hydroxy-3-phenylpropiophenone [(+)-2] and ca. 10% of 3-hydroxy-3-phenylpropriophenone [(+)-3] which were separated by LC (30 cm. $\frac{3}{8}$ in. o.d., Lichrosorb Si 60, 5 μm/CH_2Cl_2). (+)-3 ($[\alpha]^{rt}_{578}$ +18° (CH_2Cl_2)) gave spectral data as above. (+)-2 gave: ^1H NMR ($CDCl_3$) δ 7.9–6.9 (10 H), 5.2 (m, 1 H), 3.6 (d, OH), 3.3–2.6 (m, 2 H); IR (Nujol) 1760 (C=O) and 3500 (OH) cm^{-1}; $[\alpha]^{rt}_{589}$ +3.8° (c 0.58, acetone).

Methyl Ester of L(−)-β-Phenyllactic Acid[13] [(−)-5]. To a solution of 0.83 g (5 mmol) of L(−)-β-phenyllactic acid in 25 mL of ether was added at 0 °C 1 equiv of a diazomethane solution in ether. The solvent was evaporated resulting in 0.89 g (99%) of (−)-5: ^1H NMR ($CDCl_3$) δ 7.3–7.1 (5 H), 4.5–4.2 (m, 1 H), 3.7 (s, 3 H), 3.0 (m, 2 H), 1.8–1.6 (d, OH); IR (Nujol) 1745, 1730 (C=O), and 3400–3200 (OH) cm^{-1}; $[\alpha]^{rt}_{578}$ −15.3° (c 0.62, CH_2Cl_2).

L(−)-β-Phenyllactamide [(−)-6]. To a solution of 2.9 g (16 mmol) of (−)-5 in 10 mL of methanol was added an excess of liquid ammonia. After the solution stood for a week at room temperature, 2.6 g (15.7 mmol) of product was obtained by evaporating the solvent and the ammonia: yield 98%; mp 109–112 °C; ^1H NMR ($CDCl_3$) δ 7.4–7.2 (5 H), 4.5–4.2 (m, 1 H), 3.1 (m, 2 H), 2.0 (br, s, NH_2); IR (Nujol) 1685 (C=O), and 3500–3200 (OH) cm^{-1}; $[\alpha]^{rt}_{578}$ −85.0° (c 1.24, EtOH).

L(−)-2-Hydroxy-3-phenylpropiophenone [(−)-2]. To a refluxing suspension of 0.38 g of activated Mg and an I_2 crystal in 10 mL of ether was added a solution of 2.4 g of bromobenzene in 5 mL of ether. After the reaction had started, refluxing was continued for half an hour. This mixture was added to a solution of 0.5 g of (−)-6 in ether. After the solution was refluxed for 6 h, 20 mL of a saturated NH_4Cl solution was added, the mixture was acidified, and the organic layer was extracted with 3 × 20 ml of water and 1 × 20 mL of a saturated NaCl solution. After the solution was dried ($MgSO_4$) and the solvent removed, 0.56 g of crude product was obtained. Purification by thick-layer chromatography (silica gel/CH_2Cl_2) gave 0.28 g of (−)-2 (42%): mp 50–52 °C; ^1H NMR ($CDCl_3$) δ 7.9–6.9 (10 H), 5.2 (m, 1 H), 3.6 (d, OH), 3.3–2.6 (m, 2 H); IR (Nujol) 1670 (C=O) and 3500 (OH) cm^{-1}; $[\alpha]_{589}^{rt}$ −13° (c 0.14, acetone).

Registry No.—(−)-1, 61840-92-4; (+)-2, 69897-44-5; (−)-2, 69897-45-6; (+)-3, 69897-46-7; (−)-4, 20312-36-1; (−)-5, 13673-95-5; (−)-6, 69897-47-8; chalcone, 94-41-7; bromobenzene, 108-86-1.

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Electron-Transfer Processes: Oxidation of Naphthalene and *p*-Cymene by Peroxydisulfate

Claudio Giordano* and Aldo Belli

Montedison, Istituto Donegani, Novara, Italy

Attilio Citterio* and Francesco Minisci

Istituto di Chimica del Politechnico, Milano, Italy

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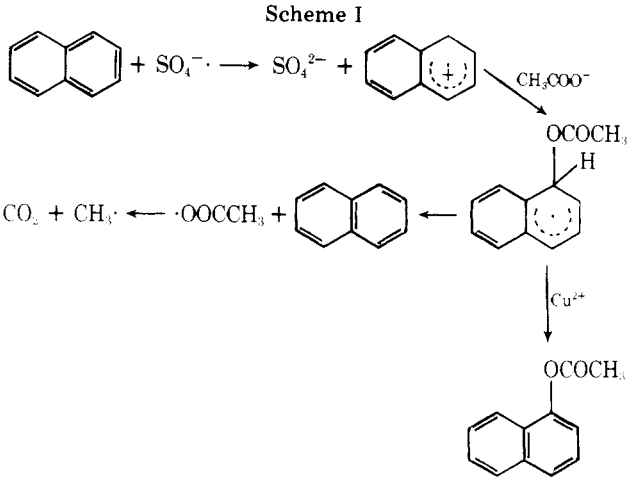
A recent report[1] shows that the oxidative acetoxylation of aromatic compounds by Ag(II) complexes in acetic acid can be made catalytic in the presence of an excess of peroxydisulfate, but no acetoxylation takes place in the absence of silver salt and in the presence of Cu(II) salts. We have found that direct aromatic acetoxylation of naphthalene by peroxydisulfate (Scheme I) occurs also in the absence of silver salt and in the presence of Cu(II) salts.

