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Metalation of Phosphine Imides with Organolithium Compounds

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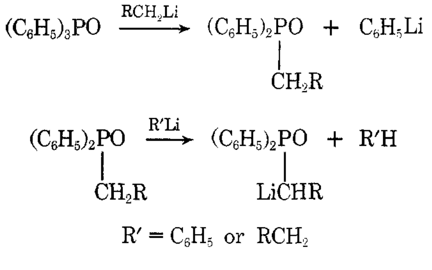
Phenyllithium metalates triphenylphosphine *N*-phenylimide (**1a**) in the ortho position of a *P*-phenyl group and diphenylalkylphosphine *N*-phenylimides on the α carbon of the alkyl group. Alkyllithium reagents react with triphenylphosphine *N*-phenylimide to give the ortho-metalated imide in addition to a competitive reaction which involves an initial displacement of phenyl by alkyl followed by α-metalations on the alkyl carbon (**9a** and **9b**). Displacement of a phenyl group is more pronounced with methyllithium than with *n*-butyllithium. Halogen-metal exchange is not observed in the reaction of *n*-butyllithium with triphenylphosphine *N*-(4-bromophenyl)imide.

Metalation of triphenylphosphine by *n*-butyllithium gives, subsequent to carbonation, an 8% yield of 3-carboxyphenyldiphenylphosphine.[1] Phenylsodium and triphenylphosphine yield 10% 5-phenyldibenzophosphole, presumably through the intermediacy of an ortho-metalated compound.[2] Alkylithium compounds metalate benzyldiphenylphosphine[3] and alkyldiphenylphosphines[4] on the α-alkyl carbon, methyl hydrogen being more easily displaced than methylene hydrogen. Alkylphosphine oxides metalate easily on an α carbon.[5a,b] Gilman and Brown reported that triphenylphosphine oxide is not metalated by phenyllithium or phenylmagnesium bromide.[1] Seyferth et al.[6a,b] have shown that alkyl Grignard or alkyllithium reagents displace a phenyl group from triphenylphosphine oxide, ultimately yielding an α-metalated diphenylalkylphosphine oxide. They present evidence that the overall reaction takes place in two steps:



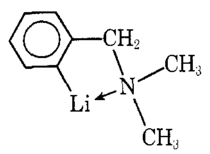
$$(C_6H_5)_3PO \xrightarrow{RCH_2Li} \underset{\displaystyle CH_2R}{(C_6H_5)_2PO} + C_6H_5Li$$

$$\underset{\displaystyle CH_2R}{(C_6H_5)_2PO} \xrightarrow{R'Li} \underset{\displaystyle LiCHR}{(C_6H_5)_2PO} + R'H$$

$$R' = C_6H_5 \text{ or } RCH_2$$

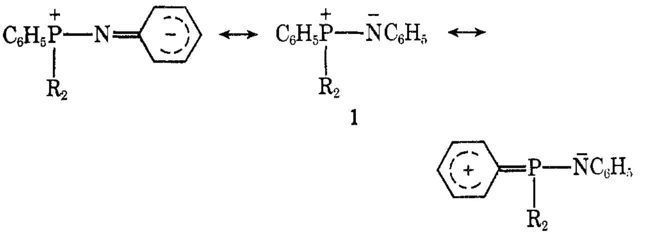
Similar results were observed with triphenylphosphine sulfide.[7]

Intramolecularly directed metalation through coordination with nitrogen has been demonstrated in *N*,*N*-dimethylbenzylamine,[8] dimethylaminomethyl- and dimethylaminoethylferrocene,[9a,b] dimethylaminomethylpyridines,[10] and arylcarboxamides.[11,12] Further, many examples of the ortho-metalation reaction with transition metal complexes having nitrogen and phosphorous donor ligands exist.[13]

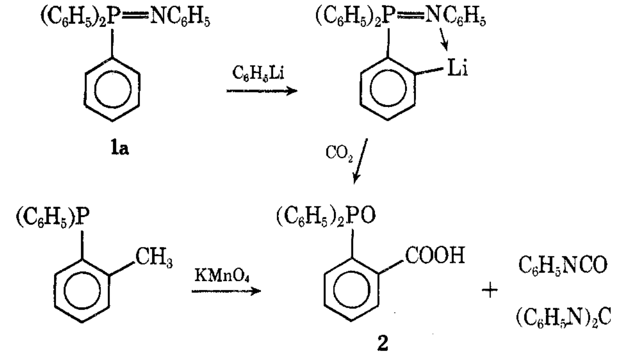


Since arylphosphine *N*-arylimides (**1**) are amenable to intramolecularly directed metalation through coordination on nitrogen and, more importantly, exhibit strong electronic effects in the rings attached to both nitrogen and phosphorous, they are interesting substrates for the study of electrophilic and nucleophilic metalations. The present paper describes our initial work pertaining to the reaction of organolithium compounds with phosphine N-arylimides.

