4-Dimethylamino-4'-bromobenzhydrol, m.p. 104–105° (reported[2] m.p. 107°), and 4-dimethylamino-4'-chlorobenzhydrol, m.p. 105° (reported[2] m.p. 103–104°), were prepared as previously described.[2] 1,1-Diphenylvinyl bromide, m.p. 49–50° (reported[3] m.p. 46–47°), and 1-bromo-4-pentene, b.p. 128–129° (reported[4] b.p. 128°), were prepared as previously described.[4]

Preparation of the aldehydes. The experimental procedure for the preparation of the aldehydes has been already described.[1]

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Syntheses of Benzophenone and Benzaldehyde Methyl Ethyl and Dimethyl Acetals by an Electrolytic Method

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The electrolyses of di- and triphenylacetic acids in methanol failed to undergo the normal Kolbe reaction. Instead of the dimers, the respective methyl ethers were obtained. Working with diphenylacetic acid in methanol-pyridine V. d. Hoek and Nauta[1] obtained diphenylmethyl methyl ether in 35% yield.

Linstead, Shephard, and Weedon,[2] by electrolysis of triphenylacetic acid in methanol alone, obtained triphenylmethyl methyl ether in 60% yield. More recently, Finkelstein and Petersen[3] have obtained an improved yield (80%) of diphenylmethyl methyl ether using triethylamine instead of sodium methoxide.

No description of the electrolysis of α-alkoxy acids in methanol could be found in the literature. The study of the electrolyses of this class of compounds was initiated in order to find out whether it would lead to the acetals. Therefore some α-alkoxyphenyl- and -diphenylacetic acids have been investigated.

The electrolysis of α-methoxyphenylacetic acid in absolute methanol afforded in 61.6% yield of benzaldehyde dimethyl acetal. When α-methoxydiphenylacetic acid was electrolyzed, in a similar way, benzophenone dimethyl acetal was obtained in 74% yield.

It seemed that the anodic methoxylation could be also a possible route to the mixed acetals, which have been described very rarely in the literature. In fact, when α-ethoxyphenylacetic acid was electrolyzed in absolute methanol, benzaldehyde methyl ethyl acetal was obtained in 71.4% yield. The electrolysis of α-ethoxydiphenylacetic acid afforded benzophenone methyl ethyl acetal in 74% yield.

Work is under way to find out to what extent this method might be applied to the syntheses of aliphatic aldehyde and ketone acetals and of the thio analogs.

EXPERIMENTAL

All melting and boiling points are uncorrected.

Preparation of the alkoxy acids and their intermediates. *α-Methoxyphenylacetic acid* (m.p. 67–70°) was prepared by reaction of mandelic acid with dimethyl sulfate, using the procedure described by Reeve and Christoffel.[4]

Methyl α-methoxydiphenylacetate (b.p. 166–167/1 mm.) was prepared by reaction of benzilic acid with phosphorus pentabromide, followed by addition of absolute methanol, using the procedure described by Klinger and Nickell.[5]

α-Methoxydiphenylacetic acid (m.p. 107–110°) was prepared by stirring of the corresponding ester with excess aqueous potassium hydroxide solution (40%) for 25 hr. The melting points of 111–112°[6] and 107°[7] have been reported for this acid.

α-Ethoxyphenylacetic acid (b.p. 172°/17 mm.) was prepared by reaction of benzilic acid with ethyl iodide and silver oxide, following the indication of Mackenzie.[8]

Ethyl α-bromodiphenylacetate was prepared by treatment of ethyl benzilate with phosphorus tribromide and bromine, using the method described by Carothers.[9]

Ethyl α-ethoxydiphenylacetate. The crude ethyl α-bromodiphenylacetate (34 g.) was stirred with absolute ethanol (218 ml.) for 3 hr. The distillation of the residue afforded a liquid (27.6 g., 91% yield), b.p. 150°/ 1 mm.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.0; H, 7.0. Found: C, 76.2; H, 6.9.

α-Ethoxydiphenylacetic acid. Ethyl α-ethoxydiphenylacetate (9 g.) was heated under reflux for 5 hr. with potassium hydroxide (7.6 g.) in absolute ethanol (72 ml.). The solution, worked up in the usual way, gave α-ethoxydiphenylacetic acid (7.7 g., 95% yield), m.p. 113–116° (from carbon disulfide–light petroleum). A m.p. of 113–114° has been reported for this acid.[10]

Electrolyses procedure. The electrolysis cell consisted of a cylindrical glass vessel contining two parallel platinum plate electrodes, placed 1–2 mm. apart. They measured 3.5 × 2.5 cm. In each case absolute methanol was used, to which sufficient sodium had previously been added to neutralize about 3% of the acid. While the cell was cooled in an ice bath, a current of 1.2 amp. was passed until the electrolyte became slightly alkaline. This process usually required about twice as long as expected considering the current and the amount of acid employed.

