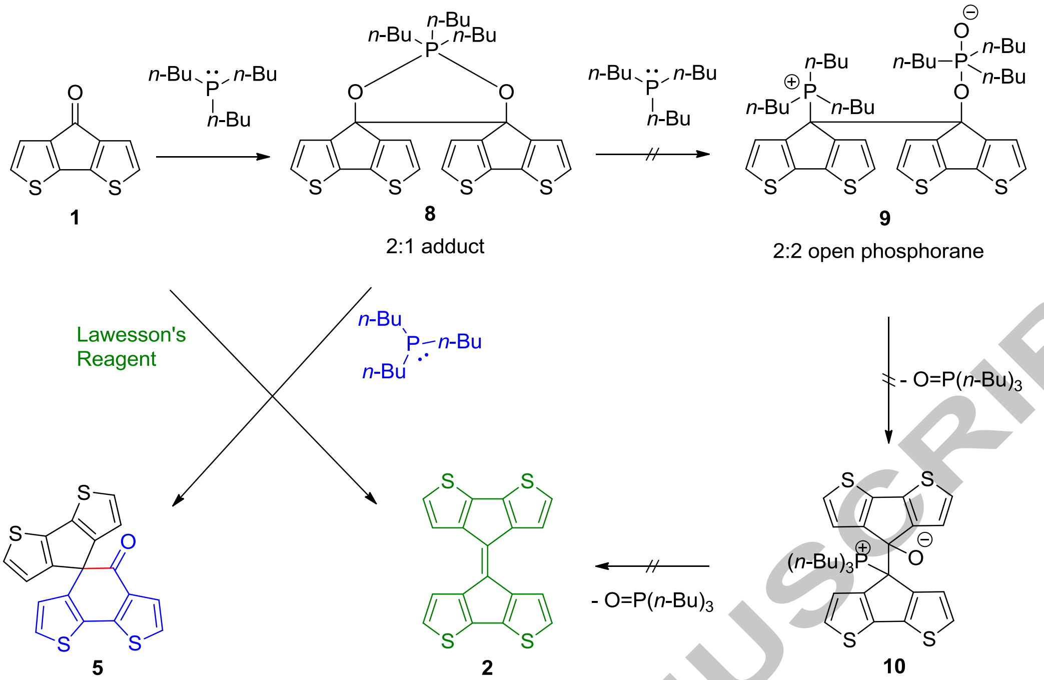
The reaction of CPDT-one **1** with two equivalents of triethyl phosphite in refluxing *o*-xylene afforded a novel compound, tentatively assigned (upon analogy with the fluorenone case) as 5*H*-spiro(benzo[1,2-*b*:6,5-*b'*]dithiophene-4,4'-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen)-5-one (**5**) (Scheme 2), in 61% yield, together with triethyl phosphate and very low amounts of starting material. The formation of a pinacol rearrangement product in one step starting from the corresponding CPDT-one has, to the best of our knowledge, not yet been reported in the CPDT series. Such reactions are known to proceed *via* a three-step mechanism (Scheme 2): i) Attack of the phosphorus free electron pair on the oxygen atom of the cyclic ketone, which results in the formation of a 1:1 dipolar adduct, an intramolecular phosphonium salt in which the negative charge is stabilized by delocalization, here in cyclopentadienide **6**. ii) The reaction of adduct **6** with another equivalent of CPDT-one **1**, leading to the formation of the 2:1 adduct **7** in which a pentacovalent oxyphosphorane is generated. iii) Thermal decomposition of **7** into spiro compound **5** (the pinacol rearrangement product) and triethyl phosphate, a reaction for which the expulsion of the pentacovalent phosphate ester is the driving force.[14] Analogous isomeric CPDT-pinacolones were previously synthesized in two steps passing by the corresponding 1,2-diols, which undergo chemical rearrangement in the presence of Brønsted acids.[15]

Surprisingly, the application of tri(*n*-butyl)phosphine also led to the formation of pinacolone **5**, the expected bicyclidene derivative **2** not being detected in the reaction mixture (Scheme 3). Unlike for the fluorenone case, the reductive dimerization reaction did not occur.[13] Most probably, attack of the phosphine on the initially formed 2:1 adduct **8**, leading to the formation of a so-called open dipolar phosphorane **9**, and subsequent rearrangement and expulsion of tributyl phosphinoxide failed to take place or was not competitive with the fast rearrangement of adduct **8** to the isolated pinacolone **5**. Application of triphenyl- or tricyclohexylphosphine in refluxing *o*-xylene afforded, even after three days, only the unreacted CPDT-one **1**. This result is in agreement with the findings of Borowitz *et al.*, who also mentioned a lack of reactivity of 9-fluorenone (**3**) toward the above-mentioned phosphines.[13]

The spiro structure of the isolated product **5** was initially confirmed by IR, MS and NMR analysis. The carbonyl function was readily identified in the IR spectrum, showing a characteristic C=O stretching band at 1664 cm^{-1}, and was confirmed by the δ = 190.1 ppm quaternary carbon resonance in the APT spectrum. MS analysis provided the molecular mass of the product (*m/z* = 368) and indicated CO loss, and compound identity was further confirmed by HRMS. ^{1}H NMR analysis showed the presence of eight aromatic protons, the lowest field one at δ = 7.43 ppm being assigned to the proton in β-position of the carbonyl function (see Supplementary Material).



