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THE REACTION OF BICYCLIC PHOSPHINE OXIDES, CONTAINING A HINDERED DOUBLE BOND WITH *m*-CHLOROPERBENZOIC ACID

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Abstract—The reaction between *m*-chloroperbenzoic acid and phosphabicyclic phosphine oxides (e.g. 8-phenyl-8-oxo-8-phosphabicyclo[3.2.1]oct-6-ene) was investigated and the structure and stereochemistry of the compounds elucidated. It could be shown that compounds possessing the allyl-P(O) R(or Ar) site, in which the double bond is hindered enough to prevent a usual epoxidation, are oxidised by the peracid to the corresponding phosphinate. Furthermore, when the resulting compounds are still strained the phospinates are unstable. The suggested mechanism for the oxidation is a process similar to the Bayer-Villiger oxidation, which is known for ketones.

In a previous report[1] the great steric hindrance of the C_6–C_7 double bond in 8 - alkyl(aryl) - 8 - oxo - 8 - phosphabicyclo[3.2.1]oct - 6 - enes was described, and the rate of obstruction towards attack of this double bond, by bulky reagents established as: C-3α-H > Ph-P > Me-P > O=P. Among other reactions which were attempted on these compounds, was also the epoxidation with *m*-chloroperbenzoic acid. It could be shown that only the compound possessing the P=O group in the equatorial position (towards the phosphorinane ring) underwent epoxidation, at room temperature. If an alkyl or aryl group were found to occupy the equatorial position, epoxidation occurs only after heating for several days in EtOAc (or other polar solvents) in the presence of great excess of the peracid and even then in low yields, together with other unexpected compounds. In the case of 8 - phenyl - 8 - oxo - 8 - phosphabicyclo[3.2.1]oct - 6 - ene (**1**) the epoxide (**2**) was accompanied by compounds **3** and **4**, the structure of which will be the subject of this report.

Elemental analysis as well as the mass spectra showed that **3** and **4** possess the $C_{13}H_{15}O_3P$ formula, i.e. both contain an additional oxygen atom when compared with epoxide **2**. The IR spectra showed neither OH nor CO groups, which could have been responsible for the additional oxygen. In the NMR spectra of **3** and **4** (Fig 1) four down-field protons were observed (Experimental),

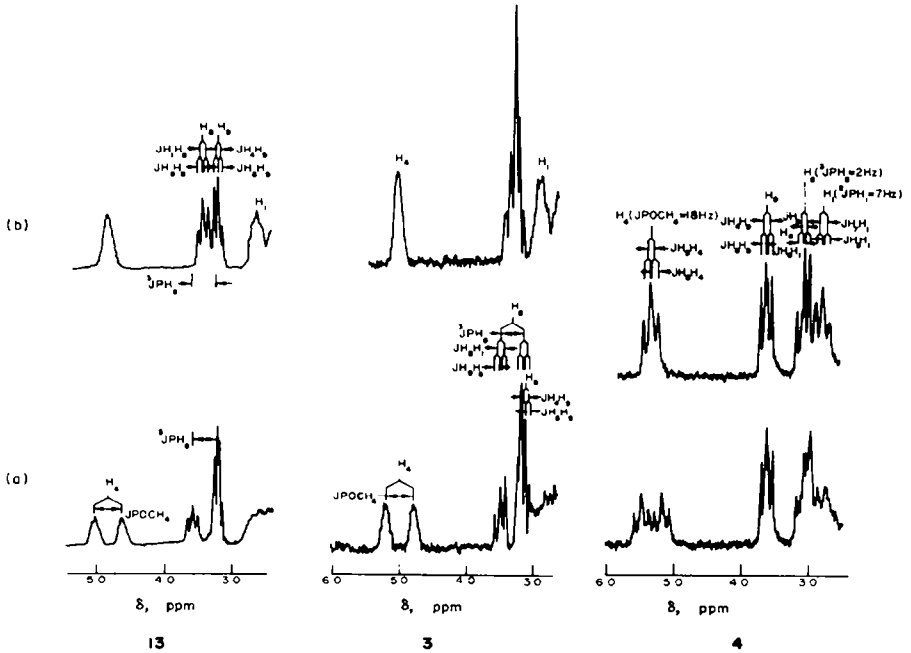
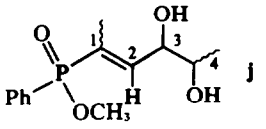


Fig. 1. Partial NMR spectrum of compounds **3**, **4** and **13** (60 MHz). a. normal spectrum b. phosphorus spin decoupled.

