In summary, we have found the first *preparative* method for direct iodination of hydrocarbons. The procedure is simple yet efficient and even normally completely unreactive straight chain alkanes can be iodinated easily. Further developments of this method are likely to find application in the widely used biochemical radioiodination[25] techniques and in the production of speciality chemicals for the pharmaceutical industry. Elaborate mechanistic studies are well underway in our laboratories.

Experimental Section

Representative preparative procedure for liquid and solid hydrocarbons: a) Iodocyclohexane (**5a**): Powdered NaOH (10.0 g) and iodoform (7.0 g, 17.8 mmol) were added to cyclohexane (100 mL). The solution was stirred for 24 h at room temperature. The organic phase was separated from the solid phase by filtration; vacuum distillation gave pure **5a** (2.8 g, 13.4 mmol, 75% relative to HCI_3). b) 1-Iodoadamantane (**11a**): Solid NaOH (2.4 g) was added to a solution of iodoform (0.79 g, 2.0 mmol), CH_2Cl_2 (20 mL), and substrate (0.27 g, 2.0 mmol). The solution was stirred for 96 h. The organic phase was separated from the solid phase by filtration, and the solid phase was washed with CH_2Cl_2 (3×20 mL); volatile components were removed by vacuum distillation. The products were purified by column chromatography (silica gel, petroleum ether, b.p. $< 60\,^{\circ}C$, R_f (**11a**) = 0.48; R_f (**11b**) = 0.25) to give 1-iodoadamantane (**11a**) (0.28 g, 1.1 mmol, 53%) and 1,3-diiodoadamantane (**11b**) (0.04 g, 0.1 mmol, 5%). All products were identified by GC, MS, and NMR analysis and were found to be identical to standard samples. Preparative yields are given in Table 1. Complete mass balances were determined for cyclohexane and adamantane.

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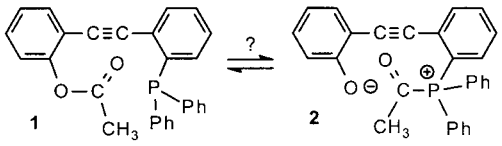
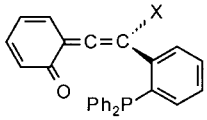
Unusual Oxaphosphoranes by Acyl Transfer from *o*-Acetoxy-*o′*-diphenylphosphanyltolane**

Edwin Vedejs* and Peter L. Steck

As part of a study on phosphane-catalyzed acylations,[1] we were interested in the chemistry of the *o*,*o′*-disubstituted tolane **1**. The linear acetylene linker provides for close proximity between the phosphorus atom and the carbonyl group,[2] perhaps sufficient to promote bonding interactions





3a, X = $C(O)CH_3$
3b, X = H

that would lead to the P-acyl derivative **2** by intramolecular acyl transfer. In its zwitterionic resonance form, **2** is formally analogous to the *P*-acylphosphonium carboxylate ion pair that is the reactive intermediate in the acylation of phosphanes with anhydrides.[1a] If **1** is capable of O to P acyl transfer, then **2** might function as an acyl donor towards external nucleophiles and could also serve as a geometrically restricted mechanistic analogue of *P*-acylphosphonium car-

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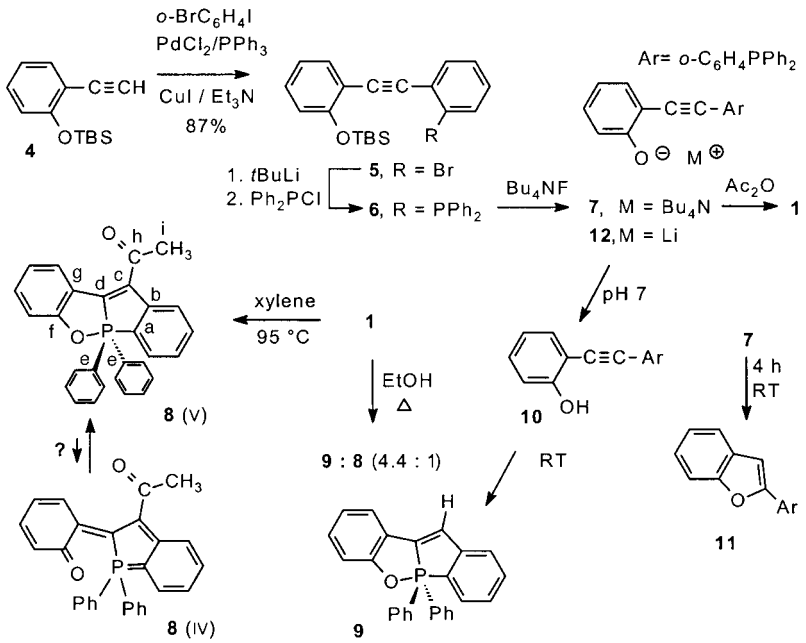
boxylate intermediates. Alternatively, **2** might undergo internal acylation to generate the reactive intermediate **3a**. These possibilities stimulated the attempt to prepare **1** and to study its reactivity.

