precipitate (0.0363 g.) was filtered off. The water was removed from the filtrate at water pump pressure on a warm water bath, leaving a yellowish mass which was washed with several portions of ether, partially dissolved in water, and acidified with concentrated hydrochloric acid, thus yielding a yellow oil. Crystallization of the oil was induced by cooling and scratching the sides of the flask. Pale yellow crystals were collected, washed with water, and dried *in vacuo* overnight: whitish crystals, m.p. 135.5–138.0°, weighed 1.337 g. (89.9%). Crystallization from a 2:1 mixture of benzene and petroleum ether (b.p. 60–75°) yielded 0.837 g. (56%) of white crystals, m.p. 140–141°. The analytical sample, white crystals, m.p. 141–142°, was obtained by recrystallization from benzene–petroleum ether (b.p. 60–75°).

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found (K): C, 75.93; H, 4.80.

The infrared spectrum of the sodium salt has a medium band at 1695 cm.$^{-1}$ and a strong band at 1620 cm.$^{-1}$

The 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol: yellow crystals, m.p. 221–222° dec.

Anal. Calcd. for $C_{22}H_{16}N_4O_6$: C, 61.11; H, 3.73. Found (S): C, 60.91; H, 4.10.

Alkaline cleavage of 9,10-dihydroanthracene-9-glyoxylic acid. A solution of 0.100 g. (0.000396 mole) of 9,10-dihydroanthracene-9-glyoxylic acid in 2.0 ml. of 1.96*N* sodium hydroxide (6 equivalents) was heated for 3 min., precipitating a white solid. The reaction mixture was filtered, and the white crystals were washed with water. The product, m.p. 107.0–108.5°, weighed 0.070 g. (96%) and the mixture m.p. with 9,10-dihydroanthracene was 107.0–108.5°. The filtrate was neutralized with concentrated hydrochloric acid and 1 ml. of 10% calcium chloride solution was added, precipitating a white powder. The calcium oxalate monohydrate was washed with 1 ml. of water and dried to constant weight, 0.057 g. (99%) at 100°. A spot test[18] established the identity of the oxalate.

Alkaline cleavage of IV. A solution of 0.470 g. (0.000218 mole) of IV in 15.0 ml. of 1.78*N* ethanolic potassium hydroxide was refluxed for an hour. Ten ml. of water was added to the reaction mixture, which was then cooled and concentrated to 10 ml. The addition of concentrated hydrochloric acid to the mixture precipitated white crystals which were filtered off, washed with water, and dried. The white crystals, m.p. 166–168°, weighed 0.490 g. (94%). A crystallization from ethanol-water yielded 0.466 g. (89%) of white needles, m.p. 167.0–168.5°. May and Mosettig[19] reported m.p. of 9,10-dihydroanthracene-9-acetic acid as 168.0–169.5°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found (K): C, 80.51; H, 5.98.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MONTANA STATE UNIVERSITY]

Anodic Oxidation of Aryl Activated Methylene Groups[1]

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Anodic oxidation produced alcohols and ketones from activated methylene groups. Tertiary butyl ethers were also formed in some cases when *tert*-butyl alcohol was present.

Since few attempts have been made to use electrochemical methods for the partial oxidation of aryl activated methylene groups, it was of interest to study the products formed from such reactions, and to obtain information concerning the mechanisms of the reactions occurring. Emphasis was placed on the oxidation of tetralin, 6-methoxytetralin, and indan because previous studies have shown that the α-methylene group of these compounds is readily oxidized to the ketone by other methods.[2,3]

The effects of the following reaction variables on the products formed and the current efficiency were studied: the form of the anode (gauze or foil), the presence of a diaphragm, the *p*H and character of the reaction medium, temperature, current density, and carriers.

