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PERMUTATIONAL ISOMERIZATION OF CAGED POLYCYCLIC OXYPHOSPHORANES

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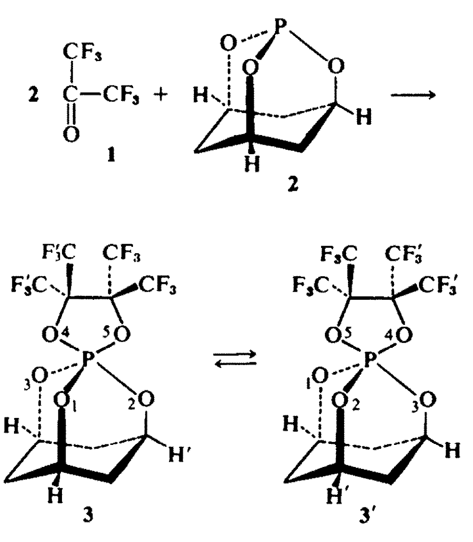
Abstract—The reaction of 1-phospha-2,8,9-trioxaadamantane with hexafluoroacetone gives a crystalline caged polycyclic pentaoxyphosphorane. The ambient temperature fourier transform ^{13}C NMR spectrum of the phosphorane in CH_2Cl_2 solution, with proton noise-decoupling, shows one singlet for three equivalent methine carbons, and one singlet for three equivalent methylene carbons. Hence, the phosphorane undergoes a rapid permutational isomerization, which is confirmed by the observation of equivalency of the three methine protons and of the three groups of methylene protons in the ^1H NMR, and of equivalency of the four CF_3 groups in the ^{19}F NMR. The variable temperature ^{19}F NMR spectra in a vinyl chloride-$CHFCl_2$ solvent system disclose that the permutational isomerization of this phosphorane cannot be prevented even at − 165°, although there is a progressive line-broadening indicative of a decrease in the exchange rate. The ^{31}P NMR spectrum of the phosphorane has a signal at a higher magnetic field ($\delta^{31}P = +42{\cdot}4$ ppm) than H_3PO_4; the shift is nearly identical in CH_2Cl_2 and in the acidic $(CF_3)_2CHOH$. The remarkably low energy barrier (< *ca* 5 kcal/mole) for the permutational isomerization of a compound as constrained as the caged oxyphosphorane is attributed to: (1) A small deviation from the perfect trigonal bipyramidal configuration, which raises the ground state energy. (2) The existence of a barrier configuration which can accommodate the constrains of the caged molecule, and is therefore of relatively low energy. The barrier configuration is deduced from the turnstile rotation mechanism of permutational isomerization.

INTRODUCTION

The first example of a caged polycyclic pentaoxyphosphorane, 3, has been reported in the form of preliminary notes.[2-7] This paper furnishes the experimental data for the synthesis of this compound. The manuscript also provides the experimental details of variable temperature ^{19}F and ^1H NMR of 3, which were given in the preliminary notes[2-7] as the basis for the introduction of a new mechanism of permutational isomerization of trigonal bipyramidal 5-coordinate phosphorus compounds. Moreover, this manuscript provides unpublished additional support for the new mechanism of permutational isomerization, on the basis of ^{13}CFT NMR of 3.



RESULTS

Synthesis of the caged polycyclic oxyphosphorane, 3, and NMR spectra at ambient temperature

Hexafluoroacetone (1) reacts with the adamantanoid phosphite,[8] 2, to give the crystalline oxyphosphorane, 3, in about 70% of the theoretical yield. The ^{31}P NMR spectrum of 3 exhibits the strongly positive chemical shift which is characteristic of molecules with five O atoms covalently bonded to phosphorus.[9,10] Table 1 shows that the ^{31}P shift of 3 is insensitive to the nature of the solvent. This is particularly significant in the case of the relatively acidic hexafluoroisopropyl alcohol.

