Anal. Calcd. for $C_{20}H_{32}Si_2Sn$: Si, 12.57; Sn, 26.44; M.R., 122.22. Found: Si, 12.35, 12.45; Sn, 26.33, 26.34; M.R., 123.51.

Dimethylbis(trimethylsilylmethyl)stannane. In the same manner, the Grignard reagent from 24.5 g. (0.2 mole) of chloromethyltrimethylsilane reacted with 11.0 g. (0.05 mole) of dimethyldichlorostannane yielding dimethylbis-(trimethylsilylmethyl)stannane, b.p. 146.5–147.3° (65 mm.), n_D^{25} 1.4644, d_4^{25} 1.0559, yield 51%.

Anal. Calcd. for $C_{10}H_{28}Si_2Sn$: Si, 17.45; Sn, 36.62; M.R., 84.12. Found: Si, 17.33, 17.07; Sn, 36.43, 36.41; M.R., 84.47.

Triphenyl-p-trimethylsilylphenylstannane. The corresponding disilicon compound has already been prepared.[16] Triphenyl-p-trimethylsilylphenylstannane could not be prepared by the interaction of trimethyl-p-bromosilane, triphenylchlorostannane and sodium in boiling toluene. The principal product obtained was hexaphenyldistannane. Accordingly, the Grignard reagent was prepared from the silicon compound, using the method of Campagna and Post,[7] from 22.9 g. (0.1 mole) of trimethyl-p-bromophenylsilane. After solution of the magnesium, 19.5 g. (0.05 mole) of triphenylchlorostannane was added dropwise and the mixture refluxed for 24 hr. The resulting system was hydrolyzed, the ethereal layer evaporated to dryness, and the residue recrystallized three times from alcohol, giving triphenyl-p-trimethylsilylphenylstannane, m.p. 132.5–133.5°, yield 71.5%.

Anal. Calcd. for $C_{27}H_{28}SiSn$: Si, 5.63; Sn, 23.77. Found: Si, 5.60, 5.43; Sn, 23.71, 23.57.

Diphenylbis(p-trimethylsilylphenyl)stannane. The same method used for the preparation of triphenyl-p-trimethylsilylstannane was followed here with the following materials: 45.8 g. (0.2 mole) of the trimethyl-p-bromophenylsilane, 4.8 g. (0.2 g. atom) of magnesium and 17.2 g. (0.05 mole) of diphenyldichlorostannane. The ethereal solution, after hydrolysis, was dried over calcium chloride and frac-

tionated yielding needle like crystals of diphenylbis(p-trimethylsilylphenyl)stannane, m.p. 95–96°, yield 23.5%.

Anal. Calcd. for $C_{30}H_{36}Si_2Sn$: Si, 9.82; Sn, 20.62. Found: Si, 9.90, 9.92; Sn, 20.50, 20.47.

Analytical. The analyses of these compounds were carried out by a determination of the total weight of the metallic oxides (silicon and tin oxides), obtained by the method of Gilman and King[17] and then determining the percentage of tin from the mixture of oxides by gravimetric or iodometric method.

The percentage of silicon was calculated from these results.

The gravimetric method consists in separating stannic oxide from silica by treating the mixture of oxides with sodium hydroxide and sulfur whereupon soluble sodium thiostannate was formed and solution filtered.

Stannic sulfide was precipitated from the boiling filtrate by the action of acetic acid. Then with sodium hydroxide the sulfide was converted once more to sodium thiostannate, soluble, while the excess of insoluble sulfur was filtered off.

Sodium thiostannate was oxidized to sodium stannate by hydrogen peroxide (boiling) and its solution neutralized with nitric acid using methyl orange and ammonium nitrate. Stannic acid precipitated quantitatively and was converted by heat to stannic oxide.

Iodometrically the tin was determined by extraction of the oxides with sodium hydroxide and collecting the sodium stannate and silicate formed in an Erlenmeyer flask, with the help of a stream of hot water.

