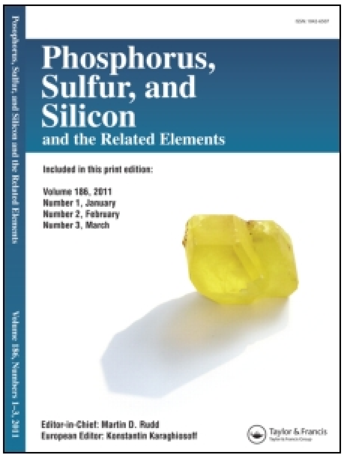

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ELECTRON-TRANSFER PROCESSES. PART 40. REACTION OF ALKYL RADICALS WITH DIPHENYLPHOSPHIDE ANION

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ELECTRON-TRANSFER PROCESSES. PART 40. REACTION OF ALKYL RADICALS WITH DIPHENYLPHOSPHIDE ANION

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The anion Ph_2P^- (K^+, 18-crown-6) reacts with *t*-BuHgCl in HMPA to form Ph_2PCMe_3 by a free radical chain mechanism. In Me_2SO, $Ph_2P(O)CMe_3$ is produced. Reaction of Ph_2P^- with $PhCOCH_2HgCl$ yields the oxidative dimerization product isolable from HMPA but readily converted to $Ph_2P(O)P(O)Ph_2$ in Me_2SO.

INTRODUCTION

Alkyl radicals can react with delocalized carbanions via addition or electron transfer. With nucleophilic radicals such as $Me_3C^{\cdot}$, addition is the preferred

$$R^{\cdot} + C^{-} \longrightarrow \begin{cases} R - C^{\cdot -} \\ R:^{-} + C^{\cdot} \end{cases}$$

route if reaction is going to occur.[1] On the other hand, with an electrophilic radical such as $PhCOCH_2^{\cdot}$, electron transfer from easily oxidized carbanions is the observed course of the reaction.

RESULTS AND DISCUSSION

A convenient source of alkyl radicals in the presence of carbanions has been found to be the alkylmercury halide. When addition of the alkyl radical to the carbanion occurs, a free radical chain reaction of the S_{RN}-type can propagate (Scheme 1).[1,2] Thus, the photostimulated reaction of *t*-BuHgCl with

$$R^{\cdot} + C^{-} \rightarrow R - C^{\cdot -}$$
$$R - C^{\cdot -} + RHgX \rightarrow R - C + R^{\cdot} + Hg^0 + X^{-}$$

SCHEME 1

$PhCOC(Ph)_2^-$ yields $PhCOC(Ph)_2CMe_3$ via Scheme 1[1] while $PhCOCH_2HgCl$ reacts readily with this carbanion to form $PhCOCH_3$ and $PhCOC(Ph)_2C(Ph)_2COPh$, presumably via Scheme 2. Photostimulation or the presence

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$$C^- + RHgX \rightarrow C^{\cdot} + R^{\cdot} + Hg^0 + X^-$$
$$R^{\cdot} + C^- \rightarrow R{:}^- + C^{\cdot}$$
$$2C^{\cdot} \rightarrow C-C$$

SCHEME 2

of free radical traps such as $(t\text{-}Bu)_2NO^{\cdot}$ have little effect on this oxidative dimerization reaction. The *tert*-butyl radical reacts via Scheme 1 and not by Scheme 2 even with such easily oxidized anions as 2,4-di-*tert*-butylphenoxide.

