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Free Radical Chain Reactions of [1.1.1]Propellane. High Affinity of Bicyclo[1.1.1]pent-1-yl Radicals for Three-Coordinate Phosphorus Molecules

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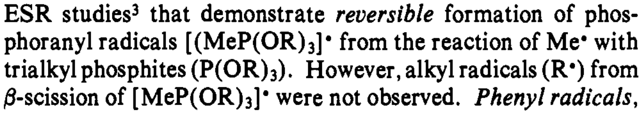
The strained hydrocarbon [1.1.1]propellane (**1**) readily reacts with a variety of free radicals to generate 3-substituted bicyclo[1.1.1]pent-1-yl radicals such as **8** and **14**.[1,2] While it is generally assumed that the bicyclo[1.1.1]pent-1-yl radical should be more reactive than an unconstrained tertiary radical, e.g., *tert*-butyl, few studies that make specific comparisons are available. We report here reaction sequences that demonstrate that these highly pyramidal, strained, tertiary radicals show a propensity toward oxidative addition to three-coordinate phosphorus (PX_3) greater than that of primary alkyl radicals and similar to that shown by phenyl radicals. In two systems, **1** traps benzyl radicals, which are themselves unreactive toward phosphorus but which as 3-(phenylmethyl)bicyclo[1.1.1]pent-1-yl radicals (**8**) react with **5** and **12**, leading to novel phosphorus-containing products, **10** and **16a**, formed by radical chain processes. Furthermore, radical-induced reaction of phosphonite **13** with **1** gives insertion product **16b** by a process in which 3-substituted bicyclo[1.1.1]pent-1-yl radicals displace primary *n*-pentyl radicals (eq 9).


1

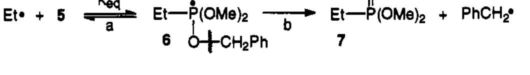
$PhCH_2O\ddot{P}(OMe)_2$ **5**

Recently Michl and co-workers reported[2b] that the 3-(methoxycarbonyl)bicyclo[1.1.1]pent-1-yl radical (**2**) reacts with $(EtO)_3P$ to give phosphonate **4**. Presumably **4** arises via β-scission of phosphoranyl radical **3**. By contrast, we find that *tert*-butyl, isopropyl, and even ethyl radicals, generated by the photolysis of the appropriate azoalkane (0.27 M) in the presence of $(MeO)_3P$ or $(EtO)_3P$ (0.28 M) in degassed benzene at 24 °C, fail to give any phosphorus-containing products. This is consistent with the ESR studies[3] that demonstrate *reversible* formation of phosphoranyl radicals $[(MeP(OR)_3]^\bullet$ from the reaction of $Me^\bullet$ with trialkyl phosphites ($P(OR)_3$). However, alkyl radicals ($R^\bullet$) from β-scission of $[MeP(OR)_3]^\bullet$ were not observed. *Phenyl radicals*, by contrast, are known to react rapidly with $P(OMe)_3$ ($k_p = 3.5 \times 10^8$ M^{-1} s^{-1} [4b,c]) to yield $PhP(O)(OMe)_2$ essentially quantitatively.[4] Their reaction with $(RO)_3P$ is *irreversible* and *strongly exothermic*,[4] presumably due to the high *s*-character of the orbital containing the odd electron and the strength of the bond to phosphorus. Thus, 3-substituted bicyclo[1.1.1]pent-1-yl radicals exhibit a propensity to undergo radical Arbuzov reactions with $(RO)_3P$ parallel to that of phenyl radicals. This can be understood in terms of their being strained, highly pyramidal σ radicals which, like phenyl radicals, form strong bonds to phosphorus in *irreversible* fashion.



