Rearrangement and Decomposition of Phosphoranyl Peroxides Produced *in situ* from Alkylidenephosphoranes and *t*-Alkylperoxy Anions

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The reactions of alkylidenephosphoranes (I), produced *in situ* from the corresponding phosphonium salts and sodium ethoxide, with sodium salt of *t*-butyl hydroperoxide (II) were carried out in absolute ethanol. Carbanion (III) of phosphoranyl peroxide, formed by the reaction of I with II, underwent a rearrangement to produce *t*-butyl phenyl ether, alkyl *t*-butyl ether, and two kinds of phosphine oxides. Phosphoranyl peroxide (IV), formed by abstraction of proton from ethanol, decomposed in homolytic fashion to yield *t*-butyl alcohol and hydroxyphosphorane (V) as an intermediate, the decomposition of which gave benzene, hydrocarbon and corresponding phosphine oxides. Homolytic decomposition of IV was supported by the reaction of tetraphenylphosphonium bromide with II. The contribution of III was confirmed by the effect of base concentration on the amounts of rearrangement products. The reaction with cumylperoxy anion gave similar results. The mechanisms of these reactions were discussed.

There are a few reports on phosphorus peroxides such as diphenylphosphinyl peroxide[1] and *t*-butyl alkylperphosphonates,[2] but no report on the phosphoranyl peroxides.

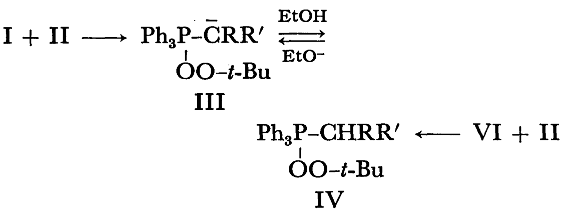
We carried out the reactions of alkyltriphenylphosphonium bromides with sodium salt of *t*-butyl hydroperoxide in the presence of sodium ethoxide in ethanol in order to investigate the chemical behavior of *t*-butyl alkyltriphenylphosphoranyl peroxides.

Under the above conditions the following reactions would be expected to occur.

$$t\text{-BuOOH} + \text{EtO}^-\text{Na}^+ \rightleftarrows \text{EtOH} + \underset{\text{II}}{t\text{-BuOO}^-\text{Na}^+} \quad (1)$$

$$\text{Ph}_3\overset{+}{\text{P}}\text{CHRR}'\ \text{Br}^- \underset{\text{EtOH}}{\overset{\text{EtO}^-}{\rightleftarrows}} \text{Ph}_3\text{P=CRR}' \quad (2)$$

VIa: R=Ph, R′=H   Ia: R=Ph, R′=H
VIb: R=R′=Ph   Ib: R=R′=Ph
VIc: R=*n*-Pr, R′=H   Ic: R=*n*-Pr, R′=H



$$\text{I} + \text{II} \longrightarrow \underset{\text{III}}{\text{Ph}_3\text{P}\underset{|\atop \text{OO-}t\text{-Bu}}{-}\bar{\text{C}}\text{RR}'} \underset{\text{EtO}^-}{\overset{\text{EtOH}}{\rightleftarrows}} \underset{\text{IV}}{\text{Ph}_3\underset{|\atop \text{OO-}t\text{-Bu}}{\text{P}}\text{-CHRR}'} \longleftarrow \text{VI} + \text{II} \quad (3)$$

This paper describes the difference in the decompositions of *t*-butyl alkyltriphenylphosphoranyl peroxides (IV) and the corresponding carbanions (III).

Results and Discussion

Sodium salt of *t*-butyl hydroperoxide (II) was produced *in situ* by addition of *t*-butyl hydroperoxide to absolute ethanol containing four times moles of sodium ethoxide. The position of the equilibrium (1) lies about 10^4 times to the side of II under the conditions given by Everett and Minkoff.[3]

To the solution was then added phosphonium bromide (VI) at room temperature under nitrogen to produce *in situ* alkylidenephosphorane (I), the formation of which was indicated by appearance of yellow color (in the case of Ia and Ic) or of reddish orange precipitate (in the case of Ib).