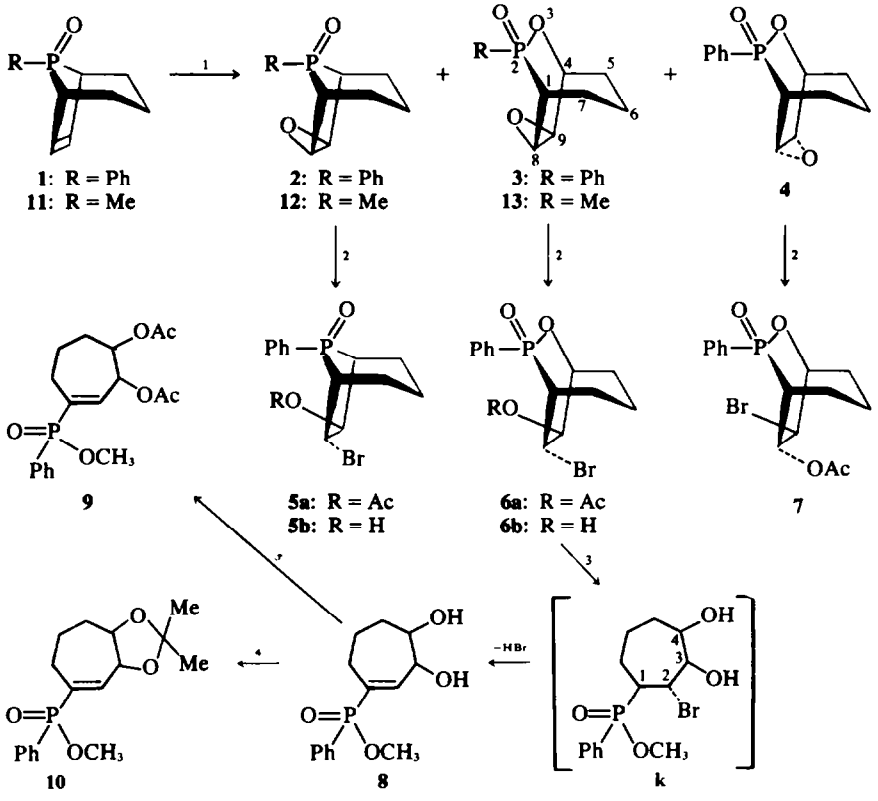
among which the signals at δ3·18 and 3·40 for **3** and 3·05 and 3·59 for **4** may be attributed to protons α to an epoxide moiety, thus suggesting the existence of this site in compounds **3** and **4** as well. To ascertain this possibility the two compounds were submitted to several acidic conditions previously[1] used for the opening of the epoxy ring in compound **2** to give the bromoacetate **5a**, namely a solution of 48% HBr in acetic acid (milder acidic conditions i.e. 7% $HClO_4$ in acetone or BF_3-etherate in benzene, left compounds **3** and **4** as in the case of **2** unchanged). Actually both compounds (**3** and **4**) resulted in bromoacetates **6a** and **7** respectively, as could be seen from the mass spectra, elemental analysis as well as the NMR spectrum (Experimental). As the chemical behaviour and spectral data of **3** and **4**, as well as **6a** and **7**, were very similar, the structure elucidation was carried out on compound **6a** only, this being the one which could be obtained in better yields.

spectrum, from which the following functional moiety (j) could be suggested:



The existence of the signals at δ3·75d (J_{POCH_3} = 11 Hz) and 3·78d (J_{POCH_3} = 11 Hz)* which was unexpected in this NMR, together with the P–Ph signal (7·35–8·0 m; 5H) could be attributed only to a Ph–P(O)OCH_3 group.

Furthermore this functional group must be attached to a double bond whose vinylic proton (H-2) appears as a double doublet at δ6·90 dm ($^3J_{PH_2}$ = 22·5 Hz, being confirmed by a double irradiation experiment) establishing its



SCHEME 1. 1. *m*-chloroperbenzoic acid; 2. 48% HBr–HOAc; 3. 1% KOH–MeOH; 4. $(CH_3)_2CO$, $CuSO_4$; 5. Ac_2O, Pyr.

Submitting the bromoacetate **6a** to mild basic conditions (1% KOH, MeOH), in order to hydrolyse the acetate group, gave the clue compound **8**. Most significant for the structure elucidation of compound **8** was its NMR

*The duplicity of the OMe-group may originate from two possible diastereomers, according to the P-configuration.

β-*cis* position relative to the PhP(O)OCH_3 group.[2] The additional hydroxyl groups in **j**, could be suggested on the basis of the signals at δ4·10 m and 4·58 m; these signals are thus attributed to the C-3, C-4- two vicinal protons in **j**. In order to confirm this assumption a diacetate **9** as well as an acetonide **10** were prepared (Experimental). The C-1, C-4 atoms of the fragment j must be connected by

three additional C atoms to give the original cycloheptanic ring; thus the 3,4-dihydroxycyclohept-1-enyl-phenylmethoxyphosphinate structure is suggested for **8**. Compound **8** is believed to be obtained by HBr-elimination from an intermediate **k** (see scheme 1); the bromine being abstracted from C-2 while the hydrogen comes from the C-1 proton which is expected to be acidic enough for the elimination to occur. The C-3-OH group must therefore be the one derived from the acetate hydrolysis, suggesting the source of the second C-4-OH group to be the third unknown oxygen of molecule **6a** (or **3**). P–C bonds are known to be quite stable under basic conditions, all the more so under the mild conditions used in our case. Compounds **1**, **2** and other related systems remain unchanged even under 10% KOH in MeOH; thus suggesting that some more meaningful changes had already occurred in compounds **3** (and **4**, see below) before the alkaline hydrolysis.