The solution was treated with excess of 6N HCl (sodium stannate passed to stannic chloride and sodium silicate to insoluble silicic acid), and Sn^{4+} was reduced to Sn^{2+} by the action of nickel wire, in carbon dioxide ambient, boiling for 0.5 hr. Sn^{+2} was titrated with a standard solution of iodine.

BUFFALO, N. Y.

Studies in the Dibenzobicyclo[2.2.2]octadiene System

WYMAN R. VAUGHAN AND MASAO YOSHIMINE[1,2]

A number of 2- and 2,3-oxygenated derivatives of dibenzobicyclo[2.2.2]octadiene have been prepared, and the anomalous reactions encountered when attempts to rearrange them to derivatives of 9,10-methano-9,10-dihydroanthracene (dibenzobicyclo[2.2.1]heptadiene) failed are described. Especially noteworthy is the unusually mild alkaline cleavage of the 2,3-diketo derivative to give 9,10-dihydroanthracene and oxalate ion.

In a preliminary study of approaches to the synthesis of 9,10-methano-9,10-dihydroanthracene[3,4] three molecular rearrangements were considered: the benzilic acid rearrangement applied to dibenzobicyclo[2.2.2]octadiene-2,3-dione (I), the pinacol rearrangement applied to the *cis* glycol (II) derivable therefrom, and the pyrolysis of the sulfite ester (III) of II. As will appear in the sequel these approaches did not afford the desired methanoanthra-

cene structure, but a number of interesting reactions were encountered.

The preparation of I involved selenium dioxide oxidation of dibenzobicyclo[2.2.2]octadien-2-one (IV), an independent synthesis[5] of which appeared subsequent to our isolation of the compound. Both procedures involve Oppenauer oxidation of the corresponding carbinol, the published one[5] employing cyclohexanone and ours employing benzoquinone. The carbinol in turn was obtained essentially by the procedure of Alder and Rickert[6] by

(1) Abstracted from a portion of the Ph.D. Dissertation of Masao Yoshimine, University of Michigan, 1955.

(2) Edgar C. Britton Fellow in Organic Chemistry, 1955.

(3) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **21**, 263 (1956).

(4) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

(5) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(6) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1940).

hydrolysis of the acetate prepared by the Diels-Alder reaction of vinyl acetate with anthracene.

Conversion of I into II was effected by lithium aluminum hydride reduction, and the *cis* configuration of II was demonstrated by comparison with an authentic sample prepared by hydrolysis of the Diels-Alder adduct of vinylene carbonate[7] with anthracene.[8] In addition, a sample of II obtained by reduction was partially converted to the carbonate[8] with phosgene and to the sulfite (III) by means of thionyl chloride.

The possibility of a Favorskii-type rearrangement[9] applied to 3-bromodibenzobicyclo[2.2.2]octadien-2-one (V) was considered briefly but was abandoned when no readily characterizable product could be isolated upon treatment of the bromoketone with silver nitrate.[9]

The anticipated rearrangements are illustrated schematically in Chart I, wherein the 1,2,3 and 4 carbons of dibenzobicyclo [2.2.2]octadiene are represented by dots.
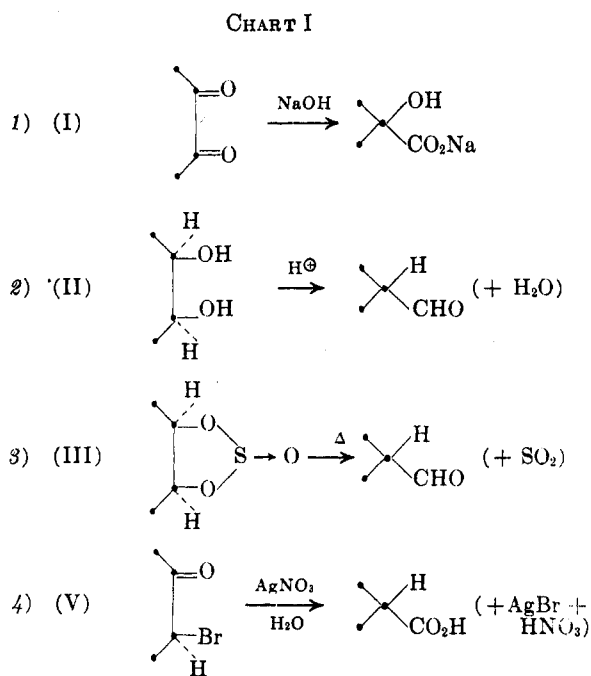
<div style="text-align:center">CHART I</div>

