Reactions of t-Butyl Peroxy Esters. X. Preparation of Dialkyl t-Butyl Phosphates from Dialkyl t-Butylperoxy Phosphates, Dialkyl Phosphorochloridates, and Dialkyl Phosphorochloridites[1]

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Dialkyl t-butyl phosphates (1, R = Me, Et, i-Pr) are produced in low yield by the reaction of the corresponding dialkyl t-butylperoxy phosphines (2) with triphenylphosphine (4), and by the reaction of the corresponding dialkyl phosphorochloridites (8) with t-butyl hydroperoxide (7) in the presence of pyridine. Esters 1 (R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, Ph, PhCH₂) are produced in high yield by the reaction of the corresponding dialkyl phosphorochloridates (6) with potassium t-butoxide at 8–10° under anhydrous conditions.

Although alkoxy derivatives of phosphorus are, in general, quite stable, t-butoxy derivatives are usually unstable and their preparation has often presented difficulty.[2] A survey of the literature reveals that the majority of the work reported on t-butoxy derivatives of phosphorus deals with di- and tri-t-butoxy phosphorus compounds.[2f–h,3]

As part of another investigation, it was of interest to develop a general method for the preparation of dialkyl t-butyl phosphates (1, R = alkyl). The literature survey showed that only two compounds of this type (1, R = Me, Et) have been prepared,[4] the rest of the

$$(RO)_2P(O)OCMe_3$$
1

reported mono-t-butoxy phosphorus compounds being either derivatives of trivalent phosphorus[3i,5] or other derivatives of pentavalent phosphorus.[3h–k,4a,6]

During our investigation of the decomposition of di-n-butyl t-butylperoxy phosphate (2, R = n-Bu), a product was suggested to be 1 (R = n-Bu).[7] It was of interest, therefore, to synthesize this compound for verification of its structure.

$$(RO)_2P(O)OOCMe_3$$
2

The reduction of peroxy esters of carboxylic acids (3) to the corresponding esters by triphenylphosphine (4) has been described.[8]

$$RC(O)OOCR'_3 + Ph_3P \longrightarrow RC(O)OCR'_3 + Ph_3P(O)$$
3   4   3   5

R = alkyl, aryl, aralkyl; R' = alkyl

As part of a general investigation of the chemistry of 2, an attempt was made to prepare 1 (R = n-Bu) by the reaction of the corresponding peroxy phosphate (2, R = n-Bu) with 4. However, since our previous experience had shown that, in homologous series of dialkyl phosphorochloridates, dialkyl phosphates, tetraalkyl pyrophosphates, and dialkyl t-butylperoxy phosphates, the di-n-butyl member of the series is usually the most difficult to handle, the investigation was commenced on other peroxy phosphates which had proved to be more stable. Thus, the reaction of 2 (R = Me, Et, i-Pr) with an ethereal solution of 4 gives 5 and the corresponding dialkyl t-butyl phosphate 1 in 9 to 36% yields.

$$(RO)_2P(O)OOCMe_3 + 4 \longrightarrow (RO)_2P(O)OCMe_3 + 5$$
2   1

R = Me, Et, i-Pr

Removal of 5 and unreacted 4 from the reaction mixture presents difficulty. Filtration and column chromatography on neutral alumina remove only a portion of 4 and 5. In the cases of 1 (R = Me, Et, i-Pr) the esters are stable enough so that distillation in the presence of 4 and 5 is possible. When esters 1 (R = n-Bu, i-Bu) are distilled in the presence of 4 and 5 the esters decompose and intractable residues are obtained. Thus, it appears that although 1 (R = Me, Et, i-Pr) can be prepared in low yield by the reduction of the corresponding 2 with 4, esters 1 (R = n-Bu, i-Bu) cannot be prepared by this method.

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In order to circumvent the purification difficulties encountered in the reactions with **4**, other reducing agents for peroxides were investigated. Although several methods for the reduction of various types of carbon peroxides have been developed,[9] little is known about the reduction of organometallic and organometalloid peroxides.[10] For example, reduction of trimethyl-(*t*-butylperoxy)silane[11] and unsymmetrical tin peroxides[12] with sodium sulfite have been reported. Reaction of **2** (R = *i*-Pr) with anhydrous sodium sulfite at 35° for 24 hr does not proceed, and the peroxy phosphate is recovered in high yield. The reaction of **2** (R = *i*-Pr) with sodium bisulfite in refluxing carbon tetrachloride for 2 hr produces **1** (R = *i*-Pr) only in trace amounts. Prolonged reaction times and elevated temperatures effect no improvement in yield. Thus, this reduction method is not applicable to this type of phosphorus peroxide.

