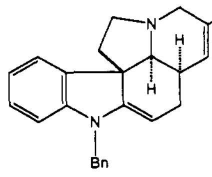

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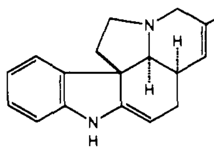

14

of lithium 4,4′-di-*tert*-butylbiphenylide[9] in tetrahydrofuran at −5 °C provided after 1 h an 87% yield of **14**. Installation of the C(3) carbomethoxy group was realized in 35% yield by treatment [−78 °C (30 min) → 0 °C (15 min)] of **14** with lithium diisopropylamide in tetrahydrofuran followed by addition of excess methyl chloroformate at −78 °C and warming to ambient temperature (30 min). The spectral properties (^{1}H NMR, IR, UV, MS) of synthetic pseudotabersonine were found to be identical with those of an authentic sample of (−)-pseudotabersonine.

The synthesis of pseudotabersonine is noteworthy in that it features (1) a novel use of the spiroaziridinium salt **6**, (2) a unique tandem retro Diels–Alder/intramolecular aza Diels–Alder sequence [**7** (R = Bn) → **8** + **9**], and (3) an unprecedented oxindole-based strategy leading to the in situ generation of dehydrosecodine **11**.

Acknowledgment. This investigation was supported by a Public Health Service Research Grant from the National Institute of General Medical Sciences (GM 33605). We are grateful to Professor Martin Kuehne for providing the ^{1}H NMR spectrum of (+)-pseudotabersonine and Professor Jean Lêvy for an authentic sample of (−)-pseudotabersonine.

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[9] Freeman, P. K.; Hutchinson, L. L. *J. Org. Chem.* **1980**, *45*, 1924.

The β-(Phosphonooxy)alkyl Radical Rearrangement[†]

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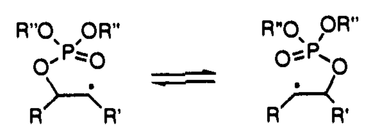
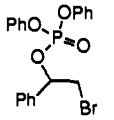
Scheme I



The acyloxy and allylhydroperoxy migrations originally described by Surzur[1] and Schenck,[2] respectively, have been the subjects of much investigation[3,4] over a number of years. We considered that an analogous 1,2-migration of phosphate esters (Scheme I) must exist and present here the results of our experiments which demonstrate that this is indeed the case.[5,6]

Reaction of styrene bromohydrin with diphenyl phosphorochloridate gave the bromo phosphate **1**. Dropwise addition of a benzene solution of tributyltin hydride (TBTH) and 10 mol % of AIBN over 25 h into a solution of **1** in benzene at reflux under nitrogen cleanly gave the reduction product (**2**) and the rearrangement product (**3**) in a ratio of 1:4.[7] Under more concentrated conditions or with more rapid addition of the stannane, greater amounts of the simple reduction product (**2**) were observed; nevertheless, even simple heating of a mixture of **1** (0.025 M) and TBTH (0.05 M) to reflux in benzene with AIBN resulted in the isolation of 23% of **3**. Mindful that **2** could also have arisen by 1,2-migration of the phenyl group, the deuterio analogue (**4**) of **1** was prepared and treated with stannane and AIBN under the optimum conditions determined for **1**, resulting in the clean formation of **5** with no trace of **6** as determined by 300-MHz ^{1}H NMR examination of the crude reaction mixture.[8] Evidently the phosphonooxy migration is significantly faster than a neophyl rearrangement. In a second example, a mixture of the bromo phosphate **7** and TBTH were heated to reflux, with AIBN initiation, in benzene leading cleanly to the rearrangement product (**8**) essentially quantitatively. The difference in rate between this example and the rearrangement of **1** to **3** was marked and probably reflects the imposed favorable orientation both of the first-formed radical and of the scissile benzylic C–O bond.



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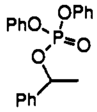

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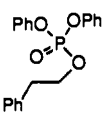

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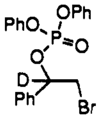

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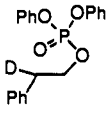

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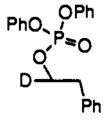

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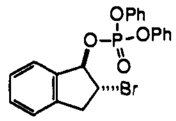

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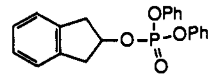

8

A third example was provided by the phosphorylated bromohydrin **9** which reacted with TBTH and AIBN under the standard

---

[†] Dedicated respectfully to Professor Jean-Marie Surzur on his retirement.