Conventional Sonogashira coupling[3] of **4** with *o*-BrC_6H_4I gave **5**, and lithiation followed by treatment with Ph_2PCl afforded **6** in 70% overall yield (Scheme 1). Initial attempts to deprotect **6** with Bu_4NF encountered unexpected complications, but using Bu_4NF in the presence of Ac_2O produced **1** in



Scheme 1. Synthesis and transformation of **1**. TBS = *t*$BuMe_2Si$.

94% yield as a colorless, crystalline substance. However, **1** proved to have unusual properties. Upon storage in $CDCl_3$ or C_6D_6, **1** slowly developed a striking orange color. The color change was more dramatic at 95 °C in xylene, and conversion was complete after 4 h. The transformation was also observed on heating solid **1** above 100 °C in a melting-point apparatus. In all of these procedures, the same intensely colored product was formed, and isolation afforded red crystals. According to X-ray crystallography, the red substance is the phosphorane **8**(V) with an unusual bicyclic structure.[4]

The exploration of acyl-transfer reactions was restricted by the thermal rearrangement of **1** to **8**, but there was a further complication. Heating **1** in absolute ethanol mainly led to deacylation, as anticipated if **2** were generated as an intermediate, and an orange-red color was observed. Formation of **8** as a by-product (ca. 20–25%) was confirmed, but the ethanolysis experiment produced a second intensely colored product **9** that resembled **8** in several respects, including stability (both **8** and **9** are stable to air, water, and chromatography) and spectroscopic data.[5] The appearance of a distinct new down-field signal for a vinylic hydrogen atom at $\delta = 7.92$ ($^3J_{P,H} = 52.8$ Hz) suggested a deacylated benzophosphole subunit, and this was confirmed by X-ray crystallography. The P–O bonds of **9** (1.95 Å) and **8** (1.90 Å) are somewhat long compared to those of typical phosphoranes (1.75–1.85 Å),[6] although shorter than in "bonding betaine"[7] or analogous dipolar structures.[4] Reported examples of the latter species have extensive delocalization and distinct visible chromophores, as do **8** and **9**. Therefore, the ^{13}C NMR spectra were studied in detail to better define the solution structures.

Extensive heteronuclear multiple quantum coherence (HMQC) experiments allowed the assignment of the quaternary carbon atoms directly bound to phosphorus in **8** and **9**. If the structures in solution have substantial contributions from tautomers containing tetravalent phosphorus, such as **8**(IV), then all of the $^1J_{P,C}$ values should be similar. On the other hand, pentacovalent **8**(V) should have characteristically large differences in $^1J_{P,C}$ for the endocyclic aryl carbon atom C_a (apical) and the exocyclic aryl carbons C_e (equatorial). The latter situation was confirmed for both **8** and **9**: C_a of **8**: $^1J_{P,C} = 29.2$ Hz; C_a of **9**: $^1J_{P,C} = 32.2$ Hz; C_e of **8**: $^1J_{P,C} = 141.1$ Hz; C_e of **9**: $^1J_{P,C} = 141.1$ Hz. Furthermore, the endocyclic phosphole carbon atom C_d has a $^1J_{P,C}$ value of 124 Hz in both **8** and **9**. This large coupling constant is expected for equatorial C–P bonds at trigonal-bipyramidal phosphorus atoms.[8] The NMR data provide no clear evidence of tetravalent structures in solution, although a small contribution by **8**(IV) would help explain the red color.