The preparation of dialkyl *t*-butylperoxy phosphates (**2**) by the reaction of the corresponding dialkyl phosphorochloridates (**6**) with *t*-butyl hydroperoxide (**7**) in the presence of pyridine has been described.[13]

$$(RO)_2P(O)Cl + Me_3COOH \xrightarrow{\text{pyridine}}$$
$$67$$

$$(RO)_2P(O)OOCMe_3 + Py \cdot HCl$$
$$2$$

R = alkyl, Ph, PhCH$_2$

However, the analogous reaction of dialkyl phosphorochloridites (**8**, R = Me, Et, *i*-Pr) with **7** in the presence of pyridine produces the corresponding dialkyl *t*-butyl phosphate (**1**) and tetraalkyl pyrophosphate (**9**) instead of the trivalent peroxide (**10**).

$$(RO)_2PCl$$
$$8$$
$$+ \xrightarrow{\text{pyridine}} (RO)_2P(O)OCMe_3 + (RO)_2P(O)OP(O)(OR)_2$$
$$7 1 9$$
$$ (RO)_2POOCMe_3$$
$$ 10$$

R = Me, Et, *i*-Pr

Similarly, the reaction of diphenylchlorophosphine (**11**) with **7** gives diphenyl *t*-butyl phosphinate (**12**) and diphenylphosphinic acid (**13**).

$$Ph_2PCl + 7 \xrightarrow{\text{pyridine}} Ph_2P(O)OCMe_3 + Ph_2P(O)OH$$
$$11 12 13$$

Further attempts to prepare peroxide **10** (R = Et) by the reaction of diethyl phosphorochloridite with so-

dium *t*-butyl peroxide were unsuccessful and produced triethyl phosphate (**14**, R = Et) as the only isolable

$$(RO)_2PCl + NaOOCMe_3 \longrightarrow (RO)_3P(O)$$
$$8 14$$

$$R = Et$$

product. This result seems to exclude the possibility of formation of **1** *via* the rearrangement of **10** under the present experimental conditions.

On the basis of these results, the following reaction scheme for the formation of **1** is proposed. Reduction of **7** by **8** probably proceeds *via* the intermediate shown[14] to produce dialkyl phosphorochloridate (**6**) and *t*-

$$(RO)_2PCl + Me_3COOH \longrightarrow$$
$$8 7$$

$$[(RO)_2\overset{+}{P} \longrightarrow O \cdots \bar{O} \cdot CMe_3] \longrightarrow$$
$$\overset{|}{Cl}\overset{|}{H}$$

$$(RO)_2P(O)Cl + Me_3COH$$
$$6$$

butyl alcohol. Reaction of **6** with *t*-butyl alcohol in the presence of pyridine produces **1**, whereas the reaction of **6** with *t*-butyl alcohol at room temperature in the absence of pyridine is reported[15] not to proceed.

$$6 + Me_3COH \xrightarrow{\text{pyridine}} (RO)_2P(O)OCMe_3$$
$$1$$

Simultaneously, **6** reacts with **7** in the presence of pyridine to produce perester **2**. Under the experimental conditions it is not possible to isolate **2**, since we have found[7,16] that **2** undergoes a facile decomposition to give the corresponding dialkyl phosphate **15**, trialkyl phosphate (**14**), and tetraalkyl pyrophosphate (**9**).

$$(RO)_2P(O)OOCMe_3 \longrightarrow$$
$$2$$

$$(RO)_2P(O)OH + (RO)_3P(O) + (RO)_2P(O)OP(O)(OR)_2$$
$$15 14 9$$

Heating of ester **1** (R = *i*-Pr) at 50° and 0.1 mm for 7 hr in the presence of pyridine produced no change in composition. The reaction of **6** (R = Et) with pyridine under anhydrous conditions at room temperature also did not proceed. Thus, it seems that **9**, **14**, and **15** are not derived from ester **1** or peroxide **10**. It appears, therefore, that oxidation of **8** occurs as the first step in its reaction with **7** and that the products are derived from the subsequent reaction of oxidation product **6** with either *t*-butyl alcohol or *t*-butyl hydroperoxide.

On the basis of these results, it is evident that neither the reduction of **2** with triphenylphosphine nor the reaction of **8** with *t*-butyl hydroperoxide is a general method for the preparation of **1**.

The kinetics of the reaction of **6** (R = Ph) with potassium *t*-butoxide have been described; however, no isolation of **1** (R = Ph) has been reported.[17] In

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contrast, the reaction of 6 (R = Me) with sodium *t*-butoxide yields[4a] 1 (R = Me), and the reaction of 6 (R = Et) with a mixture of sodium and boiling *t*-butyl alcohol yields[4b] 1 (R = Et).