Form of the anode. Because of the high oxygen overvoltage obtainable, anodes of smooth platinum were used throughout. For most runs a #150-mesh gauze (0.0016-in. wire) was used. Foil and a #45-mesh gauze (0.0075-in. wire) were also tried. Previous work had shown that the current efficiency of a cathode was a function of wire size[4] and this was also found to be the case with the platinum anode. An accurate determination of the current efficiency of the anode was impossible because of the diversity of the reactions occurring but the current efficiency of the fine gauze electrode was estimated to be at least twice that of the foil (Table I). There was less difference in current efficiency between the coarse and the fine gauze. This effect may be explained by an increase in overvoltage with decreasing electrode diameter as it has been shown for mercury cathodes that the overvoltage is an inverse function of the radius of the drops.[5]

Character of the reaction medium. Since emulsions of the compounds in aqueous alkali were not attacked, it was necessary to use a homogeneous medium containing reductant, water, auxiliary sol-

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vent, and electrolyte. The choice of solvent, which had to be inert to oxidation as well as a good blending agent, was limited. *tert*-Butyl alcohol was found to be the most effective and was used in most runs. Dioxane was less effective as a blending agent and an excessive amount of tarry by-product was obtained with pyridine.

Since practically no oxidation occurred either in acid or buffered alkaline medium, the choice of electrolyte was limited to strong bases. The addition of more than a trace of inorganic base caused the separation of the organic layer, so quaternary ammonium bases had to be used. Of the bases tried, cyclohexyltrimethylammonium hydroxide was the most satisfactory as a blending agent and electrolyte. About one quarter of the base was destroyed during an average run, trimethylamine being one of the products formed. With the above base present it was also possible to add small amounts of sodium hydroxide without causing a separation of the organic layer. The *p*H of the medium was the most important factor in determining the yields of the products isolated. In general, appreciable reaction occurred only in unbuffered alkaline medium and the oxidizing power of the anode increased with an increase in base concentration. When the concentration of base was low, the product contained a larger proportion of alcohol; when high, the product ketone underwent further reaction so that the overall yield of primary oxidation products was lowered (Table I).

Use of a diaphragm. It was found inconvenient to use a diaphragm in alkaline media because the anolyte passed into the cathode compartment so rapidly that it was difficult to maintain proper reaction conditions. However, the fact that the proportion of alcohol formed was higher with a diaphragm than without indicated that the alcohol was not a secondary reduction product.

Temperature. Reaction temperature varied from 15° to 70°. Results indicated that it was not an important factor in determining the yields of the products.

Current density. Current density was found to have little effect on the yields of the products formed. In general, reactions run with moderate current densities (4–5 amp./dm.^{2}) at 40–50° gave optimum results.

Use of carriers. The addition of sodium vanadate was found to have no effect on the reaction.

Current efficiency. In most runs a 10–20% excess of the theoretical current (4F per mole) needed to oxidize the methylene group to the ketone was used. Under these conditions about 40% of the tetralin, 30% of the indan, and 20% of the 6-methoxytetralin were recovered. A 100% current excess (8F per mole) used up more of the starting material but did not give a proportionate increase in the yields of primary oxidation products because further attack on these products was also increased (compare runs 1 and 4; Table I).

In a reaction of this type, the yields of oxidation products depend on their relative stability toward further oxidation compared with the reactivity of the starting material. In general it was found that the yields of ketone and alcohol were low where oxidizing conditions were severe (high base concentration) or if the products underwent oxidation easily compared with the starting material (indan; Table I). Besides the expected α-substituted ketones and alcohols an additional product was isolated when indan and tetralin were oxidized in *tert*-butyl alcohol solution. This was shown to be the corresponding *tert*-butyl ether by its failure to react with ketone or alcohol reagents and by the ease with which it was cleaved to *tert*-butyl alcohol and hydrocarbon when heated with palladium-charcoal catalyst. Tetralin was found to give the