Further investigations focused on the role of transient intermediates in the unusual rearrangements of **1**. The early experiments to deprotect **6** with Bu_4NF were repeated with greater care taken to intercept the phenol **10**. However, a variety of protic quenching agents gave only the red product **9** and/or a colorless isomer **11** (see Scheme 1; ^{31}P NMR: $\delta = -9.32$; structure by X-ray crystallography).[9] The latter was the sole product if the reaction mixture of **6** with Bu_4NF was allowed to stand for 4 h at room temperature before quenching, as expected from a literature precedent.[2e] However, quenching with NH_4Cl after two minutes gave **9** as the only detectable product. The initially formed tetrabutylammonium phenoxide **7** was observed prior to quenching (^{31}P NMR: $\delta = -8.02$, C_6D_6), but **10** could not be isolated without cyclization to **9**. A similar result was obtained after treatment of **1** with MeLi at −78 °C followed by workup with KH_2PO_4/Na_2HPO_4 buffer at pH 7. In this case a transient ^{31}P NMR signal was observed ($\delta = -9.62$, THF) that may correspond to the elusive **10**, but removal of the solvent gave only **9**.

We found little precedent to explain the formation of **8** or **9**. However, there is a proposal that a phosphorus center may add to an adjacent triple bond to generate a dipolar intermediate.[10] The analogous process for **1** might lead to **13a**, and subsequent acyl transfer to give **14a**, interconversion with the rotamer **15a**, and P–O bond formation would account for the thermal rearrangement of **1** to **8**. This could be a plausible mechanism in xylene, but we are skeptical that acyl transfer from **13a** to **14a** could compete with protonation of **13a** when the reaction is performed in absolute ethanol. The latter experiment gave **8** and **9** in a 1:4.4 ratio, a result that calls for a different explanation.

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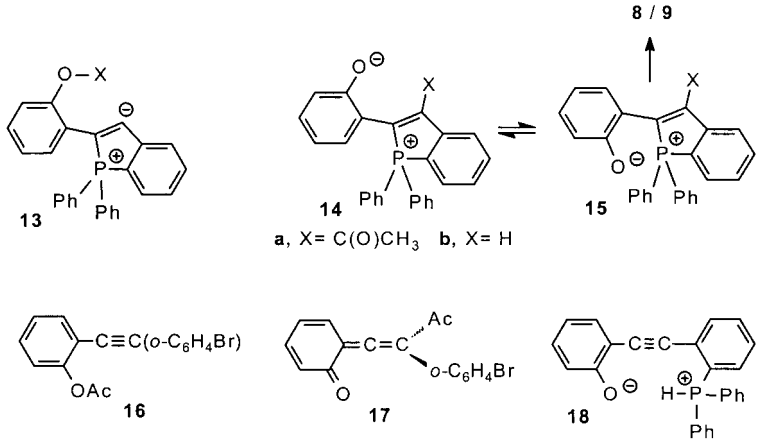

One possibility would be to invoke an unusual internal acyl transfer from **1** to directly give **3a**, followed by a precedented [2*n*+4π] cyclization to give **8** (Scheme 1).[11] The first step of this mechanism is suspect because it requires a linear sp-hybridized carbon atom in a six-center transition state and produces a new C–C bond in **3a** that is orthogonal to the original π system, geometrical features that would disfavor a concerted process. Furthermore, control experiments with the model compound **16** revealed no sign of any reaction at 95 °C in xylene. If **17** had been generated, surely the highly reactive *ortho*-quinone methide subunit would have encountered opportunities for self-destruction. This experiment indicates that phosphorus plays a key role in the rate-determining step. One possibility is acyl transfer concerted with C–P bond formation in **1** to directly give **14**, but we prefer the alternative path via *P*-acylphosphonium salt **2**. Subsequent P-to-C acyl transfer should provide a low-energy pathway to **3a** and internal [2+4] addition would then give **8**(V).[11]

Similar mechanistic possibilities can be considered for the rapid conversion of phenol **10** to **9** at room temperature via the quinone methide intermediate **3b**. However, concerted cyclization of **10** to give **14b** becomes increasingly plausible, because a similar concerted proton transfer/nucleophilic attack mechanism has been established by Letsinger et al. for the transformation of diphenylacetylene-*o*,*o*′-dicarboxylic acid into a substituted pyrone.[2b] The phenolic proton in **10** is clearly important for the exceptional reactivity, and so is the phosphorus atom.[12] In the corresponding acetate **1**, the carbonyl group is the best available electrophile, and the rearrangement is much slower. We cannot formally distinguish between mechanistic options that proceed directly from **10** to **14** versus the alternatives based on **3b** or **18**, nor can we rule out eight-membered ring phosphorane intermediates derived from **18** by P–O bond formation.[13]