Since sodium *t*-butoxide is not a readily available starting material, and reaction of 6 (R = *i*-Pr) with sodium in refluxing *t*-butyl alcohol did not produce the desired product, the reactions of 6 (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, Ph, PhCH₂) with commerically available potassium *t*-butoxide were investigated.

$$(RO)_2P(O)Cl + KOCMe_3 \longrightarrow (RO)_2P(O)OCMe_3$$
$$\quad\ 6 \qquad\qquad\qquad\qquad\qquad\qquad 1$$
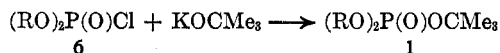
R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, Ph, PhCH₂

The reaction proceeds smoothly in all cases at 10° to produce 1 in good to excellent yield. It has been found, however, that it is necessary to maintain *strictly anhydrous conditions* during the reaction.

Esters 1 (R = Me, Et, *n*-Pr, *i*-Pr) are moderately stable and can be readily distilled under vacuum. However, esters 1 (R = *n*-Bu, *i*-Bu) can be distilled only in small quantities through a short-path distillation head and can be stored for only a few hours at −20°. Esters 1 (R = Ph, PhCH₂) are unstable at −20° and cannot be distilled; they have been identified by nmr.

Comparison of the physical constants and spectral characteristics (ir, nmr) of 1 (R = *n*-Bu) with those of the material which we have previously[7] reported to be 1 (R = *n*-Bu) indicates that these materials are not identical. We have now identified this material[7] to be tri-*n*-butyl phosphate 14 (R = *n*-Bu). This result is more compatible with other data of our investigation on the decomposition of dialkyl *t*-butylperoxy phosphates (2). The results of that study will be described at a later date.[16]

Experimental Section

Boiling points and melting points are uncorrected. Nmr spectra were obtained on a Varian HA-100 spectrometer on 10% (v/v) samples in carbon tetrachloride using an internal TMS standard. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Mr. W. Saschek. Molecular weight determinations were performed cryoscopically in benzene.

t-Butyl hydroperoxide (Lucidol Division, Wallace and Tiernan, Inc.) was concentrated by discarding the fraction up to bp 40° (40 mm). Pyridine was distilled under nitrogen and stored over sodium hydroxide. Triethyl phosphate was obtained from Eastman Kodak and was purified by distillation before use. All other materials were best commercial grade used without further purification. The petroleum ether used had bp 20–40°.

Dialkyl phosphorochloridates (6) and dialkyl *t*-butylperoxy phosphates (2) were prepared by the methods described in an earlier paper.[13b]

Tetraethyl pyrophosphate (9, R = Et), bp 104° (0.1 mm), n^{25}D 1.4166, was prepared as described in an earlier paper[7] from diethyl *t*-butylperoxy phosphate (2, R = Et).

Anal. Calcd for C₈H₂₀O₇P₂: C, 33.00; H, 6.93. Found: C, 32.96; H, 6.84.

Tetraisopropyl pyrophosphate (9, R = *i*-Pr), bp 110° (0.1 mm), n^{25}D 1.4163, was prepared as above from diisopropyl *t*-butylperoxy phosphate (2, R = *i*-Pr).

Anal. Calcd for C₁₂H₂₈O₇P₂: C, 41.67; H, 8.20. Found: C, 41.93; H, 8.37.

Sodium *t*-butyl peroxide was prepared by the method of Bartlett and McBride.[18] Thus, 90 g (1.0 mol) of *t*-butyl hydroperoxide was added at room temperature to a slurry of 24 g (0.5 mol) of sodium hydride (50% dispersion in oil). The mixture was

stirred at room temperature for 24 hr and filtered. The precipitate was dried at room temperature (10 mm) for 24 hr.

Anal. Calcd for C₄H₉O₂Na: active oxygen, 14.3; equiv wt, 112. Found: active oxygen, 13.9; equiv wt, 108.

Dialkyl Phosphorochloridites. A General Procedure.[19]—To 87 ml (1.0 mol) of phosphorus trichloride in 750 ml of benzene was added at −5 to 0° 80 ml (1.0 mol) of pyridine. The mixture was stirred at 0° for 15 min and then a solution of 160 ml (1.0 mol) of N,N-diethylaniline and 1.0 mol of the required alcohol was added at 0–5°. The mixture was stirred at 0–5° for 15 min and another 1.0 mol of alcohol was added at 0–5°. The mixture was stirred at 10–15° for 1.5 hr and filtered. The filtrate was concentrated [30–40° (30 mm)] and distilled giving dialkyl phosphorochloridite (8), Table I.