Scheme I



Under similar conditions in the presence of Fe(III) salts, no acetoxylation takes place, but α-(hydroxymethyl)-naphthalene acetate (1) is obtained as the main reaction product of naphthalene.

p-Cymene gives *p*-isopropylbenzyl acetate (2) by copper-catalyzed oxidation under the same conditions.

The oxidation of *p*-cymene with peroxydisulfate in the presence of *p*-benzoquinone gives the 2-(*p*-isopropylbenzyl)-benzoquinone in 40% yield; moreover, *p*-isopropylbenzyl alcohol and *p*-isopropylbenzaldehyde have been formed in an additional 30% yield.

These results provide further evidence concerning the formation of aromatic radical cations in the interaction of the sulfate radical anion, $SO_4^{-}\cdot$, with aromatics.[2-7] The absence of acetoxynaphthalene in the absence of Cu(II) salts could be explained by the competitive routes of Scheme I.

The formation of 1 could arise from the oxidation by $S_2O_8^{2-}$ of methylnaphthalene or of naphthylacetic acid, formed in situ from naphthalene and $CH_3\cdot$, and from naphthalene and $\cdot CH_2COOH$, respectively. The presence of both methyl and $\cdot CH_2COOH$ radicals in the reaction medium has been evidenced by trapping these radicals with quinoxaline or styrene under the reaction conditions.[8] Methylquinoxaline and γ-phenylbutyrolactone[9] have been identified among the reaction products.

Experimental Section

Acetoxynaphthalenes. Potassium peroxydisulfate (0.01 mol) was added to a well-stirred solution of $Cu(OAc)_2$ (0.02 mol), KOAc (0.04 mol), and naphthalene (0.02 mol) in acetic acid (50 mL) at 113 °C under a nitrogen atmosphere. The reaction mixture was stirred at 113 °C for 5 h. An internal standard was added to the reaction mixture, which was then extracted with ether and water. The organic layer was dried and analyzed by GLC. The acetoxynaphthalenes (α/β = 93:7) were identified by comparison with authentic samples (GLC, IR, MS). The yield based on converted naphthalene was 90%. The yield based on peroxydisulfate was 39%.

α-(Hydroxymethyl)naphthalene Acetate. The procedure was identical with that utilized for acetoxynaphthalenes with the only difference being that basic ferric acetate (0.005 mol) was used instead of cupric acetate and the reaction mixture was refluxed for 6 h. GLC revealed the presence of α-(hydroxymethyl)naphthalene acetate, identified by comparison with an authentic sample. The yield based on converted naphthalene was 60%; the yield based on peroxydisulfate was 18%.

***p*-Isopropylbenzyl Acetate.** Starting from *p*-cymene, the copper-catalyzed procedure was identical with that used for naphthalene. Conversion of *p*-cymene was 32%; the yield based on converted *p*-cymene was 70%: NMR δ 1.05 (d, 6 H), 2.05 (s, 3 H), 2.75 (m, 1 H), 5.03

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(s, 2 H), 7.1–7.2 (m, 4 H); MS *m/e* 192 (M^+), 177, 150, 117, 107, 91, 43.

2-(*p*-Isopropylbenzyl)-*p*-benzoquinone. The procedure described for toluene in ref 10 has been used with *p*-cymene. The yield of isolated 2-(*p*-isopropylbenzyl)-*p*-benzoquinone was 40%: mp 51–52 °C; NMR δ 1.2 (d, 6 H), 2.85 (m, 1 H), 3.8 (d, 2 H), 6.35 (m, 1 H), 6.7 (s, 2 H), 7.1–7.2 (m, 4 H); MS *m/e* 238 (M^+), 237, 223, 197, 165, 139, 128, 115, 102, 91, 77.

p-Isopropylbenzyl alcohol and *p*-isopropylbenzaldehyde, obtained in the same reaction, were isolated by preparative GLC and identified by comparison with authentic samples.

Registry No.—**1**, 13098-88-9; **2**, 59230-57-8; naphthalene, 91-20-3; α-acetoxynaphthalene, 830-81-9; β-acetoxynaphthalene, 1523-11-1; 2-(*p*-isopropylbenzyl)-*p*-benzoquinone, 69897-58-1; *p*-isopropylbenzyl alcohol, 536-60-7; *p*-cymene, 99-87-6; *p*-isopropylbenzaldehyde, 122-03-2.