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[5] **8**: Red prisms from methanol, m.p. 247 °C; UV/Vis: $\lambda_{max} = 430$ nm, $\varepsilon = 7500$; HR-MS calcd for $C_{28}H_{21}O_2P$ [M^+]: 420.12790; found: 420.1271; elemental analysis calcd for $C_{28}H_{21}O_2P$: C 79.98, H 5.04; found: C 79.77, H 5.20; ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.75 - 7.65$ (4H, m), 7.41 – 6.96 (12H, m), 6.73 – 6.64 (2H, m), 2.75 (3H, s); partial ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 205.0$ ($^3J_{P,C} = 22.9$ Hz, C_h), 159.5 ($^2J_{P,C} = 1.9$ Hz, C_f), 146.6 ($^2J_{P,C} = 16.5$ Hz, C_c), 146.0 ($^1J_{P,C} = 29.2$ Hz, C_a), 136.4 ($^2J_{P,C} = 24.8$ Hz, C_b), 133.7 ($^1J_{P,C} = 141.8$ Hz, C_e), 125.3 ($^1J_{P,C} = 124.0$ Hz, C_d), 117.8 ($^2J_{P,C} = 23.5$ Hz, C_g), 31.0 (C_i); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -41.4$. **9**: Red prisms from methanol, m.p. 239 °C; UV/VIS: $\lambda_{max} = 422.0$ nm, $\varepsilon = 9670$; HR-MS calcd for $C_{26}H_{19}OP$ [M^+]: 378.11740; found: 378.1184; elemental analysis calcd for $C_{26}H_{19}OP$: C 82.52, H 5.07, P 8.18; found: C 82.22, H 5.30, P 8.02; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.92$ (1H, dd, $^3J_{P,H} = 52.8$, $J = 0.7$ Hz), 7.74 – 7.66 (5H, m), 7.40 – 7.27 (7H, m), 7.22 (1H, tt, $J =$ 7.5, 1.1 Hz), 7.16 – 7.11 (1H, m), 7.09 – 7.02 (1H, m), 7.00 – 6.98 (1H, m), 6.71 (1H, tt, $J = 7.5$, 1.5 Hz), 6.63 (1H, d, $J = 7.9$ Hz); partial ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 159.4$ ($^2J_{P,C} = 1.9$ Hz, C_f), 146.5 ($^2J_{P,C} = 31.2$ Hz, C_b), 139.3 ($^1J_{P,C} = 26.1$ Hz, C_a), 134.3 ($^2J_{P,C} = 17.2$ Hz, C_c), 133.3 ($^1J_{P,C} = 141.1$ Hz, C_e), 129.2 ($^1J_{P,C} = 124.0$ Hz, C_d), 119.6 ($^2J_{P,C} = 23.5$ Hz, C_g); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = -39.8$. Oxaphosphorane **9** was stable under neutral conditions in aqueous solution, but exposure to HCl/H_2O resulted in rapid formation of a yellow phosphonium salt corresponding to O-protonation of **14** (UV/Vis: $\lambda_{max} = 393$ nm, $\varepsilon = 4870$; ^{31}P NMR (121 MHz, CD_3OD): $\delta = 33.7$). Treating the salt with $Et_3N/CDCl_3$ regenerated red **9**.

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[9] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-112758 (**8**), -112759 (**9**), and -112760 (**11**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] The C protonation and C–P bond formation in **10** is complete within 2 min in the presence of NH_4Cl. If the phenol is protected, as in **6**, then no reaction occurs upon treatment with NH_4Cl/H_2O at room temperature (30 min). An *o*,*o*′-dihydroxy analogue of **10** is quite stable.[2e] Hence, the nucleophilicity of the phosphanyl group and the proton-donor capability of the phenol are important for the high reactivity of **10**.