RESULTS

Reaction 3, Chart I, was attempted with the production of sulfur dioxide and a carbonyl compound tentatively characterized by 2,4-dinitrophenylhydrazone formation (different from that of IV) and by the infrared spectrum which possessed a band at 1730 cm.$^{-1}$ The compound itself was not obtained in good yield (considerable starting material was

recovered) and resisted satisfactory purification. However, the nature of the sulfite pyrolysis reaction[10] suggests that it may well have been the expected aldehyde, since no other obvious reaction can account for a carbonyl compound. Owing to the unsatisfactory nature of the product and the difficulty of obtaining adequate quantities of the sulfite ester (considerable dimeric material was obtained simultaneously), further investigation of the reaction was not undertaken.

While Reaction 2, Chart I, did not afford the expected product, a 50% yield of a product with a molecular formula $C_{32}H_{28}O_2$ (VI) was obtained by treating II with 25% sulfuric acid. Three structural isomers (VIa, VIb, and VIc) can reasonably be produced under these conditions. Structure VIb was
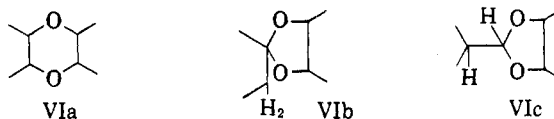
eliminated explicitly by its synthesis from IV and II in 20% yield, and it melted some 44° lower. Next, the compound in question was subjected to treatment with 48% hydrobromic acid, which should cleave VIc (or VIb), and since VI was recoverable intact, it was assigned the structure VIa.

The reaction between I and sodium hydroxide (Chart I, Reaction I) proved to be the most interesting. When I was suspended in excess 2.2N sodium hydroxide and warmed on the steam bath for 4 min., a white flocculent precipitate appeared which proved to be 9,10-dihydroanthracene (91.7% yield). From the filtrate there was obtained a 91.3% yield of calcium oxalate monohydrate.

There appears to be no precedent for this reaction—at least under such mild conditions. In fact, mild alkaline treatment of 1,2,3,4-tetrachloro-5,6-diketo-7-phenylbicyclo[2.2.2]octene-2   affords the salt of 2,3-dichloro-5-phenyl-3,6-dihydroterephthalic acid[11] while similar treatment of 1,2,3,4,5-pentaphenylbicyclo[2.2.1]hept-2-en-7-one   affords the salts of 1,2,3,4,6- and 1,2,3,4,5-pentaphenyl-2-cyclohexene-1-carboxylic acid.[12] Only one equivalent of base was essential for the latter reaction, which most nearly resembles ours. Consequently, I was warmed on the steam bath with 1.1 equivalents of sodium hydroxide, and there was obtained a sodium salt whose infrared spectrum possessed a band of medium strength at 1690 cm.$^{-1}$ and a strong band due to carboxylate ion at 1620 cm.$^{-1}$ The presence of the carbonyl group was confirmed by preparation of a 2,4-dinitrophenylhydrazone. The acid was characterized as 9,10-dihydroanthracene-9-glyoxylic acid by subsequent mild alkaline cleavage to

(7) Very kindly furnished by Prof. M. S. Newman and Dr. R. W. Addor, who provided procedural details in advance of publication (*cf.* ref. 8).

(8) M. S. Newman and R. W. Addor, *J. Am. Chem. Soc.,* **77**, 3789 (1955).