The addition of limited amounts of water to a solution of 3 has no appreciable effect on the ^{31}P NMR shift, which is another indication of the relatively high degree of stability of this phosphorane. Table 1 includes comparable data for the monocyclic pentaoxyphosphorane, 4, made from trimethyl phosphite and hexafluoroacetone,[11] and for other

Table 1. ^{31}P NMR shifts^{a} of stable and unstable oxyphosphoranes^{b} under various conditions

			∂^{31}P in Anhydrous solvents					∂^{31}P in CDCl$_3$ + 1 Moleq of water	
Compd No	Trivalent phosphorus compound	Carbonyl compound	CDCl$_3$	DMF^{c}	HFIP^{c}	CDCl$_3$ + 0·5 moleq of HFIP	CDCl$_3$ + 1 moleq of HFIP	After 0·5 hr	After 24 hr
3	$C_6H_9O_3P^{d}$	Hexafluoro-acetone	+42·4^{e}	+41·2	+44·1^{f}	+42·3	+42·4	+42·0^{e}	+42·0
4	$(CH_3O)_3P$	Hexafluoro-acetone	+49·7^{g}	+48·9	+48·3^{f}	+49·4	+49·6	+49·9^{g}	+49·8
5	$(CH_3)_2PC_6H_5$	Hexafluoro-acetone	+10·9	—	−96.8^{f,h}	+9·5	+9·0	−41·8^{i}	—
6	$(CH_3)_2PC_6H_5$	Phenanthrenequinone^{j}	+1.5^{k}	—	−85.3^{f,l}	−28·7	−53·4	−39·9^{f,i}	—

[a] ^{31}P shifts in ppm *vs* $H_3PO_4 = 0$, at 25°.

[b] The oxyphosphoranes are made from the reaction of a trivalent phosphorus compound with a carbonyl compound.

[c] DMF = dimethylformamide: HFIP = hexafluoroisopropyl alcohol.

[d] 1-Phospha-2,8,9-trioxaadamantane.

[e] *ca* 0·2M soln.

[f] *ca* 1M soln.

[g] *ca* 2M soln.

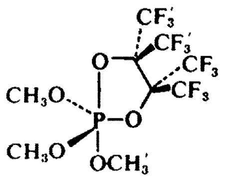
[h] Probable structure: $[(CH_3)_2(C_6H_5)\overset{+}{P}\text{-}O\text{-}C(CF_3)_2OH][(CF_3)_2CH\bar{O}]$.

[i] Probable structure: $(CH_3)_2(C_6H_5)PO$.

[j] The $(CH_3O)_3P$-Phenanthrenequinone adduct has $\partial^{31}P = +44{\cdot}7$ ppm (in CDCl$_3$).

[k] The analogous $(C_2H_5)_2(C_6H_5)P$-phenanthrenequinone adduct has: $\partial^{31}P = -10{\cdot}8$ ppm (in CH$_2$Cl$_2$) but −0·9 ppm (in benzene) showing some ^{31}P NMR solvent dependence.

[l] Acyclic dipolar ion.



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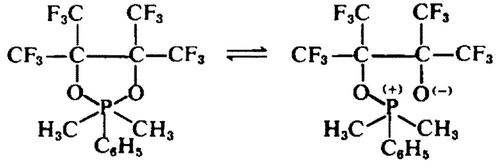
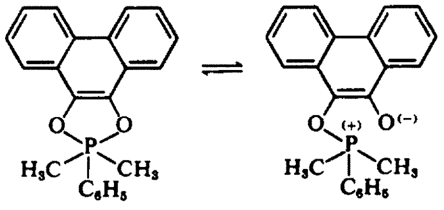


5 **5a**



6 **6a**

related compounds[12] that will becomes pertinent to further discussion, *i.e.*, **5**, **5a** and **6**, **6a**.

The ^{31}P signal of **3** is a quartet with a relatively large[9,10] $\underline{P}OC\underline{H}$ coupling, $J = 28$ Hz. The signal becomes a singlet with $\delta^{31}P = +42{\cdot}6$ ppm when the ^1H is decoupled with a frequency of 1022000 Hz. The ^{31}P signal of the precursor phosphite **2** appears as a singlet at $\delta^{31}P = -136{\cdot}4$ ppm, under the same ^1H decoupling frequency.

