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).

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Practical Synthesis of Dichloroacetylene

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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.

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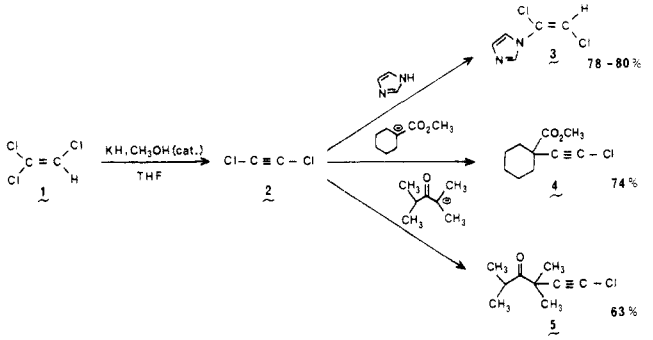
exception of that recently disclosed by Kende and Fludzinski,[2] all suffer from serious drawbacks such as operational difficulty, irreproducibility, or product contamination. Although the procedure developed by Kende and Fludzinski is a notable improvement over the previous methods, it is nevertheless time-consuming and requires a potentially eventful distillation for the separation of the dichloroacetylene from hexamethyldisilazane.

We have found that dichloroacetylene is rapidly and cleanly generated in high yield from a mixture of trichloroethylene and potassium hydride (1.2–1.3 equiv) in tetrahydrofuran at room temperature on the addition of a catalytic amount of methanol (1–2 μL/mmol of Cl_2CCHCl). The reaction is over in less than 1 h (VPC,[3]



cessation of H_2 evolution). The dichloroacetylene-containing supernatant is virtually free of potassium chloride and residual potassium hydride, which are insoluble in tetrahydrofuran, and hence no distillation is required.

The dichloroacetylene so formed has been unambiguously identified by IR (strong absorption at 983 cm^{-1})[2] and through known[2] chemical transformations: on reaction with imidazole, it produces *N*-(1,2-dichlorovinyl)imidazole (**3**) in 78–80% yield (three runs);[4,5] chloroethynylation of methyl cyclohexanecarboxylate and 2,4-dimethyl-3-pentanone with **2** affords the expected adducts **4** and **5** in yields of 74% and 63%, respectively.

This highly convenient preparation of dichloroacetylene should enhance the attractiveness of much of its unique chemistry.[1]

Experimental Section

Preparation of Dichloroacetylene (2). *Warning*—although we have used the following procedure repeatedly without the slightest incident, it is strongly recommended that all work with dichloroacetylene be conducted in a good hood and behind a safety shield. To a stirred suspension of oil-free potassium hydride (from 1.24 g of a ca. 42% dispersion, ca. 13 mmol) in 9.1 mL of dry tetrahydrofuran under argon at 25 °C are added 900 μL (1.32 g, 10.0 mmol) of trichloroethylene and then 10 μL (7.9 mg, 0.25 mmol) of methanol. The hydrogen evolution ceases after ca. 1 h, at which time VPC analysis[3] indicates a complete reaction. The supernatant (ca. 1 M[6]), which is employed in all subsequent work, is either used immediately or stored at −25 °C.

The reactions of dichloroacetylene with imidazole,[2,4] methyl cyclohexanecarboxylate,[2] and 2,4-dimethyl-3-pentanone[2] were performed essentially as described in the literature.

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Registry No. **2**, 7572-29-4; trichloroethylene, 79-01-6.

(2) Kende, A. S.; Fludzinski, P. *Synthesis* **1982**, 455–456 and references cited therein. See also: Kende, A. S.; Fludzinski, P.; Hill, J. H.; Swenson, W.; Clardy, J. *J. Am. Chem. Soc.* **1984**, *106*, 3551–3562. Pielichowski, J.; Popielarz, R. *Synthesis* **1984**, 433–434.

(3) Conditions: 10% SE 30 on Chromosorb W, 2.5 m × 2 mm, column temperature 50 °C, injection temperature 150 °C, N_2 flow rate 33 mL/min. No significant amount of any byproduct was detected.

(4) One equivalent of dichloroacetylene, based on a quantitative conversion of **1** to **2**, was used. It has been reported[2] that this reaction, when run in the presence of an excess of **2**, affords **3** in 76% yield.

(5) We have performed this transformation with dichloroacetylene–THF taken from a reaction mixture that had been stored at −25 °C for 3 days and obtained essentially the same result (75% yield).

(6) This is based on VPC and on the conversion of **2** to **3**. Similar concentrations were obtained in 50- and 100-mmol preparations (2 μL of CH_3OH/mmol of Cl_2CCHCl was used).

Preparation of Small Ring Carbocycles via Intramolecular Oxidative Coupling of Bisenolates Derived from α,ω-Diesters[1]

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Recently, a method for the preparation of carbocycles of general structure **4** was reported[2] that involved oxidative coupling of bisenolates derived from certain α,ω-diesters **2**. Unfortunately, this oxidative cyclization of dicarboxylate dienolates was reported[2] to be lacking in generality and appeared to be effective only in preparation of three- and six-membered ring systems. For example, attempts to generate cyclobutanoid **4a** by applying this methodology to dimethyl adipate (**2a**) led instead to a quantitative yield of the Dieckmann condensation product **7a**. Although addition of *N,N,N′,N′*-tetramethylethylenediamine was reported[2] to suppress completely the unwanted Dieckmann cyclization, subsequent treatment of the dienolate derived from dimethyl adipate (**2a**) with excess cupric bromide or chloride failed to produce any oxidative cyclization product.

Despite the fact that the above results would seem to preclude any success in such a venture, we decided to examine whether this intramolecular oxidative coupling reaction could be applied to di-*tert*-butyl adipate (**3a**), for which the competitive Dieckmann reaction would be somewhat sterically impeded (Scheme I). To our amazement, by use of cupric chloride as an oxidant at a reaction temperature of −78 °C, cyclobutanoid **5a** was obtained in approximately 20% isolated yield, accompanied by unreacted starting material (17%) and the corresponding Dieckmann condensation product (**8a**, approximately 30% yield[3])! Consistent with the previous studies[2] involving dimethyl adipate (**2a**), attempts to effect this oxidative coupling at higher temperatures (e.g., −20 or 0 °C) resulted in low yields (≤5%) of cyclobutanoid **5a** and a substantial amount of nondistillable product.

In order to confirm formation of the four-membered carbocycle in the above process, diester **5a** was saponified with potassium hydroxide in refluxing ethylene glycol, affording the corresponding diacid (**6a**), whose melting

(1) Abstracted from: Sarussi, S. J. M.S. Thesis, Loyola University of Chicago, Jan 1986.

(2) Chung, S. K.; Dunn, L. B., Jr. *J. Org. Chem.* **1983**, *48*, 1125.

(3) In a series of experiments designed to optimize production of cyclobutanoid **5a**, the yield of the undesired Dieckmann condensation product **8a** was found to be remarkably constant (30 ± 5%) both when the reaction temperature was varied from −78 to 0 °C and when the reaction time subsequent to the addition of the metallic oxidant was increased from 0.5 to 3.0 h. Such results indicate that the Dieckmann condensation is probably occurring during the formation of the bisenolate, prior to the addition of cupric chloride. At a reaction temperature of −78 °C, however, the isolated yield of **5a** did increase significantly with time (5% at 0.5 h after addition of cupric chloride vs. 21% after a reaction time of 3.0 h).

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