the major product with bromine, for example, is 1-BrB_5H_8. The derivative chemistry of $C_5H_5BeB_5H_8$ will be discussed more extensively later.

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NMR Evidence for C_3 Ground-State Conformations and Multiple Site Exchange Processes in Systems of the Type *t*-Bu_3MX

Sir:

The chemical consequences of intramolecular crowding in molecules of the type *t*-Bu_3MX have attracted considerable interest. Members in this class of stereochemically correspondent[1] molecules are found, by computational methods (EFF[2-5] and CNDO/2[6]) and gas-phase electron diffraction,[7,8] to possess ground states in which the *tert*-butyl groups are twisted in the same sense and to the same extent, resulting in structures with C_3 symmetry. The methyls on each of the three homotopic *tert*-butyl groups are thus rendered symmetry nonequivalent (diastereotopic). However, although there has been much interest in hindered rotation in these systems, the expected three methyl resonances have hitherto eluded observation under conditions of slow rotation in the variable-temperature NMR spectra.[4,5,9-11] We now report the first such observation in two systems, $[t\text{-}Bu_3PCH_3]^+I^-$ (**1**) and *t*-Bu_3CH (**2**), and present experimental evidence,the first of its kind for a system of the type *t*-Bu_3MX, that **1** undergoes two independent site exchange processes.

The 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of **1**[12] in 5:1 $CHF_2Cl/CHFCl_2$ at −144 °C displays three *tert*-butyl methyl singlets of equal intensity at δ_{Me_4Si} 25.7, 28.8, and 31.2 ppm. With an increase in temperature, the two downfield signals coalesce, and at −109 °C the *tert*-butyl methyl region of the spectrum consists of two sharp singlets in a 2:1 ratio, δ_{Me_4Si} 30.3 and 26.1 ppm, respectively. The calculated barrier ($\Delta G^{\ddagger}_{-138}$)[13] for this process is 6.3 ± 0.8 kcal/mol.[15] With a further increase in temperature, the two remaining singlets coalesce, and at −48 °C the spectrum consists of a singlet for the *tert*-butyl methyl carbons, δ_{Me_4Si} 29.4 ppm, and doublets for the *P*-methyl and quaternary carbons, δ_{Me_4Si} 1.8 ($^1J_{CP}$ = 45 Hz) and 38.5 ppm ($^1J_{CP}$ = 32 Hz), respectively. The calculated barrier ($\Delta G^{\ddagger}_{-72}$)[13] for this second process is 9.5 ± 0.5 kcal/mol.[17,18]

The processes responsible for the two coalescence phenomena may be described in terms of the mechanisms elaborated for analogous permutational rearrangements in the stereochemically correspondent *t*-Bu_3SiH (**3**).[4] Accordingly, the lower energy process, which results in coalescence of two of the three methyl signals, corresponds to an *SSS* mechanism in which each of the *tert*-butyl groups undergoes net conrotation through a staggered (*S*) conformation. The three *tert*-butyl groups librate about an all-staggered C_{3v} structure, and this process thus results in enantiomerization. In the higher energy *ESS* process, one of the *tert*-butyl groups rotates through an eclipsed (*E*) conformation, whereas the other two rotate in the opposite direction through *S* conformations. This pathway, or an alternative topomerization, renders all three *tert*-butyl methyl sites equivalent.[19]

The three diasterotopic methyls in the *tert*-butyl groups of **2** were also found to be observably anisochronous at the slow exchange limit: the 25.2-MHz $^{13}C\{^1H\}$ NMR spectrum of **2**[20] in CF_2Cl_2 at −127 °C exhibits three methyl singlets at δ_{Me_4Si} 26.3, 38.6, and 39.3 ppm. This observation provides the first evidence that the C_3 conformation observed in the gas phase[8] and calculated by a wide variety of force fields[3] also corresponds to the ground state in solution. At −34 °C the methyl carbons exhibit only one singlet at δ_{Me_4Si} 35.1 ppm; singlets for the quaternary and methine carbons appear at δ_{Me_4Si} 39.1 and 65.2 ppm, respectively. Preliminary dynamic NMR studies indicate that the barrier for internal rotation lies between 7 and 9 kcal/mol.[21]