Triphenylphosphine *N*-phenylimide (**1a**) is metalated by phenyllithium to give, after carbonation, a 62% yield of 2-diphenylphosphinylbenzoic acid (**2**).



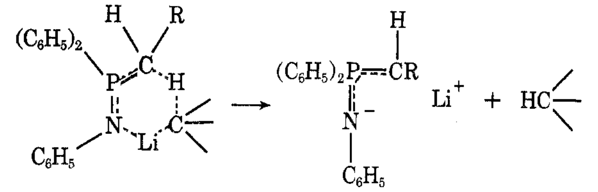
1



1a

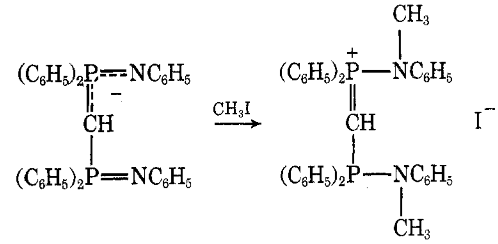
2

Phenyllithium metalates diphenylmethyl- and diphenyl-*n*-butylphosphine *N*-phenylimide on the carbon α to phosphorous. Lateral metalation is preferred to ring metalation because the incipient carbanion in the transition state (3) is resonance stabilized and collapses to the similarly stabilized carbanion (4).[14]



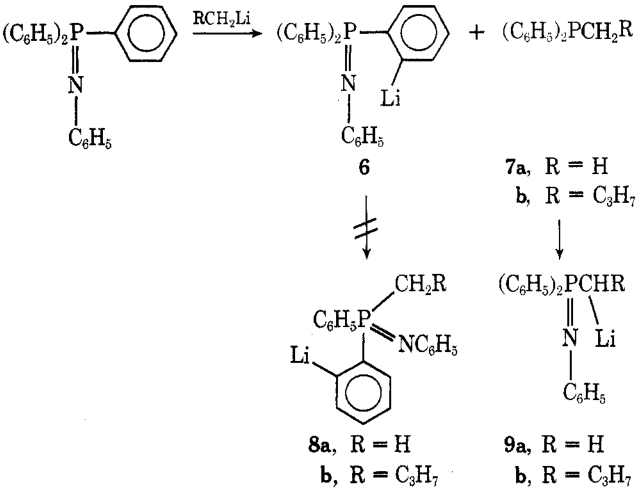
3 4

Evidence for the existence of a stabilized anion similar to 4 is presented by Kovtun et al.[15] who treated the lithium derivative of methylenebisdiphenylphosphine *N*-phenylimide with excess methyl iodide and obtained the N,N-dimethylated product (5). Alkylation at nitrogen rather than carbon may be due to steric factors. An analogous situation exists for $[(C_6H_5)_2]_2CHLi$, which undergoes P-alkylations only.[16]



5

Triphenylphosphine *N*-phenylimide reacted with methyllithium to produce, subsequent to carbonation, 10% of 2-diphenylphosphinylbenzoic acid and a mixture of acids derived from a metalation-exchange sequence (**6–8a**) and/or the reverse (**7a–9a**). Conversion of **6** to **8a** was ruled out because chromatographic analysis of the mixture of carboxylic acids derived from the lithiated compounds showed the presence of derivatives of **6** and **9a** only (see Experimental Section). Furthermore, **6** was isolated from the reaction of phenyllithium with the parent ylide and then treated in separate reactions with methyl- and *n*-butyllithium, respectively. Mild hydrolysis of the reaction mixtures gave a quantitative recovery of triphenylphosphine *N*-phenylimide. The reason for the relative unreactivity of **6** may be its insolubility in the reaction medium.