Electrolysis of α-methoxyphenylacetic acid. The solution of α-methoxyphenylacetic acid (8.1 g.) in methanol (180 ml.), was electrolyzed. The solvent was evaporated under re-

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duced pressure and the residue distilled, giving benzaldehyde dimethyl acetal (4.5 g., 61.6%), b.p. 196° (reported[11] b.p. 198–199°).

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.0; 7.9. Found: C, 71.2; H, 8.1.

This acetal was hydrolyzed by boiling with 2% hydrochloric acid, yielding benzaldehyde, which was identified as its 2,4-dinitrophenylhydrazone, m.p. 237°, undepressed on admixture with an authentic specimen.

Electrolysis of α-methoxydiphenylacetic acid. The solution of α-methoxydiphenylacetic acid (4.6 g.) in methanol (100 ml.) was electrolyzed. During the electrolysis an insoluble colorless solid was deposited at the bottom of the vessel. The methanol was evaporated under reduced pressure and the residue dissolved in ether. The ethereal solution, washed successively with saturated sodium carbonate solution, dried and evaporated, afforded, after recrystallization from methanol, benzophenone dimethyl acetal (3.2 g., 74%) m.p. 105–107°. A m.p. of 106.5–107° has been reported[12] for this acetal.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.9; H, 7.0. Found: C, 79.2; H, 6.8.

Addition of concd. sulfuric acid to this acetal afforded benzophenone, m.p. 47–49°, undepressed on admixture with an authentic specimen.

Electrolysis of α-ethoxyphenylacetic acid. The solution of α-ethoxyphenylacetic acid (3.8 g.) in methanol (90 ml.) was electrolyzed. The methanol was evaporated under reduced pressure and the residue distilled. A colorless liquid was collected as the main fraction (2.5 g., 71.4%), b.p. 205°, $n_D^{19.0}$ 1.4878.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.3; H, 8.4. Found: C, 72.5; H, 8.6.

This acetal was hydrolyzed by boiling with 2% hydrochloric acid, yielding benzaldehyde, which was identified as its 2,4-dinitrophenylhydrazone, m.p. 237°, undepressed on admixture with an authentic specimen.

Electrolysis of α-ethoxydiphenylacetic acid. The solution of α-ethoxydiphenylacetic acid (5.5 g.) in methanol (150 ml.) was electrolyzed. During the electrolysis an insoluble colorless solid was deposited at the bottom of the vessel. The methanol was evaporated under reduced pressure and the residue disolved in ether. The ethereal solution was washed successively with saturated sodium carbonate solution, dried, and evaporated. The residue, distilled under reduced pressure, yielded as a main fraction a colorless liquid (3.05 g., 74%), b.p. 133–135°, $n_D^{22.5}$ 1.9432. The liquid solidified when refrigerated overnight and, after crystallization from methanol, melted at 32–33°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.3; H, 7.4. Found: C, 79.3; H, 7.1.

This substance, when treated with concd. sulfuric acid, gave benzophenone, m.p. 48°, undepressed on admixture with an authentic specimen.

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Periodate Oxidation of Sulfides to Sulfoxides. Scope of the Reaction

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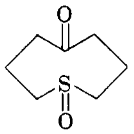
Since the first recorded synthesis of a sulfoxide by Märcker[2] in 1865, numerous methods have been developed for the transformation of sulfides to sulfoxides,[3] utilizing reagents such as nitric acid,[2,4] hydrogen peroxide,[5] dinitrogen tetroxide,[6] chromic acid,[7] ozone,[8] peracids,[9] hydroperoxides,[10] manganese dioxide,[7a] selenium dioxide,[11] and iodosobenzene.[12] We wished to synthesize a particular sulfoxide, 1-thiacycloöctan-5-one 1-oxide (I), from the corresponding sulfide in order to investigate its chemical and physical properties,[13] in continuation of our study of transannular effects in mesocyclic systems.[14] Difficulties experienced earlier in this laboratory in obtaining the sulfoxide (I) free from contaminating sulfide and/or sulfone by the usual oxidation methods were resolved when we turned to sodium metaperiodate as the oxidant.



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