TABLE I
DIALKYL PHOSPHOROCHLORIDITES (8)

R	Bp, °C (mm)	n^{25}D	Yield, %	Lit.[19] bp, °C (mm)
Et	55–57 (25)	1.4365	28	54 (25)
i-Pr	58–60 (12)	1.4260	40	62–64 (12)
n-Pr	69–71 (8)	1.4385	19	80 (17)

Reduction of Dialkyl *t*-Butylperoxy Phosphate. A. Reaction of Dimethyl *t*-Butylperoxy Phosphate (2, R = CH₃) with Triphenylphosphine (4).—To a solution of 26.2 g (0.1 mol) of triphenylphosphine in 200 ml of ether was added at 35° a solution of 19.8 g (0.1 mol) of dimethyl *t*-butylperoxy phosphate in 50 ml of ether. After the addition was complete, the mixture was stirred and refluxed for 2 hr and filtered. The filtrate was concentrated and distilled giving 2 g (11%) of dimethyl *t*-butyl phosphate (1, R = CH₃): bp 53–55° (0.2 mm); n^{25}D 1.4074 [lit.[4a] bp 60° (0.07 mm)]; nmr δ 1.44 [s, 9, (CH₃)₃CO], 3.61 [d, J = 11 Hz, (CH₃O)₂P(O)].

B. Reaction of Diethyl *t*-Butylperoxy Phosphate (2, R = Et) with Triphenylphosphine (4).—To a refluxing solution of 13.1 g (0.05 mol) of triphenylphosphine in 125 ml of ether was added dropwise over 30 min a solution of 11.3 g (0.05 mol) of diethyl *t*-butylperoxy phosphate in 50 ml of ether. The mixture was refluxed for 3.5 hr after the addition was completed and was treated as above giving 1.45 g (9.1%) of diethyl *t*-butyl phosphate (1, R = Et): bp 48–50° (0.02 mm); n^{25}D 1.4092 [lit.[4b] bp 63–66° (1 mm); n^{35}D 1.4042].

Anal. Calcd for C₈H₁₉O₄P: C, 45.71; H, 9.11; mol wt, 210. Found: C, 45.98; H, 9.19; mol wt, 204.

C. Reaction of Diisopropyl *t*-Butylperoxy Phosphate (2, R = *i*-Pr) with Triphenylphosphine (4).—To a solution of 13.1 g (0.05 mol) of triphenylphosphine in 100 ml of ether was added at 25° a solution of 12.7 g (0.05 mol) of diisopropyl *t*-butylperoxy phosphate in 100 ml of ether. After the addition was completed, the mixture was stirred at ambient temperature for 4 hr and was treated as above giving 4.28 g (36%) of diisopropyl *t*-butyl phosphate (1, R = *i*-Pr): bp 53–55° (0.1 mm); n^{25}D 1.4079.

Anal. Calcd for C₁₀H₂₃O₄P: C, 50.41; H, 9.73; mol wt, 238. Found: C, 50.23; H, 9.77; mol wt, 225.

D. Reaction of Di-*n*-butyl *t*-Butylperoxy Phosphate (2, R = *n*-Bu) with Triphenylphosphine (4).—To a solution of 2.62 g (0.01 mol) of triphenylphosphine in 100 ml of ether was added at room temperature a solution of 2.82 g (0.01 mol) of di-*n*-butyl *t*-butylperoxy phosphate in 50 ml of absolute ether. After the addition was complete, the mixture was stirred at ambient temperature for 15 hr and was treated as above, giving 2.63 g of an unresolvable mixture of triphenylphosphine oxide (5), di-*n*-butyl phosphate (15, R = *n*-Bu), and tetra-*n*-butyl pyrophosphate (9, R = *n*-Bu), which were identified by tlc on silica gel G.

E. Reaction of Diisopropyl *t*-Butylperoxy Phosphate (2, R = *i*-Pr) with Sodium Bisulfite. 1.—A solution of 12.7 g (0.05 mol) of diisopropyl *t*-butylperoxy phosphate, 50 ml of ether, 10.4 g (0.1 mol) of sodium bisulfite, and 50 ml of water was stirred at 30° for 25 hr. The aqueous layer was separated and extracted with ether (two 50-ml portions). The combined organic solutions were concentrated and distilled giving 8.5 g (67%) of diisopropyl *t*-butylperoxy phosphate [bp 63–66° (0.05 mm); n^{25}D 1.4135] and traces of diisopropyl *t*-butyl phosphate, which was identified by tlc on silica gel G.