6

7a, R = H
b, R = C_3H_7

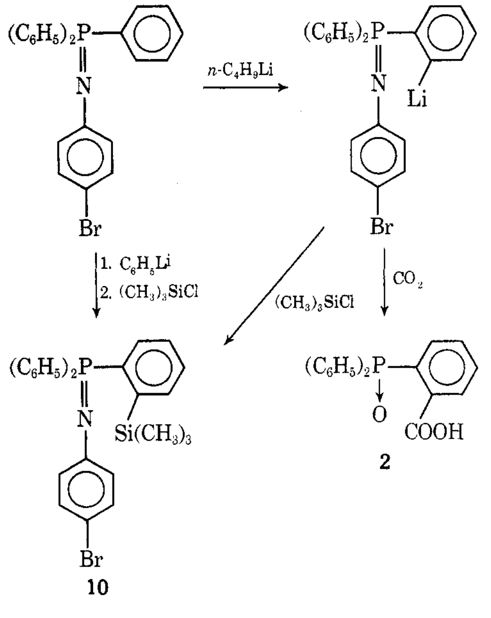
8a, R = H
b, R = C_3H_7

9a, R = H
b, R = C_3H_7

With *n*-butyllithium the exchange reaction is much less pronounced. The primary metalation product amounted to 40%, and was accompanied by a very small yield (less than 5%) of the exchange–metalation product (**9b**). These results are in contrast to the metalation of triphenylphosphine oxide with alkyllithium compounds, in which exchange followed by metalation was the only observed sequence.[6] We are proposing the two-step reaction by analogy to the triphenylphosphine oxide work[6] and because tetraphenyllead was isolated after triphenyllead chloride was added to the reaction mixture between triphenylphosphine *N*-phenylimide and *n*-butyllithium, thus proving the intermediacy of phenyllithium.

Halogen–metal interchange does not compete with metalation in the reaction of triphenylphosphine *N*-(4-bromophenyl)imide with *n*-butyllithium at 0 °C. When the reaction mixture was treated with trimethylsilyl chloride the only product to be isolated was diphenyl-2-trimethylsilylphenylphosphine *N*-(4-bromophenyl)imide (**10**). Acid hydrolysis of the residual reaction mixture yielded enough *p*-bromoaniline to show that very little, if any, bromine was displaced from the phenyl ring. This was not unexpected in view of the high electron density in the *N*-aryl ring of the imide (1). The structure of the silylphosphine imide was proved by the transformations shown in Scheme I.

Scheme I



2

10

Experimental Section

Preparation of Phosphine Imides. Phosphine imides were prepared according to the method of Horner and Oediger.[17]

(a) Triphenylphosphine *N*-phenylimide: yield 62%; mp 125–126 °C.

(b) Triphenylphosphine *N*-(*p*-bromophenyl)imide: yield 58%; mp 126–127 °C.[18]

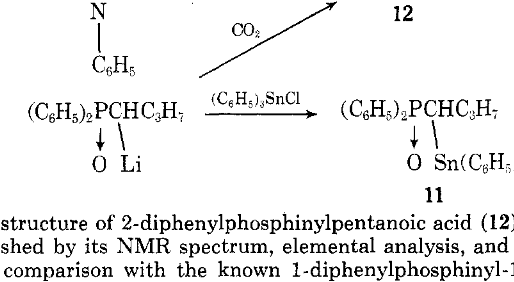
(c) Diphenylmethylphosphine *N*-phenylimide: yield 29%; mp 100–101 °C (crystallized from heptane). Anal. Calcd for $C_{19}H_{18}NP$: C, 78.4; H, 6.18; 4.77. Found: C, 78.36; H, 6.29; N, 4.67.

(d) *n*-Butyldiphenylphosphine *N*-phenylimide: yield 27%; mp 92–93.5 °C (crystallized from cyclohexane). Anal. Calcd for $C_{22}H_{24}NP$: C, 79.28; H, 7.21; N, 4.21. Found: C, 79.50; H, 7.10; N, 4.35.

