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.

Acknowledgment.—It is a pleasure to acknowledge support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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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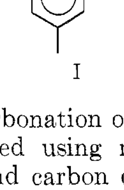
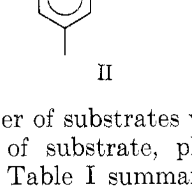
Received July 5, 1973

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

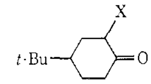
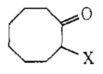


II

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%.

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.

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]

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.

Acknowledgment.—This work was assisted financially by a grant from the National Science Foundation.

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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Received July 27, 1973

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

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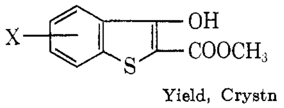
[1] P. Friedlander, *Justus Liebigs Ann. Chem.*, **351**, 390 (1906).

TABLE I

METHYL 3-HYDROXYBENZO[*b*]THIOPHENE-2-CARBOXYLATES



Registry no.	X	Mp, °C	Yield, %	Crystn solvent[a]	Temp, °C; time, hr
13134-76-4	H	109–110[b]	61	A	0, 0.5; 25, 2.5
33851-22-8	6-Cl	147–149	75	B	0, 0.5; 25, 1
33851-23-9	7-Cl	133–134	80	B	0, 0.5; 25, 2
42087-77-4	4-NO_2	185–186.5	85	B	0, 0.5
42087-78-5	7-NO_2	226–228	73	B	0, 0.5
42087-79-6	7-OCH_3	118–119	50	A	0, 0.5; 25, 3

[a] A, alcohol–water; B, alcohol. [b] Lit.[1] mp 104°.

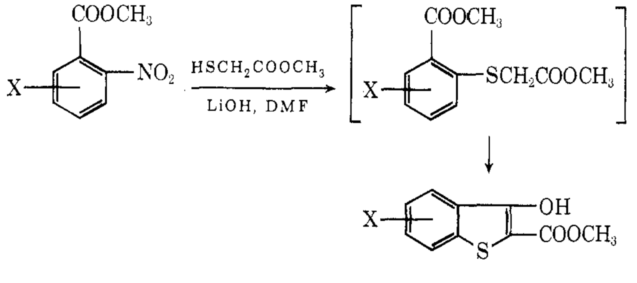
TABLE II

MICROANALYTICAL DATA

X	Empirical formula	Calcd, % C	H	N	S	Found, % C	H	N	S
H	$C_{10}H_8O_3S$	57.68	3.87		15.40	57.91	3.94		15.51
6-Cl	$C_{10}H_7ClO_3S$	49.48	2.91		13.21	49.31	2.82		13.16
7-Cl	$C_{10}H_7ClO_3S$	49.48	2.91		13.21	49.70	2.87		13.31
4-NO_2	$C_{10}H_7NO_5S$	47.43	2.79	5.53	12.66	47.47	2.77	5.52	12.76
7-NO_2	$C_{10}H_7NO_5S$	47.43	2.79	5.53	12.66	47.59	2.74	5.47	12.61
7-OCH_3	$C_{11}H_{10}O_4S$	55.45	4.23		13.46	55.67	4.14		13.59

The compound was formed by base-catalyzed cyclization of the bis methyl ester of *o*-[(carboxymethyl)thio]-benzoic acid, which was obtained in three steps from *o*-mercaptobenzoic acid. There are many modifications of this general synthesis, and these have been reviewed.[2] The free acids are readily decarboxylated to form benzo[*b*]thiophen-3(2*H*)-ones (thioindoxyls), which are precursors to thioindigo dyes. In a previous communication,[3] the author reported a direct synthesis of methyl 3-aminobenzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzonitriles and methyl benzo[*b*]thiophene-2-carboxylates from *o*-nitrobenzaldehydes. This synthesis has now been extended for the conversion of methyl *o*-nitrobenzoates to methyl 3-hydroxybenzo[*b*]thiophene-2-carboxylates (Scheme I).

SCHEME I



Under the conditions of the reaction, the nitro group, activated by the adjacent carbomethoxyl function, is readily displaced by methyl thioglycolate anion (lithium salt) in DMF, and this is followed by a base-catalyzed cyclization as in the Friedlander synthesis. The conditions are mild and the yields, which are based upon crystallized products, are high (Table I). The major side reaction appears to be hydrolysis of the starting ester, and this can probably be overcome by rigorous drying of the DMF and lithium hydroxide. Other examples of the synthetic utility of activated nitro displacement will be the subject of further communications.

Experimental Section[4]

Materials.—All benzoic acids utilized are commercially available from the Aldrich Chemical Co. The methyl esters were prepared by standard procedures in the literature.

General Procedure for Methyl 3-Hydroxybenzo[*b*]thiophene-2-carboxylates.—To a well stirred, cold solution (ice bath) containing 30 mmol of the substituted methyl *o*-nitrobenzoate and 4.0 ml of methyl thioglycolate in 60 ml of DMF was added slowly, portionwise, 2.5 g of lithium hydroxide. The mixture was stirred in the cold for 0.5 hr and then at room temperature for the time period shown in Table I. It was poured into ice water and the solution was acidified. The crude product was collected and crystallized from the appropriate solvent (Table I). Microanalytical data are summarized in Table II.

Acknowledgments.—The author wishes to thank Mr. Paul Unger and associates for spectral measurements and Mr. George Maciak and associates for microanalytical data.

Registry No.—Methyl *o*-nitrobenzoate, 606-27-9; methyl 4-chloro-2-nitrobenzoate, 42087-80-9; methyl 3-chloro-2-nitrobenzoate, 42087-81-0; methyl 2,6-dinitrobenzoate, 42087-82-1; methyl 2,3-dinitrobenzoate, 42087-83-2; methyl 3-methoxy-2-nitrobenzoate, 5307-17-5; methyl thioglycolate, 2365-48-2.

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(2) (a) H. D. Hartough and S. L. Meisel, "The Chemistry of Heterocyclic Compounds," A. Weissberger, Ed., Interscience, New York, N. Y., 1954, pp 67, 138; (b) B. Iddon and R. M. Scrowston, *Advan. Heterocycl. Chem.*, **11**, 229 (1970).

(3) J. R. Beck, *J. Org. Chem.*, **37**, 3224 (1972).

(4) Melting points were determined on a Mel-Temp apparatus and are uncorrected.

Synthesis and Properties of 3,3,6,6-Tetramethyl-1-oxacycloheptane-4,5-dione

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Received May 21, 1973

Our interest in charge-transfer phenomena in heteroatom containing medium ring ketone[1a] and α-dione[1b,c] substrates has led us to synthesize oxa α-dione **1**[2] in order to compare its uv spectra, mass spectral frag-

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(1) (a) P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1970); (b) P. Y. Johnson, *Tetrahedron Lett.*, 1991 (1972); (c) P. Y. Johnson and I. Jacobs, *Chem. Commun.*, 925 (1972).

(2) Since submitting this manuscript a second report of the synthesis of **1** has been published. See A. Krebs and G. Eurgdorfer, *Tetrahedron Lett.*, 2063 (1973).