Towards $(EtO)_2PO^-$ neither $Me_3C^{\cdot}$ nor $PhCOCH_2^{\cdot}$ have appreciable reactivity.[3] However, towards $Ph_2P^-K^+$/18-crown-6 in hexamethylphosphoric triamide (HMPA) reactions occur analogous to those observed with an easily oxidized carbanion. The reaction with *t*-BuHgCl occurs by a photostimulated chain reaction to yield Ph_2PCMe_3, whereas towards $PhCOCH_2HgCl$ a thermal reaction occurs readily yielding $(Ph)_2PP(Ph)_2$ (Table I). In Me_2SO similar reactions occur, but the only products isolable are the phosphine oxides ($Ph_2P(O)CMe_3$ and $Ph_2P(O)\text{-}P(O)Ph_2$) apparently formed by oxygen transfer from Me_2SO to the phosphines. In an independent experiment, it was demonstrated that in an argon atmosphere $(Ph)_2PP(Ph)_2$ is converted to the dioxide in 30 min at 25°C.

Phosphide anions participate in the free radical-electron transfer processes of Schemes 1 and 2 in a manner completely analogous to carbanions. The yield of Ph_2PCMe_3 prepared in this manner is higher than the yield reported in the reaction of Ph_2PCl with *t*-BuMgCl in THF at −78°C.[4]

TABLE I

Reactions of Ph_2PK with RHgCl

R	Conditions[a]	Product (Yield)
Me_3C	Me_2SO, 2 h	$Ph_2P(O)CMe_3$ (38,[b] 35%[c])
Me_3C	HMPA, 2 h	Ph_2PCMe_3 (42,[b] 37%[c]) $Ph_2P(O)CMe_3$ (7%[b])
$PhCOCH_2$	Me_2SO, 0.5 h	$Ph_2P(O)P(O)Ph_2$ (53,[b] 45%[c])
$PhCOCH_2$	HMPA, 0.5 h	$(Ph)_2PP(Ph)_2$ (58,[b] 47%[c])

[a] Reactions were performed in N_2-purged solvents in the presence of equimolar amounts of 18-crown-6, with irradiation from a 275 W sunlamp positioned ca. 15 cm from the Pyrex reaction flask.

[b] Yields determined by ^1H NMR and GLC on a 1 mmol scale for reactions 0.1 *M* in RHgX and Ph_2PK.

[c] Isolated yields.

EXPERIMENTAL

Solutions of Ph_2PK were prepared immediately before use by the reaction of Ph_2PH with molar equivalents of Me_3COK and 18-crown-6 under nitrogen. After deoxygenation by N_2 bubbling for 15–30 min, the mercurial was added. Irradiated experiments employed a 275 W sunlamp ca. 15 cm from the Pyrex flask. Product isolation involved treatment with 50–100 mL of deoxygenated water followed by extraction with deoxygenated Et_2O. Yields of products were obtained by GLC or ^1H NMR analysis of the concentrated Et_2O extracts using internal standards. Pure samples of the reaction products were obtained by distillation or crystallization. The ^{31}P chemical shifts are reported as referenced to external 85% H_3PO_4 with resonances deshielded from the reference being reported as positive values.

Diphenyl-(1,1-dimethylethyl)phosphine Oxide

Reaction of 10 mmol of Me_3CHgCl, $Ph_2P^-K^+$ and 18-crown-6 in 60 mL of Me_2SO with sunlamp irradiation had an induction period of ~5 min after which Hg^0 precipitated from the solution. After 2 h, the solution was decanted from the Hg^0 and added to 50 mL deoxygenated H_2O. The Et_2O extract was dried over $MgSO_4$ and the solvent removed under vacuum. Recrystallization of the product from benzene gave 0·90 g (35%) of $Ph_2P(O)CMe_3$, mp 132°C (lit.[5] mp 131–132°C); ^1H NMR ($CDCl_3$) δ 1.24 (D, 9H, $J_{PCCH} = 15$ Hz), 7.2–8.3 (m, 10H); ^{31}P NMR ($CDCl_3$) δ 38.77; GCMS (rel. intensity) 258 (M^+, 0.54), 202 (100), 183 (4.4), 155 (16.1), 125 (5.76), 77 (9.69), 57 (2.13), 51 (5.38), 47 (13.95).