The reaction soon took place, the temperature of the mixture rose slightly, and the color of the solution gradually became pale. The reaction products were determined by vapor phase chromatography (vpc) and column chromatography. Peroxides (IV) could not be obtained under the reaction conditions.

Alkylphosphonium salts and alkylidenephosphoranes have been reported to react with sodium ethoxide in ethanol under reflux for several hours to give phosphine oxide and hydrocarbon:[4]

$$\text{Ph}_3\text{P=CRR}' \text{ or } \text{Ph}_3\overset{+}{\text{P}}\text{-CHRR}' \xrightarrow[\text{EtOH}]{\text{EtO}^-} \text{Ph}_3\text{P=O} + \text{RR}'\text{CH}_2 + \text{EtOEt} \quad (4)$$

This type of reaction occurred to a small extent in the case of Ia and appreciably in the case of Ib under the reaction conditions. The yields of products in Table 1 were roughly corrected for the contribution of the reaction (4), based on results of blank tests.

It is difficult to distinguish which of I and VI reacted with II, but we inferred that the reaction of I with II predominates in the present case, because the reaction rates was in the order Ib>Ia>Ic. This is also supported by the fact that II is a soft base whereas I is a softer acid than VI.[5]

The mechanisms for the formation of products are postulated as follows.

Carbanion (III) of pentacovalent phosphorus per-

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[1] R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965).

[2] a) A. Rieche, G. Hilgetag, and G. Schramm, *Chem. Ber.*, **95**, 381 (1962); b) T. I. Yurzhenko and B. J. Kaspruk, *Dokl. Akad. Nauk SSSR*, **168**, 113 (1966); *Chem. Abstr.*, **65**, 7210e (1966).

[3] A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953). For pK_a value of ethanol, 17—18 was assumed.

[4] M. Grayson and P. T. Keough, *J. Amer. Chem. Soc.*, **82**, 3919 (1960).

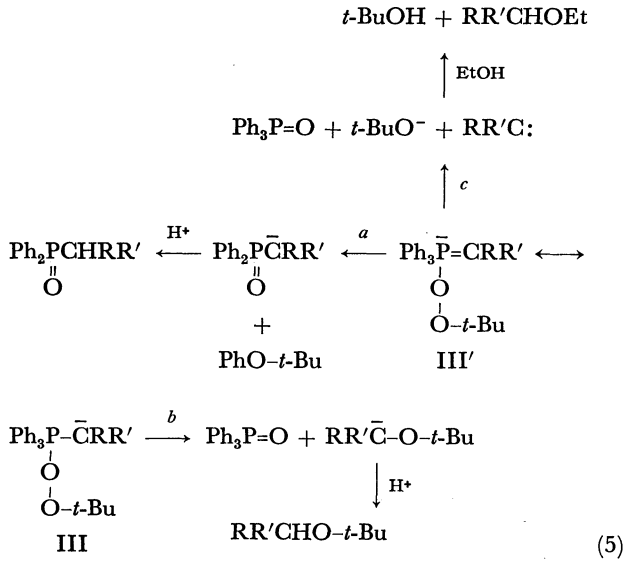
[5] R. G. Pearson, *ibid.*, **85**, 3533 (1963); *Chem. Brit.*, **1967**, 103.

TABLE 1. YIELDS OF REACTION PRODUCTS (mol%, by vpc)

Phosphorane R R′	Ia Ph H		Ib Ph Ph		Ic *n*-Pr H		$Ph_4P^+Br^-$ (VIII)	
$RR'CH_2$	65.0	63.8	90.2	83.9	0[a]	0[a]	0	0
PhO-*t*-Bu	15.5	12.6	9.1	10.8	0	0	0	0
RR′CHO-*t*-Bu	16.3	11.0	0	0	trace	trace	0	0
RR′CHOEt	2.4	2.1	0	0	<2	<2	0	0
PhH	7.6	7.4	trace	trace	80.2	78.5	81.8	72.1
t-BuOH	64.9	68.4	84.2	78.5	70.2	98.0	100	98.4
$Ph_3P{=}O$	61.2	62.0	81.3	80.7	16.9	20.0	68.8[b]	90.2 55.2[b]
$Ph_2P({=}O)CHRR'$	c)	c)	5.7	8.0	68.3	76.2	0	0

a) Not detected as evolved gas.
b) Amount isolated by column chromatography.
c) Formation was detected, but the determination was unsuccessful due to insufficient resolution under various conditions.

oxide, first formed by the reaction of II with I, is in the equilibrium (3) with the corresponding phosphoranyl peroxide (IV). Carbanion (III) undergoes a rearrangement of the phenyl or alkyl group to β-oxygen of the peroxide bond to yield *t*-butyl phenyl ether, alkyl *t*-butyl ether and corresponding phosphine oxides as shown in course *a* in the following scheme.



