58.5 (d), 83.6 (s), 224.4 (s); mass spectrum (70 eV), m/z (relative intensity) 202 (molecular ion, 12.6), 109 (8.9), 108 (100), 107 (31.8), 95 (22.0), 91 (12.2), 79 (16.5), 77 (19.6).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.47; H, 7.00.

Method B. Compound **3a** (500 mg, 1.44 mmol) and sodium chloride (300 mg, excess) were suspended in dimethyl sulfoxide (DMSO, 30 mL). The reaction mixture was heated at 150 °C for 1.5 h; slight darkening of the reaction mixture occurred, and a gas was evolved slowly during this period. The reaction mixture was then cooled to room temperature and water (150 mL) was added. The resulting mixture was extracted with methylene chloride (3 × 25 mL), and the combined organic layers were washed with water (3 × 30 mL), dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford crude **4** as a white solid. Vacuum sublimation of this material [150 °C (0.05 mmHg)] afforded pure **4** (285 mg, 97%).

Dimethyl 3,6-Dichloropentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-trideca-2,6-diene-2,7-dicarboxylate (6). A suspension of **3a** (1.0 g, 2.9 mmol) in phosphorus trichloride (6 mL) was cooled via application of an external ice bath. To this stirred suspension was added phosphorus pentachloride (3.00 g, 14.3 mmol) in small portions during 30 min. The reaction mixture was stirred for 1 h after all of the PCl_5 had been added. The reaction mixture was then refluxed overnight. The resulting mixture was cooled to room temperature and poured over crushed ice (100 g). The resulting suspension wax extracted with methylene chloride (3 × 50 mL), and the combined organic layers were washed with water (3 × 50 mL), dried (anhydrous magnesium sulfate), and filtered. The filtrate was concentrated in vacuo to afford crude diacid **5** as a light brown microcrystalline solid. This material was dissolved in methanol (10 mL) that contained concentrated sulfuric acid (2 drops), and the resulting solution was refluxed overnight. The reaction mixture was cooled and diluted with water (60 mL), and the resulting mixture was extracted with methylene chloride (3 × 30 mL). The combined organic layers were washed with water (4 × 50 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. Crude **6** was thereby obtained as a light brown microcrystalline solid. This material was recrystallized from ether to afford pure **6** as colorless prisms (369 mg, 36%): mp 138–139 °C; IR (KBr) 2949 (s), 2890 (s), 2849 (m), 1722 (s), 1698 (s), 1626 (s), 1610 (m), 1440 (s), 1255 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.51 (AB, J_{AB} = 10.5 Hz, 1 H), 1.60 AB, J_{AB} = 10.5 Hz, 1 H), 2.42 (m, 2 H), 2.80 (m, 2 H), 3.15 (m, 2 H), 3.70 (s, 6 H), 3.78 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.2 (d), 37.0 (t), 39.7 (d), 40.5 (d), 51.9 (d), 53.2 (q), 126.9 (s), 141.5 (s), 165.8 (s); mass spectrum (70 eV), m/z (relative intensity) [no molecular ion] 184.0 (100.0), 124.9 (93.4).

Anal. Calcd for $C_{17}H_{16}Cl_2O_4$: C, 57.48; H, 4.54. Found: C, 57.39; H, 4.37.

Attempted Intramolecular [2 + 2] Photocyclization of 6. A solution of **6** (200 mg) in degassed ethyl acetate (250 mL) was irradiated with a 450-W Hanovia medium-pressure mercury lamp (Pyrex filter) for 24 h. Removal of solvent in vacuo afforded only unchanged starting material (194 mg). No reaction occurred even when considerably longer irradiation times were employed (i.e., 48 and 72 h, respectively).

Acknowledgment. Financial support of this study by the Air Force Office of Scientific Research (Grant AFO SR-84-0085), The Robert A. Welch Foundation (Grant B-963), and the North Texas State University Faculty Research Committee is gratefully acknowledged. The X-ray crystallographic structure determination of **3a** was supported in part by the Office of Naval Research Mechanics Division.

Registry No. 1, 2958-72-7; **3a**, 108744-07-6; **4**, 108744-08-7; **5**, 108744-09-8; **6**, 108744-10-1; ethyl diazoacetate, 623-73-4.

Supplementary Material Available: A list of atomic coordinates and equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, and H-atom coordinates and isotropic displacement parameters for **3a** (5 pages). Ordering information is given on any current masthead page.