Diphenyl-(1,1-dimethylethyl)phosphine

The photostimulated reaction of 15 mmol of *t*-BuHgCl, $Ph_2P^-K^+$ and 18-crown-6 in 60 mL HMPA for 2 h yielded by distillation 1.34 g (37%) of Ph_2PCMe_3, bp 141–144°C at 2 torr (lit.[4] bp 144–146°C at 2 torr); ^1H NMR ($CDCl_3$) δ 1.15 (d, 9H, $J_{PCCH} = 12.2$ Hz), 7.15–8.2 (m, 10H); ^{31}P NMR (CH_2Cl_2) δ 16.98; HRMS: 242.12238 (M^+) (calcd. 242.12257).

The above reaction in the presence of 10 mol % $(t\text{-Bu})_2NO^{\cdot}$ yielded only 4% of Ph_2PCMe_3.

Tetraphenyldiphosphine

In a glove box under an argon atmosphere, $PhCOCH_2HgCl$ (10 mmol) was added to the red solution of 10 mmol of Ph_2PH, Me_2COK and 18-crown-6 in 50 mL of HMPA. The color was discharged immediately. After 30 min of sunlamp irradiation, the solution was added to 50 mL of deoxygenated H_2O. Extraction with deoxygenated Et_2O followed by distillation gave 0.87 g (47%) of $(Ph)_2PP(Ph)_2$, bp 260–263°C at 1 torr, mp 120°C (lit.[6] mp 120.5°C); ^{31}P NMR (C_6H_6) δ 15.5 (lit.[7] δ 15.2).

Tetraphenyldiphosphine Dioxide

Repetition of the above experiment in Me_2SO as solvent yielded upon recrystallization from toluene 0.91 g (45%) of $Ph_2P(O)P(O)Ph_2$, mp 167–168°C (lit.[8] mp 166–167°C); ^{31}P NMR (C_6H_{12}) $\delta = 25.92$ (lit.[8]) δ 25.9).

Reaction of Tetraphenyldiphosphine with Dimethyl Sulfoxide

Tetraphenyldiphosphine (5 mmol) was stirred in 30 mL of Me_2SO for 30 min under argon with sunlamp irradiation. After 30 min a 78% yield of $Ph_2P(O)P(O)Ph_2$ was detected by g.l.p.c. Upon isolation a 72% yield of $Ph_2P(O)P(O)Ph_2$ was obtained. Under similar conditions in HMPA no more than 6% of $Ph_2P(O)P(O)Ph_2$ was formed in 1 h.

Reaction of t-BuHgCl with 2,4-(t-Bu)$_2$C$_6$H$_3$OK

Reaction of 1 mmol of *t*-BuHgCl with molar equivalents of 2,4-(*t*-Bu)$_2C_6H_3OK$ and 18-crown-6 in 10 mL of deoxygenated solvent with sunlamp irradiation for 2 h at 35–40°C produced 2,4,6-tri-*t*-butylphenol in 47% yield in Me_2SO and 58% in HMPA. In HMPA in the presence of 0.1 mmol of (*t*-Bu)$_2NO^•$, the yield was reduced to 8%.

Reaction of PhCOCH$_2$HgCl with PhCOCPh$_2$Li

Although the reaction of *t*-BuHgCl with $PhCOC(Ph)_2Li$ or $PhCOC(Ph)_2K$ yielded only $PhCOC(Ph)_2CMe_3$,[1] the reaction of $PhCOC(Ph)_2Li$ with $PhCOCH_2HgCl$ in deoxygenated HMPA at 35–40°C yielded $PhCOCH_3$ and $PhCOC(Ph)_2$-$C(Ph)_2COPh$ in the presence or absence of irradiation. The presence of 10 mol % of *t*-$Bu_2NO^•$ did not appear to have any significant effect on the reaction. Reaction for 3 h on a 1 mmol scale in 10 mL of HMPA yielded $PhCOC(Ph)_2$-$C(Ph)_2COPh$ in 71% isolated yield, mp 146.5–147.5°C from MeOH-C_6H_6 (lit.[9] mp 148–151°C).

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