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); $^1$H 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); $^1$H 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); $^1$H 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.

(17) We assume that this value must be misprinted.

## Cathodic Reductions of Aroyl Chlorides

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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, $^1$H 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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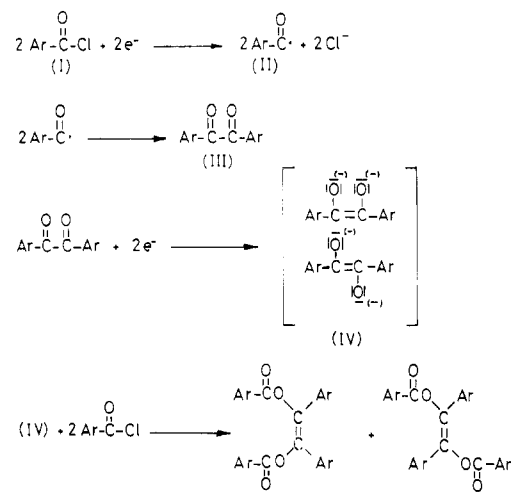
0022-3263/82/1947-0142$01.25/0 

Scheme I



However, they were easily differentiated by their melting points, chromatographic retention times, and their UV spectra, in which the lower melting isomer showed a bathochromic effect at $\lambda_{max}$ as compared with the higher melting isomer.

The structures of the electrolysis products were corroborated as *cis*- and *trans*-stilbenediol dibenzoates by comparison with authentic samples (melting points, mixture melting points, and IR, UV, and mass spectra). The ratio of cis to trans isomers was 32:68.

**Electrolysis of Naphthoyl Chlorides.** Cathodic reductions of 1-naphthoyl and 2-naphthoyl chlorides gave 1,2-dinaphthyl-1,2-ethenediol dinaphthoates, on the basis of elemental analyses and IR, UV, mass, and $^1H$ NMR spectra. Electron consumptions were 1 F/mol of substrate.

These products could not be analyzed by GC because of their high molecular weight. Nevertheless, after several recrystallizations from different solvents their melting points were unchanged, and each gave only one spot by TLC and only one peak in their UV spectrum at $\lambda_{max}$. These results indicate that only one isomer was formed in each of the electrolytic reductions. Since reduction of benzoyl chloride gave predominantly the trans isomer, it appears that the more bulky naphthyl groups lead to the formation of only the trans isomer.

The practically quantitative yields and the mild reaction conditions make the electrolytic method a very convenient procedure for preparing 1,2-diaryl-1,2-ethenediol diaroylates.

**Mechanism.** Considering that every molecule of electrolytic product requires four molecules of aroyl chloride for its formation and that coulometric measurements indicate that 1 F is consumed per mole of substrate, it follows that four electrons must be involved in the formation of each molecule of reaction product. The most rational way to fulfill these conditions is shown in Scheme I.

In the first step, the cleavage of the carbon–halogen bond generates an aroyl free radical (II). Dimerization of II leads to a diaroyl intermediate (III), which, having a lower reduction potential than the aroyl chloride, undergoes reduction to form the 1,2-diaroyl-1,2-ethenediolates (IV), which are then acylated by two molecules of the aroyl chloride.

The participation of bibenzoyl as an intermediate was shown by using the reduction potentials shown in Table I. When solutions containing bibenzoyl and benzoyl chloride were electrolyzed, selecting the cathode potential so that only the bibenzoyl was reduced and so that benzoyl chloride would participate only in the acylation of the dianions IV, the current consumption was 2 F/mol of bibenzoyl. The products formed in this experiment were compared with those obtained by electrolysis of benzoyl chloride solutions; the IR and mass spectra were identical, but GC, melting point, and UV spectral data showed that the cis isomer was formed exclusively. This difference in isomer ratio indicates a different mode of interaction of the bibenzoyl molecule with the electrode in the two cases.

When bibenzoyl is electrolyzed, it must diffuse from the solution to the mercury surface negatively charged. Thus, the molecule will approach with its oxygen atoms (with negative charge density because of the dipoles, $\delta + C = O\delta^-$, of the carbonyl groups) as far away as possible from the electrode. Accordingly, when the carbon–carbon double bond is formed, only the cis isomer is produced. On the other hand, when bibenzoyl is formed through the dimerization of electrogenerated benzoyl radicals at the surface of the electrode, it will be reduced immediately, and both cis and trans isomers are formed.

## Experimental Section

**Starting Materials.** Bibenzoyl, anhydrous lithium perchlorate, and the acyl chlorides were obtained from Fluka A-G and were used without purification. Acetone was dried at least 24 h over anhydrous $K_2CO_3$ and then distilled according to the procedure of Weissberger and Proskauer.[13]

**Instruments**: Polarograph, Amel 452; potentiostat, Amel 557; integrator; Amel 558; IR spectrometer, Perkin-Elmer 177; UV spectrometer, Varian 634; NMR spectrometer, Hitachi Perkin-Elmer R600; mass spectrometer, Hewlett-Packard 5980A; analytical gas chromatograph, Hewlett-Packard 5710A.