The existence of the P–OMe group after the hydrolysis, together with the second C-4-OH group, originating from the third oxygen of the molecule *vide supra*, suggests that a phosphinate moiety is included in **6a** (and obviously also in **3**), i.e. the phospholenic ring of **1** was altered under the influence of the *m*-chloroperbenzoic acid into the 2-oxo-phosphorinane ring in **3**. Upon hydrolysis this P–O bond undergoes methanolysis to give from one side the P–O–Me group and on the other the hydroxyl. The suggested structure for **3** is therefore a 2 - phenyl - 2 - oxo - 2 - phospha - 3 - oxa - 8,9 - epoxy - bicyclo[3.2.2]nonane.

Further evidence for the phosphinate structure, of **3** (and **4**, **6a** and **7**) could be obtained from the mass spectrum showing strong fragmentations of *m/e* 141 ($PhP(O)(OH)$); 142 ($PhP(OH)_2$) and 143 ($PhPH(OH)_2$)[3] (or *m/e* 79 ($MeP(O)(OH)$); 80 ($MeP(OH)_2$) and 81 ($MePH(OH)_2$) in the case of compound **13**, *vide infra*).

Compound **4**, exhibiting a very similar NMR spectra, as well as the same kind of chemical behaviour, should be a closely related isomer of **3**; most probably differing from **3** only in the configuration around the P-atom and/or the epoxy ring.

In order to elucidate the stereochemistry of compounds **3** and **4** we prefered to start with the stereochemistry investigation of the two bromoacetates **6a** and **7**. These compounds exhibited a more conclusive NMR spectra than the starting epoxides (**3** and **4**) from which they are obtained in a well defined stereochemical process.[4*]

The NMR spectrum of compound **6a** shown in Fig 2, showed three well defined signals at δ4·23, 4·83 and 5·53. Comparison of this spectrum with that of **6b** (the corresponding bromohydrine which is obtained in small amounts during the work-up of **6a**) showed that the signal of **6a** at δ5·53 is the one near the acetate group.

According to a double irradiation experiment, the signal at δ4·83 α-to the bromine atom, could be attributed to the C-8 position, it being vicinal to the C-1 proton appearing at $\delta \sim 2{\cdot}6$.

*Epoxides are known to be opened to the *trans*-diaxial bromoacetates in which the acetate group is attached from the same direction as the original oxygen atom. Furthermore if the system can release strain by fliping to another conformer the *trans*-diequatorial compound can be the end product.

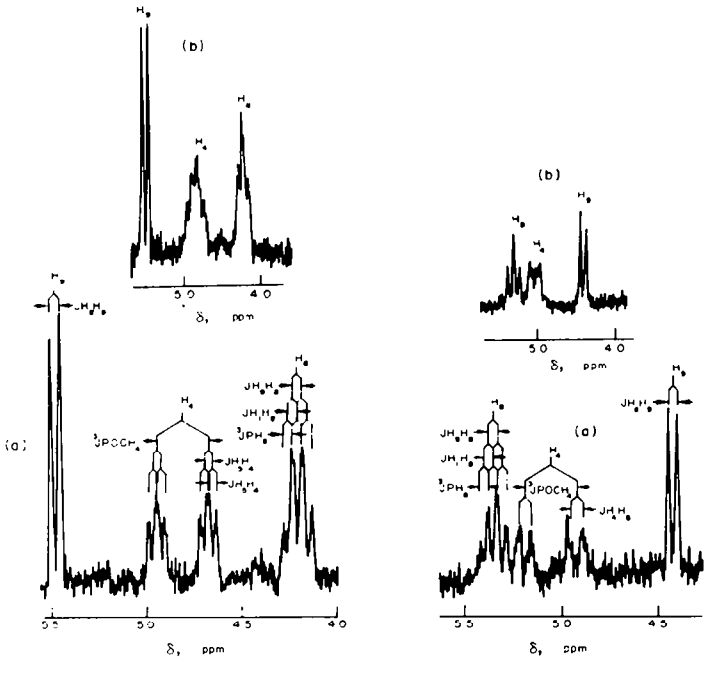


Fig. 2. Partial NMR spectra of compounds **6a** and **7**. a. normal spectra (100 MHz) b. phosphorus spin decoupled (60 MHz).