[1] (a) Surzur, J.-M.; Teissier, P. *C. R. Acad. Sci. Fr., Ser. C* **1967**, *264*, 1981. (b) Surzur, J.-M.; Teissier, P. *Bull. Soc. Chim. Fr.* **1970**, 3060. (c) Also see: Tanner, D. D.; Law, F. C. P. *J. Am. Chem. Soc.* **1969**, *91*, 7537.

[2] Schenck, G. O.; Neumuller, O. A.; Eisfeld, W. *Liebigs Ann. Chem.* **1958**, *618*, 202.

[3] Acetoxy migration: (a) Beckwith, A. L. J.; Duggan, P. J. *J. Chem. Soc., Chem. Commun.* **1988**, 1000. (b) Beckwith, A. L. J.; Radom, L.; Saebo, S. *J. Am. Chem. Soc.* **1984**, *106*, 5119. (c) Barclay, L. R. C.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1984**, *106*, 1793. (d) Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4399. (e) Korth, H. G.; Sustmann, R.; Gröninger, K. S.; Leisung, M.; Giese, B. *J. Org. Chem.* **1988**, *53*, 4364. (f) Kocovsky, P.; Stary, I.; Turecek, F. *Tetrahedron Lett.* **1986**, *27*, 1513. (g) Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615. (h) Giese, B.; Gröninger, K. S.; Witzel, T.; Korth, H.-G.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 233. (i) Giese, B.; Kopping, B. *Tetrahedron Lett.* **1989**, *30*, 681.

[4] Allylhydroperoxy migration: (a) Brill, W. F. *J. Chem. Soc., Perkin Trans. 2* **1984**, 621. (b) Brill, W. F. *J. Am. Chem. Soc.* **1965**, *87*, 3286. (c) Porter, N. A.; Wujek, J. S. *J. Org. Chem.* **1987**, *52*, 5085. (d) Porter, N. A.; Zuraw, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1472. (e) Beckwith, A. L. J.; Davies, A. G.; Davison, I. G. E.; Maccoll, A.; Mruzek, M. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 815. (f) Davies, A. G.; Davison, I. G. E. *J. Chem. Soc., Perkin Trans. 2* **1989**, 825. (g) Avila, D. V.; Davies, A. G.; Davison, I. G. E. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1847. (h) Mills, K. A.; Caldwell, S. E.; Dubay, G. R.; Porter, N. A. *J. Am. Chem. Soc.* **1992**, *114*, 9689.

[5] To our knowledge the closest analogy to the migrations described herein involves the photostimulated rearrangement of an α-keto phosphite to an enolphosphate: Griffin, C. E.; Bentrude, W. G.; Johnson, G. M. *Tetrahedron Lett.* **1969**, 969.

[6] A related intermolecular process in which methyl and phenyl radicals displace ethyl radicals from triethyl phosphate, when generated in the latter as solvent, has been described by Levin: (a) Levin, Ya. A.; Truteva, E. K.; Gozman, I. P.; Abul'khanov, A. G.; Ivanov, B. E. *Izv. Akad. Nauk SSSR Ser. Khim.* **1970**, 2844. (b) Levin, Ya. A.; Truteva, E. K.; Ivanov, B. E. *J. Gen. Chem. USSR* **1974**, *44*, 1418.

[7] Typical experimental procedure: To a solution of **1** (104 mg, 0.25 mmol) in C_6H_6 (40 mL) at reflux under N_2 was added a solution of TBTH (87 mg, 0.30 mmol) and AIBN (3.5 mg, 0.025 mmol) in C_6H_6 (20 mL) over 25 h with a motor-driven syringe pump. After the reaction was cooled to room temperature, the solvent was removed in vacuo and the residue examined by ^{1}H NMR spectroscopy at 300 MHz. The products **2** and **3** were identified by comparison with the spectra of authentic samples.

