test,[7] the configuration shown corresponds to the absolute configuration.

Registry No. 1a, 75102-66-8; **1b**, 79721-99-6; **1c**, 79722-00-2; **1d**, 79722-01-3; **1f**, 79735-20-9; **3a**, 75102-67-9; **3b**, 75102-68-0; **3c**, 79722-02-4; **3d**, 79722-03-5; **3e**, 75196-27-9; **3f**, 79722-04-6; **4a** (isomer 1), 75111-48-7; **4a** (isomer 2), 75172-29-1; **4b** (isomer 1), 79722-06-8; **4b** (isomer 2), 79722-05-7; **5a**, 79722-07-9; **5b**, 79722-08-0; **5c**, 79735-21-0; **5d**, 79735-22-1.

Supplementary Material Available: Tables listing final atomic (Table I) and final anisotropic thermal (Table II) parameters, bond lengths (Table III), bond angles (Table IV), and selected torsion angles (Table V) for **3f** (6 pages). Ordering information is given on any current masthead page.

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Deoxygenation of 7-Oxabicyclo[2.2.1]hepta-2,5-diene Systems to Substituted Benzenes by Titanium Tetrachloride–Lithium Aluminum Hydride[1]

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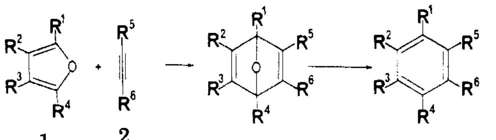
Received June 15, 1981

It is well-known that furans **1** readily undergo Diels–Alder cycloadditions with dienophiles **2** to form the oxygen-bridged six-membered carbocycles **3**. The deoxygenation of **3** appears to constitute an attractive route for the construction of substituted benzenes **4**.

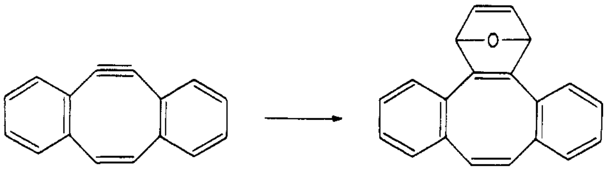


1 2 3 4

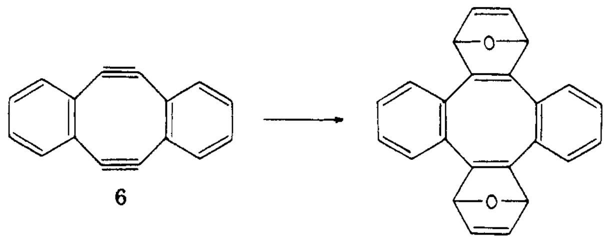
In contrast to the related cycloadditions between thiophenes and dienophiles,[3] whose adduct would subsequently expel a sulfur atom spontaneously on heating, the analogous deoxygenation process is thermodynamically less favorable. Consequently, it is important to note that thiophenes can undergo Diels–Alder reactions with only a very limited choice of dienophiles. Therefore, the utility of furans for such preparative purposes would find greater use if the final deoxygenation step can be realized synthetically.

To our best knowledge, this type of transformation has only been reported sporadically in the literature. However, the reagent used in each case is not universal for all oxygen-bridged compounds **3**. For example, when **3** is fused to a pyridine ring, lithium amalgam can, in general, effect the deoxygenation.[4] On the other hand, when **3** is extensively conjugated with aromatic systems, magnesium[5] or zinc dust in hydrochloric acid[6] can help to pull off the oxygen atom. When **3** is activated by four cyano groups, the addition of triphenyl phosphine, followed by the elimination of triphenyl phosphine oxide at 195 °C, provides tetracyanobenzene.[7] Unfortunately, none of the aforementioned reagents could furnish the benzene moiety from the unactivated furan adduct **3**. By far, the only viable method for this aromatization process is via a two-step procedure, i.e., catalytic hydrogenation of one of the two double bonds, followed by dehydration[8] upon treatment with acid.