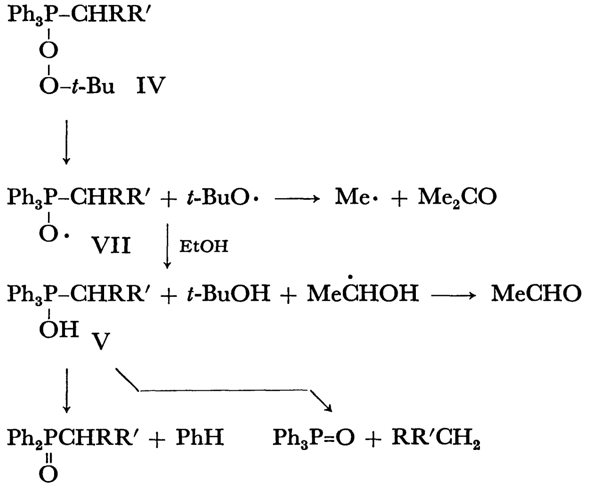
$$t\text{-BuOH} + \mathrm{RR'CHOEt} \xleftarrow{\mathrm{EtOH}} \mathrm{Ph_3P{=}O} + t\text{-BuO}^- + \mathrm{RR'C{:}} \xleftarrow{c} \mathrm{III'}$$

$$\underset{\mathrm{O}}{\overset{}{\mathrm{Ph_2PCHRR'}}} \xleftarrow{H^+} \mathrm{Ph_2P({=}O)\bar{C}RR'} + \mathrm{PhO\text{-}}t\text{-Bu} \xleftarrow{a} \underset{\mathrm{III'}}{\mathrm{Ph_3\bar{P}(O\text{-}O\text{-}}t\text{-Bu)}{=}\mathrm{CRR'}} \longleftrightarrow$$

$$\underset{\mathrm{III}}{\mathrm{Ph_3P(O\text{-}O\text{-}}t\text{-Bu)\text{-}\bar{C}RR'}} \xrightarrow{b} \mathrm{Ph_3P{=}O} + \mathrm{RR'\bar{C}\text{-}O\text{-}}t\text{-Bu} \xrightarrow{H^+} \mathrm{RR'CHO\text{-}}t\text{-Bu} \qquad (5)$$

Rearrangement of the phenyl group may imply resonance contribution of III′, which may be supported by the existence of tris(biphenylene)phosphorane anion.[6] The diphenylmethyl group did not rearrange to the peroxide bond (course *b* in Scheme (5)) to form *t*-butyl ether, probably because of the steric hindrance or low nucleophilicity. The formation of alkyl ethyl ether may be ascribed to the intermediacy of carbene which reacts with solvent ethanol (course *c*).

On the other hand, it is considered that phosphoranyl peroxide (IV) undergoes a homolytic decomposition and the resulting radical (VII) abstracts hydrogen atom from ethanol to give hydroxyphosphorane (V), which decomposes to give benzene or hydrocarbons, and corresponding phosphine oxides:

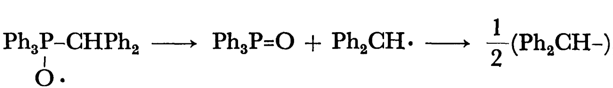


$$\underset{\mathrm{IV}}{\mathrm{Ph_3P(O\text{-}O\text{-}}t\text{-Bu)\text{-}CHRR'}} \longrightarrow \underset{\mathrm{VII}}{\mathrm{Ph_3P(O\cdot)\text{-}CHRR'}} + t\text{-BuO}\cdot \longrightarrow \mathrm{Me}\cdot + \mathrm{Me_2CO}$$

$$\xrightarrow{\mathrm{EtOH}} \underset{\mathrm{V}}{\mathrm{Ph_3P(OH)\text{-}CHRR'}} + t\text{-BuOH} + \mathrm{Me\dot{C}HOH} \longrightarrow \mathrm{MeCHO}$$

$$\mathrm{V} \longrightarrow \mathrm{Ph_2P({=}O)CHRR'} + \mathrm{PhH} \qquad \mathrm{V} \longrightarrow \mathrm{Ph_3P{=}O} + \mathrm{RR'CH_2} \qquad (6)$$

