J. Am. Chem. Soc. **1993,** *115,* 2071-2072

The solid states of **1** and **2** comprise individual molecules (Figure 1), and there are no short intermolecular contacts. The In(+2) dimer, **1**, features an In–In bond of length 2.744(2) Å. This distance is comparable to those reported for systems with short indium–indium contacts[1] and consistent with a bond order of unity. Within experimental error, both indium centers adopt trigonal planar geometries with the C–In–C angles ~3° smaller than the others. The dihedral angle between the C–In–C planes is 94.1(5)°, presumably as a consequence of minimizing steric repulsions between *o*-CF_3 groups and maximizing intramolecular In···F interactions (vide infra). As in the case of B_2R_4 derivatives,[10] there is no evidence for π-type interaction between the group 13 elements. Eight intramolecular In···F contacts (one for each *o*-CF_3 group) fall in the range 2.801(10)–2.957(13) Å and are thus shorter than the sum of van der Waals radii (3.40 Å).[11] However, the average In···F contact of 2.856(13) Å is considerably longer than the sum of covalent radii (2.16 Å)[11] or the In–F bond distances in $[InF_6]^{2-}$ and InF_3 which range from 2.03 to 2.06 Å.[12] Nevertheless, as in the cases of $(R_F)_2Sn$[13] and $(R_F)_2Pb$,[14] these interactions may contribute to the stability of **1**. The geometry of each InF_4 secondary coordination sphere of **1** is distorted tetrahedral.

The InC_3 geometry of monomeric **2** is trigonal planar. The observation that the average In–C bond distance in **2** (2.189(9) Å) is somewhat longer than that in the unfluorinated analogue Mes_3In (2.168(5) Å)[15] is presumably due to the larger steric demands of the R_F substituent. Compound **2** adopts a propeller-type conformation in which the twist angles of the aryl rings with respect to the InC_3 plane are very similar (49.4, 49.5, and 54.8° for rings 1, 2, and 3, respectively). In contrast, $(Mes)_3In$ features a conformation in which one ring is essentially perpendicular to the InC_3 plane. Such differences may result from packing forces. However, the six (trigonal prismatic) intramolecular In···F contacts from the *o*-CF_3 groups (average distance 2.762(7) Å) may also play a role in the conformational preference of **2**. Although C–H···In interactions could not be confirmed crystallographically in $(Mes)_3In$, low-temperature ^{13}C NMR data are consistent with agostic behavior. In the case of **2**, no changes were observed in the ^{19}F spectra in the temperature range −80 to 30 °C.

The analogous R_F derivatives of gallium have also been prepared. The Ga(+2) dimer $(R_F)_2GaGa(R_F)_2$ (**3**) was synthesized in 45% yield via the reaction of $Ga_2Cl_4 \cdot 2$dioxane[16] with 4 equiv of R_FLi in Et_2O solution at −78 °C. Likewise, the reaction of $GaCl_3$ with 3 equiv of R_FLi in Et_2O solution at −78 °C afforded a 35% yield of $(R_F)_3Ga$ (**4**). Compound **3** can also be prepared by reductive coupling of $(R_F)_2GaCl$[5] with Na/K alloy in hexane solution. The CIMS and NMR spectral data[7] for **3** and **4** are very similar to those of **1** and **2**, respectively, and a preliminary X-ray crystallographic study indicates that **2** and **4** are isomorphous.

In summary, the R_F ligand is capable of supporting Ga–Ga and In–In bonds as well as permitting the isolation of monomeric triaryl derivatives. As noted by Barron et al.,[17] the high nucleophilicity and low basicity of the R_F anion minimize reduction at the metal center. Moreover, electrostatic repulsions for the CF_3 groups inhibit oligomerization.[18]

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Note Added in Proof. For an interesting indium(I) complex of the R_FO ligand, see: Scholz, M.; Noltemeyer, M.; Roesky, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1383.

Supplementary Material Available: Tables of bond distances, bond angles, atomic coordinates, and thermal parameters for **1** and **2** (19 pages); listings of observed and calculated structure factors for **1** and **2** (43 pages). Ordering information is given on any current masthead page.