Intramolecular [2 + 2] Cycloadditions of Ketenes to Carbonyl Groups. A Novel Synthesis of Substituted Benzofurans

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Received February 11, 1987

There is considerable current interest in synthetic applications of intramolecular [2 + 2] cycloaddition reactions of ketenes with carbon–carbon double bonds[1] and with ketone and aldehyde carbonyl groups.[2] We recently reported that (*o*-carbonylphenoxy)acetyl chlorides can be readily dehydrochlorinated to afford the corresponding ketenes, which then undergo facile intramolecular [2 + 2] cycloadditions to form the corresponding tricyclic β-lactones. Decarboxylation of these lactones then occurs spontaneously, thereby affording the corresponding benzofuran in 53–82% yield (Scheme I).[2] In order to further delineate the scope and limitations of this novel synthesis of substituted benzofurans, we have explored new methods to generate ketene intermediates for use in intramolecular cycloaddition reactions. We now report the results of our study.

The method utilized for the synthesis of the (*o*-carbonylphenoxy)acetic acids that were employed as substrates in this study is illustrated in Scheme II for the preparation of [(*o*-formylphenoxy)phenyl]acetic acid. Williamson ether syntheses were carried out via reaction of appropriately substituted phenoxide anions with substituted α-bromoacetic acids (see Experimental Section). On occasions when oily (*o*-acylphenoxy)acetic acids were prepared that could not be recrystallized, it proved expedient to purify them via the corresponding dicyclohexylammonium salt.[3] These salts, prepared conveniently by reaction of each of the crude acids with dicyclohexylamine, could be purified simply by washing with ligroin. The salts thereby obtained proved to be suitable for direct utilization in the one-pot ketene cycloaddition procedure (method B) without the necessity of prior conversion to the free acid. Three different methods were then utilized to generate the corresponding ketenes from these (*o*-carbonylphenoxy)acetic acids, as follows.

Method A. Base-promoted elimination of hydrogen chloride from acid chlorides of the type $R_2CHC(O)Cl$ is one of the classical methods by which ketenes have been generated traditionally.[4] Thus, the (*o*-carbonylphenoxy)acetic acids were converted into the corresponding acid chlorides via reaction with 5–8 equiv of oxalyl chloride in benzene at ambient temperature for 4–8 h. Excess oxalyl chloride was removed in vacuo, and the crude acid chloride was then added very slowly to a refluxing solution of triethylamine (3 equiv) in benzene. The fact that dehydro-

(1) (a) Snider, B. B.; Hui, R. A. H. F.; Kulkarni, Y. S. *J. Am. Chem. Soc.* **1985**, *107*, 2194. (b) Marko, I.; Rosmans, B.; Hesbain-Frisque, A.; Dumas, S.; Ghosez, L.; Ernst, B.; Greuter, H. *J. Am. Chem. Soc.* **1985**, 107, 2192. (c) Snider, B. B.; Hui, R. A. H. F. *J. Org. Chem.* **1985**, *50*, 5167. (d) Brady, W. T.; Giang, Y. F. *J. Org. Chem.* **1985**, *50*, 5177. (e) Kulkarni, Y. S.; Snider, B. B. *J. Org. Chem.* **1985**, *50*, 2809. (f) Corey, E. J.; Desol, M. C. *Tetrahedron Lett.* **1985**, *26*, 3535. (g) Kulkarni, Y. S.; Burbaum, B. W.; Snider, B. B. *Tetrahedron Lett.* **1985**, *26*, 5619. (h) Ghosez, L.; Marko, I.; Hesbain-Frisque, A. M. *Tetrahedron Lett.* **1986**, *27*, 5211.

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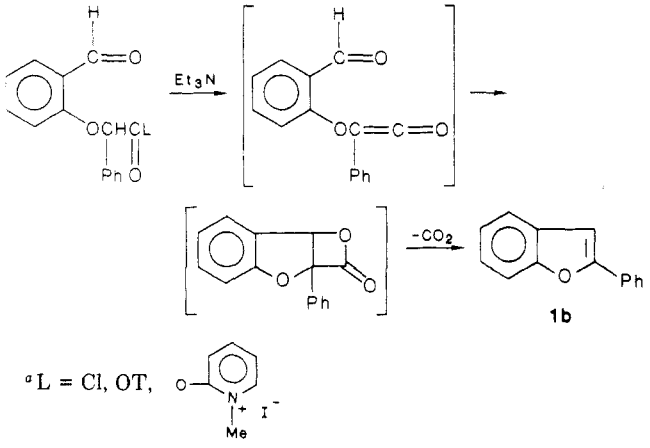
(4) (a) Sauer, J. C. *J. Am. Chem. Soc.* **1947**, *69*, 2444. (b) Sauer, J. C. *Organic Synthesis*; Wiley: New York, 1963; Collect. Vol. 4, p 560. (c) Patai, S., Ed. *The Chemistry of Ketenes, Allenes and Related Compounds*; Interscience Publications: New York, 1980.