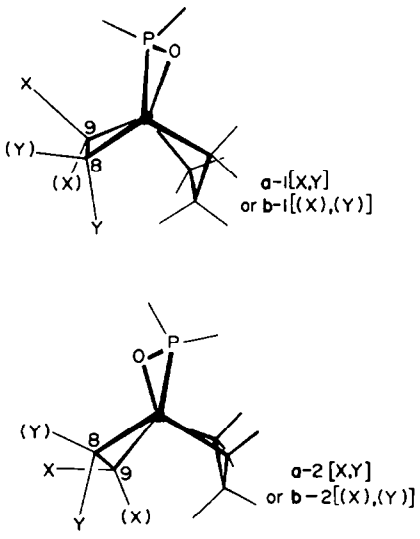


Fig. 3. The four possible structures of the bromoacetates **6a** and **7**. [**6a**, **a**-2(C-8α-Br, C-9β-OAc); **7**, **a**-2(C-8α-OAc, C-9β-Br)].

Two possible configurations for **6a** could be suggested: the C-8α-Br, C-9β-OAc configuration (**a**) and the C-8β-Br, C-9α-OAc one (**b**). Furthermore, closer inspection into the Dreiding models (Fig 3) of these two possible structures (**a** and **b**), shows that each of them can exist in two conformations: **a**-1 (the substituents being diaxial) **a**-2 (the substituents being di-equatorial) **b**-2 (di ax) and **b**-1 (di eq) respectively. The relevant dihedral angles measured from these models, in comparison with the observed J-values are given in Table 1. Upon this correlation it can

Table 1. The dihedral angles for the four possible structures (Fig 3).

φ*	a-1	a-2	b-1	b-2	J of 6a	J of 7
PO,CH_4	140°	160°	140°	160°	27	28
PC,CH_8	90°	65°	145°	180°	5	4
H_1H_8	35°	50°	90°	60°	5	5
H_8H_9	90°	145°	160°	90°	5	5
H_4H_9	60°	85°	75°	30°	0	0

*Dihedral angle.

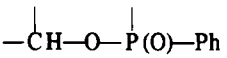
be concluded that **a**-2 (when X = OAc, Y = Br) is the correct structure; this assumption is based on the following data:

1. The $^3J_{PCCH_8}$ value (5Hz) excludes the **b**-1, **b**-2 as well as **a**-1 conformers in which the PC,CH_8 dihedral angles are 145°, 180° and 90° respectively; the latter angles demanding $^3J_{PH}$-values of approximately 28, 35 and 0 Hz respectively.[5]

2. The $J_{H_8H_9}$ value (5Hz) immediately excludes the **a**-1 **b**-2 conformers having a H_8H_9-dihedral angle of 90°, likewise **b**-1 is excluded by the $J_{H_1H_8}$ value, and **a**-1, **b**-2 and most probably also **b**-1, by the $J_{H_4H_9}$-value. (Actually Table 1 together with the δ-values should be sufficient for the structure determination). Obtaining the di-equatorial conformer is not surprising; indeed we believe that the diaxial one is initially obtained during the epoxide ring opening,[5] but in order to release strain, mainly between the 8α-acetoxy and the C-6α-H groups this conformer (**a**-1) flips over to **a**-2.

From the suggested structure of **6a**, the stereochemistry of the epoxide in **3**, namely the *exo*-(β-oriented) one follows immediately.

The NMR spectrum of **7** (Fig 2) resembles to a great extent the spectrum of **6a**, except for the fact that the chemical shifts of C-8-H and C-9-H are mutually exchanged relative to the shifts of the corresponding signals in the spectrum of **6a**. According to the homo and hetero double irradiation experiments it was obvious that in **7** the acetate group is attached to the C-8 carbon and the bromine to the C-9 carbon, vicinal to the



group as opposed to the situation in **6a**. A correlation between the J-values found for this compound with the dihedral angles (in the same manner as described for compound **6a**), (Table-1; when Y = OAc, X = Br) unequivocally established the **a**-2 conformer for **7**- again the less crowded diequatorial isomer. This 8α-acetoxy-9β-bromo-configuration for **7** confirms the *endo*-(α-oriented) structure for the epoxide of **4**.

The four down-field signals, observed in the NMR spectrum of **3** (and **4**), among which three are coupled with the P-atom (Fig 1), were assigned to the C-4, C-9, C-8, and C-1 protons, according to hetero and homo spin decoupling. Very characteristic among these signals, in the spectrum of **3**, is the one attributed to the C-4 (in α-position to a phosphinate oxygen) proton at δ5·0 (J_{POCH_4} = 24 Hz). This coupling constant, together with the $^3J_{PCCH_8}$ value (see below) confirms the *exo* structure suggested for **3**; the J-values are in much better agreement, with a value of 165° in the *exo*-isomer than with a value of 95°–110° found for the corresponding angle in the *endo* isomer (the phenomenon that the J-values in these strained compounds are smaller than the expected ones was already discussed in connection with compound **2**).[1,5]

The NMR of compound **4**, on the other hand, shows J_{POCH_4} and J_{PCCH_8} values of 18 Hz and 2 Hz respectively (see Table 2) being in accordance with the *endo* isomer values. Furthermore, a Dreiding model of **4** suggests the possibility of the existence of the two twisted conformers ("Twist 1" and "Twist 2"-Table 2) in contrast to only one in

Table 2

	Compound 4			Compound 3	
	"Twist 1"	"Twist 2"	J(Hz)[a]	†[b]	J(Hz)[a]
PO,CH_4	125°	170°	18	170°	24
PC,CH_8	95°	110°	2	165°	20

[a] The measured coupling constants.
[b] Only one conformer exists.

the case of 3. According to the values in Table 2 compound 4 may be found in an equilibrium between the two conformers; the J_{POCH_4}-value being smaller than the corresponding one in 3.