(9) A. C. Cope and E. S. Graham, *J. Am. Chem. Soc.,* **73**, 4702 (1951).

(10) C. C. Price and G. Berti, *J. Am. Chem. Soc.,* **76**, 1211 (1954).

(11) L. Horner and H. Merz, *Ann.,* **570**, 89 (1950).

(12) C. F. H. Allen, J. E. Jones, and J. A. Van Allan, *J. Am. Chem. Soc.,* **68**, 708 (1946).

9,10-dihydroanthracene and oxalate ion, precedent for which is to be found in the mild alkaline cleavage of 9-benzoyl-9,10-dihydroanthracene to benzoate and 9,10-dihydroanthracene.[13] Presumably, then, the initial cleavage is analogous, and the rate of the reaction considerably exceeds that of the expected benzilic acid rearrangement.

It is difficult to envisage a different initial step for the expected rearrangement and the observed cleavage, thus addition of the hydroxyl ion to one of the carbonyl carbons to form an anionic intermediate (VII) is a logical first step.[14]
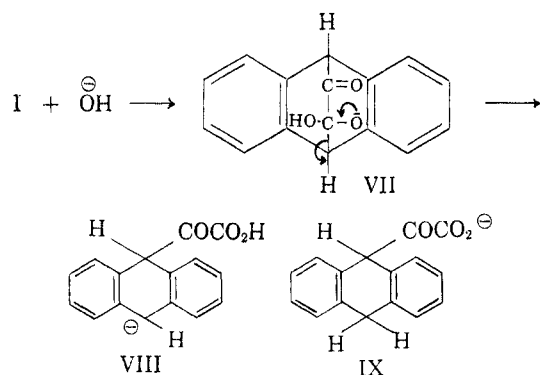
Two factors then contribute to a favorable rate for cleavage as compared with rearrangement: resonance stabilization of the carbanion (VIII) and the increase in strain in the desired methanoanthracene derivative. The facile cleavage of IV which follows, in the presence of *excess* alkali, may be pictured by similar hydroxyl addition to the remaining carbonyl (→X) with separation of the acid oxalate ion promoted by resonance stabilization of the resultant carbanion (XI):
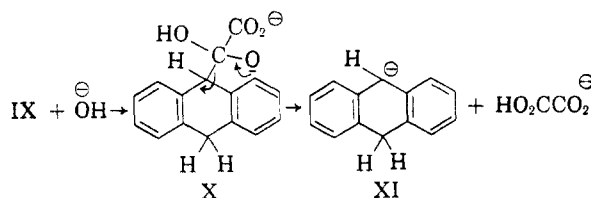
That the second carbon-carbon cleavage occurs according to the hydroxide addition mechanism would appear to be substantiated by the fact that *excess* alkali is required, since such an attack would be reversible and would possess an unfavorable equilibrium constant owing to the negative charge already present adjacent to the carbonyl group. For example, two equivalents of sodium hydroxide with the acid derived from IX affords but 32% of 9,10-dihydroanthracene and leaves considerable unreacted alkali, while six equivalents of hydroxide affords 99% cleavage in 3 min. on the steam bath.

By way of confirming the general character of this alkaline cleavage IV was treated with alcoholic potassium hydroxide, whereupon there was obtained a 94% yield of 9,10-dihydroanthracene-9-acetic acid. This, of course, is more nearly analogous to the ketone cleavage cited above;[13] and a considerably longer reaction time was required, as might be expected, since the carbonyl carbon in IV is electronically a less attractive site for hydroxide attack than in I (−I effect of adjacent carbonyl of I). The considerably less facile hydroxide fusion cleavage of diaromatic ketones[15] constitutes further support for the argument that resonance stabilization of the benzhydryl-type carbanion is in part responsible for the observed cleavages. That it may not be entirely due to such stabilization but to a combination of the latter with the steric nature of the bicyclic system would appear from the observations of Bachmann and Chu[16] who apparently were forced to use fusion to cleave 10,10-diaryl-9,10-dihydro-9-phenanthrones to salts of 2-[2′-diarylmethylphenyl]benzoic acids.