TABLE I

ANODIC OXIDATION PRODUCTS

Starting Material Recovered, %	Moles of Product per Mole of Reacted Starting Material Ketone	 Alcohol	 Ether	Conditions
Tetralin				
12	0.20	0.13	0.09	8F/mole current; #150 gauze anode
16	0.24	0.11	0.08	8F/mole current; #45 gauze anode
37	0.19	0.14	0.08	8F/mole current; foil anode
42	0.21	0.09	0.09	Optimum[a]
60	0.11	0	0.11	High base concentration
45	0.17	0.15	0.08	
1,2,3,4-Tetrahydro-1-naphthol				
15	0.50	...	0	Optimum[a]
6-Methoxytetralin				
25	0.40	0.04	0	Optimum[a]
Indan				
35	0.05	0.03	0.08	Optimum[a]
p-Propylanisole				
0	0.13	0	0	Optimum[a]

[a] 4.4–5F/mole current; 35–50°; 4-5 amp./dm.^{2}; 0.4–0.5*N* base, #150 gauze anode.

ketone, alcohol and ether in a molar ratio of about 2:1:1 with about 50% of the reacted starting material forming a polymeric product which was mostly alkali soluble. The electron releasing property of the methoxy group in 6-methoxytetralin increased the ease of oxidation of the hydrocarbon and alcohol so that the total yield was higher and the ratio of ketone to alcohol was about 10:1. No ether was isolated and about 40% of the reacted starting material formed alkali soluble by-products. Indan formed the ketone, alcohol, and ether in a molar ratio of 2:1:3 with about 80% of the reacted starting material forming acidic by-products. This reflects the ease with which the product ketone undergoes further oxidation. *p*-Propylanisole was also oxidized so as to compare the aliphatic with the alicyclic methylene. It was found to give a 13% yield of *p*-methoxypropiophenone. The remainder of the product was a neutral mixture which failed to react with palladium-charcoal catalyst or phthalic anhydride. Law and Perkin[6] found 1- and 2-phenylethanols and benzaldehyde among the products formed by the oxidation of ethylbenzene in acid medium at a platinum anode.

Several mechanisms for explaining anodic oxidation have been proposed. It has been suggested that atomic oxygen is responsible for nuclear attack and molecular oxygen for side chain oxidation.[7] Hydroxyl radicals[6] and peroxygen compounds[8] have also been proposed as oxidizing agents. There is a superficial resemblance between results from molecular oxygen oxidation and anodic oxidation of tetralin, the ketone and alcohol being formed in similar proportions and yields. However, when air was passed through the solution used in the anodic oxidation, no reaction occurred. Also, molecular oxygen had very little effect on indan and 6-methoxytetralin, in contrast to anodic oxidation. Thus, it is unlikely that molecular oxygen is the primary oxidizing agent. Tetralin was also found to be stable to a mixture of *tert*-butyl hydroperoxide and di-*tert*-butyl peroxide, indicating that peroxides were not involved. The participation of atomic oxygen in the oxidation cannot be excluded, but the effect of increasing base concentration suggests a free radical mechanism involving hydroxyl radicals. Attack by the hydroxyl radical on the hydrocarbon would form an α-radical which could unite with another hydroxyl radical to form the alcohol.[9] A repetition of this process on the same carbon atom would produce the ketone. Hydroxyl radical attack on *tert*-butyl alcohol would produce a *tert*-butoxy radical which could unite with an α-radical to form the *tert*-butyl ether. Although it appears unlikely that molecular oxygen is involved in the initial attack on the reductants, any RH· and ROH· radicals formed could react with molecular oxygen to form peroxy radicals which could undergo further transformations to form the alcohol[10] and ketone.[11]

EXPERIMENTAL[12]

Tetralin. Tetralin, obtained from the Distillation Products Co., was purified by fractional distillation through a modified Widmer column, b.p. 85–88° (12 mm.); n_D^{20} 1.5390.

Indan. Commercial indene was hydrogenated over Raney nickel catalyst. The product was washed with acid, alkali, and fractionated through a modified Widmer column, b.p. 61–64° (12 mm.); n_D^{20} 1.5285.

6-Methoxytetralin. α-Naphthylmethyl ether was reduced using the method of Stork.[13] The product was fractionated through a modified Widmer column, b.p. 90–93°; n_D^{20} 1.5458.

p-Propylanisole. Anethole was hydrogenated over Raney nickel catalyst and the product fractionated through a modified Widmer column, b.p. 83–86° (12 mm.); n_D^{20} 1.5049.