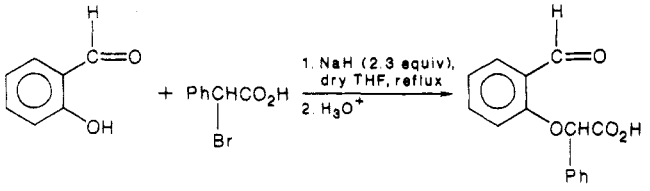
0022-3263/87/1952-3457$01.50/0

Scheme I[a]



[a] L = Cl, OT,

Scheme II



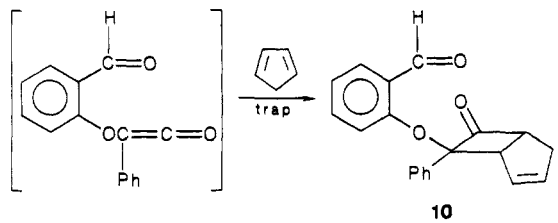
chlorination occurred was evidenced by the immediate formation of a precipitate of triethylamine hydrochloride. The reaction mixture was refluxed for 3–4 h; carbon dioxide was evolved during this period, thereby resulting in the formation of a substituted benzofuran. The application of this procedure to the synthesis of 2-phenylbenzofuran is illustrated in Scheme I.

Method B. This procedure employs tosylate rather than chloride as the leaving group. Thus, the substituted acetic acids were reacted with *p*-toluenesulfonyl chloride in the presence of triethylamine in refluxing benzene solution; the mixed anhydride, $R_2CHC(O)OTs$, that is produced initially in this reaction reacts in situ with triethylamine, thereby generating the ketene. Under the reaction conditions, the product formed via intramolecular [2 + 2] cycloaddition of the ketene to the adjacent carbonyl functionality is unstable. Carbon dioxide is spontaneously eliminated during the reaction, thereby resulting in the formation of a substituted benzofuran. Since it is not necessary to isolate the intermediate mixed anhydride, this sequence of reactions affords a simple, one-pot synthesis of a substituted benzofuran from an (*o*-acylphenoxy)acetic acid.[5] The application of this precedure to the synthesis of 2-phenylbenzofuran is illustrated in Scheme I.

A potential limitation inherent in the use of method B is that excess *p*-toluenesulfonyl chloride must be removed at the conclusion of the reaction; normally, this is accomplished by prolonged stirring with aqueous alkali. It is likely that these conditions would result in destruction of base-labile cycloadducts (e.g., β-lactones and/or β-lactams). However, this did not present any problem when this procedure was applied to the synthesis of substituted benzofurans via method B.

Method C. This procedure utilizes 2-chloro-1-methylpyridinium iodide (Mukaiyama's reagent)[6] to generate an ester via reaction with the (*o*-acylphenoxy)acetic acid. This ester then could be reacted with triethylamine, thereby generating the ketene in situ. Intramolecular [2 + 2] cycloaddition of this intermediate ketene to the adjacent carbonyl functionality then proceeded in the manner described above (cf. method B). The application of this procedure to the synthesis of 2-phenylbenzofuran is illustrated in Scheme I.

Scheme III



Results and Discussion. The results obtained by applying methods A–C to the synthesis of several substituted benzofurans are summarized in Table I. The method by which the ketenes were generated had little, if any, effect upon the yield of the substituted benzofuran.

Inspection of the data in Table I reveals that, unlike intermolecular ketene cycloadditions, our intramolecular ketene cycloadditions to carbonyl groups proceed with about equal facility regardless of whether the reaction involves a ketone or an aldehyde carbonyl group. *Intermolecular* [2 + 2] cycloaddition of benzaldehyde to phenoxyphenylketene was attempted under the same conditions that were utilized in this study for the corresponding intramolecular [2 + 2] cycloaddition reaction (cf. entry 1 in Table I). We found no evidence for the formation of β-lactone or of the decarboxylation product (i.e., 1,2-diphenyl-1-phenoxyethane) in this reaction. However, a considerable amount of black tar was formed, a result which is consistent with that reported earlier by Staudinger.[7]

The similarity of the reactions described herein to the well-known Perkin reaction for the preparation of benzofuran[8] necessitated our demonstrating that these reactions indeed proceed via ketene intermediates. This could be accomplished via an intermolecular trapping experiment that utilized cyclopentadiene as ketenophile. Thus, the application of method A to the generation of (*o*-formylphenoxy)phenylketene (entry 1 in Table I), when performed in the presence of excess cyclopentadiene, afforded the corresponding intermolecular [2 + 2] cycloadduct (**10**), Scheme III).[2] Furthermore, the Perkin reaction normally is applicable only to aromatic aldehydes and not ketones; the precedures reported herein work well with aromatic ketones (cf. entries 2, 5, 6, and 7 in Table I).