From the product ratio of hydrocarbon to benzene, the mobility of phenyl and alkyl groups fell in the order $Ph_2CH > PhCH_2 > Ph > n\text{-Bu}$. This is in good agreement with that in the reaction of phosphonium halides with hydroxide ion,[7] which proceeds through hydroxyphosphoranes of type V. Detection of small amounts of acetone and acetaldehyde by vpc indicates the intermediacy of *t*-butoxy and α-hydroxyethyl radicals, respectively. Furthermore, in the case of Ib, a trace amount of tetraphenylethane was isolated by column chromatography, indicating the presence of diphenylmethyl radicals:



$$\mathrm{Ph_3P(O\cdot)\text{-}CHPh_2} \longrightarrow \mathrm{Ph_3P{=}O} + \mathrm{Ph_2CH\cdot} \longrightarrow \frac{1}{2}(\mathrm{Ph_2CH\text{-}})_2$$

$$\text{or}\quad \mathrm{Ph_2C{:}} \xrightarrow{\mathrm{EtOH}} \mathrm{Ph_2CH\cdot} \longrightarrow \qquad (7)$$

In order to clarify whether *t*-butyl tetraphenylphosphoranyl peroxide gives *t*-butyl phenyl ether and triphenylphosphine oxide by migration of the phenyl group, tetraphenylphosphonium bromide (VIII) was allowed to react with II under similar conditions. Benzene, *t*-butyl alcohol and triphenylphosphine oxide

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[6] D. Hellwinkel, *Chem. Ber.*, **98**, 576 (1965).

[7] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.*, **1929**, 2342; H. Hoffmann, *Ann. Chem.*, **634**, 1 (1960); G. Aksness and J. Songstad, *Acta Chem. Scand.*, **16**, 1426 (1962).

were obtained as the sole reaction product (Table 1) and no *t*-butyl phenyl ether was detected by vpc. The result supports the view that ethers are produced from the carbanion (III) and hydrocarbons from the neutral peroxide (IV), because in this case no carbanion can participate in the reaction.

When VIII and silver hydroxide were allowed to react in ethanol, benzene and triphenylphosphine oxide were obtained in nearly quantitative yields. These products should be formed from tetraphenylhydroxyphosphorane (IX) as an intermediate:

$$\underset{\text{VIII}}{Ph_4\overset{+}{P}\ Br^-} + AgOH \longrightarrow AgBr + \underset{\text{IX}}{Ph_4P\text{-}OH}$$
$$\longrightarrow Ph_3P{=}O + PhH \qquad (8)$$

Thus the intermediacy of hydroxyphosphorane (V) was supported.

From the above mechanistic consideration, we can evaluate the ratio of participation of carbanion (III), the amount of which is equal to the sum of the amounts of ethers, and that of the phosphoranyl peroxide (IV), the amount of which is equal to the sum of the amounts of benzene and hydrocarbon, in the course of reaction. The results are shown in Table 2. However, it is not possible to discriminate the homolytic decomposition of III, if it take place at all, from that of IV.

Table 2. Relative ratio of participation of III and IV as intermediates

	III$^{a)}$		IV$^{b)}$		III+IV (≡100)	
Ia	34.2	25.7	72.6	71.2	106.8	96.9
Ib	9.1	10.8	~90.2	~83.9	99.3	94.7
Ic	~2	~2	80.2	78.5	82.2	80.5
			97.1$^{c)}$	98.5$^{c)}$	99.1$^{c)}$	100.5$^{c)}$

a) [PhO-*t*-Bu] + [RR′CHO-*t*-Bu] + [RR′CHOEt].
b) [PhH] + [RR′CH$_2$].
c) The amount of butane was assumed to be the same as that of triphenylphosphine oxide according to Scheme (6).