Complexation of compound 4 with $Eu(fod)_3$ suggests that the P=O group is oriented towards the epoxide, the α protons of which are mainly shifted by this shift reagent. This means a change in the P-configuration as compared to the starting material 1.

A priori, in the hitherto discussed compounds a chair⇌boat equilibrium can not be excluded. In contrast to the situation in 1 where a boat conformation should involve a strong flagpole interaction, the flip from chair to boat in the phosphinates is expected to be inseparable from a twisting of the P–O bridge, thereby releasing the possible flagpole interaction. Obviously, substituents at C-8 and C-9 will change from the axial to the equatorial position in such a conformational transition, which will render this process more difficult than in their absence.* In this respect compound 3 differs from 4, 6a and 7 as twisting in this molecule is prevented by the oxirane ring.

The above conformational mobility can explain the fact that two epoxides are obtained. The P=O enables epoxidation of the double bond of q (Scheme 2) from the β-direction while the flexibility of the system does not exclude the α-directed epoxidation.

The epoxidation of 8 - methyl - 8 - oxo - 8 - phosphabicyclo[3.2.1]oct - 6 - ene (11) has been shown to result apart from the expected epoxide (12), in an additional product (13) (Fig 1). In view of the above data, compound 13 must be the P-methyl analog of 3, being highly hygroscopic, the use of $Eu(fod)_3$ for complexation experiments was impossible preventing the P-configuration estimation.

The suggested mechanism for all these above described oxidation reactions is shown in Scheme 2.

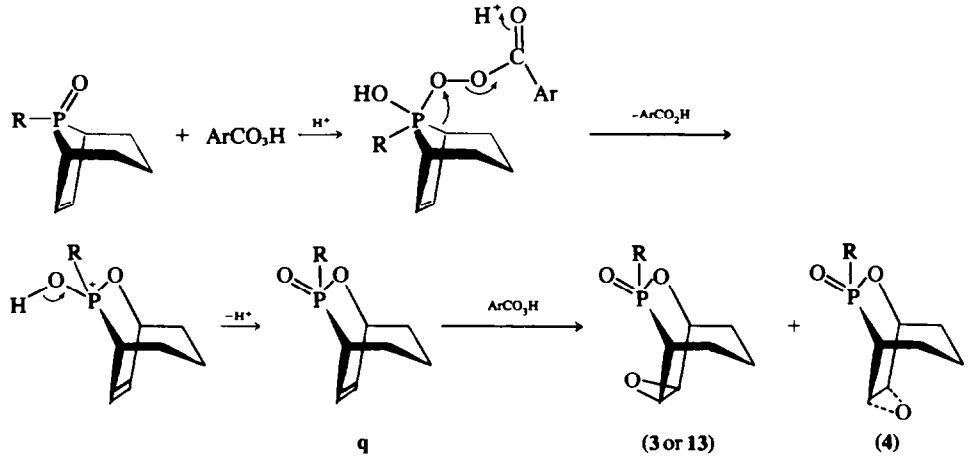
*It is worth while to mention that even if flipping of the oxo phosphepanic ring do occur, the above configurational analysis is firm and abiding.

The phosphorane intermediate in the proposed first step, namely attack of the peracid anion on the phosphoryl group, was already suggested in the case of phosphine oxide oxidations by peracids or peroxides (e.g. diphenylphosphine oxide).[6] In the second step a migration of the C-1 ring atom, to an electron deficient oxygen occurs to give intermediate q. The phosphoryl group is believed to take the place of the carbonyl, in the very similar Bayer-Villiger oxidation.[7] The last step in the synthesis of 3 and 4 is the epoxidation of q from either of its sides to give these epoxides. As far as we know this is the first case reported for such a migration; indeed a Bayer-Villiger oxidation of dialkylphosphonates has already been reported,[8] however in that case the dialkylphosphono group migrates to the carbonyl oxygen.