The fourier transform ^{13}C NMR spectrum of the caged oxyphosphorane can be determined in CH_2Cl_2 solution at ambient temperature, with proton noise-decoupling.* The spectrum shows one singlet for three equivalent methine carbons $(\dot{C}H)$, with a chemical shift of $-24{\cdot}5$ ppm downfield from internal CH_2Cl_2. The spectrum also shows one singlet for three equivalent methylene carbons $(\dot{C}H_2)$, with a chemical shift of $+20{\cdot}5$ ppm upfield from internal CH_2Cl_2.

The chemical shift of the methine carbons $(\dot{C}H)$ of the phosphorane **3** is displaced $-10{\cdot}6$ ppm to lower field, while the shift of the methylene carbons, $(\dot{C}H_2)$ is displaced $+3{\cdot}1$ ppm to higher field, relative to the shifts of the respective carbons of the phosphite ester, **2**.

The ^{19}F NMR spectrum of the phosphorane **3** in CH_2Cl_2 solution shows one sharp and very narrow doublet, $J_{\underline{F}CCO\underline{P}} = 0{\cdot}3$ Hz with $\delta^{19}F = -9{\cdot}5$ ppm (*vs* $CF_3COOH = 0$) for twelve equivalent fluorines.

The ^1H NMR spectrum of **3** in $CDCl_3$ has one doublet, $J_{\underline{H}CO\underline{P}} = 28{\cdot}0$ Hz with $\tau = 5{\cdot}00$ ppm due to three equivalent methine protons. There are also signals centered at $\tau = 7{\cdot}20$ and $8{\cdot}26$ ppm for three groups of equivalent methylene protons.

It is concluded from these data that the caged phosphorane **3** undergoes a relatively rapid positional exchange of ligands at ambient temperature, as indicated in formulas $\mathbf{3} \rightleftharpoons \mathbf{3'}$.

Variable temperature ^{19}F NMR spectra. The solvent system 70% vinyl chloride + 30% $CHFCl_2$ permits† the study of the ^{19}F NMR spectra of the caged oxyphosphorane **3** from ambient temperature to − 165°. The data are summarized in Table 2. It is concluded that the energy barrier for the positional exchange of ligands is very low, probably less than 5 kcal/mole and, therefore, the exchange process cannot be prevented even at − 165°. One can, however, observe a progressive line-broadening at low temperatures, which is consistent with a decrease in the rate of the exchange.

Variable temperature ^1H NMR spectra. No significant changes are noted in the ^1H NMR spectra of $CDCl_3$ solutions of the oxyphosphorane **3** in the temperature range + 30° to − 50° allowed by solubility considerations. In general, proton chemical shift differences are much smaller than ^{19}F chemical shift differences. In view of the results of the variable temperature ^{19}F NMR study, no further efforts were made to develop a solvent system‡ which would permit observations of ^1H NMR spectra at the lowest temperature allowed by the instrument.

DISCUSSION

The NMR data show conclusively that at ambient temperature the ligands in the caged pentaoxyphosphorane, $\mathbf{3} \rightleftharpoons \mathbf{3'}$, undergo a relatively rapid exchange among the skeletal positions of a slightly

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*The pertinent operational data are: R. F. Frequency = 55·3330 MHz; Spectral width = 10,000 Hz; acquisition time = 0·4 sec; pulse width = 7 μsec; K-transient = 21·954. Carbons other than those in the adamantanoid moiety were not observed.

†Solubility considerations prevent the study of the variable temperature ^{19}F NMR spectra of **3** in pure vinyl chloride down to − 155°; hence, the statements concerning the coalescence temperature and the changes in the ^{19}F NMR signal which appear in Refs 3*b*, 4*b*, 5*b*, 6*b*, and 7*b* are incorrect. The observations at temperatures above *ca* −50° reported in those references, 3*b*–7*b*, and the inferences therefrom, are correct.

‡The results of an initial examination of the variable temperature ^1H NMR spectra of **3** in the solvent system 3 : 1 $SO_2 : CF_2Cl_2$, in the range − 50° to − 155°, are in error. The statement concerning the coalescence temperature which appears in Ref 5*b* is therefore incorrect. The observations made above *ca* − 50° are correct.