In order to make the participation of carbanion (III) conclusive, the effect of the concentration of sodium ethoxide on the yields of the rearrangement products (*t*-butyl ethers) was examined in the case of benzylidenetriphenylphosphorane (Ia). The results are shown in Table 3. The yields of *t*-butyl phenyl ether and benzyl *t*-butyl ether increased gradually with the concentration of sodium ethoxide. This reveals the existence of equilibrium between III and IV, and the formation of *t*-butyl ethers from carbanion (III).

Table 3. Effect of concentration of sodium ethoxide on yields of *t*-butyl ethers in ethanol (mol %)
($[Ph_3\overset{+}{P}CH_2Ph\ Br^-] : [t\text{-}BuOOH] : [EtONa] = 1 : 1 : x$)

x	1	2	4	10	20
PhO-*t*-Bu	8.2	10.3	10.1	10.1	15.3
PhCH$_2$O-*t*-Bu	9.3	12.2	13.4	17.8	24.7
Total	17.5	22.5	23.5	27.9	40.0

Similarly the reaction of sodium salt of cumyl hydroperoxide with Ia was carried out in ethanol under similar conditions and similar results were obtained (Table 4), though the yield of benzyl cumyl ether decreased probably because of the steric hindrance in the cumylperoxy group.

Table 4. Yields of reaction products of Ia with sodium salt of cumyl hydroperoxide in ethanol

Product	Yield (mol%)	
$PhCH_3$	63.8	61.0
$PhOCMe_2Ph$	13.6	15.2
$PhCH_2OCMe_2Ph$	<2	<2
$PhCH_2OEt$	trace	trace
PhH	4.5	3.0
$PhCMe_2OH$	75.1	79.6
$Ph_3P{=}O$	70.7	78.8

Experimental

Materials. Alkyltriphenylphosphonium bromides were prepared by the methods reported in literature: benzylthiphenylphosphonium bromide,[8] mp 271—274°C; *n*-butyltriphenylphosphonium bromide,[9] mp 232—234°C; benzhydryltriphenylphosphonium bromide,[10] mp 238—240°C; tetraphenylphosphonium bromide,[11] mp 281—284°C. Commercially available *t*-butyl and cumyl hydroperoxides were used after distillation under reduced pressure. *t*-Butyl phenyl ether was prepared from *t*-butyl peroxybenzoate and phenylmagnesium bromide,[12] bp 44—46°C/2 mmHg, n_D^{20} 1.4923. Benzyl *t*-butyl ether (bp 60—62°C/3.5 mmHg) and cumyl phenyl ether (mp 43—46°C) were prepared similarly. Benzyl ethyl ether (bp 183—185°C), benzhydryl ethyl ether (bp 158—161°C/18 mmHg), *n*-butyl ethyl ether (bp 90—91°C), benzhydryl *t*-butyl ether (mp 53—55°C), *n*-butyl *t*-butyl ether (bp 123—125°C) and benzyl cumyl ether which could not be distilled without decomposition but was confirmed to be almost pure by vpc, were prepared by the usual method. Benzyldiphenylphosphine oxide was prepared by the procedure of Hoffmann and Tesch,[13] mp 192—193°C. Benzhydryldiphenylphosphine oxide was prepared by the method described in literature,[14] mp 305—305.5°C.

Reactions of Alkylidenetriphenylphosphoranes with Sodium Salt of t-Butyl Hydroperoxide. Only typical examples are described.

a) Benzylidenetriphenylphosphorane (Ia): Sodium salt of *t*-butyl hydroperoxide (0.05 mol) was prepared in absolute ethanol by addition of *t*-butyl hydroperoxide (5.1 m*l*, 0.05 mol) in ethanol (300 m*l*) containing excess sodium ethoxide (0.20 mol) under nitrogen atmosphere. To this solution benzyltriphenylphosphonium bromide (21.6 g, 0.05 mol) was added with stirring in one portion, and yellow color appeared instantaneously showing the formation of benzylidenetriphenylphosphorane. The color of the solution faded to pale yellow after about 15 min and a white precipitate appeared. The mixture was stirred overnight at room temperature and the