2 **3** **4**

In contrast to their unreactivity with $(MeO)_3P$ and $(EtO)_3P$, we observe that ethyl radicals, from photolysis (Kimax) of Et_2N_2 (0.23 M) over 12 h, react readily with benzyl dimethyl phosphite (**5**) (0.23 M) in degassed benzene at room temperature to give $EtP(O)(OMe)_2$ in 90% yield, based on conversion (18%) of **5** (quantitative ^{31}P NMR using tri-*n*-propyl phosphate as an internal standard). We envision this reaction to be a free radical Arbuzov process (eq 1), analogous to that reported for $Me_2N^\bullet$,[5] proceeding



$$Et^\bullet + \mathbf{5} \underset{a}{\overset{K_{eq}}{\rightleftharpoons}} \underset{\mathbf{6}\quad O+CH_2Ph}{Et-\dot{P}(OMe)_2} \xrightarrow{b} \underset{\mathbf{7}}{Et-\overset{O}{\overset{\|}{P}}(OMe)_2} + PhCH_2^\bullet \qquad (1)$$

via the phosphoranyl radical **6** that undergoes *rapid β-scission* to form phosphonate **7** and the stable benzyl radical. For cases of *reversible* radical addition to PX_3, previous work from this laboratory[6c] has identified the rate constant for subsequent α- or β-scission of the phosphoranyl radical intermediate, as in step 1b, as the key factor that determines whether a given radical will give net overall reaction.[6] Isopropyl and *tert*-butyl radicals, however (above conditions), fail to undergo free radical Arbuzov processes with **5**, a result of their greater stabilities and consequently highly unfavorable K_{eq} (eq 1a). Benzyl radicals, generated in the β scission process that yields **7** (eq 1b), also are unable to react with **5** in a process analogous to that for ethyl radicals and instead dimerize to $PhCH_2CH_2Ph$, identified by GLC.

We find, however, that if benzyl radicals formed in a β-scission (as in eq 1b) are trapped by addition to **1**, a novel chain reaction ensues. Thus, UV irradiation (Kimax) at 0 °C for 1 h of a degassed solution of **1**[7] (0.5–0.7 mmol), **5** (1.4 mmol), and bis(phenylmethyl)diazene (BPMDA,[9] 0.03 mmol) in C_6D_6 gives phosphonate **10** in 61% NMR yield (0.23 mmol), based on 28% conversion of **5** (by quantitative ^{31}P NMR) and 45% isolated yield (0.17 mmol).[7] Phosphonate **10** almost certainly arises via chain-propagating steps 3, 4, and 5 following initiation by reaction 2. *The benzyl radical from β-scission of* ***9****, though itself unreactive toward* ***5****, propagates the chain process by converting* ***1*** *into highly reactive* ***8*** (eq 3). When only 0.57 mmol of **5** is used, both **10** (45% NMR

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(1) For recent reviews on the chemistry of small-ring propellanes and the formation of bridgehead free radicals, see: (a) Szeimies, G. In *Advances in Strain in Organic Chemistry*; Halton, B., Ed.; JAI Press Ltd.: Greenwich, CT, 1992; Vol. 2, pp 1–55. (b) Walton, J. C. *Chem. Soc. Rev.* **1992**, *21*, 104–112.

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(4) (a) Fu, J.-J. L.; Bentrude, W. G. *J. Am. Chem. Soc.* **1972**, *94*, 7710–7717. (b) Fu, J.-J. L.; Bentrude, W. G.; Griffin, C. E. *J. Am. Chem. Soc.* **1972**, *94*, 7717–7722. (c) Kryger, R. G.; Lorand, J. P.; Stevens, N. R.; Herron, N. R. *J. Am. Chem. Soc.* **1977**, *99*, 7589–7600.

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(6) For reviews of phosphoranyl radicals, see: (a) Bentrude, W. G. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Sussex, 1990; Vol. 1, pp 531–566. (b) Bentrude, W. G. In *Reactive Intermediates*; Abramovitch, R. A., Ed.; Plenum: London, 1983; Vol. 3, pp 199–298. (c) Bentrude, W. G. *Acc. Chem. Res.* **1982**, *15*, 117–125. (d) Roberts, B. P. In *Advances in Free Radical Chemistry*; Williams, G. H., Ed.; Heyden and Sons: London, 1980; Vol. 6, pp 225–289.