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(12) For the preparation of **1**, see Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1967**, *100*, 692.
(13) Activation parameters were obtained by a least-squares fit to the Eyring equation of the rate data obtained by line-shape analysis using the Saunders program.[14]
(14) The computer program used was adapted from one developed by M. Saunders (see Saunders, M. In "Magnetic Resonance in Biological Systems"; Ehrenberg, A.; Malmström, B. G.; Vänngård, T., Eds.; Pergamon: New York, 1967; p 85).
(15) This value of the free energy is in agreement with $\Delta G^{\ddagger}_c$ = 6.4 ± 0.6 kcal/mol calculated by use of the Gutowsky–Holm approximation[16] for an equally populated, uncoupled AB system with $\Delta\nu$ = 59 Hz and T_c = − 138 °C.
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(17) Although all signals in the ^{13}C NMR spectra of **1** had noticeable temperature-dependent chemical shifts relative to Me_4Si, no change in the chemical-shift *difference* between the *tert*-butyl methyl resonances was seen over a 30 °C range at the slow exchange limit of the higher energy process. Solubility limitations precluded a similar study for the lower barrier; temperature-dependent chemical-shift differences were assumed to be negligible in this instance also.
(18) An analogous coalescence phenomenon for the same process was observed in the variable-temperature 100-MHz $^1H\{^{31}P\}$ NMR spectrum of **1**. The *tert*-butyl methyl singlet, δ_{Me_4Si} 1.51 ppm at −50 °C in 5:1 $CHClF_2$/$CHCl_2F$, is split into two singlets in a 2:1 ratio, δ_{Me_4Si} 1.38 and 1.56 ppm, respectively, at −113 °C.
(19) *EFF* calculations on **1** are precluded by the lack of proper parametrization for tetravalent phosphorus. It is noteworthy, however, that *EFF* calculations predict *three* rearrangement processes for *t*-Bu_3SiCH_3, which is sterically similar and stereochemically correspondent to **1**. The lower energy process (*SSS*), which averages two of the three methyl sites, requires 6.0 kcal/mol.

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The two higher energy processes, both of which have barriers of 9.2 kcal/mol, lead to exchange of all sites. These two processes correspond to an *ESS* mechanism and a topomerization, in which only one of the *tert*-butyl groups undergoes permutational rearrangement (L. D. Iroff, unpublished results).

(20) For the preparation of **2**, see Lee, H.-H. Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1971.

(21) Previously, Bartell and Bürgi[22] had estimated an activation energy of 16 kcal/mol for the enantiomerization of **2**, by use of force-field calculations in which all three *tert*-butyl groups were driven in synchrony so as to maintain C_3 symmetry throughout;[23] "whether a reaction coordinate of lower symmetry exists that corresponds to a lower activation energy was not investigated." [22]

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(23) This approach was necessitated by limitations in the dimensions of the computer program used (Bürgi, H. B., private communication).

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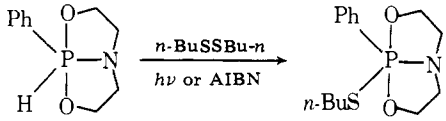
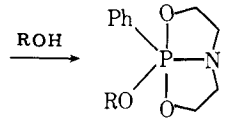
Free-Radical Alkylthiylation of a Pentacovalent P–H Compound

Sir:

The preparation of new pentacovalent phosphorus derivatives (phosphoranes) remains a synthetic challenge, even though molecules of increasingly complex structure have lately been prepared.[1] Among these are various pentacovalent P–H compounds. A recent review[2] tabulated well over 100 such molecules, including a very large fraction of bicyclic and spiro compounds. We report here the radical-initiated conversion of the bicyclic P–H compound **1**[3] to the corresponding PSR derivative **2** in high yields. This represents a hitherto un-



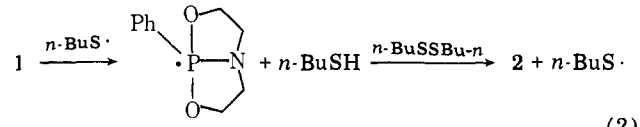
1 **2**



(1)

3, RO = *n*-PrOH
4, RO = EtOH

discovered free-radical chain reaction of such materials, which almost certainly proceeds via the phosphoranyl radical intermediate **5**. Furthermore, the structurally novel phosphorane **2** is not otherwise synthetically accessible. Such a substitution reaction, if general, holds potential promise for the functionalization of the many synthetically available pentacovalent P–H precursors[2] as their PSR derivatives.