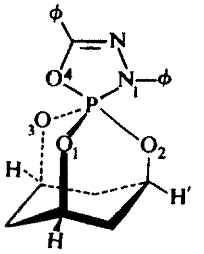
Table 2. Variable temperature ^{19}F NMR spectra of the caged polycyclic pentaoxyphosphorane, 3[a]

Temp	Oxyphosphorane frequency, Hz	Lock frequency,[a] Hz	Δ, Hz
Ambient	3143·2	2495·4	−647·8
−92·5°	3079·3	2495·7	−583·6
−112·5°	3069·3	2495·4	−573·9
−124·5°	3069·5	2495·7	−573·8
−148°	3176·0	2495·7	−680·3
−150°	3184·7	2495·5	−689·2
−155°	3188·9	2495·6	−693·3
−165°	3176·0	2495·7	−676·8

[a] Solvent: 70% vinyl chloride + 30% $CHFCl_2$.
Internal standard: $CF_3COOC_2H_5$. R.F. frequency: 94·1 MHz; sweep width: 1000 Hz; sweep time: 500 sec.

distorted TBP.* This is the geometry of the closely related caged tetraoxyazaphosphorane 7 as revealed by X-ray crystallography.[13] It is inconceivable that the observed equivalency of the methine carbons and hydrogens, and of the trifluoromethyl fluorines, are, in all cases, the result of accidental coincidences of the respective chemical shifts.

The direct observation of the temperature at which the equivalent methine and methylene proton signals, and the equivalent trifluoromethyl fluorine signal, should split as expected for a "frozen", more or less distorted TBP,* could not be achieved. Nevertheless, the progressive line-broadening of the low temperature ^{19}F spectrum is a good indication that the phenomenon of PI* does indeed occur in the caged phosphorane 3. The exact determination of the energy barrier for this PI* is beyond the present range of NMR studies. However, that barrier must be very low indeed, probably less than 5 kcal/mole.



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$\delta^{31}P = +56\cdot8$ ppm (CH_2Cl_2)
$\tau_{CH} = 5\cdot26$ ppm($CDCl_3$)
$J_{HCOP} = 26\cdot0$ Hz

The exchange of ligands between the coordination sites of TBP* five-coordinate phosphorus compounds can occur by intramolecular bond deformation processes ("regular processes"), or by breaking and making of bonds ("irregular processes")[2-7] There are several conceivable types of irregular ligand exchanges,[14-18] and some of them have actually been observed. The sum total of several observations strongly suggest, although do not rigorously prove, that the ligand exchange in 3 occurs by an intramolecular bond deformation or regular process. First, note the insensitivity of the ^{31}P NMR shift to the nature of the solvent; Table 1. Hexafluoroisopropyl alcohol is relatively acidic and should affect the ^{31}P shift if there were dipolar ions with 4-coordinate phosphorus in equilibrium with the pentaoxyphosphorane structure. This effect is indeed observed in the case of the less stable dioxyphosphorane, 5, 5a, made from the reaction of dimethylphenylphosphine with hexafluoroacetone.[12] In this case, the shift is strongly displaced toward lower magnetic field as the equilibrium is shifted toward the open dipolar form by solution in the alcohol. The same phenomenon is observed in the dioxyphosphorane, 6, 6a, made from dimethylphenylphosphine and phenanthrenequinone.[12] On the other hand, the ^{31}P shift of the pentaoxyphosphorane 4 made from trimethyl phosphite and hexafluoroacetone[11] is insensitive to the nature of the solvent (Table 1).

The second piece of evidence against the occurrence of facile bond ruptures in the caged phosphorane 3, and in its monocyclic analog 4, is their lack of reactivity toward water under conditions which cause the immediate decomposition of the less stable dioxyphosphoranes 5 and 6; *cf* Table 1.

Finally, the energy barrier involved in the PI* of 3 is simply too low to be accountable for in terms of bond ruptures. For example, an energy barrier of at least 25 kcal/mole has been estimated for an intermolecular exchange of ligands between two different pentaoxyphosphoranes.[14]

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*The following abbreviations will be used in the Discussion: TBP = trigonal bipyramid or trigonal bipyramidal. PI = Permutational Isomerization. BPR = Berry pseudorotation mechanism. TR = Turnstile rotation mechanism.