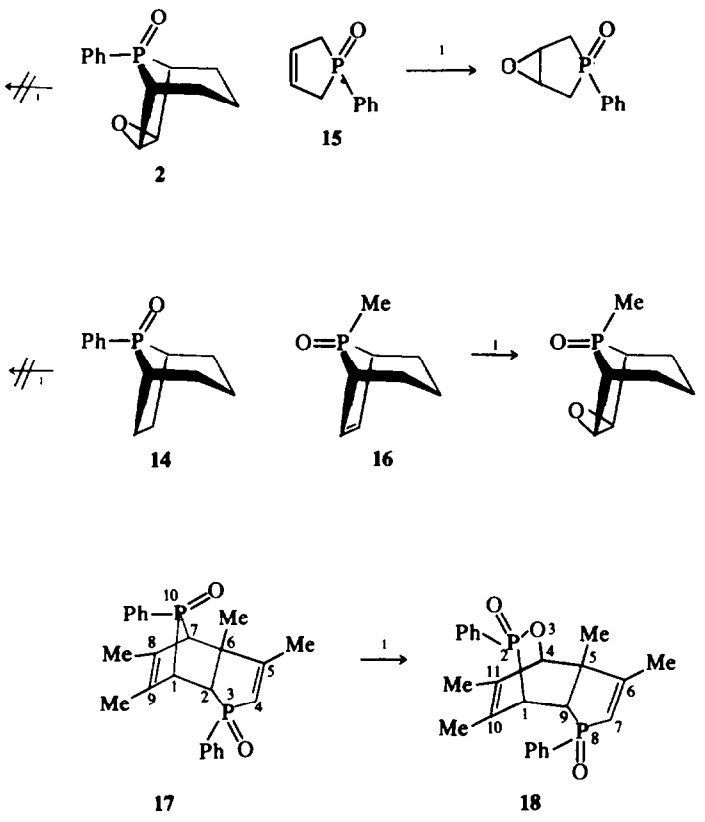
In addition to several experimental requirements i.e. polar solvent and elevated temperatures, known to be favored in the case of the Bayer-Villiger reaction, two structural features are essential: (a) the "migrating" carbon atom must be in an allylic position; compounds 2 and 8 - phenyl - 8 - oxo - 8 - phosphabicyclo[3.2.1]octane (14) did not undergo such rearrangement. (b) the essential double bond must be sterically hindered, otherwise it undergoes a normal epoxidation process, e.g. 3-phospholenes (like 15) and compound 16 gave only the normal epoxides (Scheme 3).

It can be seen that the double bond is indeed necessary, most probably for stabilization of the intermediate carbanion, furthermore this double bond must be sterically hindered to prevent normal epoxidation. A good test case for the above conclusions was the following example.

The 7-phosphabicyclo[2.2.1]heptane system is known to be very strained;[9] it was thus expected that a molecule containing this moiety as well as a double bond fulfilling the above requirements will easily undergo the oxidation. To check this assumption the dimer of 1-phenyl-1-oxo 3,4-dimethylphosphole (17)[10] was tested. The reaction started almost immediately and a phosphinate could be observed, (18). However compound 18 turned out to be



SCHEME 2.



SCHEME 3. 1. *m*-chloroperbenzoic acid.

unstable ($\tau_{1/2} \simeq 3$ hr at r.t.). The fact that **17** undergoes the oxidation may originate from a hindered double bond (by the Ph group, the stereochemistry of which as far as we know has not finally been proved) or from the fact that this molecule is so highly strained. The dissociation process of **18** in respect to other related compounds is described in detail in a following report.

EXPERIMENTAL

For general directions see Ref. 1.

2 - *Phenyl* - 2 - *oxo* - 2 - *phospha* - 3 - *oxa* - 8,9β - *epoxybicyclo*[3.2.2]*nonane and the corresponding* 8,9α-*epoxide* (**3** *and* **4**)

Compounds **3** and **4** were prepared, together with **2**, as was previously described.[1] Compound **3**, m.p. 158°–159° (benzene-hexane), ν_{max}^{KBr} 3030, 3000, 2925, 2900, 2850, 1590, 1480, 1445, 1350, 1300, 1240, 1230, 1210, 1120, 1080, 1060, 1020, 1000, 980, 960, 910, 820, 800, 760, 740, 720, 700, 600, 560, 550 cm^{-1}. Showed the following NMR spectrum: δ1·50–2·80 m (broad, H_5, H_6, H_7; 6H); 2·85 m ($^2J_{PH_1}$ = 6 Hz; $J_{H_1H_8}$ = 5 Hz; H_1); 3·18 dd ($J_{H_8H_9} = J_{H_4H_9}$ = 4 Hz; H_9); 3·40 dd ($^3J_{PH_8}$ = 20 Hz; $J_{H_1H_8}$ = 5 Hz; $J_{H_9H_8}$ = 4 Hz; H_8); 5·0 dm (J_{POCH_4} = 24 Hz; H_4); 7·43 m and 7·75 m (Ph; 5 H). (Found; C, 62·32, H, 6·10; P, 12·25; $C_{13}H_{15}O_3P$ requires: C, 62·34; H, 6·04; P, 12·38%). Mass spectrum (*m/e* (%)): 250, M^+ (75); 249 (9); 222 (19); 221 (37); 218 (10); 182 (16); 180 (78); 167 (17); 159 (38); 156 (26); 143 (27); 142 (50); 141 (55); 125 (24); 124 (10); 77 (100).