(7) [1.1.1]Propellane[8] was purified by preparative GLC.[2c] Product solutions were analyzed quantitatively by ^{31}P NMR in tubes containing a capillary of 0.32 M $(MeO)_3PO$ in C_6D_6 as external standard.

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(9) For an example of BPMDA photolysis as a source of benzyl radicals, see: Albini, A.; Fasani, E.; Sulpizio, A. *J. Am. Chem. Soc.* **1984**, *106*, 3562–3566. Use of BPMDA also avoids the photo-Arbuzov rearrangement of **5**.[10]

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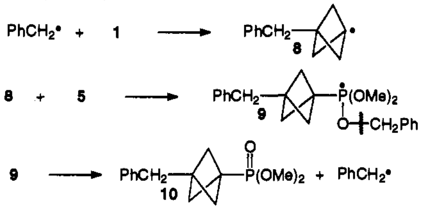
$$\underset{\text{(BPMDA)}}{PhCH_2N{=}NCH_2Ph} \longrightarrow 2\ PhCH_2^\bullet + N_2 \qquad (2)$$

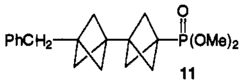


(3)

(4)

(5)

yield, 25% isolated yield) and the bis-adduct **11** (11% NMR yield, 8% isolated yield), from successive reaction of two molecules of **1**, are seen at 77% conversion of **5**. Use of [2,2′-^{2}H]bis(phenylmethyl)diazene, deuterium-labeled to the extent of about 75%, as initiator in the reactions of **5** with **1**, leads to 2–3% incorporation of ^{2}H into **10** (GC/MS). Assuming that labeled benzyl radicals initially form **8** (eq 3) and that subsequent formation of **9** involves only unlabeled benzyl radicals from step 4, an average chain length of 30–50 is estimated for the process of eqs 2–5.



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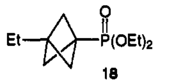

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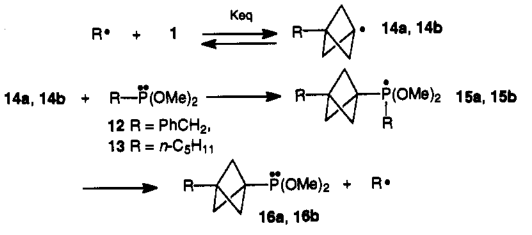
Additional evidence for the high affinity of bicyclo[1.1.1]pent-1-yl radicals for three-coordinate phosphorus is the facile displacement of the relatively stable benzyl radical in a BPMDA-initiated *insertion reaction* of **1** with dimethyl benzylphosphonite ($PhCH_2P(OMe)_2$, **12**) that results in the formation of **16a** (Scheme 1, R = $PhCH_2$). (Conditions similar to those of reaction of **1** with **5**). Phosphonite **16a** was isolated as phosphonate **10** following its oxidation (NMR yield of **10**, 46% at 31% conversion of **12**).

$$\underset{\mathbf{13}}{n\text{-}C_5H_{11}\ddot{P}(OMe)_2} + t\text{-}BuO^\bullet \longrightarrow t\text{-}BuO\ddot{P}(OMe)_2 + n\text{-}C_5H_{11}^\bullet \qquad (6)$$

The energetically favored intermediate phosphoranyl radical **15a** (R = $PhCH_2$) is the key intermediate in the radical chain reaction of **1** with **12**, defined by eqs 7–9.