An examination of molecular models reveals that the regular PI* of the caged phosphorane **3** cannot be carried out according to the Berry pseudorotation mechanism.[19]† The equatorial oxygens of the adamantanoid cage cannot function as the pivot in BPR.* As the 180° diapical angle is forced to contract toward the required 120°, the apical adamantanoid oxygen is pulled in one direction, while at the same time one equatorial adamantanoid oxygen is being pulled in the opposite direction by the expansion of the 120° diequatorial angle toward the required 180°. Since those two oxygens, together with the pivot oxygen form part of the adamantanoid cage, the motions of the BPR[16] mechanism are forbidden in **3**. Moreover, the equatorial oxygen of the five-membered ring cannot be the pivot in BPR* because this would require placing one ring of the adamantanoid cage in a diapical position.

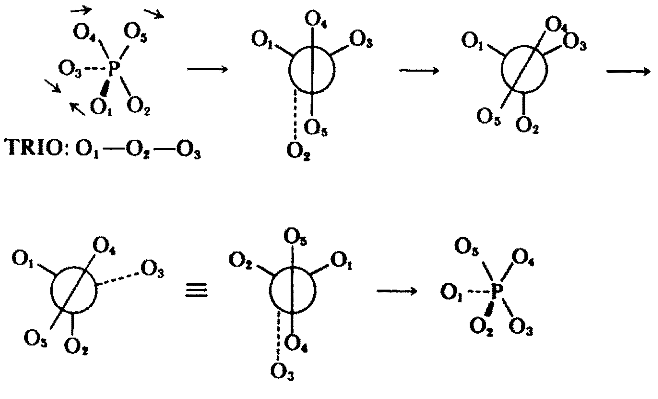
The occurrence of the extraordinarily rapid regular PI*, $\mathbf{3} \rightleftharpoons \mathbf{3'}$, can be explained by the turnstile rotation[2-7] mechanism, as shown in Scheme 1. The two 5-membered ring oxygens, O(4) and 0(5), function as the "pair", and the three caged oxygens, O(1), O(3) and 0(2), function as the "trio". In the TR* illustrated in Scheme 1, the trio-equatorial O(1) will remain equatorial in the new permutational isomer. The following motions occur simultaneously as the system moves toward the barrier configuration.

The diequatorial angle of the trio, O(1)-P-O(3) contracts from 120° to approximately 90°, while the pair, O(4), O(5) tilts as a unit approximately 9° toward the trio-apical O(2). Simultaneously, there is an internal rotation of the pair relative to the trio, which can be illustrated by means of the Newman projections in Scheme 1. In the internal rotation, the pair-equatorial O(5) points toward the trio-equatorial O(1) that will remain equatorial. The internal rotation reaches 30° at the barrier configuration, and 60° at the completion of the TR.* Past the barrier there is a simultaneous tilt of the pair, O(4), 0(5), away from the ligand that will become apical in the new permutational isomer; also, there is a simultaneous expansion of the angle that will become a new diequatorial angle, O(1)-P-O(2). The net result of these motions is to generate a new permutational isomer in which the pair, O(4), O(5), has exchange positions on the skeleton, while the trio, O(1), O(3), O(2) have *apparently* described the motions of a turnstile.‡

In the caged phosphorane **3**, the establishment of a TBP* arrangement of the phosphorus valencies involves a certain amount of distortion of the adamantanoid cage, and this requires some energy. This energy is released as the TBP* goes over into the 30°-TR barrier configuration, where the adamantanoid moiety possesses C_{3v} local symmetry. An idealized model of the 30°-TR barrier for **3** is depicted in Fig 1. The remarkably low energy barrier which accounts for the rapid PI* of **3** is due, in this hypothesis, to a relatively energetic distorted TBP* and to a favorable 30°-TR barrier configuration.

These ideas are consistent with the results of an X-ray crystallographic analysis[13] of the caged tetraoxyazaphosphorane, **7**. The main deviations from the idealized D_3h skeletal symmetry in **7** are as follows. (a) The O(1)-P-O(3) angle is 106·2 rather than 120°; this is the angle that contracts in the TR mechanism. (b) The O(4)-P-O(2) angle is 169·8° rather than 180°, and the N(1)-P-O(2) and N(1)-P-O(4) angles are, respectively, 86·4° and 83·8°, rather than 90°. These deviations are in the direction of the tilting of the pair in the TR mechanism.