Compound **4** m.p. 144°–145° (benzene-hexane); ν_{max}^{KBr} 3040, 2950, 2920, 2860, 1595, 1445, 1350, 1325, 1300, 1280, 1225, 1200, 1165, 1120, 1050, 965, 900, 865, 830, 770, 750, 700, 560, 525 cm^{-1} showed the following NMR spectrum: δ1·50–2·50 m (broad, H_5, H_6, H_7; 6H); 2·75 m ($^2J_{PH_1}$ = 7 Hz; $J_{H_1H_8}$ = 6 Hz; $J_{H_1H_7}$ = 8 Hz; H_1); 3·05 ddd ($^3J_{PH_8}$ = 2 Hz; $J_{H_1H_8}$ = 6 Hz; $J_{H_8H_9}$ = 4 Hz; H_8); 3·59 dd ($J_{H_8H_9}$ 4 Hz; $J_{H_4H_9}$ = 6 Hz; H_9); 5·30 dm (J_{POCH_4} = 18 Hz; $J_{H_4H_9}$ = 6 Hz; $J_{H_4H_5}$ = 7·5 Hz; H_4): 7·48 and 7·78 (Ph; 5H). (Found: C, 62·25; H, 6·00; P, 12·24; $C_{13}H_{15}O_3P$ requires: C, 62·34; H, 6·04; P, 12·38%). Mass spectrum (*m/e*; (%)): 250(43); 221 (19); 183 (22); 182 (39); 181 (38); 169 (47); 143 (31); 142 (38); 141 (29); 125 (17); 124 (7); 77 (100).

Acidic cleavage of compound **3** (**6***a*)

Compound **3** (100 mg) dissolved in 48% HBr/HOAc (1 ml) was kept at r.t. for 24 h. Then crusched ice (200 mg) was added, the soln neutralized (solid $NaHCO_3$) and extracted with $CHCl_3$(5 × 15 ml). The combined extracts were washed once with H_2O, then dried and evaporated to dryness, resulting in a brownish solid product (170 mg); m.p. 162°–163° (methylenechloride-cyclohexane); ν_{max}^{KBr}: 3050, 2960–2870, 1750, 1590, 1450, 1370. 1240, 1220, 1170, 1115, 1075, 1035, 1000, 980, 940, 920, 890, 840, 830, 750, 735, 615, 565, 540, 490 cm^{-1}, δ1·75–2·95 m (broad; H_1, H_5, H_6, H_7; 7H); 2·23s ($OCOCH_3$, 3H); 4·23 m ($^3J_{PH_8} = J_{H_8H_9} = J_{H_1H_8}$ = 5 Hz; H_8); 4·83 dm (J_{POCH_4} = 28 Hz; $J_{H_3H_4}$ = 4 Hz; H_4); 5·53 d ($J_{H_8H_9}$ = 5 Hz; H_9); 7·65 m (2H) and 7·93 m (3H)-Ph. Mass Spectrum (*m/e*(%)): 372/4 M^+ (2); 293 (39); 253 (59); 233 (21); 159 (19); 143 (14); 142 (8); 141 (19); 125 (13); 77 (49); 43 (100);. (Found: C, 48·40. H, 4·85; P, 8·44; Br, 21·25; $C_{15}H_{18}O_4$ PBr requires: C, 48·31; H, 4·88; P, 8·30; Br. 21·42%).

Acidic cleavage of compound **4** (**7**)

Compound **4** (180 mg) was treated with 48% HBr/HOAc (1·5 ml)

under the same conditions described for compound **3**. The product was purified on a neutral Alumina column (Merck III, EtOAc) yielding a viscous hydroscopic, clear oil (38 mg). ν_{max}^{neat}: 3030, 2940–2880, 1750, 1600, 1440, 1370, 1250, 1210, 1110, 1070, 1020, 990, 930, 880, 850, 825, 800, 770, 745, 695, 650, 600, 565, 520 cm^{-1}. Mass spectrum (*m/e*; (%)): 373 (3); 313 (11); 251 (12); 233 (18); 143 (6); 142 (8); 141 (11); 119 (16); 117 (16); 93 (15); 91 (36); 85 (34); 43 (100), δ1·60–2·80 m (H_1, H_5, H_6, H_7, 7H); 2·08s ($OCOCH_3$; 3H); 4·40 d ($J_{H_8H_9}$ = 5 Hz; H_9); 5·05 dm (J_{POCH_4} = 27 Hz; $J_{H_3H_4}$ = 6 Hz; H_4); 5·30 m ($^3J_{PH_8}$ = 4 Hz; $J_{H_9H_8} = J_{H_1H_8}$ = 5 Hz; H_8); 7·50 m & 7·95 m (Ph; 5H) ppm. (Found: M^+ 372/4; $C_{15}H_{18}O_4$ PBr requires: MW 373).