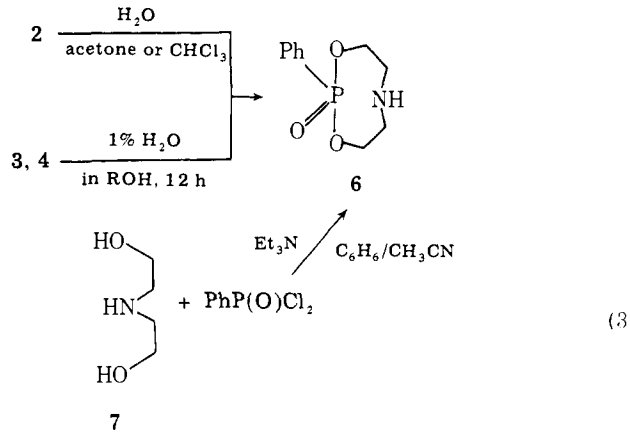
5 (2)

No reaction occurred when **1** and *n*-BuSSBu-*n* were allowed to stand 1 day in the dark at room temperature or overnight at 65 °C. However, when a benzene solution, 0.2 M in both **1** and *n*-BuSSBu-*n*, was irradiated through Pyrex with a medium-pressure 450-W Hanovia mercury lamp, **1** was completely consumed in 30 min in a very clean reaction which gave **2** in 70–80% yield (GLC, hexadecane as internal standard). A completely analogous reaction was initiated thermally at 65 °C by a trace of azobisisobutyronitrile. *n*-Butyl mercaptan was identified in the reaction mixtures but not measured quantitatively.

Pure **2** (>99%) could be isolated by rapid repeated short-column filtration chromatographies on silica gel: ^{31}P NMR δ −29.5[4] (C_6D_6); ^{1}H NMR δ (C_6D_6) 0.78 (3 H, distorted t, J_{HH} = 6 Hz, $CH_3CH_2CH_2CH_2S$), 1.10–1.74 (4 H, m, $CH_3CH_2CH_2CH_2S$), 2.56–2.92 (6 H, m, NCH_2 and $CH_3CH_2CH_2CH_2S$), 3.36–3.90 (4 H, m, OCH_2), 7.13–7.36 (3 H, m, *m*,*p*-C_6H_5), 7.90–8.23 (2 H, m, *o*-C_6H_5P); MS, *m/e* 300 (M^+, 0.7), 210 (M^+ − *n*-BuS, 100); high-resolution MS, *m/e* 210.0676, calcd 210.0684 ($C_{14}H_{23}N_2O_2PS$).

On treatment with a sixfold excess of *n*-PrOH, phosphorane **2** (~0.04 M in C_6H_6) was slowly converted to the alkoxy derivative **3**[5] (δ ^{31}P, −39.4, C_6D_6) in 16 h at room temperature in 65% yield (GLC) at 35% consumption of **2**. Similarly, from reaction with EtOH, derivative **4**[5] (δ ^{31}P, −39.4, C_6D_6) resulted in 72% yield at 65% conversion.

Phosphorane **2** was readily hydrolyzed in a few days in H_2O-saturated $CHCl_3$ or in 10 h in 2% H_2O–acetone at room temperature to the eight-membered ring phosphonate **6** (eq 3). Phosphonate **6** was also formed on hydrolysis of **3** and **4**



(3)

(~70% yields) and on reaction of amino alcohol **7** with $PhP(O)Cl_2$ (70% isolated yield): mp of **6** 57–58 °C (ligroin); high-resolution MS 227.0745, calcd 227.0712 ($C_{10}H_{14}NO_3P$); ^{1}H NMR ($CDCl_3$) δ 2.85 (2 H, d of d of d, CH_2NHCH_2) 3.22 (2 H, d of d of d, CH_2NHCH_2), 3.85–4.62 (4 H, m, OCH_2), 7.53 (3 H, m, C_6H_5P), 7.87 (2 H, m, C_6H_5P), 1.87 (1 H, s, NH).

Although phosphoranyl radicals have been generated previously by alkoxy-radical attack on pentacovalent P–H compounds,[6] the ability of a free radical so unreactive as RS· to abstract hydrogen (reaction 2) suggests that the P–H bond is very weak indeed. Nonetheless, the resulting phosphoranyl radical **5**[7] is sufficiently reactive that attack on disulfide sulfur occurs efficiently even at *n*-BuSSBu-*n* concentrations of 0.2 M and less, and a free-radical chain reaction ensues. The conversion **5** → **2** is the first example of such a displacement process involving a phosphoranyl radical. Whether its efficiency is the result of the known[9] high stability of pentacovalent phosphorus at the bridgehead position of the [3.3.0]bicyclooctane ring system remains speculative. Certain phosphoranyl radicals have earlier been shown to be intercepted by reaction[10] with O_2, by additions to olefinic double bonds,[6,11] and by spin trapping with *t*-BuNO[6] and 5,5-dimethyl-1-pyrroline 1-oxide.[12] Phosphoranyl radicals in which phosphorus is part of a five-membered ring are generally stabilized with respect to α and β scission processes.[6,13] The above thiylalkylation process therefore should be quite generally applicable to the many known spiro and bicyclic pentacovalent P–H compounds.[2,14]

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