The binding energies of various configurations of the PF_5 molecule related to the TR mechanism have been calculated by the CNDO/2 approximation of the MO-LCAO method.[5,6] The most stable 30°-TR barrier configuration model has an 85°F-P-F angle



SCHEME 1

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*See footnote on previous page.

†The extensive literature on the Berry pseudorotation mechanism has been thoroughly reviewed in Refs 2–7.

‡The reorientation in space of one of the Newman projections in Scheme 1 is not an integral part of the TR process, but a convenient device to produce a new permutational isomer with the same skeletal space orientation as in the original drawing.

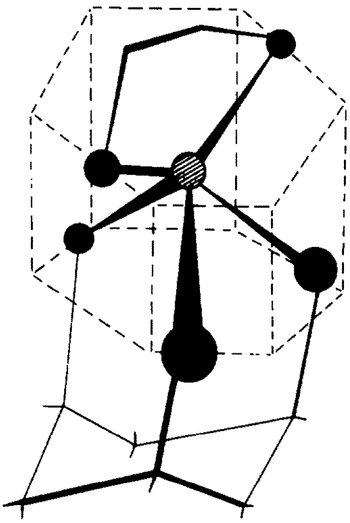

Fig 1. Model of the 30°-TR barrier situation in the adamantanoid oxyphosphorane, 3. ● = Oxygen, ⊜ = Phosphorus.

for the pair, and three 95° F-P-F angles for the trio. The angles observed for the azaphosphorane molecule 7 in the crystals are: N(1)-P-O(4) = 83·4° (the "pair"), and the set: O(1)-P-O(3) = 106·2°, O(1)-P-O(2) = 97·1°; O(2)-P-O(3) = 98·4° (the "trio"). From these data it would appear that the molecule **7**, and presumably the related **3**, need only some relatively minor adjustments to reach the 30°-TR barrier.

The value of the ^{31}P and the ^{19}F NMR of the polycyclic oxyphosphorane **3** and of its monocyclic analog[11] **4** are very similar. Moreover, as shown in Table 1 the monocyclic oxyphosphorane **4** discloses also a remarkable lack of sensitivity of the phosphorus NMR shift to the nature of the solvent and even to the addition of limited amounts of water to its solutions. The proton NMR spectrum of **4** has been followed to − 100° without significant changes. It thus appears that the oxyphosphoranes **3** and **4**, which are derived from the reactions of hexafluoroacetones with phosphide esters undergo relatively rapid regular permutational isomerizations whether or not the phosphide esters are acyclic or polycyclic.

EXPERIMENTAL

Elemental analysis are by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1-*Phospha*-2,8,9-*trioxaadamantane* (**2**). The phosphite, m.p. 200–203° (after sublimation at 100–110°, 0·05 mm) was made in 58% of the theoretical yield by the procedure in the Lit using triethylamine in CH_2Cl_2 as solvent. The phosphite had $^{31}P = -136{\cdot}5$ ppm; $\tau = 5{\cdot}76$ ppm, $J_{\underline{H}COP} = 6.3$ Hz (methine H): $\tau = 7{\cdot}10$ and $8{\cdot}07$ ppm, $H_{\underline{H}C\underline{H}} = 14$ Hz (methylene H), in agreement with the values given by Verkade *et al.*[8]

Reaction of hexafluoroacetone (**1**) *with* 1-*phospha*-2,8,9-*trioxaadamantane* (**2**). Hexafluoroacetone (3·6 ml) was added to a suspension of **2** (1·6 g) in methylene chloride (30 ml), kept at − 75°, under N_2. After 2 h at − 75°, the mixture was allowed to reach 20° within 2 h. The solvent was evaporated at 40° (20 mm) and the residue was recrystallized from methylene chloride to give **3** in 70% of the theoretical yield, m.p. 166°-dec.

Found: C, 29·2; H, 1·9; P, 6·4. Calc for $C_{12}H_9O_5PF_{12}$: C, 29·4; H, 1·8; P, 6·3%.

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