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8) K. Friedrich and H. G. Henning, *Chem. Ber.*, **92**, 2756 (1959).
9) R. Mechoulam and F. Sondheimer, *J. Amer. Chem. Soc.*, **80**, 4386 (1958).
10) L. Horner and E. Lingnaw, *Ann. Chem.*, **591**, 135 (1955).
11) J. Dodonow and H. Medox, *Ber.*, **61**, 907 (1928).
12) C. Friesell and S. O. Lawesson, *Org. Syn.*, **41**, 91 (1961).
13) A. K. Hoffmann and A. G. Tesch, *J. Amer. Chem. Soc.*, **81**, 5519 (1959).
14) H. Hoffmann, R. Grünewald, and L. Horner, *Chem. Ber.*, **93**, 861 (1960).

amount of remaining peroxide was pursued by iodometry at appropriate intervals. Finally the solution was heated at 60°C for 2 hr. About 5% of the initial hydroperoxide remained unchanged.

The precipitate (NaBr, 2.2 g) was filtered and liquid products were determined by vpc after neutralization with hydrogen chloride in ethanol. From the filtrate ethanol was distilled off and the residue was chromatographed on alumina. Triphenylphosphine oxide (8.6 g, 0.031 mol, 62.1%), mp 155—156°C, was obtained and determined by mixed mp with an authentic sample and the IR spectrum. Benzyldiphenylphosphine oxide was not determined precisely but identified by vpc, and isolated in a small amount by column chromatography.

b) *Diphenylmethylenetriphenylphosphorane (Ib)*: The reaction was carried out under the same conditions and in the same scale as those for a), but in this case the corresponding phosphorane precipitated immediately as an orange-red solid and gradually disappeared during the reaction. The reaction was faster than that of benzylidenetriphenylphosphorane and the temperature of the mixture rose to 40—50°C after 2 hr. The products were determined by vpc. Diphenylmethane was also isolated by distillation under reduced pressure and triphenylphosphine oxide (11.3 g, 81.3%) was obtained by column chromatography on alumina. Elution with ether gave 10 mg of tetraphenylethane, mp 204—208°C. The structure was determined based on spectral data and by mixed melting point with an authentic sample.

c) n-*Butylidenetriphenylphosphorane* (*Ic*): The reaction was performed under the same conditions and in the same scale as those for a), except that a gas burrette was equipped to the system in order to measure the volume of *n*-butane, which is expected to be evolved. The reaction was slower than that of benzylidenetriphenylphosphorane. No gas evolution was observed in this system, *n*-butane evolved being probably completely soluble in ethanol. *n*-Butyl ethyl ether, triphenylphosphine oxide and diphenyl-*n*-butylphosphine oxide were determined by vpc. The two oxides were also obtained by column chromatography and the melting points were 155°C and 87—93°C (lit,[15] mp 95°C), respectively.

d) *Tetraphenylphosphonium bromide* (*VIII*): This reaction was carried out in the same manner and scale as those for a). Benzene and *t*-butyl alcohol were determined by vpc and triphenylphosphine oxide (7.7 g, 55.2%) was obtained by column chromatography on alumina.

Reaction of Benzylidenetriphenylphosphorane with Sodium Salt of Cumyl Hydroperoxide. To sodium ethoxide (0.08 mol) in ethanol (150 m*l*) was added cumyl hydroperoxide (2.8 m*l*, 0.02 mol) and then 8.7 g (0.02 mol) of benzyltriphenylphosphonium bromide was added. The reaction was carried out by the same procedure as mentioned above. The products were determined by vpc.

Reaction of Tetraphenylphosphonium Bromide with Silver Hydroxide. Silver hydroxide (2.5 g, 0.02 mol) freshly prepared, was added to tetraphenylphosphonium bromide (8.4 g, 0.02 mol) in ethanol (150 m*l*) with stirring. Pale brown precipitate was simultaneously formed and stirring was continued for one hour. The precipitate (AgBr, 3.5 g, 93%) was then filtered off. From the filtrate, benzene (85.5%) was determined by vpc. After removal of ethanol, the residue was recrystallized from benzene, yielding triphenylphosphine oxide (14.8 g, 86.2%), mp 149—156°C.

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[15] W. Kuchen and H. Buchwald, *Chem. Ber.*, **92**, 227 (1959).