**General Electrolysis Procedure.** Electrolyses were carried out in cells with compartments separated by a porous glass diaphragm. The temperature was controlled at 18 °C, and stirring was magnetic. A mercury pool was used as the cathode and a platinum plate as the anode. The electrolyte was anhydrous acetone 0.4 M in anhydrous lithium perchlorate. For prevention of the accumulation of acid in the anode compartment, 4 g of anhydrous $Na_2CO_2$ was put on the glass diaphragm. The $Na_2CO_3$ prevented diffusion of protons into the cathode compartment, forming benzoin benzoate or naphthoin naphthoates, which occurred when electrolyses were run without it.

Electrolyses were carried out under controlled cathodic potential, and coulometric measurements were made with an electronic integrator coupled to the potentiostat. When current started passing, the surface of the mercury cathode became yellow, and after a short time the catholyte solution became turbid because the reaction products are only sparingly soluble in acetone and precipitate. Crude reaction products were obtained by removing the acetone and adding water to dissolve the electrolyte, leaving a white solid that was collected by vacuum filtration.

**Reduction of Benzoyl Chloride.** Solutions of 1.4 (10 mmol) or 2.81 g (20 mmol) of benzoyl chloride were electrolyzed under a cathodic potential of −1.45 V vs. SCE. The electron consumption was 1 F $mol^{-1}$. Stilbenediol dibenzoates were obtained in an overall yield of 95%. GC determination of the isomer ratio by using an internal standard showed 68% trans isomer and 32% cis isomer. Samples of both pure isomers were obtained by fractional crystallization, dissolving the mixture in $CH_2Cl_2$, and adding diethyl ether. When the solution was cooled, the trans isomer (mp 188 °C) crystallized. After filtration, the solvent were distilled, and the residue was crystallized from methanol to give the cis isomer, mp 160 °C. On admixture with authentic samples, no depression in melting point was observed: IR (KBr); cis and trans isomers 1735 $cm^{-1}$; mass spectrum (cis and trans isomers); 70 eV), *m/e* (relative intensity) 420 (2), 299 (1), 105 (100), 77 (47), 51 (18); $^1H$ NMR ($CDCl_3$), only aromatic protons, broad bands centered at δ 7.4; UV ($CH_3OH$) $\lambda_{max}$ 230 nm (cis), 234 (trans). On analytical GC with an OV-17 column (0.32 cm × 2 m), the trans isomer had

(13) A. Weissberger and E. Proskauer, "Organic Solvents", Oxford Press, London, 1935, p 143.

a longer retention time than the cis. Anal. Calcd for $C_{28}H_{20}O_4$: C, 79.98; H, 4.79. Found (cis isomer): C, 79.50; H, 4.81. Found (trans isomer): C, 79.65; H, 4.83.

**Reduction of 1-Naphthoyl Chloride.** Solutions of 1.9 (10 mmol) or 3.81 g (20 mmol) of 1-naphthoyl chloride were electrolyzed under a cathodic potential of -1.30 V vs. SCE. The electron consumption was 1 F $mol^{-1}$. *trans*-1,2-Bis(1-naphthyl)-1,2-ethenediol di-1-naphthoate was obtained in 93% yield. After crystallization from $CH_3OH$–$CHCl_3$ it had the following mp 241 °C; IR (KBr) 1730 $cm^{-1}$. UV ($CHCl_3$) $\lambda_{max}$ 242 nm; $^1H$ NMR ($CDCl_3$), absence of signals for nonaromatic protons, broad band centered at $\delta$ 7.6; mass spectrum (70 eV), *m/e* (relative intensity) 620 (5), 449 (3), 326 (1), 265 (30), 155 (95), 127 (100), 101 (20), 77 (27). Anal. Calcd for $C_{44}H_{28}O_4$: C, 85.14; H, 4.55. Found: C, 85.34; H, 4.49.

A sample prepared by the procedure of Trisler and Kawasaki[8,9] showed the same properties as the product obtained by electrolysis.

**Reduction of 2-Naphthoyl Chloride.** Samples of 2-naphthoyl chloride (10 or 20 mmol) were electrolyzed under a potential of -1.40 V vs. SCE, and *trans*-1,2-bis(2-naphthyl)-1,2-ethenediol di-2-naphthoate was obtained in 92% yield. The electron consumption was 1 F $mol^{-1}$. The product was crystallized from $CHCl_3$: mp 292 °C; IR (KBr) 1733 $cm^{-1}$; UV ($CHCl_3$) $\lambda_{max}$ 247 nm; $^1H$ NMR ($CHCl_3$) did not give satisfactory results because of the low solubility of the compound, but in deuterioacetone a weak band centered at $\delta$ 8.05 was observed; mass spectrum (70 eV), *m/e* (relative intensity) 620 (3), 449 (2), 265 (4), 155 (43), 127 (100), 101 (21), 77 (34). Anal. Calcd for $C_{44}H_{28}O_4$: C, 85.14; H, 4.55. Found: C, 85.31; H, 4.59.