Scheme 2. Proposed reaction mechanism for the synthesis of pinacolone **5**.



Scheme 3. Reaction of CPDT-4-one **1** with tri(*n*-butyl)phosphine.

A series of detailed NMR experiments (^{1}H, ^{13}C, APT, short and long-range HETCOR) was then performed for structure confirmation, allowing complete chemical shift assignment of the ^{1}H and ^{13}C resonances of pinacolone **5** (see Supplementary Material). The experimental values were also compared with those obtained from theoretical chemical shift calculations[16] and were found to be in close agreement (see Supplementary Material). The [IEFPCM($CHCl_3$)/B3LYP/6-311+G(d,p)] ground state optimized structure of **5** shows that the CPDT core is almost perpendicular to the benzodithiophenone core, the dihedral angle between the planes being 89° (Figure 1).

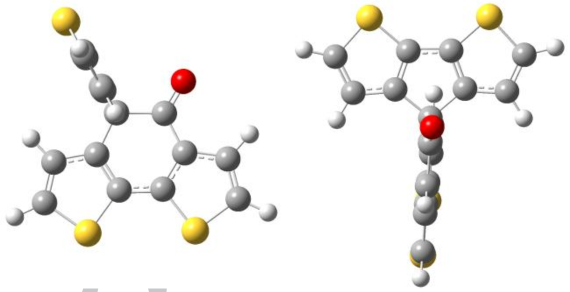


Figure 1. Optimized structure of pinacolone **5**, viewed along the CPDT plane (left) and along the benzodithiophenone plane (right).

Final unambiguous structural proof was only afterwards provided by single-crystal X-ray diffraction (Figure 2). The structure is characterized by disorder; the cyclopentadithiophene is always in the same position, but the benzodithiophenone is rotated 180° with respect to the spiro bond (74/26%). Both fused heterocycles are in an almost perpendicular conformation (88.47(4)° and 89.00(7)°, respectively; the central atom was omitted in the calculation of the planes). Despite the orthogonal arrangement of the two planes, the molecular point group cannot be classified as C_s (mirror plane) as the CPDT is inclined about 15° when looking along the plane formed by the benzodithiophenone. Upon comparison of the experimental and calculated structures, one observes only minor deviations. Indeed, the largest bond length difference is as small as 0.038 Å (with an average of 0.015 Å), while the deviation for all C-S-C bond angles is below 1.0° and the difference for the dihedral angles is only ~1.5° (see Supplementary Material).

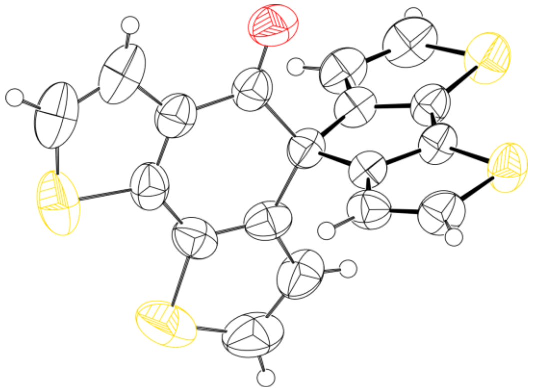


Figure 2. ORTEP representation of 5*H*-spiro(benzo[1,2-*b*:6,5-*b'*]dithiophene-4,4'-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen)-5-one (**5**), with thermal displacement ellipsoids drawn at the 50% probability level (the disorder is omitted for clarity).

In summary, in this paper we have reported on the reaction of 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (**1**) with a series of trivalent organophosphorus reagents. The results show that such a protocol exclusively leads to the formation of the pinacol rearrangement product, *i.e.* 5*H*-spiro(benzo[1,2-*b*:6,5-*b'*]dithiophene-4,4'-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen)-5-one (**5**), when either triethyl phosphite or tri(*n*-butyl)phosphine is applied, whereas no reaction is seen with triphenyl- or tricyclohexylphosphine. A noticeable difference in reactivity between CPDT-4-one **1** and the structurally resembling 9-fluorenone (**3**) was observed. Thorough NMR characterization enabled full ^{1}H and ^{13}C chemical shift assignment of the CPDT-pinacolone product and theoretical chemical shift calculations corroborated well with the experimentally observed values. A single-crystal X-ray structure of the pinacolone was finally obtained as well, with a solid-state conformation matching closely to the calculated optimized structure.

Acknowledgments

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Supplementary Material

Crystallographic data (excluding structure factors) for the structure in this Letter have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **906131**. A copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc-cam.ac.uk). Further supplementary data associated with this article (experimental data, detailed description of the NMR chemical shift assignments and associated theoretical calculations, and more details on the X-ray analysis) can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.xxx.

*Graphical Abstract (for review)