tube and was extracted with three 1-ml portions of diethyl ether by means of a Pasteur pipet. The combined extracts were dried over a mixture of equal parts of anhydrous $MgSO_4$ and anhydrous Na_2CO_3. The dried extract was decanted into a test tube, and excess diazomethane was added.[7] Excess diazomethane was removed by means of a stream of nitrogen, and 50- to 100-μl samples of the solution were analyzed by glpc (6-ft 10% Carbowax 20M on Chromosorb W, 80–100 mesh at 150°, He flow 60 ml/min). A correction factor for the extraction and analysis was determined using a synthetic mixture of pure **2** and **3**. Control experiments demonstrated that epimerization of the products did not occur under the conditions of the decarboxylation.

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Registry No.—**1**, 35113-49-6; **2**, 42031-28-7; **3**, 42031-29-8.

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[7] H. Schlenk and J. L. Gellerman, *Anal. Chem.*, **32**, 1412 (1960).

Carboxylation Reactions Using the Reagent Lithium 4-Methyl-2,6-di-*tert*-butylphenoxide

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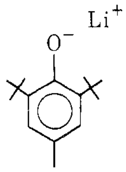
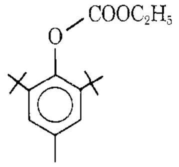
This research was initiated in order to develop a system for the carboxylation of weakly acidic substances such as ketones by the use of a base which is protected sterically from attack on carbon dioxide but able to deprotonate the substrate for carboxylation. The base chosen for initial studies was the 4-methyl-2,6-di-*tert*-butylphenoxide ion (I). It was found that the lithium salt I was readily generated from the phenol in ethereal solution by treatment with 1 equiv of *n*-butyllithium. Although solutions of I in ether did take up carbon dioxide, the rate of absorption was quite slow. It was determined, for example, that exposure of I in ethereal solution to carbon dioxide at 760 mm for 12 hr followed by quenching with triethyloxonium fluoroborate gave only 15% of the carbonated derivative II together with much recovered phenol.



I



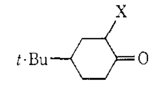
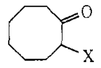
II

The carbonation of a number of substrates was then investigated using mixtures of substrate, phenoxide base I, and carbon dioxide. Table I summarizes the results obtained for three ketones, a terminal acetylene, and a sulfone. No carbonation was observed for isoamyl acetate, *N*-acetylpiperidine, phenylacetamide, or 1-nonyne. Methyl phenylacetate, phenylacetonitrile, and γ-butyrolactone underwent carbonation to some extent with yields in the range 20–50%.

In summary, the above data would suggest that the reagent I can be used to promote the carboxylation of ketones, but that it is ineffective toward less acidic substrates. The reagent I has also been applied to dithiocarboxylation reactions using carbon disulfide as reactant.[1]

TABLE I

REACTION OF SUBSTRATES WITH CARBON DIOXIDE AND LITHIUM 4-METHYL-2,6-DI-*tert*-BUTYLPHENOXIDE[a]

Substrate registry no.	Substrate, X = H; product, X = COOH	Product registry no.	Yield, %	Reaction time, hr
98-53-3		42031-70-9	89	16
502-49-8		25731-69-7	77	16
98-86-2	$C_6H_5COCH_2X$	614-20-0	75	24
536-74-3	$C_6H_5C{\equiv}CX$	637-44-5	74	16
3112-85-4	$C_6H_5SO_2CH_2X$	3959-23-7	65	24

[a] Reaction conditions: 760 mm of CO_2, 4 equiv of I/equiv of substrate, ether solvent.

Experimental Section

2-Carboxy-4-*tert*-butylcyclohexanone.—This preparation can be used to illustrate the general procedure applied to the substrates listed in Table I. Lithium 4-methyl-2,6-di-*tert*-butylphenoxide (4 mmol) was generated by slow addition of 4 mmol (2 ml, 2 *M* in hexane) of *n*-butyllithium to 4.2 mmol (924 mg) of 4-methyl-2,6-di-*tert*-butylphenol in 25 ml of ether at −78° under argon. The resulting white precipitate dissolved completely when the mixture was allowed to warm up to room temperature. The flask containing this reagent was then attached to a hydrogenation apparatus, which was prefilled with excess carbon dioxide, and 0.9 mmol (139 mg) of 4-*tert*-butylcyclohexanone in 1 ml of ether was added. The resulting mixture was well stirred for 16 hr (the solution became turbid after 90 min). The mixture was diluted with 20 ml of ice water at 0° and extracted with ether. The aqueous layer was acidified to pH 3–4 using 0.1 *M* aqueous hydrochloric acid at 0° and extracted with two portions of ether. The ethereal extract was dried over sodium sulfate and concentrated *in vacuo* to give a thick oil (89% yield) which slowly crystallized in a cold room at 5°. Thin layer chromatographic analysis of this product revealed no impurities. The infrared spectrum ($CHCl_3$ solution) exhibited bands at 3400–2800, 1715 (m), 1660 (s), and 1598 cm^{-1} (m), indicating a predominance of the enol form. The product lost carbon dioxide upon warming with formation of 4-*tert*-butylcyclohexanone.

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Registry No.—Carbon dioxide, 124-38-9; lithium 4-methyl-2,6-di-*tert*-butylphenoxide, 42031-71-0.

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[1] E. J. Corey and R. H. K. Chen, *Tetrahedron Lett.*, in press.

Synthesis of Methyl 3-Hydroxybenzo[*b*]thiophene-2-carboxylate Esters by Nitro Displacement

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The first synthesis of methyl 3-hydroxybenzo[*b*]thiophene-2-carboxylate was reported by Friedlander.[1]

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[1] P. Friedlander, *Justus Liebigs Ann. Chem.*, **351**, 390 (1906).