In addition to the foregoing applications of methods A–C for the synthesis of substituted benzofurans, we have also attempted to promote intramolecular [2 + 2] ketene cycloadditions to carbonyl groups in other systems. Thus, ketenes were generated from keto acids **11**[14] (via method A), **12**[9] (via method A), and **13**[15] (via method B).

Despite the favorable proximity of reacting groups, yields of the expected cycloadducts were poor or nonexistent in the systems studied. Several factors may be responsible for these observations, e.g.: (i) anticipated strain in the expected product, i.e., the cage β-lactone that would be formed were the ketene derived from **11** to un-

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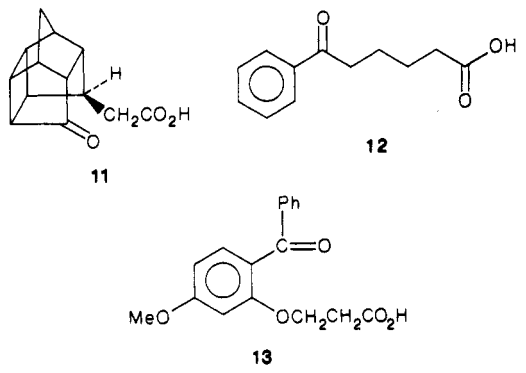
(9) Brady, W. T.; Giang, Y.-S. F.; Weng, L.; Ong. W.; Marchand, A. P.; Wu, A.-H., submitted for publication.



dergo intramolecular cycloaddition to the neighboring carbonyl carbon atom and (ii) lack of reactivity of the aldoketenes derived from carboxylic acids **11–13**. In addition, the formation of an aromatic system that provides an important driving force for the formation of substituted benzofurans is absent in the products that would be expected to arise via intramolecular cycloaddition of the ketenes derived from keto carboxylic acids **11–13**.

In conclusion, the syntheses of substituted benzofurans via intramolecular [2 + 2] ketene cycloadditions to aldehyde and ketone carbonyl groups reported herein appear to be generally useful and to offer an improvement over existing methods for the preparation of this important class of heterocyclic compounds.

Experimental Section

Melting points are uncorrected.

General Procedures for the Preparation of (*o*-Acylphenoxy)acetic Acids. Method I. Method I was utilized for the syntheses of **1a**, **4a**, **5a**, **6a**, **8a**, and **9a**. Sodium hydride (60% dispersion in mineral oil, 115 mmol) was added slowly with effective stirring to a mixture of the appropriate *o*-acylphenol (50 mmol) and α-halo carboxylic acid (50 mmol) in dry tetrahydrofuran (THF, 100–200 mL). The resulting mixture was stirred at room temperature for 20 min and then refluxed for 12–24 h. The reaction mixture was then cooled, quenched by addition of water (200 mL), and washed with chloroform (3 × 40 mL). The aqueous solution was then acidified to pH 1 via addition of dilute aqueous hydrochloric acid solution and extracted with benzene (3 × 60 mL). The combined benzene extracts were washed sequentially with water and with brine, dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The crude (*o*-acylphenoxy)acetic acid thereby obtained was recrystallized from methylene chloride–hexane mixed solvent. In the case of compound **9a**, purification of the crude product was carried out either (i) via column chromatography (silica gel stationary phase, 12% ethyl acetate–hexane mixed solvent as eluent) or (ii) via conversion to the corresponding dicyclohexylammonium salt (see method III, below).

Method II. This method was utilized for the syntheses of keto acids **2** and **7**. The procedure employed in method II was identical with that in method I with the exception that cold solutions of sodium *o*-acylphenolate and of sodium α-halo carboxylate were prepared separately. These solutions were then mixed together and heated to reflux.

Method III. This method was utilized in connection with the synthesis and purification of compound **9a**. The procedure employed in method III was identical with that in method I with the exception that the crude product was purified via conversion to the corresponding dicyclohexylammonium salt. Thus, a portion of the crude product was dissolved in a small amount of ethanol. To this solution was added ca. 1 equiv of dicyclohexylamine, whereupon the corresponding ammonium salt crystallized immediately. Ligroin was then added, and the dicyclohexylammonium salt was isolated via suction filtration. The material thereby obtained was then utilized as starting material for the intramolecular ketene cycloaddition study (vide infra).

(*o*-Formylphenoxy)phenylacetic Acid (1a). Compound **1a** (9.98 g, 78%) was obtained as a colorless microcrystalline solid: mp 140–142 °C; IR (Me_2SO-d_6) 3650–2700 (s), 1742 (s), 1665 cm^{-1} (s); ^1H NMR (Me_2SO-d_6) δ 5.95 (s, 1 H), 6.85–7.67 (m, 9 H), 10.55 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 78.1 (d), 114.7 (d), 121.7 (d), 125.3 (s), 127.4 (d), 127.9 (d), 128.8 (d), 128.9 (d), 135.7 (s), 136.1 (d), 159.5 (s), 170.5 (s), 189.3 (d).