Scheme 1



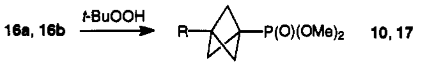
(7)

(8)

(9)

($\mathbf{14a}$ - $\mathbf{16a}$, R = $PhCH_2$, $\mathbf{14b}$ - $\mathbf{16b}$, R = $n\text{-}C_5H_{11}$)

A further example (eqs 6–9, R = $n\text{-}C_5H_{11}$) is the photoinitiated insertion reaction at 0 °C of **1** with $n\text{-}C_5H_{11}P(OMe)_2$ (**13**) (0.67 mmol **13**, 0.5–0.8 mmol **1**, 0.02 mmol di-*tert*-butyl peroxide, 100 μL of C_6D_6, quartz), which yields phosphonite **16b** (R = $n\text{-}C_5H_{11}$). The formation of phosphoranyl radical **15b** (R = $n\text{-}C_5H_{11}$) again is a favored process, and the *weaker* phosphorus–carbon bond *to the n-pentyl group* in **15b** undergoes α-scission to form **16b**. Evidently, the energetically favored process, eqs 8 and 9, is that in which the *tertiary* radical **14b** *displaces a primary radical*, *n*-pentyl, from **13**. Oxidation of **16b** afforded phosphonate **17** (eq 10) in 27% NMR yield (0.12 mmol, based on 69% conversion of **13**) and 12% isolated yield (HPLC). The structures of **10**, **17**,



(10)

and **18** (see below) were identified by their ^{31}P, ^1H, and ^{13}C NMR spectra and HRMS data. Phosphonites **16a** and **16b** were characterized by ^{31}P NMR spectroscopy and conversion to **10** and **17** (supplementary material).

Attempts to carry out an azobisethane-initiated free radical chain reaction *at 0 °C* of **1** with $(EtO)_3P$, under the above conditions, led to formation of waxy polymeric material. However, when near-stoichiometric amounts of azobisethane (0.66 mmol) and **1** ($\sim$1 mmol) in benzene (3.0 mL) in the presence of excess triethyl phosphite (12 mmol) are irradiated with UV light (Pyrex) *at 24 °C* for 12 h, formation of phosphonate **18** is observed (0.15 mmol based on ^{31}P NMR, 0.063 mmol isolated). This reaction involves a chain process identical to that depicted in eqs 3–5, but with an ethyl group in place of benzyl in the phosphoranyl radical intermediate analogous to **9**. Compared to the α- and β-scissions of the chain reactions of **5**, **12**, and **13**, the β-scission of this radical is relatively slow ($k = 3 \times 10^2\ s^{-1}$ at 0 °C from activation parameters[3]) and in our system evidently leads to inefficient chain propagation. Thus, the reaction can proceed only at higher temperatures and requires the use of a large amount of the initiator. The observed formation of polymer from **1** in the reaction at 0 °C likely is initiated in part by the addition of a relatively stable **9**-like radical to **1**, a reaction we have shown to proceed readily with suitably stabilized phosphoranyl radicals.[11]

In summary, we have demonstrated that *3-substituted bicyclo[1.1.1]pent-1-yl radicals have a propensity for oxidative addition to three-coordinate phosphorus similar to that of phenyl radicals*. This behavior reflects the strained, pyramidal nature of the bicyclo[1.1.1]pent-1-yl radical, the high *s*-character in the bridgehead orbital bearing the odd electron,[12] and the strong phosphorus–carbon bond formed between the bridgehead carbon center and phosphorus.[14] The ready interception of radicals by [1.1.1]propellane (**1**) and the reactivity of the 3-substituted bicyclo[1.1.1]pent-1-yl radicals thus formed allow efficient and unusual free radical chain Arbuzov (eqs 3–5) and insertion processes to occur (eqs 7–9) in which novel phosphorus-containing molecules are formed.

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Supplementary Material Available: Experimental details, along with mass spectral and NMR data for all new compounds (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) Dockery, K. P.; Bentrude, W. G. *Abstracts of Papers*, 204th National Meeting of the American Chemical Society; Washington, DC, August 1992; American Chemical Society: Washington, DC, 1992; ORGN 375.

(12) While direct measurements of *s*-character by ESR ^{13}C hfs have not been reported, bridgehead $^1J_{CH}$ values of products reflect high *s*-character (e.g., 33% *s*-character for bicyclo[1.1.1]pentane itself[13]).

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