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Preparation and Reactivity of 3,7-*endo*-Diphenylbicyclo[3.3.0]octane Derivatives

Daniel Gardette and Jean Lhomme*[1]

Department of Chemistry, University of Clermont, 63170, Aubière, France

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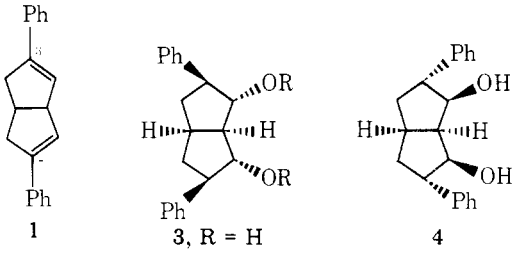
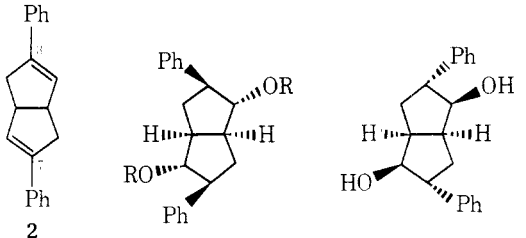
We wish to report a study of 3,7-*endo*-diphenylbicyclo[3.3.0]octane derivatives, i.e., systems of the Ar_1–C_n–Ar_2 type, in which two aromatic rings are fixed on the endo side of the "U-shaped"[2] *cis*-bicyclo[3.3.0]octane skeleton. This work was undertaken as part of a project aimed at the study of ring–ring interactions between aromatic molecules. In recent work,[3] we described the stacking interactions between aromatic moieties (nucleotide bases and antimalarial quinolines) by preparing Ar_1–$(CH_2)_3$–Ar_2 models, in which the aromatic residues are linked by a trimethylene bridge, which allows, but does not impose, the intramolecular ring–ring stacking. In a search for more rigid linking systems which could favor to a larger extent this type of interaction, we have examined a series of polycyclic skeletons and have finally turned to the *cis*-bicyclo[3.3.0]octane system, since in one of the possible conformations (as indicated by molecular models) the endo C_3-H and C_7-H bonds are nearly parallel at a distance of 3.5 to 4 Å, i.e., close to the width of an aromatic ring. There are few data in the literature on the conformation of 3,7-disubstituted bicyclooctane derivatives;[4] consequently, we have prepared as models the simplest compounds in the series, the diphenyl derivatives **11–23**, in order to ascertain whether these systems can achieve conformations in which the aromatic moieties interact. We describe here the preparation and some spectroscopic and reactivity data of these compounds.

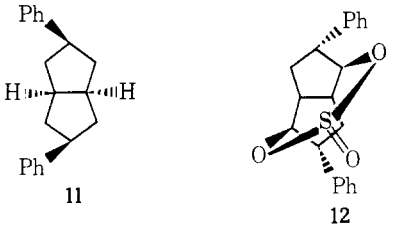
Results and Discussion

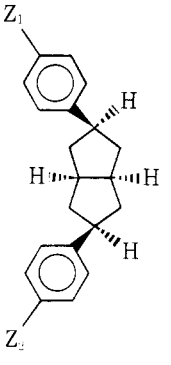
cis-Bicyclo[3.3.0]octane-3,7-dione was reacted with phenylmagnesium bromide to give a dihydroxy compound which was dehydrated in methanolic hydrochloric acid to a 50:50 mixture of the isomeric dienes **1** and **2**[5] which could be separated on silica impregnated with silver nitrate. The "endo-endo" positioning of the benzene rings was accomplished by taking advantage of the more accessible (exo) face of the double bonds:[2] treatment of diene **1** with diborane, followed by H_2O_2 oxidation led to an ca. 15:1 mixture of two isolable diols, **3** and **4**. Treated similarly, diene **2** gave **5** and **6** in the same 15:1 ratio. The NMR spectra of the four diols and the corresponding derivatives, namely the acetates **7** and **8** and the tosylates **9** and **10**, were recorded in different solvents or in the presence of $Eu(dpm)_3$ (for the diols themselves). Con-

exo: ┈┈ endo: ◄









11, $Z_1 = Z_2 = H$
13, $Z_1 = H$; $Z_2 = COCH_3$
14, $Z_1 = Z_2 = COCH_3$
15, $Z_1 = H$; $Z_2 = COPh$
16, $Z_1 = Z_2 = COPh$
17, $Z_1 = H$; $Z_2 = CO(CH_2)_2CH_3$
18, $Z_1 = Z_2 = CO(CH_2)_2CH_3$
19, $Z_1 = H$; $Z_2 = CO_2H$
20, $Z_1 = Z_2 = CO_2H$
21, $Z_1 = H$; $Z_2 = CO_2CH_3$
22, $Z_1 = Z_2 = CO_2CH_2CH_3$
23, $Z_1 = H$; $Z_2 = NO_2$

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