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Detection of Reaction Selectivity on Catalyst Libraries by Spatially Resolved Mass Spectrometry**

Matthias Orschel, Jens Klein, Hans-Werner Schmidt, and Wilhelm F. Maier*

While combinatorial chemistry has established its importance for drug development,[1–3] combinatorial methods are just starting to be applied increasingly in the field of materials research and catalyst development.[4–6, 16] In analogy to the development of new drugs, the major problems are not centered on the synthesis of new libraries—25 000 different components on a few square centimeters have already been realized[4]—but on the reliable, fast, and spatially resolved detection of the desired properties of the library components.[7, 8]

For the combinatorial development of new catalyst materials, the catalytic activity and selectivity of the library components have to be determined quickly and reliably. Very few examples for the determination of reactivity behavior of the components of combinatorial libraries have been reported. A very sensitive and fast method for investigating catalytic activity is emissivity-corrected IR thermography,[9] which allows the reliable and spatially resolved detection of the heat change on heterogeneous catalysts in gas-phase reactions[9] as well as the heat change of homogeneously catalyzed reactions in the liquid phase.[10] Although the relative activity of catalysts is easily determined by such thermographic methods, no information on catalytic selectivity is obtained. A mass spectrometer specially developed for high-throughput screening in combinatorial catalyst development has been applied by Weinberg et al. to catalyst libraries generated in situ by evaporation techniques.[11, 12] Disadvantages of such a solution are its high cost and that it is not accessible to general synthetic or academic laboratories. Although mass spectrometry should be able to identify reaction selectivities, only catalytic activities have been reported. The identification of selectivity differences of heterogeneous catalysts on libraries by spatially resolved mass spectrometry has not yet been demonstrated.

The aim of our study was the detection of selectivity changes on the different components of a catalyst library in the product distribution of a gas-phase reaction by spatially resolved mass spectrometry. The components used for this task were a commercially available gas analyzer and a synthesis robot. The basic idea was to exchange the pipetting unit of the robot for the capillary of the inlet system of a conventional gas analyzer. This combination allows use of the spatial library information of the synthesis robot for the product analysis. To allow the investigation of general gas-phase reactions the MS capillary had to be combined with another capillary providing the feed gas (capillary bundle).

In Figure 1 the experimental setup is shown schematically. The pipetting unit of the commercial robot (spatial resolution in *x*,*y*,*z* direction 0.1 mm) was exchanged for the capillary

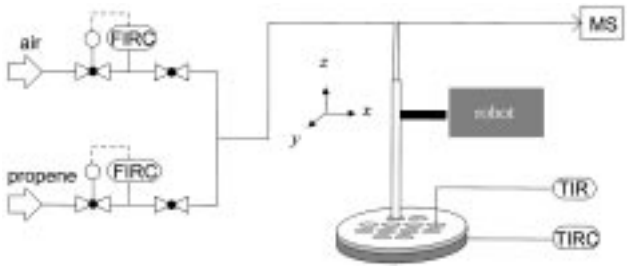

Figure 1. Schematic representation of the setup for spatially resolved mass spectrometry on a catalyst library with control of the capillary bundle with a pipetting robot. FIRC = mass-flow controller, TIR = temperature indicator, TIRC = temperature controller.

bundle (Figure 2). The capillary bundle (length 15 cm) consists of an outer steel capillary (outer diameter 2.0 mm, inner diameter 1.5), two inner steel capillaries (outer diameter

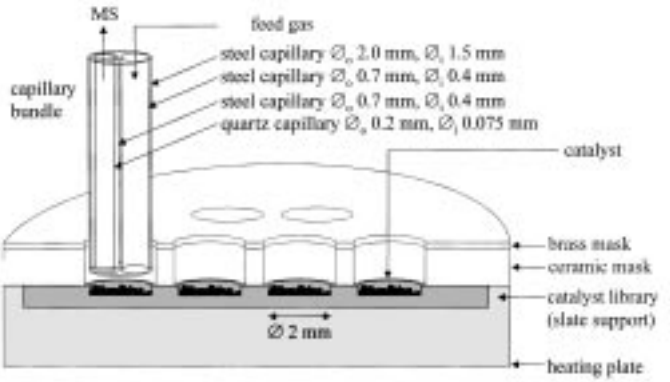

Figure 2. Schematic representation of the positioning of the capillary bundle in the library compartments. $\varnothing_o$ = outer diameter, $\varnothing_i$ = inner diameter.

0.7 mm, inner diameter 0.4 mm), and the MS capillary (quartz capillary, outer diameter 0.2 mm). One of the inner capillaries is used for feed gas supply, and the other one is principally available for other uses, depending on the reaction conditions. In the present case the second inner steel capillary simply

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