Metalation of Triphenylphosphine *N*-Phenylimide with Phenyllithium. To 3.5 g (0.01 mol) of triphenylphosphine *N*-phenylimide suspended in 50 ml of ether was added 6 ml of phenyllithium (2.3 M in benzene–ether). The mixture was stirred at room temperature. The imide dissolved immediately and after 5 min a yellow precipitate formed. After 3 h the mixture was poured on pulverized dry ice suspended in dry ether. After the CO_2 had evaporated, the mixture was hydrolyzed with water, the phases were separated, and the aqueous phase was acidified with dilute HCl. The precipitated acid was collected on a filter, dried, and crystallized from 95% ethanol, yield 2.0 g (62%), mp 263–268 °C. A second crystallization raised the melting point to 266–268 °C. Schindlbauer[19] prepared 2-diphenylphosphinylbenzoic acid by oxidation of diphenyl-*o*-tolylphosphine with $KMnO_4$ in aqueous pyridine and reported a melting point of 242–249 °C. In a similar preparation we obtained an acid melting at 266–268 °C after several crystallizations from ethanol. The neutral equivalent and NMR spectrum were consistent with the structure assigned by Schindlbauer. A mixture melting point with the metalation product was undepressed. The ether layer from the hydrolysis of the carbonated mixture was evaporated, and the semisolid residue was triturated with ethanol. The residue, crystallized from ethanol, melted at 234–236 °C. The mixture melting point with diphenylurea was 235–236 °C.

Metalation of Diphenylmethylphosphine *N*-Phenylimide with Phenyllithium. To 1.5 g (5.0 mmol) of phosphine imide in 25 ml of ether was added 3 ml of phenyllithium in benzene–ether (2.3 M). After 3 h at room temperature the mixture was poured on dry ice–ether. After hydrolysis the aqueous layer was acidified with dilute HCl and the oily precipitate extracted with chloroform. The solution was dried over anhydrous sodium sulfate and placed on a silica gel column. The column was eluted successively with chloroform and chloroform–methanol (15:5 v/v). The first component (0.2 g) to be eluted was diphenylmethylphosphine oxide, mp 111–113 °C. The second component, after crystallization from dilute ethanol, melted at 143–145 °C. The yield was 0.65 g (52%). A mixture with diphenylphosphinylacetic acid[5b] melted at 143–145 °C.

Metalation of *n*-Butyldiphenylphosphine *N*-Phenylimide with Phenyllithium. To 1.4 g (4.2 mmol) of phosphine imide was added 3 ml of a 2 M solution of phenyllithium in ether. After 3 h at room temperature, the mixture was treated in the usual manner to yield, after crystallization from dilute ethanol, 1.0 g (83%) of an acid melting at 121–123°. Anal. Calcd for $C_{17}H_{19}O_3P$: C, 67.55; H, 6.29. Found. C, 67.40; H, 6.19. NMR 2.5 (m, 10 H), 6.4 (m, 1 H), 8.5 (m, 4 H), 9.5 (m, 3 H), −1.6 ppm (s, 1 H). A mixture melting point with 2-diphenylphosphinylpentanoic acid, prepared by metalation of *n*-butyldiphenylphosphine oxide (see below), was undepressed.



The structure of 2-diphenylphosphinylpentanoic acid (**12**) was established by its NMR spectrum, elemental analysis, and by indirect comparison with the known 1-diphenylphosphinyl-1-triphenylstannylbutane (**11**).[6b]

Preparation of 2-Diphenylphosphinylpentanoic Acid (12). To 0.025 mol of phenyllithium in 50 ml of ether was added 5.16 g (0.02 mol) of *n*-butyldiphenylphosphine oxide. After 1 h at room temperature one-half of the mixture was poured on a suspension of pulverized, solid CO_2 in ether and the other half was added to 4.8 g (0.01 mol) of triphenyltin chloride in 15 ml of ether. The carbonated mixture was processed in the usual manner and the acidic product after crystallization from dilute ethanol melted at 121–123 °C (yield 75%).

The organotin solution was treated with 25 ml of H_2O, the ether layer was separated, and the ether was evaporated. Crystallization of the residue from ether gave 4.0 g (70%) of 1-diphenylphosphinyl-1-triphenylstannylbutane (**11**), mp 148–150 °C.[6b]

Metalation of Triphenylphosphine *N*-Phenylimide with Methyllithium. Metalation of 3.5 g (0.01 mol) of imide was carried out as described above for phenyllithium. The acidified aqueous layer from the carbonation was extracted with four 10-ml portions of chloroform. The chloroform was evaporated and the crude, sticky product, 2.3 g, was crystallized from aqueous ethanol, then from acetic acid, and finally from ethanol. The yield of 2-diphenylphosphinylbenzoic acid was 0.24 g (10%), mp 265–267 °C.

The filtrate from the first crystallization was evaporated in a rotary still, and yielded after purification via the sodium salt[5b] and several crystallizations from dilute ethanol, diphenylphosphinylacetic acid, melting at 143–144 °C.