EXPERIMENTAL

Dibenzobicyclo[2.2.2]octadiene-2,3-dione (I). A mixture of 5.32 g. (0.0242 mole) of dibenzobicyclo[2.2.2]octadien-2-one (IV),[17] 4.04 g. (0.0363 mole) of sublimed selenium dioxide and 10 ml. of ethanol was heated, with stirring, for 2 hr. at 145–150°. The yellowish-black reaction mixture was partially dissolved in ethanol and 1.86 g. of black selenium was collected by filtration. The filtrate was concentrated under an air jet to a dark yellow oil which was partially dissolved in ether, and the resulting solution was washed with several portions of water to remove the excess selenium dioxide. The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the solvent was removed to leave a dark orange semisolid. The crude product was crystallized from carbon tetrachloride to yield 2.53 g. of yellow-orange crystals, m.p. 188–198°. A second crystallization from benzene afforded 1.92 g. (33%) of yellow crystals, m.p. 199.0–201.5°, after sintering above 194°.

Anal. Calcd. for $C_{16}H_{10}N_2$: C, 82.04; H, 4.30. Found (K): C, 81.87; H, 4.49.

The infrared spectrum shows strong absorptions at 1750 cm.$^{-1}$ and 1730 cm.$^{-1}$

A quinoxaline was prepared by means of o-phenylenediamine: m.p. 291.5–292.0°, from 95% ethanol.

Anal. Calcd. for $C_{22}H_{14}N_2$: C, 86.25; H, 4.61. Found (G): C, 86.25; H, 4.49.

A mono-2,4-dinitrophenylhydrazone was also prepared: m.p. 217–218° dec., from benzene–petroleum ether (60–75°).

Anal. Calcd. for $C_{22}H_{14}N_4O_5$: C, 63.77; H, 3.41; N, 13.52. Found (G): C, 63.49; H, 3.52; N, 13 52.

(13) J. W. Cook, *J. Chem. Soc.*, 1677 (1926).

(14) C. K. Ingold, *Ann. Rep. Chem. Soc.*, **25**, 124 (1928); cf. E. R. Alexander, *Ionic Organic Reactions*, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 199–200.

(15) M. R. Delange, *Bull. soc. chim.*, [3] **29**, 1131 (1903).

(16) W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **57**, 1095 (1935).

(17) Prepared essentially as in ref. 5, but using benzoquinone as hydrogen acceptor in place of cyclohexanone. A 2,4-dinitrophenylhydrozone was prepared: m.p. 210.5–211.5°, from 95% ethanol. *Anal.* Calcd. for $C_{22}H_{16}N_4O_4$: C, 65.99; H, 4.03; N, 13.99. Found (G): C, 65.77; H, 4.04; N, 13.77.

Dibenzobicyclo[2.2.2]octadiene-cis-2,3-diol (II). A Soxhlet extractor, containing 6.00 g. (0.0256 mole) of I, and a slurry of 0.971 g. (0.0256 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether, was heated under reflux with stirring for 18 hr. The excess hydride was destroyed by dropwise addition of water. To the reaction mixture was added 100 ml. of 5% sodium hydroxide with stirring. The ethereal layer was separated, washed with several portions of water, dried over anhydrous magnesium sulfate, and filtered. The ether was removed by an air jet leaving 5.78 g. of pale yellow material, m.p. 194–198°. Crystallization from 20% petroleum ether (b.p. 60–75°)-benzene mixture yielded 4.93 g. (81%) of white crystals, m.p. 199.0–200.5°. An analytical sample was prepared by repeated recrystallizations from 20% petroleum ether (b.p. 60–75°)-benzene mixture, white crystals, m.p. 200.5–201.5°. A mixture melting point with an authentic sample of II[8] showed no depression.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found (G): C, 80.50; H, 6.09.