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(9) Crystal data for **1** ($C_{36}H_8F_{36}In_2$): triclinic, space group $P\bar{1}$ with a = 11.647(2) Å, b = 12.166(2) Å, c = 16.861(3) Å, α = 73.12(3)°, β = 77.83(3)°, γ = 74.40(3)°, V = 2179.1(6) Å^3, Z = 2, d_{calcd} = 2.064 g cm^{-3}, μ(Mo Kα) = 1.242 mm^{-1}. Crystal data for **2** ($C_{27}H_6F_{27}In$): a = 9.010(2) Å, b = 12.920(3) Å, c = 15.391(3) Å, α = 103.72(3)°, β = 102.66(3)°, γ = 105.00(3)°, V = 1604.3(6) Å^3, Z = 2, d_{calcd} = 1.983 g cm^{-3}, μ(Mo Kα) = 0.914 mm^{-1}. Totals of 7607 and 4184 independent reflections were collected for **1** and **2**, respectively, on a Siemens R3m/V diffractometer at 298 K using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Both structures were solved by direct methods and refined by full-matrix least squares (SHELXTL PLUS). The final R values were 0.0796 and 0.0556 for **1** and **2**, respectively.

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(18) There are several F···F contacts <3.0 Å, the shortest being 2.619 Å for F(32)–F(49) in **1** and 2.572 Å for F(11)---F(31) in **2**.

Elemental White Phosphorus as a Radical Trap: A New and General Route to Phosphonic Acids

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We report that white phosphorus is a remarkably efficient trap for carbon radicals. This provides a new and convenient route for the conversion of carboxylic acids into the corresponding phosphonic acids. The latter often show interesting biological activity.[1]

The bond angles in white phosphorus (P_4) are unusually small (60°), and the phosphorus–phosphorus bonds are bent as in cyclopropane.[2] On this basis, one could argue that this highly strained molecule might be chemically very reactive, as stated in most chemistry textbooks.[3] Surprisingly, we have found that many organic compounds in CH_2Cl_2–CS_2 under dry argon at room temperature are not reduced by white phosphorus with or without

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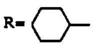
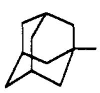
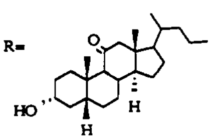
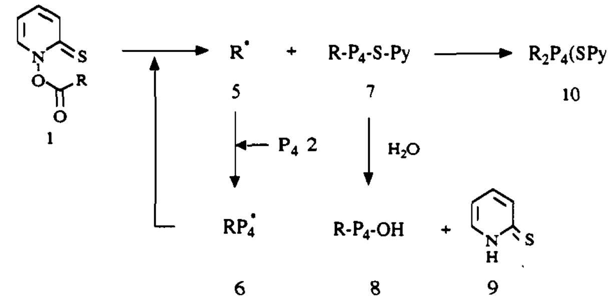
Table I. Results of the Transformation from Carboxylic Acids to Alkylphosphonic Acids

Entry	Starting material	Isolated Yield of Product	m.p.°C (lit.)
1	1a R=$PhCH_2CH_2$-	3a 74.7%	136-138 (137.5-139)[10]
2	1b R=$C_{15}H_{31}$-	3b 71.4%	92-94 (95.5-101.9)[11]
3	1c R= 	3c 73.5%	165-166 (166-167)[12]
4	1d R= 	3d 86.5%	304-307 (308-310)[13]
5	1e R= 	3e 80.7%	230-232

Scheme I



irradiation by visible light.[4,5] All reactions in the sequel were also run under dry argon.