(*o*-Acetylphenoxy)phenylacetic Acid (2a). Compound **2a** (6.89 g, 51%) was obtained as a colorless microcrystalline solid: mp 185–187 °C; IR (Me_2SO-d_6) 3700–2930 (s), 1735 (s), 1675 cm^{-1} (s); ^1H NMR (Me_2SO-d_6) δ 2.59 (s, 3 H), 5.49 (s, 1 H), 6.46–7.35 (m, 9 H), 9.47 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 31.8 (q), 77.9 (d), 113.8 (d), 121.2 (d), 127.6 (d), 128.8 (d), 128.9 (d), 129.8 (d), 133.5 (d), 135.7 (s), 156.1 (s), 170.5 (s), 199.2 (s).

2-(2-Formyl-6-methoxyphenoxy)butanoic Acid (4a). Compound **4a** (8.45 g, 71%) was obtained as a colorless microcrystalline solid: mp 113.0–114.5 °C; IR (Me_2SO-d_6) 3700–2850 (s), 1728 (s), 1690 cm^{-1} (s); ^1H NMR (Me_2SO-d_6) δ 0.98 (t, J = 5.6 Hz, 3 H), 1.86 (m, 2 H), 3.64 (s, 3 H), 4.75 (t, J = 5.2 Hz, 1 H), 6.31–6.74 (m, 3 H), 10.49 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 6.8 (q), 25.3 (t), 58.2 (q), 85.1 (d), 126.9 (d), 132.9 (s), 139.4 (d), 161.2 (s), 163.7 (s), 186.8 (s), 206.5 (s).

(2-Benzoyl-5-methoxyphenoxy)phenylacetic Acid (5a). Compound **5a** (16.8 g, 93%) was obtained as a colorless microcrystalline solid: mp 129–131 °C; IR ($CDCl_3$) 3750–2600 (s), 1734 (s), 1665 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.62 (s, 3 H), 5.47 (s, 1 H), 6.39–7.92 (m, 13 H), 8.73 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 54.7 (q), 77.9 (d), 105.4 (d), 120.9 (d), 126.0 (d), 127.4 (d), 127.6 (d), 128.2 (d), 129.1 (d), 131.7 (d), 132.1 (s), 134.3 (s), 138.2 (s), 156.5 (s), 162.8 (s), 170.2 (s), 195.0 (s).

(2-Benzoyl-5-methoxyphenoxy)acetic Acid (6a). Compound **6a** (12.2 g, 85%) was obtained as a colorless microcrystalline solid: mp 110–112 °C; IR (film) 3700–2550 (s), 1742 (s), 1670 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 3.62 (s, 3 H), 4.25 (s, 2 H), 6.24–7.68 (m, 8 H), 9.12 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 55.3 (q), 66.0 (t), 100.4 (d), 105.9 (d), 121.1 (s), 127.8 (d), 128.0 (d), 128.4 (d), 129.6 (d), 132.3 (d), 132.6 (d), 138.1 (s), 158.1 (s), 163.3 (s), 169.7 (s), 195.2 (s).

[*o*-(3-Phenylpropionyl)phenoxy]phenylacetic Acid (7a). Compound **7a** (16.4 g, 91%) was obtained as a colorless microcrystalline solid: mp 115–117 °C; IR ($CDCl_3$) 3700–2600 (s), 1739 (s), 1668 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.87–3.53 (m, 4 H), 5.68 (s, 1 H), 6.75–7.64 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 30.2 (t), 44.2 (t), 79.5 (d), 122.2–129.3 (complex, 14 C), 134.0 (d), 134.5 (s), 141.0 (s), 155.9 (s), 172.3 (s), 202.1 (s).