2.—A slurry of 10.4 g (0.10 mol) of sodium bisulfite and 12.7 g (0.05 mol) of diisopropyl *t*-butylperoxy phosphate was stirred

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(19) J. Michalski, T. Modro, and A. Zwierzak, *J. Chem. Soc.*, 4904 (1961).

for 168 hr at room temperature and distilled giving 6.2 g (49%) of diisopropyl *t*-butylperoxy phosphate.

3.—A mixture of 10.4 g (0.1 mol) of sodium bisulfite, 25 ml of water, 12.7 g (0.05 mol) of diisopropyl *t*-butylperoxy phosphate, and 50 ml of carbon tetrachloride was refluxed for 2 hr. The aqueous layer was separated and extracted with ether (two 50-ml portions). The combined organic solutions were concentrated and distilled giving 9.7 g (76%) of diisopropyl *t*-butylperoxy phosphate.

F. Reaction of Diisopropyl *t*-Butylperoxy Phosphate (2, R = *i*-Pr) with Sodium Sulfite.—A mixture of 25.2 g (0.2 mol) of sodium sulfite, 12.7 g (0.05 mol) of diisopropyl *t*-butylperoxy phosphate, and 25 ml of ether was refluxed for 24 hr and filtered. The filtrate was concentrated and distilled giving 10 g (79%) of diisopropyl *t*-butylperoxy phosphate.

Reaction of Dimethyl Phosphorochloridite (8, R = Me) with *t*-Butyl Hydroperoxide (7) and Pyridine.—The reaction flask was charged with 12.8 g (0.01 mol) of dimethyl phosphorochloridite and 250 ml of petroleum ether (bp 20–40°) in a nitrogen-filled glove box and was then removed and rapidly fitted with thermometer, dropping funnel, stirrer, and condenser. A slow stream of nitrogen was started and a solution of 9.0 g (0.10 mol) of *t*-butyl hydroperoxide and 7.9 g (0.10 mol) of pyridine was added dropwise at 8–12°. The mixture was warmed to room temperature over 1 hr and filtered. The filtrate was concentrated and fractionated through a 10-cm Vigreux column giving 3.42 g (19%) of dimethyl *t*-butyl phosphate (1, R = CH₃): bp 44–48° (0.1 mm); n^{25}D 1.4075.

Reaction of Diethyl Phosphorochloridite (8, R = Et) with *t*-Butyl Hydroperoxide (7) and Pyridine. 1.—To a solution of 15.6 g (0.10 mol) of diethyl phosphorochloridite and 100 ml of pentane was added under nitrogen at −15° a solution of 10 g (0.11 mol) of *t*-butyl hydroperoxide and 10 ml (0.12 mol) of pyridine. The mixture was stirred at −5 to 5° for 2 hr and then filtered. The filtrate was concentrated and an ethereal solution of the residual oil was washed with 10% (v/v) aqueous sodium bicarbonate, dried (Na₂SO₄), concentrated, and distilled giving 3.5 g (16%) of diethyl *t*-butyl phosphate (1, R = Et): bp 48–51° (0.14 mm); n^{25}D 1.4095.

2.—To a solution of freshly distilled diethyl phosphorochloridite (11.7 g, 0.075 mol) in 100 ml of petroleum ether was added at −20 to −15° a solution of 7.20 g (0.08 mol) of *t*-butyl hydroperoxide in 5.92 g (0.075 mol) of pyridine. The reaction was carried out in a nitrogen filled glove box and a slow stream of dried (H₂SO₄) nitrogen was passed through the reaction vessel during the addition. The mixture was warmed to room temperature over 3 hr and was filtered in the glove box. The filtrate was concentrated and distilled giving 2 g (17%) of tetraethyl pyrophosphate (9, R = Et) [bp 119–121° (0.2 mm); n^{25}D 1.4223] and 7.0 g (44%) diethyl *t*-butyl phosphate (1, R = Et) [bp 53–55° (0.3 mm); n^{25}D 1.4109].

Reaction of Diisopropyl Phosphorochloridite (8, R = *i*-Pr) with *t*-Butyl Hydroperoxide (7) and Pyridine.—To a solution of 18.5 g (0.10 mol) of diisopropyl phosphorochloridite in 100 ml of petroleum ether was added under nitrogen at −15 to −10° a solution of 10 g (0.11 mol) of *t*-butyl hydroperoxide and 10 ml of (0.12 mol) pyridine in 25 ml of petroleum ether. The mixture was stirred for 0.75 hr at 0° and filtered. The filtrate was washed with aqueous sodium bicarbonate (4:1, v/v, 25 ml) and then with 25 ml of water. The organic layer was dried (Na₂SO₄), concentrated, and distilled giving 3.0 g (13%) of diisopropyl *t*-butyl phosphate (1, R = *i*-Pr) [bp 45–46° (0.15 mm), n^{25}D 1.4092] and 2.9 g (17%) of tetraisopropyl pyrophosphate (9, R = *i*-Pr) [bp 114° (0.25 mm), n^{25}D 1.4196].