[8] The bromo phosphates **1**, **13**, **15** and the glycoside **9** were each recovered unchanged after 24 h at reflux in benzene, indicating that the reactions observed did not occur by an ionic rearrangement to their regioisomers followed by reduction with the stannane.

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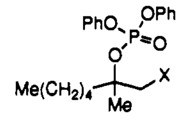
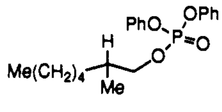
conditions to give the rearrangement product **10** in 75% isolated yield. Examination of the crude reaction mixture indicated complete absence of the simple reduction product **11**. On the other hand, reaction of the bromo phosphate **12** with TBTH and AIBN under the standard conditions led to the clean formation of the simple reduction product **13**, with none of the rearrangement product being observed in the ^{1}H NMR of the crude reaction mixture. Evidently, the rearrangement only proceeds at a measurable rate when it leads to the formation of a relatively stabilized radical.



9 X = Br
11 X = H



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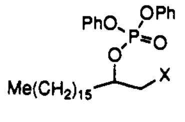
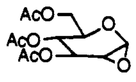


12 X = Br
13 X = H

Finally, Brigl's anhydride (**14**)[9] was opened with thiophenol to give the β-thio glycoside **15**, which on phosphorylation gave the crystalline phosphate ester **16**. Reaction of this species with TBTH and AIBN in benzene at reflux under conditions similar to those described above resulted in the clean formation of triacetyl D-glucal (**17**). The simple reduction product (**18**) was not observed under the dilute conditions used.[4e,10,11] The formation of **17** may be interpreted in terms of a migration of the type outlined in Scheme I to give **19** followed by its rapid in situ decomposition.[12] Alternatively, in the light of the recent report of Giese[13] on related nucleotide radicals, it is possible that the initial anomeric radical expels the diphenyl phosphate anion, giving a radical cation which then evolves into the observed product.



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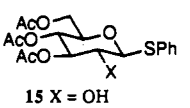
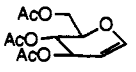


15 X = OH
16 X = OP(O)(OPh)$_2$



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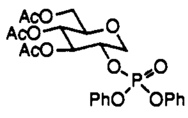

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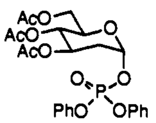
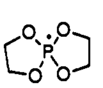


19

Turning to the mechanism of rearrangement, the reaction of **1** and TBTH was conducted in the presence of indene and that of **7** and TBTH in the presence of styrene. Both reactions were clean and in neither case were the crossover products **8** and **3**, respectively, observed. The intramolecular nature of the rearrangement is thus firmly established. As in the case of the acyloxy and allylperoxy rearrangements, where the possibility of 1,3-dioxolan-2-yl and 1,2-dioxolan-4-yl radicals, respectively, as intermediates has been conclusively ruled out, 5-membered cyclic phosphoranyl radicals are probably not intermediates as evidenced by the known stability of inter alia **20**.[14] Rather it is probable that the rearrangements proceed either via a cyclic transition state (**21**) or a tight radical ion pair (**22**).



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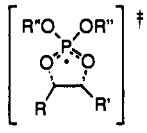

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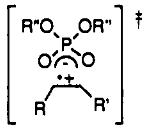

22

The mechanism of this novel rearrangement and the possibility that it plays a role in the degradation of oligonucleotides by free radicals are being actively investigated in this laboratory.

Supplementary Material Available: 300-MHz ^{1}H and ^{13}C NMR spectra in CDCl$_3$ of compounds **1-3**, **7-10**, **12**, **15**, **16**, and **18** (22 pages). Ordering information is given on any current masthead page.

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(9) (a) Brigl, P. *Z. Physiol. Chem.* **1922**, *122*, 245. (b) Lemieux, R. U.; Howard, J. *Methods Carbohydr. Chem.* **1963**, *2*, 400. (c) Halcomb, R. L.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 6661.

(10) The related migration of the 2-acetoxy group on treatment of acetobromoglucose with tributyltin hydride giving 1α,3,4,6-tetraacetyl-2-deoxyglucopyranose has been observed by Giese: Giese, B.; Gilges, S.; Gröninger, K. S.; Lamberth, C.; Witzel, T. *Liebigs Ann. Chem.* **1988**, 615.