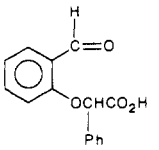
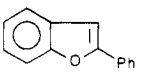
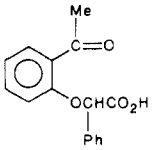
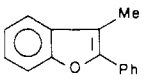
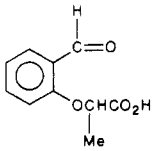
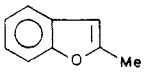
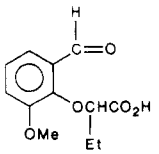
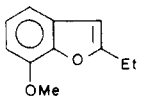
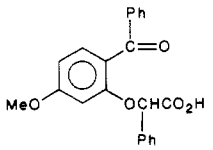
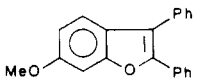
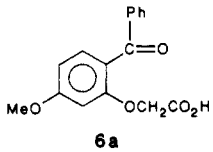
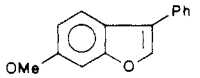
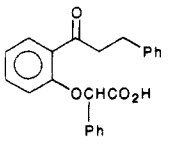
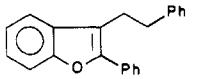
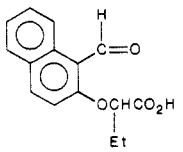
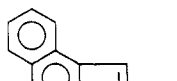
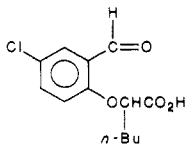
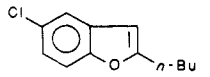
2-(1-Formyl-2-naphthoxy)butanoic Acid (8a). Compound **8a** (8.39 g, 65%) was obtained as a colorless microcrystalline solid: mp 115–118 °c; IR ($CDCl_3$) 3700–2680 (s), 1732 (s), 1671 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 1.15 (t, J = 7.0 Hz, 3 H), 2.12 (m, 2 H), 4.91 (t, J = 6.3 Hz, 1 H), 6.88–7.79 (m, 6 H), 9.25 (s, 1 H), 10.97 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 9.4 (q), 26.0 (t), 78.3 (d), 113.6–131.5 (complex, 7 C), 137.7 (s), 139.2 (s), 161.9 (s), 174.9 (s), 193.3 (d).

2-(2-Formyl-4-chlorophenoxy)hexanoic Acid (9a). Compound **9a** (10.28 g, 76%) was obtained as a colorless oil: IR (neat) 3650–2180 (s), 1738 (s), 1685 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.74–2.25 (m, 9 H), 4.62 (t, J = 5.6 Hz, 1 H), 6.83 (d, J = 8.2 Hz, 1 H), 7.21 (d, J = 8.2 Hz, 1 H), 7.53 (s, 1 H), 10.42 (s, 1 H), 11.08 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.5 (q), 24.1 (t), 27.1 (t), 32.0 (t), 53.5 (d), 114.8 (d), 126.2 (s), 126.8 (s), 127.7 (d), 135.0 (d), 158.6 (s), 174.6 (s), 188.6 (d).

Dicyclohexylammonium 2-(2-Formyl-4-chlorophenoxy)hexanoate. This compound was prepared by treating **9a** with dicyclohexylamine; method III, above, was utilized for this purpose. The dicyclohexylammonium salt thereby synthesized was obtained as a colorless microcrystalline solid: mp 183–184 °C; IR (film) 3280–2150 (s), 1678 (s), 1639 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 0.84–2.07 (m, 31 H), 2.63 (m, 2 H), 4.46 (t, J = 6.2 Hz, 1 H), 6.84–7.38 (m, 2 H), 7.77 (s, 1 H), 10.51 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.0 (q), 22.6 (t), 24.6 (t), 25.1 (t), 28.1 (t), 28.8 (t), 32.9 (t), 52.2 (d), 79.8 (d), 115.4 (d), 125.4 (s), 125.5 (s), 126.9 (d), 134.6 (d), 160.1 (s), 174.5 (s), 188.7 (d).

General Procedures for Intramolecular Cycloadditions of Ketenes to Carbonyl Groups. Method A. Benzofurans **1b–6b** were synthesized via this procedure. The appropriate acyl acid in each case (5–10 mmol) was converted to the corresponding acid chloride via reaction with oxalyl chloride (5–8 equiv) in benzene (10–15 mL) at ambient temperature for 4–8 h. Excess oxalyl chloride was removed in vacuo. Benzene (150–250 mL) was added to the residue, and the resulting solution was added

Table I. Synthesis of Benzofurans via Intramolecular [2 + 2] Cycloadditions of (*o*-Acylphenoxy)ketenes

entry	acid	benzofuran	yield (%)[a] method A	method B	method C
1	 **1a**	 **1b**	75	78	94
2	 **2a**	 **2b**	78		
3	 **3a**[b]	 **3b**	57		
4	 **4a**	 **4b**	53		79
5	 **5a**	 **5b**	82	84	90
6	 **6a**	 **6b**	74		
7	 **7a**	 **7b**		89	
8	 **8a**	 **8b**		74	
9	 **9a**	 **9b**		72, 70[c]	

[a] See text. [b] See ref 9 for synthesis of **3a**. [c] The tosylate was prepared via reaction of *p*-toluenesulfonyl chloride with the dicyclohexylammonium salt of the precursor aldoacid. See text.

slowly during 1.5–6 h to a refluxing solution of triethylamine (2–3 equiv) in benzene or toluene (100–200 mL). The reaction mixture was refluxed for 3–4 h after the addition of the acid chloride had been completed. The reaction mixture was cooled and then filtered, and the filtrate was concentrated in vacuo. The crude product (substituted benzofuran) was purified via column chromatography (silica gel stationary phase, 0.5–1% ethyl acetate–hexane mixed solvent as eluent).