Reaction of Diethyl Phosphorochloridite (8, R = Et) with Sodium *t*-Butyl Peroxide.—The reaction vessel was charged with 12.3 g (0.11 mol) of sodium *t*-butyl peroxide and 350 ml of petroleum ether in a nitrogen-filled glove box. The flask was fitted rapidly with dropping funnel, stirrer, thermometer, and condenser. A slow stream of nitrogen was maintained in the system during the reaction. Diethyl phosphorochloridite (15.6 g, 0.10 mol) was added over 0.5 hr at 6–10°. The cooling bath was removed and the mixture was stirred for 0.75 hr and then filtered. The filtrate was concentrated (25°) and distilled giving 2.3 g (25%) of triethyl phosphate (14, R = Et): bp 48–51° (0.15 mm); n^{25}D 1.4041; nmr (CCl₄) δ 1.34 (t, 3, J = 6 Hz, CH₃CH₂O), 4.02 (m, 2, CH₃CH₂O); ir 1280 (P=O).

Reaction of Diisopropyl *t*-Butyl Phosphate (1, R = *i*-Pr) with Pyridine.—A solution of 11.9 g (0.05 mol) of diisopropyl *t*-butyl phosphate and 3.95 g (0.05 mol) of pyridine was heated at 50°

(0.1 mm) for 7 hr and distilled giving 10.6 g (89%) of diisopropyl *t*-butyl phosphate (1, R = *i*-Pr): bp 54–56° (0.25 mm); n^{25}D 1.4078.

Reaction of Diethyl Phosphorochloridate (6, R = Et) with Pyridine.—A solution of 17.25 g (0.10 mol) of diethyl phosphorochloridate, 8.69 g (0.11 mol) of pyridine, and 50 ml of petroleum ether was stirred under nitrogen at room temperature for 3 hr and distilled yielding 16.5 g (96%) of diethyl phosphorochloridate (6, R = Et), bp 48–50° (0.8 mm) [lit.¹³ᵇ bp 42° (0.2 mm)].

Reaction of Diphenylchlorophosphine (11) with *t*-Butyl Hydroperoxide (7) and Pyridine. 1.—To a solution of 22.1 g (0.1 mol) of diphenylchlorophosphine in 100 ml of petroleum ether was added at −15 to −5° a solution of 10 g (0.11 mol) of *t*-butyl hydroperoxide and 10 ml (0.12 mol) of pyridine. The mixture was filtered giving 22 g of a white solid which was washed with water and recrystallized from methanol–benzene giving 12 g (55%) of diphenyl phosphinic acid (13), mp 193.5–194°.

Anal. Calcd for C₁₂H₁₁O₂P: C, 66.05; H, 5.08. Found: C, 65.50; H, 5.23.

The filtrate was evaporated to dryness (0.15 mm) leaving 5 g (18%) of diphenyl-*t*-butyl phosphinate (12), mp 111.5–112° (MeOH–H₂O).

Anal. Calcd for C₁₆H₁₉O₂P: C, 70.07; H, 6.98; mol wt, 275. Found: C, 70.22; H, 7.07; mol wt, 265.

2.—An analogous reaction of 19 ml (0.1 mol) of diphenylchlorophosphine, 10 g (0.11 mol) of *t*-butyl hydroperoxide and 100 ml of petroleum ether gave 20.5 g (94%) of diphenylphosphinic acid (13).

3.—A similar reaction of 19 ml (0.1 mol) of diphenylchlorophosphine, 10 ml (0.12 mol) of pyridine, and 100 ml of petroleum ether gave 1.2 g of an unidentified polymeric material, 8 g of pyridinium hydrochloride, and 9.4 g (49%) of unchanged diphenyl chlorophosphine (11): bp 108–110° (0.3 mm); n^{25}D 1.5888.