(11) An authentic sample of **18**, prepared by reduction of 3,4,6-triacetylglucopyranosyl chloride[9a] with TBTH/AIBN and phosphorylation, was stable under the standard reaction conditions.

(12) The presumed decomposition of **11** to **10** is reasonable in the light of the well-known instability of 2-deoxyglycopyranoside derivatives and, in particular, the anomeric phosphates toward oxenium ion formation: (a) Williams, N. R.; Wander, J. D. In *The Carbohydrates*; Pigman, W., Horton, D., Eds.; Academic Press: New York, 1980; Vol. IB, p 761. (b) Percival, M. D.; Withers, S. G. *Can. J. Chem.* **1988**, *66* 1970.

(13) Giese, B.; Burger, J.; Kang, T. W.; Kesselheim, C.; Wittmer, T. *J. Am. Chem. Soc.* **1992**, *114*, 7322.

(14) (a) Grechkin, N. P.; Gubanova, G. S. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1970**, 2803. (b) Roberts, B. P. *Adv. Free Radical Chem.* **1980**, *6*, 225.

Reactions of Organometallic Complexes with Singlet Oxygen. Photooxidation of Vaska's Complex

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Received October 22, 1992

Singlet oxygen can both react with (k_R) and be physically quenched by (k_Q) substrates. Many organometallic complexes physically quench singlet oxygen in solution;[1] recently, several gold(I) complexes[2] have been shown to do so with high efficiency. It has been suggested by Corey[2,3] and Detty[4] that the quenching by these complexes occurs by electron donor-acceptor interaction between the nucleophilic metal and the electrophilic singlet oxygen and possibly by heavy atom-promoted intersystem crossing by spin-orbit coupling. Corey et al. have suggested an unstable gold(III) peroxy intermediate.[2] However, no products have been isolated, and chemical reaction has not been separated from the total (physical + chemical) singlet oxygen quenching rate constant for the gold complexes. To the best of our knowledge, there are no reports of chemical reactions of singlet oxygen with metal centers in organometallic complexes. We now report the reaction and rate constants for both physical and chemical interactions of singlet oxygen with Vaska's complex, Ir(CO)Cl(PPh$_3$)$_2$ (**1**).

$$\mathrm{A} + {}^3\mathrm{O}_2 \xleftarrow[\mathrm{A}\,(k_Q)]{} {}^1\mathrm{O}_2 \xrightarrow[\mathrm{A}\,(k_R)]{} \mathrm{AO}_2$$

The oxidative addition of triplet oxygen to **1** and related derivatives has been well studied,[5-9] in part because this system is simple and the formation of the peroxide Ir(CO)Cl(PPh$_3$)$_2$O$_2$ (**2**) is reversible. However, we have found that deoxygenation of **2** is principally photochemical. Bubbling argon through a solution of **2** in the dark for 70 h at room temperature gave only 0.7% conversion to **1**, whereas complete conversion occurred within a few minutes upon irradiation with a Cermax 300-W xenon lamp under the same conditions. Although photochemical reductive elimination of H$_2$ is known in some related Ir complexes,[10] this possibility was apparently not taken into account when the kinetic and equilibrium parameters for loss of O$_2$ from the peroxide **2** and its derivatives were determined.[6,8]

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(1) Wilkinson, F.; Brummer, J. *J. Phys. Chem. Ref. Data* **1981**, *10*, 809-999 and references cited therein.

(2) Corey, E. J.; Mehrotra, M. M.; Kahn, A. U. *Science* **1987**, *236*, 68-69.

(3) Corey, E. J.; Kahn, A. U. *Tetrahedron Lett.* **1990**, *31*, 1389-1392.

(4) Detty, M. R. *Organometallics* **1992**, *11*, 2310-2312.

(5) Vaska, L. *Science* **1963**, *140*, 840-841.

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(8) Valentine, J. S. *Chem. Rev.* **1973**, *73*, 235-245 and references cited therein.

(9) Vaska, L. *Acc. Chem. Res.* **1976**, *9*, 175-183.

(10) Ferraudi, G. J. *Elements of Inorganic Photochemistry*; Wiley-Interscience: New York, 1988; pp 184-185.

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