**Reduction of Bibenzoyl in the Presence of Benzoyl Chloride.** Solutions containing 2.10 g (10 mmol) of bibenzoyl and 2.81 g (20 mmol) of benzoyl chloride were electrolyzed under a -0.9-V cathodic potential vs. SCE, a potential at which only the bibenzoyl is reduced. The electron consumption was 2 F $mol^{-1}$ of bibenzoyl. The product had the same physical, spectroscopic, and GC properties as *cis*-stilbenediol dibenzoate and showed no depression in melting point when mixed with an authentic sample. The yield was quantitative based on bibenzoyl.

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**Registry No.** Benzoyl chloride, 98-88-4; *cis*-stilbenediol dibenzoate, 1924-28-3; *trans*-stibenediol dibenzoate, 1924-29-4; 1-naphthoyl chloride, 879-18-5; *trans*-1,2-bis(1-naphthyl)-1,2-ethenediol di-1-naphthoate, 79722-54-6; 2-naphthoyl chloride, 2243-83-6; *trans*-1,2-bis(2-naphthyl)-1,2-ethenediol di-2-naphthoate, 79722-55-7; bibenzoyl, 134-81-6.

## Carbon-13 Nuclear Magnetic Resonance as a Probe for the Structural Assignment of 1,4,5-Trisubstituted Imidazoles

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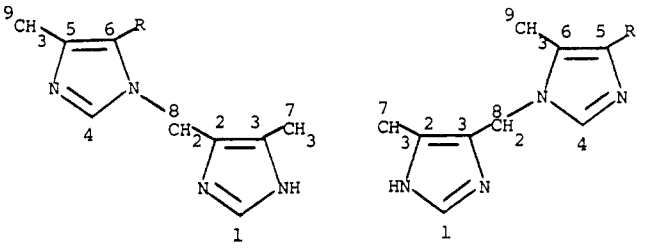
We have synthesized a pair of 1,4,5-trisubstituted imidazole esters, **1a** and **1b**, by the alkylation of 4-methyl-5-carbethoxyimidazole with 4-methyl-5-(chloromethyl)-imidazole. A marked solvent effect on the ratio of **1a** to **1b** was observed. When the reaction was carried out in dimethylformamide, **1a** was favored by a 3:1 ratio, whereas **1b** was favored (4:1) in methoxyethanol. We were unable to study this solvent effect in other solvents because of the low solubilities of the imidazoles.



**1a** R = $CO_2Et$ **1b** R = $CO_2Et$

**4a** R = $^{10}CH_2OH$ **4b** R = $^{10}CH_2OH$

In an attempt to establish the structure of these pairs of constitutional isomers, we examined their proton magnetic resonance spectra; but the evidence was inconclusive. Methods for distinguishing between 1,4- and 1,5-disubstituted imidazoles by cross-ring coupling constants,[1] use of lanthanide shift reagents,[2] and carbon-13 chemical shifts have been reported,[3] and only the last of these methods was useful to us. We have extended the use of the carbon-13 chemical shift method by making use of model compounds to carry out statistical chemical shift correlations to establish the structure. This approach involved synthesizing the model compounds and using measurements from them to estimate the carbon-13 chemical shifts expected for **1a** and **1b**. Statistical analysis was then applied to correlate these estimated chemical shifts with experimental values obtained from measurements with the two isomers of compound **1** (experimentally labeled **1x** and **1y**) which were to be identified. This method eliminates the necessity of making unambiguous assignments.

Scheme I illustrates how the model compounds were selected. Moiety C is a common structural feature to both **1a** and **1b**. The readily available 4-methyl-5-(hydroxymethyl)imidazole (**3**) was used as a model for this moiety.

Compounds **2a** and **2b** were synthesized unambiguously (see below) and used as models for moieties A and B, respectively. Carbon-13 chemical shifts observed for **2a** and **3** were used to estimate shifts for **1a**, neglecting the bridging methylene carbon. Similarly, shifts observed with **2b** and **3** were used to estimate shifts for **1b**.

The rationale for the described analysis required the unambiguous syntheses of 1,4-dimethyl-5-carbethoxyimidazole (**2a**) and 1,5-dimethyl-4-carbethoxyimidazole (**2b**). The synthesis of **2a** was reported by Staab and Schwalbach,[4] who methylated 4-methyl-5- carbethoxyimidazole with methyl sulfate.

The structure of the product (**2a**), which was an oil [bp 96 °C (1 torr)], was confirmed by the reaction of 4-methyl-5-carbethoxyoxazole with methylamine. We treated 4-methyl-5-carbethoxyimidazole with $NaH/CH_3I$ in THF at 0 °C and obtained a mixture of an oil [bp 95 °C (0.1 torr)] and a solid (mp 81 °C). While the proton NMR spectrum of the oil was identical with that of compound **2a** prepared by Staab and Schwalbach, the proton NMR spectrum of the solid showed this to be the isomeric compound **2b**. Finally, **4a**, **4b**, and model compound **3** were obtained by reducing **1a**, **1b**, and 4-methyl-5-

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