Preparation of Dialkyl *t*-Butyl Phosphates (1) by the Reaction of Dialkyl Phosphorochloridates (6) with Potassium *t*-Butoxide. Dimethyl *t*-Butyl Phosphate (1, R = Me).—The reaction flask was charged with a mixture of 12.1 g (0.11 mol) of potassium *t*-butoxide and 250 ml of petroleum ether in a nitrogen-filled glove box. The flask was removed and rapidly fitted with thermometer, stirrer, condenser, and dropping funnel. A stream of dry nitrogen was maintained during the reaction. Dimethyl phosphorochloridate (14.4 g, 0.10 mol) was added at 5–8°. The mixture was stirred for 15 min and filtered. The filtrate was concentrated and distilled giving 7.9 g (43%) of dimethyl *t*-butyl phosphate (1, R = Me): bp 40–42° (0.15 mm); n^{25}D 1.4073.

Anal. Calcd for C₆H₁₅O₄P: C, 39.56; H, 8.30. Found: C, 39.60; H, 8.29.

Diethyl *t*-Butyl Phosphate (1, R = Et).—As above, 17.25 g (0.1 mol) of diethyl phosphorochloridate, 12.32 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react, giving 15 g (71%) of diethyl-*t*-butyl phosphate (1, R = Et): bp 53–55° (0.05 mm); n^{25}D 1.4028; nmr δ 1.32 (t, 6, CH₃CH₂O), 1.44 [s, 9, (CH₃)₃CO], 3.98 (m, 4, CH₃CH₂O).

Di-*n*-propyl *t*-Butyl Phosphate (1, R = *n*-Pr).—As above, 20.0 g (0.10 mol) of di-*n*-propyl phosphorochloridate, 12.1 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react, giving 18.8 g (79%) of di-*n*-propyl *t*-butyl phosphate (1, R = *n*-Pr): bp 66–67° (0.1 mm); n^{25}D 1.4156; nmr δ 0.96 [t, 6, J = 8 Hz, (CH₃CH₂O)₂P(O)], 1.45 [s, 9, (CH₃)₃CO], 1.65 [m, 4, (CH₃CH₂CH₂O)₂P(O)], 3.86 [m, 4, J = 8 Hz, (CH₃CH₂CH₂O)₂P(O)].

Anal. Calcd for C₁₀H₂₃O₄P: C, 50.33; H, 9.73. Found: C, 50.41; H, 9.73.

Diisopropyl *t*-Butyl Phosphate (1, R = *i*-Pr).—As above, 20.05 g (0.1 mol) of diisopropyl phosphorochloridate, 12.32 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react, giving 17.1 g (72%) of diisopropyl *t*-butyl phosphate (1, R = *i*-Pr): bp 51–52° (0.2 mm); n^{25}D 1.4070; nmr δ 1.29 [d, 12, J = 6 Hz, [(CH₃)₂CHO]₂P(O)], 1.46 [s, 9, (CH₃)₃CO], 4.50 [m, 2, (>CHO)₂P(O)].

Di-*n*-butyl *t*-Butyl Phosphate (1, R = *n*-Bu).—As above 22.85 g (0.10 mol) of di-*n*-butyl phosphorochloridate, 12.32 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react, giving after distillation in small batches 22 g (84%) of di-*n*-butyl *t*-butyl phosphate (1, R = *n*-Bu): bp 97–99° (0.2 mm); n^{25}D 1.4212; nmr δ 0.96 [t, 6, (CH₃CH₂CH₂-CH₂O)₂P(O)], 1.48 [s, 9, (CH₃)₃CO], 1.60 [m, 8, (CH₃CH₂CH₂-CH₂O)₂P(O)], 3.91 [m, 4, (CH₃CH₂CH₂CH₂O)₂P(O)].

Anal. Calcd for $C_{12}H_{27}O_4P$: C, 54.12; H, 10.22. Found: C, 53.42; H, 10.16.

Diisobutyl *t*-Butyl Phosphate (1, R = *i*-Bu).—As above, 22.85 g (0.1 mol) of diisobutyl phosphorochloridate, 12.32 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react, giving after distillation in small batches 18.2 g (69%) of diisobutyl *t*-butyl phosphate (1, R = *i*-Bu): bp 87–89° (0.3 mm); $n^{25}D$ 1.4171; nmr δ 0.97 {d, 12, J = 6 Hz, [(CH₃)₂CHCH₂O]₂P(O)]}, 1.46 [s, 9, (CH₃)₃CO], 1.91 [m, 2, (>CHCH₂O)₂P(O)], 3.75 [m, 4, (>CHCH₂O)₂P(O)].

Anal. Calcd for $C_{12}H_{27}O_4P$: C, 54.12; H, 10.22. Found: C, 53.63; H, 10.09.