A portion of the glycol (II) was converted into its carbonate ester by means of phosgene in dioxane containing pyridine. The product melted at 253.0–253.5° and failed to depress the melting point of an authentic sample.[8] The infrared spectra were identical.

Attempted pinacol rearrangement of II. A suspension of 1.101 g. (0.00460 mole) of II in 18 ml. of 25% sulfuric acid was refluxed for a week. The suspension was cooled, and a white powder was collected by filtration and washed with sodium bicarbonate solution and water. The dried, crude product, m.p. 238–254°, 0.901 g., was crystallized from ethanol yielding 0.508 g. (50%) of white, glistening plates, m.p. 258.5–260.0°. The analytical sample, glistening white plates, m.p. 259.5–260.5°, was obtained by several recrystallizations from ethanol.

Anal. Calcd. for $C_{32}H_{28}O_2$: C, 87.24; H, 5.49; mol. wt. 440. Found (G): C, 87.19; H, 5.77; mol. wt. (Rast with borneol) 460.

A second crop of 0.222 g. of white crystals, m.p. 190.5–196.0°, was obtained from the filtrate. The infrared spectrum was identical with that of the starting material.

Ketal of II with IV. A solution of 0.320 g. (0.00137 mole) of II, 0.302 g. (0.00137 mole) of IV, and a trace of *p*-toluenesulfonic acid was refluxed for 24 hr., removing a water-benzene azeotropic mixture. The reaction mixture was washed with sodium bicarbonate solution and with water, dried over anhydrous magnesium sulfate, and concentrated to a yellow oil. The oil was triturated with a mixture of ethanol and petroleum ether (b.p. 60–75°) to obtain 0.162 g. of crude white crystals, m.p. 208–215°. One crystallization from ethanol yielded 0.125 g. (20%) of white crystals, m.p. 214–215°. The analytical sample, white crystals, m.p. 214.5–215.0°, was obtained by two recrystallizations from petroleum ether (b.p. 60–75°).

Anal. Calcd. for $C_{32}H_{28}O_2$: C, 87.24; H, 5.49. Found (G): C, 87.30; H, 5.53.

Attempted cleavage of VI. A suspension of 0.401 g. (0.000910 mole) of VI, in 30 ml. of 48% hydrobromic acid was heated on a steam bath for a week. The reaction mixture was cooled, and pale yellow crystals were collected and washed with sodium bicarbonate solution and with water. The pale yellow crystals, m.p. 252–258°, weighed 0.366 g. (91% recovery). The infrared spectrum was identical with that of the starting material.

Reaction of II with thionyl chloride. (A) Dimeric sulfite. To a solution of 0.976 g. (0.00409 mole) of II, in 1.395 g. (0.0163 mole) of dried pyridine, 35 ml. of dried, purified dioxane and 20 ml. of dried benzene cooled to 10° was added dropwise to a solution of 0.973 g. (0.00818 mole) of thionyl chloride and stirred for 5 hr., allowing the temperature to rise to 18°. The removal of the solvent from the reaction mixture left a whitish mass which was partially dissolved in hot benzene. Pyridine hydrochloride was filtered off and was washed with several portions of benzene. The solvent

was stripped from the filtrate, leaving a yellow mass which was partially dissolved in ethanol. White crystals, m.p. 234.0–234.5° dec., weighing 0.214 g. (18%), were collected by filtration, washed with ethanol, and dried.

Anal. Calcd. for $C_{32}H_{24}O_6S_2$: C, 67.62; H, 4.25; mol. wt. 568. Found (G): C, 67.29; H, 4.36; mol. wt. (Rast) 558.

(B) *Monomeric sulfite* (III). The filtrate and ethanol washings of the disulfite were combined, and the mixture evaporated to dryness, giving a white mass. One crystallization from ethyl acetate yielded 0.687 g. of white crystals, m.p. 172–185°. Recrystallization from ethanol gave 0.345 g. (29%) of fine white needles, m.p. 191.2–192.2°.