Basic hydrolysis of compound **6a** (**8**)

Compound **6a** (64 mg) dissolved in 1% methanolic KOH (1 ml) was kept at r.t. for 15 h. The neutralized (3% HCl/isopropanol) soln was evaporated under reduced pressure, and the obtained solid boiled in EtOAC (10 ml). After filtration, removing of the solvent, and refiltration through a short alumina column a viscous clear oil was obtained.

Compound **7**; ν_{max}^{neat}: 3450–3200 (broad), 2935–2840, 1640, 1590, 1440, 1200, 1120, 1100, 1060, 1030, 1000, 965, 920, 880, 750, 720, 690 cm^{-1}. Showed the following NMR spectrum: δ1·30–2·70 m (Broad; H_5, H_6, H_7; 6H); 3·75 d ($^3J_{P-OCH}$ = 11 Hz); 3·78 d ($^3J_{POCH_3}$ = 11 Hz); 4·10 m (H_4); 4·58 m (H_3); 6·90 dm ($^3J_{PH_2}$ = 22·5 Hz; H_2); 7·35–8·00 m (Ph, 5H) (Found: M^+ 275; $C_{14}H_{12}O_4P$ requires: MW 275).

Acetylation of compound **8** (**9**)

Compound **8** (16 mg) was dissolved in Ac_2O (0·05 ml) and dry C_6H_5N (0·05 ml). After 24 h the solvents were removed under high vaccum, yielding a yellow viscous oil, δ1·30–2·70 m (broad; H_5, H_6, H_7: 6H); 2·05s ($OCOCH_3$; 6H); 3·75 d (J_{POCH_3} = 11 Hz; P–OCH_3; 3H); 5·20 m (H_4, 1H); 5·70 m (H_3, 1H); 6·70 dm ($^3J_{PH_2}$ = 21 Hz; H_2; 1H); 7·40–8·00 m Ph–H; 5H) ppm.

Acetonide formation from compound **8** (**10**)

A soln of compound **8** (164 mg) in dry acetone (50 ml) was refluxed in the presence of anhyd $CuSO_4$ (1·5 gr) for 36 h. After cooling, the solid was filtered and the solvent removed under reduced pressure. The resulting viscous yellow oil was purified twice on a neutral alumina column ($CHCl_3$), to give a viscous, clear oil (185 mg). ν_{max}^{neat}: 3050, 2975–2830, 1640, 1590, 1460, 1400, 1350, 1200, 1120, 1070, 1020, 995, 950, 900, 870, 835, 800, 755, 725, 700, 650, 620 cm^{-1}, δ1·33s (3H) and 1·45s (3H)-the two acetonide methyls; 1·20–2·40 m (broad: H_5, H_6, H_7; 6H); 3·70 d (J_{POCH_3} = 11 Hz; P = OCH_3) 4·15 m (H_4); 4·95 m ($^4J_{PH_3} \simeq 2$ Hz; $J_{H_4H_3}$ = 7·5 Hz; $J_{H_2H_3}$ = 3 Hz; H_3) 6·55 dm $^3J_{PH_2}$ = 20 Hz; H_2); 7·30–7·90 m (Ph–H; 5H) ppm (Found: M^+ 315; $C_{17}H_{16}O_4P$ requires: MW 315)

2 - *Methyl* - 2 - *oxo* - 2 - *phospha* - 3 - *oxa* - 8,9β - *epoxy* - *bicyclo*[3.2.2.]*nonane* (**13**)

The reaction conditions for the preparation of compounds **13**, obtained together with the epoxide **12**, were previously described.[1]

Compound **13** (was purified on a neutral alumina coulum, (Merck, III, MeOH–EtOAc 5:95) yielding a viscous clear oil. (Hygroxopic) ν_{max}^{neat}; 2930, 2850, 1450, 1370, 1330, 1290, 1240, 1190, 1090, 1060, 1040, 1005, 985, 970, 920, 910, 870,820, 810, 780, 760, 710, 680 cm^{-1}. δ1·50–2·50 m (broad; H_6, H_7, H_5; 6H); 1·80 d ($^2J_{PH}$ = 13·5 Hz; P–CH_3; 3H); 2·65 m (H_1, 1H); 3·20 dd ($J_{H_8H_9}$ = $J_{H_4H_9}$ = 3·5 Hz; H_9; 1H); 3·42 ddd ($^3J_{PH_8}$ = 20 Hz; $J_{H_9H_8}$ = 3·5 Hz; $J_{H_1H_8}$ = 5 Hz; H_8; 1H); 4·84 dm (J_{POCH_4} = 24 Hz; H_4; 1H) ppm. Mass spectrum (*m/e*; (%)): 188 (3); 159 (15); 131 (6); 120 (8); 117 (25); 97 (13); 91 (34); 84 (23); 81 (37); 80 (24); 79 (49); 63 (25); 39 (100). (Found: M^+ 188; $C_8H_{13}O_3P$ requires: MW. 188).

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