We have long been interested in the cycloaddition reactions between furans and strained acetylenes, e.g., 5,6-didehydrodibenzo[*a*,*e*]cyclooctene (**5**) and 5,6,11,12-tetradehydrodibenzo[*a*,*e*]cyclooctene (**6**), from which 5,8-epoxy-5,8-dihydrotribenzo[*a*,*c*,*e*]cyclooctene (**7**) and 1,4,9,12-diepoxy-1,4,9,12-tetrahydrotetraphenylene (**8**) were isolated.[9] The compounds **7** and **8** seem to be probable precursors for the preparation of tribenzo[*a*,*c*,*e*]cyclooctene (**9**) and tetraphenylene (**10**), respectively. We have tried the single-step deoxygenation of **7** and **8** with a variety of deoxygenation reagents, e.g., triphenyl phosphine, triphenyl arsine, zinc–copper couple, and magnesium as well as zinc dust etc., without success. After some experimentation, we finally discovered that titanium tetrachloride–lithium aluminum hydride[10] was effective for such deoxygenation reactions.[11] To this end, we first chose to apply this reagent pair to three model oxygen-bridged compounds, namely, dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**11**),[12] dimethyl 1-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**12**), and dimethyl 1,4-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**13**).[3] Thus, when the compounds **11–13** were allowed to react with a mixture of titanium tetrachloride (6.5 molar equiv), lithium aluminum hydride (2.5 molar equiv), and triethylamine (1 molar equiv) in THF for 24 h under nitrogen at room temperature and following the usual workup, the corresponding phthalates **14**, **15**,[13] and **16**[3,12] were isolated in moderate yields.[15]



5 7



6 8

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[1] Dedicated to the memory of the late Professor Franz Sondheimer.

[2] Formerly spelled as H. N. C. Wong.

[3] Kuhn, H. J.; Gollnick, K. *Chem. Ber.* **1973**, *106*, 674.

[4] Kaufmann, T. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 543.

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[10] (a) Ishida, A.; Mukaiyama, T. *Chem. Lett.* **1976**, 1127. (b) During the preparation of this manuscript, Professor H. Hart independently reported similar procedures which applied low-valent forms of iron, tungsten, and titanium to effect deoxygenation of similar systems; see: Hart, H.; Nwokogu, G. *J. Org. Chem.* **1981**, *46*, 1251.

[11] Titanium trichloride–lithium aluminum hydride can effect the deoxygenation of epoxides to olefins; see: McMurry, J. E.; Fleming, M. P. *J. Org. Chem.* **1975**, *40*, 2555.

[12] Stork, G.; van Tamelen, E. E.; Friedman, L. J.; Burgstahler, A. *J. Am. Chem. Soc.* **1953**, *75*, 384.

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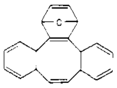
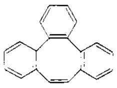
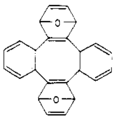
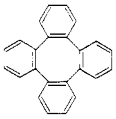
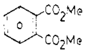
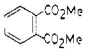
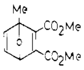
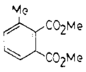
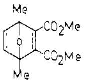
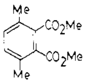
[14] Buckle, D. R.; Morgan, N. J.; Ross, J. W.; Smith, H.; Spicer, B. A. *J. Med. Chem.* **1973**, *16*, 1334.

0022-3263/82/1947-0140$01.25/0 © 1982 American Chemical Society

Table I

precursor	product	% yield	bp, °C (pressure, mm)	mp, °C
 7	 9	57		141-142 (lit.[16] 139-140)
 8	 10	50		237-239 (lit.[9] 239-240)
 11	 14	64	82-84 (0.2)	
 12	 15	77	92-94 (0.2)	
 13	 16	54	98 (0.2) [lit.[14,17] 178 (0.5)]	73-75 (lit.[3] 72-75)

Tribenzo[*a*,*c*,*e*]cyclooctene (**9**)[16] and tetraphenylene (**10**)[9] were also obtained from **7** and **8**, respectively, under similar conditions.[15] The isolation of **9** and **10** involved only direct recrystallization.

Studies of the mechanism of this deoxygenation reaction are in progress. The possibility of applying this strategy to the preparation of other highly interesting substituted benzene systems is also under investigation in our laboratories.