Anal. Calcd. for $C_{16}H_{12}O_3S$: C, 67.62; H, 4.25. Found (G): C, 67.48; H, 4.30.

Pyrolysis of III. The pyrolysis of 0.0810 g. (0.000287 mole) of III was carried out in a Pyrex tube plugged with Pyrex glass wool. The sulfite was heated in a stream of nitrogen at 285–300° for 1 hr., yielding 0.045 g. of a mixture of white needles and a pale yellow powder. The initial decomposition temperature of 280° was detected by the formation of a barium sulfate precipitate in the gas exhaust trap, which contained a solution of hydrogen peroxide and barium nitrate. The infrared spectrum of the mixture indicated the presence of undecomposed starting material and a compound with a medium absorption band at 1727 cm.$^{-1}$ Attempts to purify the mixture were not successful. A 2,4-dinitrophenylhydrazone of the crude product was prepared, and two recrystallizations of the crude hydrazone gave trace amounts of yellow-orange, glistening crystals, m.p. 214.0–214.5°. A mixture m.p. with the 2,4-dinitrophenylhydrazone of IV was 185–192°. Insufficient material was available for analysis.

3-Bromo-dibenzobicyclo[2.2.2]octadien-2-one (V) To a solution of 5.00 g. (0.0227 mole) of V, in 100 ml. of carbon tetrachloride was added a solution of 3.80 g. (0.0238 mole) of bromine in 75 ml. of carbon tetrachloride. The reaction mixture was allowed to stand overnight at room temperature, then was treated with sulfur dioxide, washed with water and filtered through a Celite-Norit–anhydrous magnesium sulfate mixture. The removal of the solvent at water pump pressure left 6.17 g. of partially crystalline material. A crystallization from ethanol yielded 5.42 g. (79%) of white needles, m.p. 124–126°. Recrystallization from ethanol gave 4.54 g. (67%) of white needles, m.p. 124–126°.

Anal. Calcd. for $C_{16}H_{11}BrO$: C, 64.21; H, 3.71. Found (K): C, 63.90; H, 3.93.

Alkaline cleavage of I. A suspension of 0.256 g. (0.00109 mole) of I in 5.0 ml. of 2.2*N* sodium hydroxide (5 equivalents) was heated on the steam bath, with stirring. A white flocculent precipitate appeared in 1 min., but the heating was continued for 3 min. The reaction mixture was cooled, and the crude product was collected by filtration, washed and dried, yielding 0.180 g. (91.5%) of white crystals, m.p. 104.5–106.5°. Two crystallizations from ethanol afforded long, white needles, m.p. 107.0–108.5°. A mixture m.p. with 9,10-dihydroanthracene was 106.5–108.5°, and the infrared spectra were identical.

The yellowish reaction filtrate was neutralized with dilute hydrochloric acid, and 2 ml. of 10% calcium chloride solution was added, forming a white precipitate. The white powder was collected, washed with 2 ml. of water and dried at 100° to constant weight. The white powder, calcium oxalate monohydrate, weighed 0.145 g. (91.3%). A spot test, according to the procedure of Feigl,[18] established the identity of the oxalate.

Preparation of 9,10-dihydroanthracene-9-glyoxylic acid. A suspension of 1.380 g. (0.00590 mole) of I in 5.45 ml. of 1.19*N* sodium hydroxide (1.1 equivalent) was heated on the steam bath, with stirring for 4 min. An unidentified tan

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(18) F. Feigl, *Qualitative Analysis by Spot Test*, Third English Ed., Elsevier Publishing Co., Inc., New York, N. Y., 1946, p. 403.

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-dihydro-anthracene-9-glyoxylic acid in 2.0 ml. of 1.96N 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 1.78N 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.

Ann Arbor, Mich.

(19) E. L. May and E. Mosettig, *J. Am. Chem. Soc.*, 70, 1077 (1948).

Anodic Oxidation of Aryl Activated Methylene Groups[1]

RICHARD E. JUDAY

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 pH 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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