When the crude mixture of acids was converted to the methyl esters with ethereal diazomethane and then subjected to gas chromatography[20] the results showed a 12% yield of **6** and 44% of **9a**.

Metalation of Triphenylphosphine *N*-Phenylimide with *n*-Butyllithium. The reaction was carried out as described for the metalation with methyllithium and yielded 1.3 g (40%) of 2-diphenylphosphinylbenzoic acid and less than 5% of 2-diphenylphosphinylpentanoic acid. Gas chromatography[20] of the methyl esters gave 45% of **6** and 5% of **9b**.

Attempted Exchange Reaction between *o*-Lithiophenyldiphenylphosphine *N*-Phenylimide (6) and *n*-Butyllithium. To a suspension of 5.2 g (0.015 mol) of triphenylphosphine *N*-phenylimide (**1a**) in 50 ml of ether was added 7 ml of 2.2 M phenyllithium in benzene–ether and the mixture was stirred for 3 h at room temperature. The yellow, crystalline lithio compound (**6**) was collected on a filter in a dry N_2 atmosphere. The filtrate was hydrolyzed with H_2O and 1.2 g (0.0034 mol) of starting imide (**1a**) was recovered from the organic layer.

The lithio derivative (**6**) (identity had been established previously by conversion to the corresponding acid) was suspended in 50 ml of ether and, after addition of 7 ml of 2 M *n*-butyllithium in hexane, was stirred for 3 h at room temperature. The mixture was hydrolyzed with H_2O, 25 ml of benzene was added, and the organic layer was separated, dried over Na_2SO_4, and evaporated. The yield of recovered imide (**1a**) was 3.79 g (0.011 mol), giving a total of 0.0144 mol (96%) of recovered imide. A blank run in which *n*-butyllithium was omitted gave a 95% recovery of imide; thus no appreciable exchange took place between **6** and *n*-butyllithium.

Methyllithium. In an identical experiment methyllithium was stirred with a suspension of the lithio derivative (**6**). Ninety-four percent of the starting imide (**1a**) was recovered.

Trapping of Phenyllithium with Triphenyllead Chloride. To 0.02 mol of *n*-butyllithium in 50 ml of ether was added 3.53 g (0.1 mol) of triphenylphosphine *N*-phenylimide. After 3 h 7.1 g (0.015 mol) of triphenyllead chloride was added. The mixture was refluxed for 1 h, hydrolyzed with water, and filtered. The residue was crystallized from benzene, giving 2.5 g (48%) of tetraphenyllead, mp 228 °C.

Diphenyl-2-trimethylsilylphenylphosphine *N*-(4-Bromophenyl)imide (10). A. To 0.034 mol of *n*-butyllithium in 80 ml of ether was added 14.7 g (0.034 mol) of triphenylphosphine *N*-(4-bromophenyl)imide in 175 ml of ether at 0 °C. After the mixture was stirred for 1 h at 0 °C, 3.67 g (0.034 mol) of trimethylsilyl chloride was added. The cooling bath was removed and the mixture was refluxed for 2 h. Water was added and the layers were separated. The ether was evaporated and the residue was stirred with 50 ml of ethanol and was refrigerated overnight. The white solid which separated was crystallized from ligroin, yielding 1 g of starting imide. The ethanol filtrate was concentrated to a viscous residue which was dissolved in 75 ml of methanol. Water was added to incipient turbidity and the mixture stored at 0 °C overnight. The mixture was then filtered and the residue crystallized from cyclohexane, giving 1.85 g (10%) of diphenyl-2-trimethylsilylphosphine *N*-(4-bromophenyl)imide. Anal. Calcd for $C_{27}H_{27}BrNPSi$: C, 64.32; H, 5.35; N, 2.77. Found: C, 64.65; H, 5.50; N; 2.66.

The residues from the above crystallizations were combined and refluxed for 6 h with 8 ml each of concentrated HCl and ethanol. The mixture was diluted with water and extracted with ether. The aqueous layer was neutralized with sodium hydroxide and extracted with ether, and the ether evaporated. The oily residue was treated with acetic anhydride to yield 5.9 g (0.029 mol) of *p*-bromoacetanilide which, after crystallization from aqueous ethanol, melted at 165–167 °C. Thus at least 95% of the bromine in the starting imide remained intact during the reaction with *n*-butyllithium.