Diphenyl *t*-Butyl Phosphate (1, R = Ph).—As above, 21.3 g (0.08 mol) of diphenyl phosphorochloridate,[13b] 9.8 g (0.09 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react. The filtrate was concentrated at −20° (0.1 mm) leaving 23.1 g (95%) of diphenyl *t*-butyl phosphate (1, R = Ph) identified by nmr: nmr δ 1.46 [s, 9, (CH₃)₃CO], 6.82 [s, 10, (C₆H₅O)₂P(O)].

Dibenzyl *t*-Butyl Phosphate (1, R = PhCH₂).—As above 28.33 g (0.096 mol) of dibenzyl phosphorochloridate,[13b] 12.32 g (0.11 mol) of potassium *t*-butoxide, and 250 ml of petroleum ether were allowed to react. The filtrate was concentrated at −20°

(0.1 mm) giving 22 g (68%) of dibenzyl *t*-butyl phosphate (1, R=PhCH₂) identified by nmr: nmr δ 1.47 [s, 9, (CH₃)₃CO], 4.71 [d, 4, (C₆H₅CH₂O)₂P(O)], 6.87 [s, 10, (C₆H₅CH₂O)₂P(O)].

Polar Effects on the Formation of Imines from Isobutyraldehyde and Primary Aliphatic Amines[1]

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The following dimensionless equilibrium constants for the formation of imines and water from isobutyraldehyde and primary amines were determined in aqueous solution at 35°: MeO(CH₂)₃NH₂, 3600; PhCH₂NH₂, 2500; MeOCH₂CH₂NH₂, 2060; Me₂NCH₂CH₂NH₂, 1700; HC≡CCH₂NH₂, 1400; (MeO)₂CHCH₂NH₂, 1380; H₂N-CH₂CONH₂, 621; H₂NCH₂CN, 548; CF₃CH₂NH₂, 238. The equilibrium constants decrease with increasing electron-withdrawing power of the substituents. A plot of log K vs. the pK_a values of the conjugate acids of the amines gives a satisfactory straight line for amines of the type RNH₂ where R contains an sp³-hybridized β-carbon atom. Deviations from this line in the cases of the imines derived from aminoacetonitrile and propargylamine are attributed to the particular stability of a conformer in which the carbon–nitrogen double bond of the imine is eclipsed by a cyano or ethynyl group. This conclusion is supported by nmr data.

We have previously described methods for determining equilibrium constants for the formation of imines from isobutyraldehyde and primary amines by uv measurements at the aldehyde maximum or at the imine maximum or by measurements of the effect of added aldehyde on the pH of amine buffer solutions.[2] Equilibrium constants were reported for methyl-, ethyl-, isopropyl-, *t*-butyl-, *n*-propyl-, and *n*-butylamine, and the conformational equilibria of the resultant imines were discussed on the basis of their nmr spectra. In these compounds, where polar effects were held relatively constant, differences in ease of formation and in conformational preferences were attributed almost entirely to steric effects. We have now determined the equilibrium constants for the formation of imines from isobutyraldehyde and primary amines of the type RCH₂NH₂, in which steric effects are kept fairly constant and polar effects varied widely.

Results

The equilibrium constant for imine formation is that defined previously[2]

$$K = IW/AB \qquad (1)$$

where I, W, B, and A are the equilibrium concentrations of imine, water, amine, and aldehyde (including both free aldehyde and aldehyde hydrate), respectively. For the ultraviolet method of determining K, eq 2 was used when measurements were made at the imine maximum.

$$A_0/[D - A_0\epsilon_A - (B_0 - B')\epsilon_B] =$$
$$\{1/(\epsilon_I - \epsilon_A - \epsilon_B)\} + \{W/[KB(\epsilon_I - \epsilon_A - \epsilon_B)]\} \qquad (2)$$

ϵ_I, ϵ_A, and ϵ_B are the extinction coefficients of the imine, aldehyde, and amine at the wavelength used, A_0 and B_0 are the initial concentrations (before imine formation) of aldehyde and amine, B' is the concentration of amine in the reference cell, and D is the absorbance. In order to calculate the real concentrations of amines present (that is, to correct for the amounts present in the protonated forms), it was necessary to know their ionization constants at the ionic strengths and temperatures used. This knowledge was vital in cases where equilibrium constants were determined by pH measurements. The ion-product constant of water was calculated as described previously.[2] The ionization constants of 2-methoxyethylamine, 3-methoxypropylamine, 2,2-dimethoxyethylamine, 2,2,2-trifluoroethylamine, benzylamine, propargylamine, and 2-dimethylaminoethylamine were determined at 35°. Literature values at 25° were corrected to 35° by the

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(2) J. Hine and C. Y. Yeh, *J. Amer. Chem. Soc.*, **89**, 2669 (1967).