Experimental Section

Melting points were determined on a hot-stage microscope and are uncorrected. ^{1}H NMR spectra were recorded on either a Varian EM-360L (60 MHz), a Perkin-Elmer R32 (90 MHz), or a Varian XL-200 (200 MHz) spectrometer with $CDCl_3$ solutions unless otherwise stated, Me_4Si being used as an internal standard. Mass spectra were recorded on either a JEOL D-300 or a Finnigan 4021 spectrometer. Solvents were purified and dried by standard methods. All evaporations of solvents were carried out under reduced pressure.

Dimethyl 7-Oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (11). Dimethyl acetylenedicarboxylate (11.72 g, 0.083 mol) and furan (4.00 g, 0.06 mol) were placed in a sealed tube, which was heated at 100 °C for 20 h. The reaction mixture was distilled under vacuum. The endoxide **11** was obtained as a light yellow oil: 7.90 g (47%); bp 113–115 °C (0.7 mm) [lit.[12] bp 130–133 °C (2 mm)]; ^{1}H NMR (CCl_4) δ 3.80 (s, 6 H), 5.62 (s, 2 H), 7.25 (s, 2 H); mass spectrum, *m*/*e* 210 (M^+).

Dimethyl 1-Methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (12). Dimethyl acetylenedicarboxylate (2.84 g, 0.02 mol) and 2-methylfuran (1.23 g, 0.015 mol) were placed in a sealed tube, which was heated at 100 °C for 17 h. The endoxide **12** (3.17 g, 70.8%) was obtained by distillation: bp 96–100 °C (0.4 mm); ^{1}H NMR δ 1.80 (s, 3 H), 3.80 (s, 3 H), 3.86 (s, 3 H), 5.64 (d, 1 H, J = 2 Hz), 7.00 (d, 1 H, J = 2 Hz), 7.22 (dd, 1 H, J = 2, 4 Hz); mass spectrum, *m*/*e* 224 (M^+).

Dimethyl 1,4-Dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (13). Dimethyl acetylenedicarboxylate (5.68 g, 0.04 mol), 2,5-dimethylfuran (2.88 g, 0.03 mol), and dioxane (5 mL) were refluxed at 101 °C for 17.5 h. The reaction mixture was distilled under vacuum to yield the endoxide **13**: 5.8 g (81%); bp 102–105 °C (0.4 mm) [lit.[3] bp 120–160 °C (4 mm)]; ^{1}H NMR δ 1.80 (s, 6 H), 3.82 (s, 6 H), 6.98 (s, 2 H); mass spectrum, *m*/*e* 238 (M^+).

Dimethyl Phthalate (14). THF (20 mL) was added carefully to stirred titanium tetrachloride (7.6 mL, 0.065 mol) at 0 °C under N_2. A suspension of lithium aluminum hydride (1.00 g, 0.026 mol) in THF (30 mL) was added carefully to the above suspension. Then triethylamine (1.00 g, 0.01 mol) in THF (5 mL) was added. The mixture was stirred and refluxed at 65 °C for 0.5 h. It was allowed to cool to room temperature. The endoxide **11** (2.00 g, 0.0095 mol) in THF (5 mL) was added dropwise. The mixture was stirred for 24 h. It was then poured into 20% aqueous K_2CO_3 solution (400 mL) and filtered. The filter cake was washed with CH_2Cl_2 several times. The filtrate was extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated. The residue was distilled under vacuum to give the phthalate **14**: 1.186 g (64%); bp 82–84 °C (0.2 mm); ^{1}H NMR (CCl_4) δ 3.74 (s, 6 H), 7.20–7.60 (AA′BB′, 4 H); mass spectrum *m*/*e* 194 (M^+).

Dimethyl 3-Methylphthalate (15). THF (20 mL) was added dropwise to titanium tetrachloride (7.6 mL, 0.065 mol) at 0 °C under N_2. A suspension of lithium aluminum hydride (1.00 g, 0.026 mol) in THF (30 mL) was added dropwise to the above suspension carefully at 0 °C and was followed by triethylamine (0.94 g, 0.009 mol) in THF (5 mL). The mixture was refluxed at 65 °C for 0.5 h. Then it was allowed to cool to room temperature, and endoxide **12** (2.22 g, 0.01 mol) in THF (10 mL) was added. The reaction mixture was stirred for 24 h, and then it was poured into 20% aqueous K_2CO_3 (400 mL) and H_2O (100 mL). The resulting mixture was filtered, and the filter cake was washed thoroughly with CH_2Cl_2. The filtrate was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated. The residue was distilled under vacuum to afford the phthalate **15**: 1.61 g (77.8%); bp 92–94 °C (0.2 mm); ^{1}H NMR (CCl_4) δ 2.26 (s, 3 H), 3.76 (s, 6 H), 7.15–7.26 (m, 2 H), 7.47–7.77 (m, 1 H); mass spectrum, *m*/*e* 208 (M^+).