B. To 4.32 g (0.01 mol) of triphenylphosphine *N*-(4-bromophenyl)imide suspended in 50 ml of ether was added 10 ml of 1.8 M phenyllithium in benzene–ether. After 3 h one-half of the solution was treated with CO_2 in the usual manner, yielding 67% of 2-diphenylphosphinylbenzoic acid. The other half was treated with 0.005 mol of trimethylsilyl chloride, as described in A above, and yielded 1.25 g (50%) of diphenyl-2-trimethylsilylphosphine *N*-(4-bromophenyl)imide, identical with the product from A, thus establishing the position of the trimethylsilyl group.

Registry No.—**1a**, 2325-27-1; **2**, 2572-40-9; **6**, 57901-16-3; **10**, 57901-17-4; **11**, 57901-18-5; **12**, 57901-19-6; triphenylphosphine *N*-(*p*-bromophenyl)imide, 14987-96-3; diphenylmethylphosphine *N*-phenylimide, 57901-20-9; *n*-butyldiphenylphosphine *N*-phenylimide, 57901-21-0; phenyllithium, 591-51-5; diphenylmethylphosphine oxide, 2129-89-7; diphenylphosphinylacetic acid, 1831-63-6; *n*-butyldiphenylphosphine oxide, 4233-13-0; methyllithium, 917-54-4; *n*-butyllithium, 109-72-8; triphenyllead chloride, 1153-06-6; tetraphenyllead, 595-89-1; *p*-bromoacetanilide, 103-88-8.

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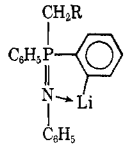
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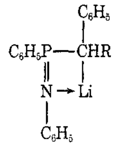
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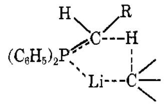
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Reactions of Carboxylic Acids with Organolithium Compounds

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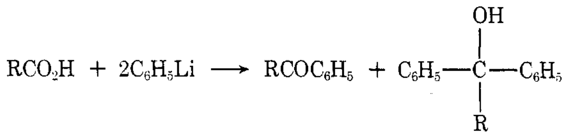
A series of carboxylic acids, RCO_2H, has been treated with a series of organolithium compounds, R′Li, to give, in most cases, a mixture of ketones, RCOR′, and carbinols, $R'_2C(OH)R$. A scheme is presented to account for the formation of these products and evidence in its support is given.

Recently we reported[1] that the interaction of equivalents of lithium carboxylates and organolithium compounds for a 24-h period gave mixtures of ketones and carbinols. It was anticipated that similar results would arise from the interactions of carboxylic acids (1 equiv) and organolithium compounds (2 equiv);[2] however, quite different results were obtained (vide infra).

In the present study a series of aliphatic acids (1 equiv) and one aromatic acid (1 equiv) were allowed to react with phenyllithium (2 equiv) for 0.5 h. In all cases mixtures of ketones and carbinols were obtained.



$$RCO_2H + 2C_6H_5Li \longrightarrow RCOC_6H_5 + C_6H_5-\overset{\displaystyle OH}{\underset{\displaystyle R}{C}}-C_6H_5$$

It was thought that refluxing the carboxylic acids with phenyllithium for periods greater than 0.5 h might lead to only ketonic products as was found[1] in the reactions of preformed lithium carboxylates with phenyllithium. However, refluxing *n*-butyric acid or benzoic acid (1 equiv) with phenyllithium (2 equiv) for varying periods of time gave essentially the same yields of ketone and tertiary alcohol (Table I).

Table I. Reactions of *n*-Butyric and Benzoic Acids with Phenyllithium

		Products, % yield	
RCO_2H, R	Reflux time, h	C_6H_5COR[a]	$(C_6H_5)_2C(OH)R$[b]
n-C_3H_7	0.5	57	25
n-C_3H_7	24	60	29
C_6H_5	0.5	54	25
C_6H_5	24	66	25
C_6H_5	96	63	25

[a] Physical constants agree with literature values [C. R. Hauser, W. J. Humphlett, and M. J. Weiss, *J. Am. Chem. Soc.*, **70**, 426 (1948)]; in each case the carboxylic acid (1 equiv) was added to phenyllithium (1 equiv). [b] Physical constants agree with literature values [H. Masson, *C. R. Acad. Sci.*, **135**, 534 (1902)].

Several other aliphatic, aromatic, and heterocyclic acids were treated with phenyllithium to give mixtures of ketones and carbinols (Table II). In addition, the reactions of benzoic acid with six aliphatic organolithium compounds