Quaternary ammonium bases. Cyclohexyltrimethylammonium hydroxide. Dimethylcyclohexylamine was made by hydrogenating dimethylaniline in methanol solution over Raney nickel catalyst. The product was fractionated through a modified Widmer column. The amine was converted to the methiodide by treating with excess methyl iodide. A water solution of the methiodide was treated with excess freshly precipitated silver oxide and the reaction mixture filtered through a sintered glass funnel. The filtrate was evaporated *in vacuo* (12 mm.) until the boiling point of the solution reached 35°. It was allowed to stand overnight in the refrigerator and refiltered through Filter-cel. The solution was then titrated to determine the concentration of base which ran from 50–55%.

Tetraethylammonium hydroxide. A similar procedure starting with triethylamine and ethyl iodide was used. It was found to be an inferior blending agent.

Benzyltrimethylammonium hydroxide. A practical grade water solution of this base was obtained from the Distillation Products Co. It was found to be too unstable under the conditions used in the reaction.

Anodic oxidations. Apparatus. Reactions were run in a 200-ml. Berzelius beaker equipped with a rubber stopper having holes drilled for a condenser, thermometer, stirrer and anode leads. The cathode lead entered through the condenser. A propeller type stirrer was used. The anodes were cylinders 25 mm. wide and 140 mm. in circumference with leads of #22 platinum wire welded on. The cathode was a #45 mesh platinized platinum gauze cylinder 40 mm. wide and 15 mm. in diameter.

Reactions. A solution of 10–11 g. of reductant, 15–18 ml. of quaternary base solution, 20–30 ml. of water, up to 4 ml. of 20% sodium hydroxide solution, and 75 ml. of *tert*-butyl alcohol was placed in the beaker. The solution was stirred and cooled in a water bath while the desired amount of current was passed through. Current densities varied from 2 to 9 amp./dm.^{2} Since some of the base was destroyed during the reaction, and some neutralized by acidic products, it was necessary to make small additions of base during the reaction in order to maintain a proper conduc-

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tivity. These additions usually totaled about 4 ml. of quaternary base and up to 2 ml. of 20% sodium hydroxide solution. The reaction product was diluted with 300 ml. of water and extracted twice with benzene or ligroin. The alkali soluble products could then be separated by acidifying the aqueous layer. In the high base concentration runs enough sodium carbonate was formed to crystallize out. The combined solvent layer was washed twice with alkali, dried over anhydrous potassium carbonate, concentrated and fractionated *in vacuo.* The combined oxidation product was then refluxed in 75–100 ml. of 5% aqueous methanol with 2–4 g. of semicarbazide hydrochloride (estimated 100% excess) and 3–6 g. of sodium acetate for 3 hr. The mixture was allowed to stand overnight, filtered, and the precipitate washed thoroughly with ether and ligroin to remove unreacted materials. The combined filtrate was diluted with water and extracted twice with ether. The ether solution was washed with dilute sodium hydroxide, dried over potassium carbonate, evaporated, and distilled *in vacuo.* This product was then warmed for 10 min. with 1–2 g. of phthalic anhydride in 3–4 ml. of pyridine. The product was poured into sodium bicarbonate solution and washed twice with ether. The ether layer was washed with acid and worked up, as outlined above, for the *tert*-butyl ether. The aqueous layer was treated with dilute sodium hydroxide solution and allowed to stand at room temperature for 4 hr. to hydrolyze the ester. The alcohol could then be recovered by solvent extraction. This last step could be omitted when *tert*-butyl ethers were found to be absent.

Products. α-Tetralone. The ketone obtained from the oxidation of tetralin was shown to be α-tetralone by the melting point of the semicarbazone, 215–217°. Hydrolysis of the semicarbazone gave a product identical with that obtained from air oxidation.