Dimethyl 3,6-Dimethylphthalate (16). THF (30 mL) was added carefully to titanium tetrachloride (7.6 mL, 0.065 mol) at 0 °C under N_2. A suspension of lithium aluminum hydride (1 g, 0.026 mol) in THF (20 mL) was added to this suspension and was followed by triethylamine (1.01 g, 0.01 mol) in THF (5 mL). The mixture was refluxed at 65 °C for 0.5 h and was allowed to cool to room temperature. The endoxide **13** (2.5 g, 0.01 mol) in THF (10 mL) was added. The mixture was stirred at room temperature for 24 h. It was then poured into 20% aqueous K_2CO_3 (400 mL) and filtered. The filter cake was washed thoroughly with CH_2Cl_2, and the filtrate was extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated. The residue was chromatographed on a silica gel column (EtOAc–hexane, 1:3) to provide the phthalate **16**: 1.25

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(15) All isolated compounds exhibited spectroscopic properties identical with those of the corresponding authentic samples and/or literature reports.

(16) Huang, N. Z. *Chem. Ind.* (*London*) **1981**, 364.

g (54%); bp 98 °C (0.2 mm); [lit.[14,17] bp 178 °C (0.5 mm)]; mp 73–75 °C (lit.[3] mp 72–73 °C); ^1H NMR (CCl_4) δ 2.40 (s, 6 H), 3.90 (s, 6 H), 7.20 (s, 2 H); mass spectrum, *m/e* 222 (M^+).

Tribenzo[*a*,*c*,*e*]cyclooctene (9). Lithium aluminum hydride (25 mg, 0.66 mmol) was added carefully to titanium tetrachloride (0.2 mL, 1.71 mmol) in THF (10 mL) at 0 °C under N_2 and was followed by triethylamine (25 mg, 0.25 mmol). The mixture was refluxed for 5 min and was allowed to cool to room temperature. The endoxide 7[9] (69.5 mg, 0.26 mmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. It was then poured into 20% aqueous K_2CO_3 solution (30 mL) and filtered. The filter cake was washed with CH_2Cl_2, and the filtrate was extracted with CH_2Cl_2 (3 × 20 mL). The combined CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated. The residue was extracted with pentane (10 mL), and the pentane solution was filtered through a thin layer of Celite and evaporated. The residue was recrystallized from absolute EtOH to furnish tribenzo[*a*,*c*,*e*]cyclooctene (**9**): 37.3 mg (57%); mp 141–142 °C (lit.[16] mp 139–140 °C); ^1H NMR δ 6.74 (s, 2 H), 6.96–7.42 (m, 12 H); mass spectrum, *m/e* 254 (M^+).

Tetraphenylene (10). Lithium aluminum hydride (23.3 mg, 0.61 mmol) was added carefully to titanium tetrachloride (0.18 mL, 1.54 mmol) in THF (10 mL) at 0 °C under N_2 and was followed by triethylamine (23.4 mg, 0.23 mmol). The mixture was refluxed for 5 min and was allowed to cool to room temperature. The endoxide 8[9] (39.3 mg, 0.12 mmol) in THF (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h. It was then poured into 20% aqueous K_2CO_3 solution (30 mL) and filtered. The filter cake was washed with CH_2Cl_2, and the filtrate was extracted with CH_2Cl_2 (2 × 20 mL). The combined CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated. The residue was recrystallized from absolute EtOH to provide tetraphenylene (**10**): 18 mg (50%); mp 237–239 °C (lit.[9] mp 239–240 °C); ^1H NMR δ 7.26 (br s); mass spectrum, *m/e* 304 (M^+).