Method B. Benzofurans **1b**, **5b**, **7b**, **8b**, and **9b** were prepared via this procedure. Thus, the (*o*-acylphenoxy)acetic acid or its

dicyclohexylammonium salt (5–10 mmol) was dissolved in benzene (50–100 mL) and added during 5–10 h via syringe to a refluxing solution of triethylamine (4 equiv) and *p*-toluenesulfonyl chloride (2 equiv) in benzene (50–100 mL). The reaction mixture was refluxed for 6 h after the addition of the carboxylic acid (or its dicyclohexylammonium salt) had been completed. The reaction mixture was then cooled and washed with water (50 mL). The organic layer was concentrated in vacuo to a final volume of ca. 30 mL. The resulting concentrate was stirred with 5% aqueous sodium hydroxide solution (250–350 mL) for 10 h to remove excess *p*-toluenesulfonyl chloride. The benzene layer was then dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo. The residue (crude substituted benzofuran) was purified via column chromatography (silica gel stationary phase, 0.5–1% ethyl acetate–hexane mixed solvent as eluent).

Method C. Benzofurans **1b**, **4b**, and **5b** were prepared via this procedure. Thus, a mixture of the (*o*-acylphenoxy)acetic acid (10.0 mmol), 2-chloro-1-methylpyridinium iodide (Mukaiyama's reagent,[6] 2.56 g, 10.0 mmol), and dry THF (30 mL) under nitrogen was heated at 55 °C via application of an external oil bath for 6 h. The reaction mixture was then cooled to room temperature and filtered. The filtrate was then added dropwise under nitrogen to a stirred, refluxing solution of triethylamine (4.5 g, 43.2 mmol) in dry THF (20 mL) during 2 h. The resulting mixture was then refluxed under nitrogen for an additional 4 h. The reaction mixture was concentrated in vacuo; the residue was diluted with brine (50 mL) and extracted with methylene chloride (3 × 50 mL). The combined extracts were dried (anhydrous magnesium sulfate) and filtered, and the filtrate was concentrated in vacuo to afford the crude cycloadduct. The crude product was purified via column chromatography (silica gel stationary phase, 0.5–1% ethyl acetate–hexane mixed solvent as eluent).

2-Phenylbenzofuran (1b). Pure **1b** (method A, 0.85 g, 75%; method B, 0.89 g, 79%; method C, 1.82 g, 94%) was obtained as a colorless microcrystalline solid: mp 120–121 °C (lit.[10] mp 120 °C).

3-Methyl-2-phenylbenzofuran (2b). Pure **2b** (method A, 1.32 g, 78%) was obtained as a colorless microcrystalline solid: mp 34–34.5 °C (lit.[11] mp 32–34 °C).

2-Methylbenzofuran (3b). Pure **3b** (method A, 0.97 g, 57%) was obtained as a colorless oil. The ^{1}H and ^{13}C NMR[12] and infrared[13] spectra of this material were identical in all respects with values reported in the literature for authentic **3b**.

2-Ethyl-7-methoxybenzofuran (4b). Pure **4b** (method A, 0.98 g, 53%; method C, 1.39 g, 79%) was obtained as a colorless oil: IR (neat) 1625 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.57 (t, J = 7.5 Hz, 3 H), 2.61 (q, J = 7.5 Hz, 2 H), 3.72 (s, 3 H), 6.05–6.92 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 11.7 (q), 21.5 (t), 55.6 (q), 101.1 (d), 105.4 (d), 112.6 (d), 122.8 (d), 130.5 (s), 142.6 (s), 144.8 (s), 160.8 (s).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.81; H, 6.92.

6-Methoxy-2,3-diphenylbenzofuran (5b). Pure **5b** (method A, 1.36 g, 82%; method B, 1.39 g, 84%; method C, 2.7 g, 90%) was obtained as a colorless microcrystalline solid: mp 120–121 °C; IR (film) 1614 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.71 (s, 3 H), 6.68–7.89 (m, 13 H); ^{13}C NMR ($CDCl_3$) δ 55.5 (q), 111.8 (d), 117.4 (d), 120.1 (d), 123.6 (d), 126.5–129.6 (complex, 11 C), 130.8 (s), 132.9 (s), 149.5 (s), 154.9 (s), 158.4 (s).

Anal. Calcd for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37. Found: C, 84.09; H, 5.34.

6-Methoxy-3-phenylbenzofuran (6b). Pure **6b** (method A, 1.28 g, 84%) was obtained as a colorless microcrystalline solid: mp 43–44 °C; IR ($CDCl_3$) 1624 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.68 (s, 3 H), 6.70–7.74 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 55.3 (q), 96.1 (d), 112.0 (d), 119.6 (s), 120.4 (d), 121.9 (s), 127.1 (d), 128.8 (d), 132.1 (s), 140.1 (d), 156.8 (s), 158.1 (s).

Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.32; H, 5.40. Found: C, 79.96; H, 5.43.

2-Phenyl-3-(2-phenylethyl)benzofuran (7b). Pure **7b** (method B, 1.47 g, 89%) was obtained as a colorless oil: IR (neat) 1622 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 2.80–3.28 (m, 4 H), 6.85–7.62 (m, 14 H); ^{13}C NMR ($CDCl_3$) δ 26.3 (t), 35.6 (t), 111.0 (d), 115.3 (s), 119.5 (d), 122.3 (d), 124.3 (d), 126.1 (d), 126.8 (d), 128.0 (d), 128.4 (d), 128.5 (d), 130.3 (s), 131.1 (s), 141.3 (s), 151.1 (s), 154.0 (s).

Anal. Calcd for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.34; H, 6.13.

2-Ethylnaphtho[2,1-*b*]furan (8b). Pure **8b** (method B, 1.24 g, 74%) was obtained as a colorless oil: IR (neat) 1632 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 1.64 (t, J = 7.6 Hz, 3 H), 3.17 (q, J = 7.6 Hz, 2 H), 7.13 (s, 1 H), 7.51–8.38 (m, 6 H); ^{13}C NMR ($CDCl_3$) δ 12.1 (q), 21.9 (t), 100.1 (d), 112.1 (d), 123.8–125.8 (complex, 6 C), 128.6 (d), 130.3 (s), 151.9 (s), 160.2 (s).

Anal. Calcd for $C_{14}H_{12}O$: C, 85.68; H, 6.16. Found: C, 85.58; H, 5.91.

2-*n*-Butyl-5-chlorobenzofuran (9b). Pure **9b** (method B, 1.29 g, 72%) was obtained as a colorless oil: IR (neat) 1613 cm^{-1} (m); ^{1}H NMR ($CDCl_3$) δ 0.68–2.87 (m, 9 H), 6.02 (s, 1 H), 6.78–7.24 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 13.7 (q), 22.2 (t), 28.1 (t), 29.6 (t), 101.4 (d), 111.4 (d), 119.7 (d), 123.1 (d), 127.9 (s), 130.5 (s), 153.0 (s), 161.3 (s).

Anal. Calcd for $C_{12}H_{13}C10$: C, 69.07; H, 6.28. Found: C, 68.94; H, 6.10.

7-(2-Formylphenoxy)-7-phenylbicyclo[3.2.0]hept-2-en-6-one (10). A solution of triethylamine (2.53 g, 25 mmol) in dry hexane (10 mL) was added dropwise with stirring to a cold (0 °C) solution that contained freshly cracked cyclopentadiene (13.2 g, 0.20 mol) and [(2-formylphenoxy)phenyl]acetyl chloride that had been prepared from **1a** (5.12 g, 20 mmol) in hexane (50 mL). The resulting mixture was cooled via application of an external ice bath and stirred at 0 °C for 3 h. The reaction mixture was then warmed to room temperature and stirred for an additional 6 h. The resulting mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified via column chromatography (silica gel stationary phase, 7% ethyl acetate–hexane mixed solvent as eluent), thereby affording **10** (2.74 g, 45%) as a pale yellow oil: IR (neat) 1783 (s), 1687 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 2.28–2.80 (m, 2 H), 3.49–4.28 (m, 2 H), 5.50–5.96 (m, 2 H), 6.63–7.72 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ 34.5 (t), 51.2 (d), 59.7 (d), 98.9 (s), 117.5 (d), 121.7 (d), 124.1–135.9 (complex, 11 C), 158.0 (s), 189.5 (d), 208.7 (s).

Acknowledgment. We thank the Robert A. Welch Foundation (Grant B-220 to W.T.B., Grant B-963 to A. P.M.) and the North Texas State University Faculty Research Committee for partial financial support of this study. In addition, A.P.M. gratefully acknowledges support of this work by the Air Force Office of Scientific Research (Grant AFO SR-84-0085).

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(14) Compound **11** was synthesized via base-promoted hydrolysis of the corresponding carboxylic acid ethyl ester.[9]
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Practical Synthesis of Dichloroacetylene

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Received November 28, 1986

Recently, we required for another program a good preparation of dichloroacetylene. While a number of syntheses of this highly useful but toxic and explosive compound have already been reported,[1] with the single

(1) For a review, see: Delavarenne, S. Y.; Viehe, H. G. In *Chemistry of Acetylenes*; Viehe, H. G., Ed.; Marcel Dekker: New York, 1969; Chapter 10. For more recent work and for additional reports on the potential hazards, see ref 2.

0022-3263/87/1952-3461$01.50/0