1,2,3,4-Tetrahydro-1-naphthol. The alcohol product from tetralin oxidation gave a phenylurethane, m.p. 119–121° (121–122°).[14]

1-Indanone. The ketone obtained from indan oxidation was identical with a commercial sample, m.p. 40–41°.

1-Indanol. The alcohol obtained from the indan oxidation gave an α-naphthylurethane, m.p. 136–138° (137°).[15]

6-Methoxy-α-tetralone. Oxidation of 6-methoxytetralin gave a ketone identical with that obtained by other methods, m.p. 77–78.5°.[10]

6-Methoxy-1-hydroxy-1,2,3,4-tetrahydronaphthalene. The alcohol obtained from the oxidation of 6-methoxytetralin gave an α-naphthylurethane, m.p. 130–132° (131–133°).[16]

p-Methoxypropiophenone. The ketone obtained from the oxidation of *p*-propylanisole formed a semicarbazone identical with that from a commercial sample of the compound, m.p. 168–170°.

1-tert-Butoxytetralin. This compound was obtained from the reaction mixture after separation of the ketone and alcohol. It distilled at 135–137° (12 mm.), n_D^{20} 1.5245.

Anal. Calcd. for $C_{14}H_{20}O$: C, 82.35; H, 9.80. Found: C, 82.12; H, 9.42.

A mixture of 1.1 g. of the compound and 0.3 g. of 20% palladium-charcoal was placed in a 25-ml. distilling flask and heated gradually by oil bath, in an argon atmosphere to 150°. *tert*-Butyl alcohol started distilling at this point (identified as the α-naphthylurethane) and on continued heating to 250°, 0.3 g. of naphthalene was obtained.

A solution of 2.0 g. of the compound in 12 ml. of acetic acid to which 0.1 ml. of 85% perchloric acid[17] had been added, was hydrogenated at atmospheric pressure over 0.3 g. of 20% palladium-charcoal catalyst. The reaction ceased after the absorption of about 1 mole of hydrogen. A yield of 1.1 g. of tetralin was obtained from the reaction product.

1-tert-Butoxyindan. This compound was obtained from the reaction product after separation of the ketone and alcohol. It distilled at 120–125° (10 mm.), n_D^{20} 1.5050.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.10; H, 9.47. Found: C, 81.75; H, 9.52.

Heating with 20% palladium-charcoal catalyst, 0.3 g. of *tert*-butyl alcohol (identified as the α-naphthylurethane) was obtained and 0.6 g. of indan boiling at 175–180°, n_D^{20} 1.5372. Hydrogenation of 1.5 g. of the compound gave 1.0 g. of indan after the absorption of 1 mole of hydrogen.

Air oxidations. Tetralin. The time and temperature directions of *Organic Syntheses*[18] were followed. The air was dried by passing through a calcium chloride and was introduced under pressure through a gas dispersion tube. The reaction product was worked up using the directions of *Organic Syntheses* and the ketone separated from the alcohol through the formation of the semicarbazone. The ketone was recovered from the semicarbazone by steam distillation from an aqueous suspension acidified with oxalic acid.[19] From 485 g. of tetralin a yield of 76 g. of α-tetralone and 34 g. of 1,2,3,4-tetrahydro-1-naphthol were obtained.

Indan. Using the method outlined for tetralin and starting with 177 g. of indan, a yield of 2.5 g. of 1-indanone was obtained.

6-Methoxytetralin. Using the method outlined for tetralin and starting with 80 g. of 6-methoxytetralin, 1.2 g. of 6-methoxy-α-tetralin was obtained.

Attempted oxidation with tert-butylhydroperoxide, di-tert-butylperoxide. The *tert*-butyl hydroperoxide, di-*tert*-butyl peroxide mixture obtained from 74 g. of *tert*-butyl alcohol at 0°[20] was added to a solution of 11 g. of tetralin, 10 ml. of water, 16 ml. of quaternary base, and 50 ml. of *tert*-butyl alcohol. The mixture was allowed to stand for 24 hr. at room temperature. There was no evidence of a reaction occurring and on working up the mixture the tetralin was recovered.

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