Acknowledgment. We acknowledge with thanks the financial support from Academia Sinica, China.

Registry No. 1 ($R^1 = R^2 = R^3 = R^4$ = H), 110-00-9; 1 (R^1 = Me, $R^2 = R^3 = R^4$ = H), 534-22-5; 1 ($R^1 = R^4$ = Me, $R^2 = R^3$ = H), 625-86-5; 2 ($R^5 = R^6$ = C(O)OMe), 762-42-5; 7, 79503-92-7; 8, 79503-90-5; 9, 212-77-1; 10, 212-74-8; 11, 1829-60-3; 12, 18064-04-5; 13, 18063-93-9; 14, 131-11-3; 15, 21483-46-5; 16, 37902-49-1; titanium tetrachloride, 16028-76-5; lithium aluminum hydride, 16853-85-3.

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[17] We assume that this value must be misprinted.

Cathodic Reductions of Aroyl Chlorides

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Received July 22, 1981

Cathodic reductions of halogenated compounds have been widely studied from both synthetic and mechanistic aspects. In these processes either one or two electrons per molecule of substrate can be transferred. Cleavage of the carbon–halogen bond is common, converting the halogen to halide ion and the organic group to a free radical or a carbanion. The usual products of these reductions result from coupling,[1] transposition,[2,3] proton abstraction,[4] or combination with cathode material to form organometallic compounds.[1,5,6]

Table I. Half-Wave Potentials in Lithium Perchlorate-Acetone

compd	$E_{1/2}$, V (vs. SCE)	compd	$E_{1/2}$, V (vs. SCE)
benzoyl chloride	−1.35	2-naphthoyl chloride	−1.30
1-naphthoyl chloride	−1.20	bibenzoyl	−0.85

Cathodic reductions of acyl halides, in which cleavage of the carbon–halogen bond is also possible, have been little studied. Arthur and Lyons[7] studied several acyl halides polarographically and presumed the formation of free radicals in these reductions. We here report on cathodic reductions of aroyl chlorides on a preparative scale. We find evidence that aroyl free radicals are formed in the first step of the reduction, with a series of further processes leading to the corresponding 1,2-diaroyl-1,2-ethenediol diaroylates as the final products.

The formation of *trans*-1,2-diphenyl-1,2-ethenediol dibenzoate (*trans*-stilbenediol dibenzoate) from bibenzoyl by reaction with cyanide anion in a aprotic medium has been reported by Trisler and Frye.[8] The same reaction has been applied to asymmetric benzils by Kawasaki and Ogata.[9] Staudinger and Binkert[10] reported the preparation of stilbenediol dibenzoate (mp 159 °C) along with a small quantity of a material melting at 185–187 °C from the reaction of benzoyl chloride with potassium salt of stilbenediol. Later, Ried and Keil[11] referred to the higher melting compound as *trans*-stilbenediol dibenzoate. The compound was formed in low yield (1%) from the reaction of the benzoin-piperidine Mannich base with benzoyl chloride in pyridine. Blake, Coates, and Tate[12] reported the compound melting at 159 °C as *cis*-stilbenediol dibenzoate.

Results and Discussion

We first determined the half-wave polarographic potentials of the aroyl chlorides as well as that of bibenzoyl, which, as will be shown later, is an intermediate in the formation of *cis*- and *trans*-stilbenediol dibenzoates. In the polarographic recording, only one wave was observed from 0.0 V to the cathodic limit of the electrolyte system, −1.95 V vs. SCE. The results are shown in Table I.

Electrolysis of Benzoyl Chloride. In every electrolysis, while the quantity of the substrate was varied and the cathode potential controlled, the current consumption was consistent with the donation of one electron per molecule of benzoyl chloride. At the end of the electrolysis, a white solid was isolated from the catholyte, and its elemental analysis and IR, ^1H NMR, and mass spectra were consistent with the stilbenediol dibenzoate structure, which has cis and trans isomers. The presence of both isomers in the reaction product was shown by gas–liquid chromatography, which gave only two peaks that by GC/MS gave two mass spectra identical with each other and to the one obtained from known samples of the isomers. The isomers were separated by fractional crystallization. No significant differences between their IR spectra were observed.

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