On the basis of the facile radical ring cleavage reaction of [1.1.1]propellane and bicyclo[1.1.0]butane,[6] we conceived that white phosphorus might be a good radical trap even at low temperatures. We found that even the *O*-acyl derivatives **1** of *N*-hydroxy-2-thiopyridone (Barton PTOC esters)[7] are not reduced by white phosphorus in CH_2Cl_2–CS_2. However, on irradiation with white light (2 equiv of P_4), a rapid radical reaction takes place. No RS-2-Py is produced, so the addition reactions are very efficient. Treatment with water gives only 2-thiopyridone (**9**) (92%) in keeping with a phosphorus–2-thiopyridine bond. Photolysis of **1a–e** in the presence of P_4 (**2**) at 0 °C followed by removal of the CH_2Cl_2 and CS_2 in vacuo and oxidation with excess H_2O_2 in 1,2-dimethoxyethane under reflux gave phosphonic acids **3a–e** in good yield (Table I) as well as phosphoric acid (**4**). It is worth noting that hindered phosphonic acid **3d** can be prepared easily in high yield. An earlier radical procedure using $P(SPh)_3$ was less successful.[8] In one example (**1a**), the phosphonic acid was quantified by ^{31}P NMR and found to be 92%. ^{31}P NMR also showed that the appropriate phosphinic acid was the precursor of the phosphonic acid. Likewise, phosphorus acid was a precursor of the phosphoric acid (**4**).

A mechanistic picture (Scheme I) suggests that photolysis of **1**, as usual, produces radical R• (**5**) which reacts with P_4 (**2**) to give derived radical **6**. This, in turn, reacts with **1** to reform R• (**5**) and the product **7**. Hydrolysis of **7** with water would give **8** and 2-thiopyridone (**9**). Experimentally, there was no trace of dipyridine 2,2-disulfide by GC/MS analysis so the phosphorus radical **6** does not dimerize at all. In a control experiment, we also showed that reaction between bipyridine 2,2-disulfide and P_4 (**2**) did not produce **9**.[9]

The efficiency of white phosphorus as a radical trap was demonstrated in competition experiments. When **1a** was photolyzed in the presence of 1 equiv of P_4 (**2**) and 5 equiv of methyl acrylate, the total yield of $PhCH_2CH_2SPy$ and $Ph(CH_2)_3CH(Spy)COOMe$ was less than 3% of **1a**, and the rest was the normal adduct **7a**. Even in the presence of Tempo (**1a**:P_4:Tempo = 1:1:1), **3a** was still obtained in 56% NMR yield after oxidation.

At least 2 equiv of white phosphorus is required in order to avoid the formation of RS-2-Py for the tertiary product (**3d**). However, for the primary alkyl radicals **1a** and **1b**, 0.5 equiv of white phosphorus is enough to guarantee a good yield of phosphonic acid. It is clear that the initial adducts **7a** and **7b** react with cleavage of a second P–P bond to give the tetrasubstituted cyclotetraphosphine **10a** and **10b**, respectively. No dialkylphosphinic acid, $R_2P(O)(OH)$, could be detected by ^{31}P NMR after oxidation, so the alkyl groups must be on separate phosphorus atoms.

We also carried out kinetic studies of the reaction between **1c** and white phosphorus (**2**). Under conditions as in our prior quantum yield measurements,[14] the half-life $t_{1/2}$ for a reaction (**1c**:P_4 = 1:5) is 12.5 s. Under identical conditions, the $t_{1/2}$ for the reaction between **1c** and $BrCCl_3$ is 170 s (quantum yield 30)[14]. We can conclude that the quantum yield for the P_4 reaction is about 400.

In conclusion, a clear-cut radical reaction based on white phosphorus has been demonstrated. The oxidation of the adduct to the corresponding phosphonic acid should find application in the synthesis of naturally occurring alkylphosphonic acids,[1,15] as well as in the synthesis of phosphonic acid analogues of natural phosphates.[2a]

Acknowledgment. We thank the NIH and Schering-Plough Corporation for financial assistance. J.Z. is a Schering-Plough Scholar.

Supplementary Material Available: Experimental details and spectroscopic data for compounds **3a–e** (2 pages). Ordering information is given on any current masthead page.

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[4] The following substrates have been tested in mixed solvents CH_2Cl_2–CS_2 at room temperature under argon: cyclohexene, styrene, benzophenone, benzoyl chloride, cyclohexanone oxime, 2,2′-dinitrobiphenyl, quinone, tetrachloro-1,4-benzoquinone, α-pinene epoxide, β-pinene epoxide, styrene oxide.

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