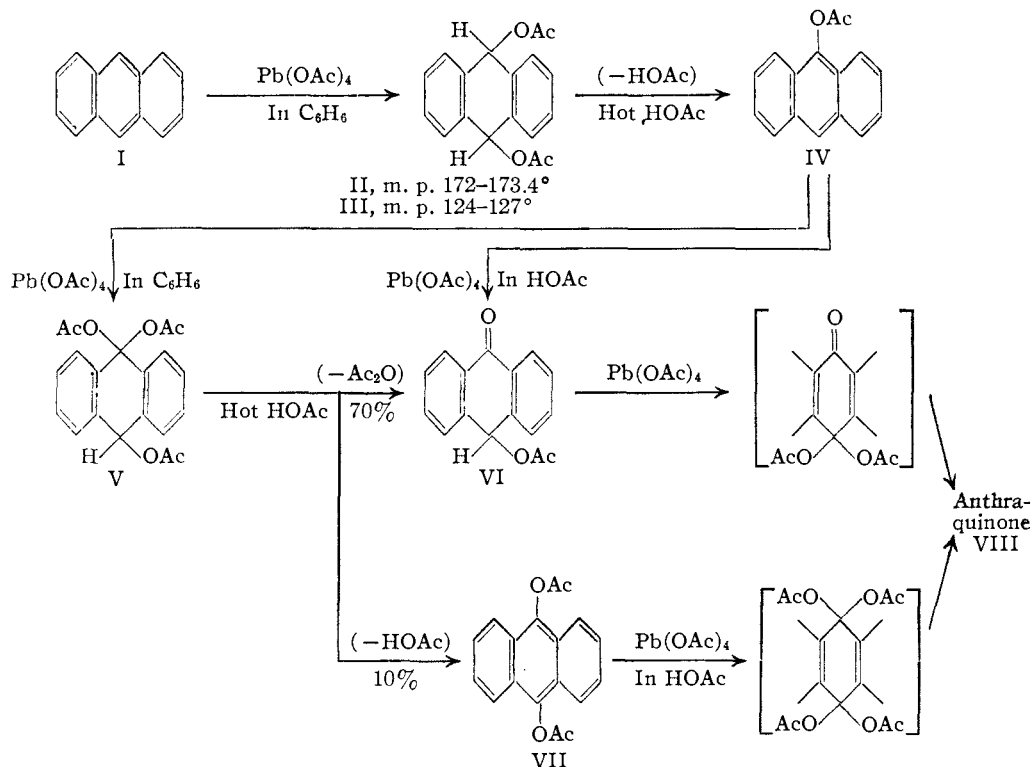


[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Mechanism of the Oxidation of Anthracene with Lead Tetraacetate¹BY LOUIS F. FIESER AND STEARNS T. PUTNAM²

Investigations of the acetoxylation of polynuclear aromatic hydrocarbons by the action of lead tetraacetate³ were suggested by an observation made by K. H. Meyer⁴ several years before lead tetraacetate had been introduced as a useful reagent by the work of Dimroth.⁵ Meyer had studied the oxidation of anthracene with a suspension of lead dioxide in acetic acid and had isolated as reaction products 9-acetoxyanthracene (IV in the chart) and oxanthrone acetate (VI). Several products similar to 9-acetoxyanthracene have been encountered in the reactions of lead tetraacetate with other hydrocarbons, but none of the type of oxanthrone acetate. The present study arose out of curiosity in regard to the manner in which the latter substance is formed.

When the temperature was controlled to 35–40° or when the reaction was conducted in benzene–acetic acid at 50–55°, a new compound melting at 173° was isolated in very small amounts. This substance proved to undergo ready alteration in warm acetic acid, and hence the oxidation was tried in dry benzene at the reflux temperature, when both the 173° compound and a second new compound melting at 127° were isolated. Both substances are colorless, sensitive to heat and light, difficult to purify and the melting points are not sharp. The two compounds are isomeric, and the composition corresponds to the introduction of two acetoxy groups without elimination of hydrogen. When a solution of either isomer in acetic acid is warmed, 9-acetoxyanthra-



In initial trials the oxidation of pure anthracene with lead tetraacetate in acetic acid solution at 50–55° gave complex mixtures from which 9-acetoxyanthracene and anthraquinone were iso-

lated. From these facts it is inferred that the substances are geometrical isomers formed by the addition of acetoxy groups to the ends of the diene system in the central ring of the anthracene molecule (Formulas II and III in the chart). Several independent syntheses of 9,10-diacetoxy-9,10-dihydroanthracene were attempted without success, but some corroboration was found in the observation that the higher-melting isomer is converted by dry hydrogen chloride in ether solution into 9-chloro-

(1) This paper is based upon results presented in the Dissertation of Stearns T. Putnam, May 1, 1942.

(2) Present address: Hercules Powder Company Experiment Station, Wilmington, Delaware.

(3) Fieser and Hershberg, *THIS JOURNAL*, **60**, 1893, 2542 (1938); Fieser and Cason, *ibid.*, **62**, 434 (1940).

(4) K. H. Meyer, *Ann.*, **379**, 37 (1911).

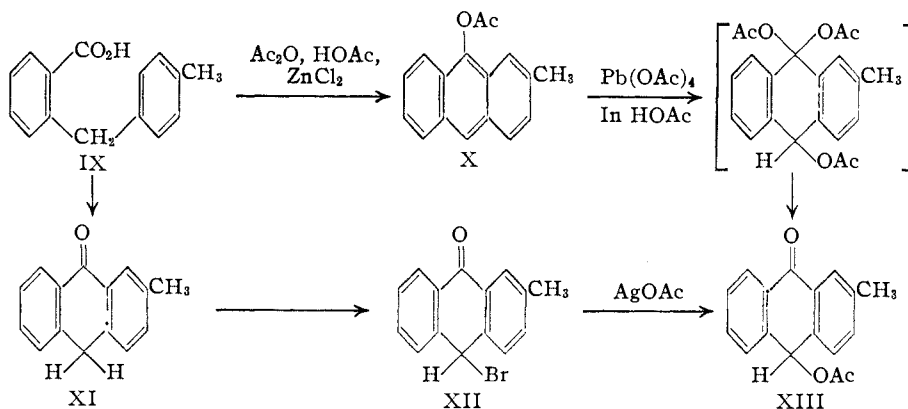
(5) Dimroth and Kammerer, *Ber.*, **53**, 481 (1920).

anthracene; the reaction must involve the replacement of at least one of the acetoxy groups of the starting material by chlorine, for 9-acetoxyanthracene, a conceivable intermediate, remains unchanged under the conditions of the experiment.

The first step in the reaction of anthracene with lead tetraacetate is thus an addition. Although this appears to be the first instance of an addition to an aromatic system, the reaction is well known in the aliphatic and alicyclic series.^{6,7}

In exploring the further course of the oxidation, we treated pure 9-acetoxyanthracene with lead tetraacetate in acetic acid solution and obtained oxanthrone acetate (VI) as the sole reaction product. 9,10-Diacetoxyanthracene could conceivably arise by a substitution reaction, but none of this substance could be found in the reaction mixture. If a second addition were involved, the initial product would have the structure V, and when the reaction was conducted in dry benzene a crystalline substance of this composition was indeed isolated. This substance, 9,9,10-triacetoxy-9,10-dihydroanthracene, when heated in acetic acid solution is converted largely into oxanthrone acetate (VI) by the loss of acetic anhydride and to a lesser extent into 9,10-diacetoxyanthracene (VII) by the loss of acetic acid. It was found further that both oxanthrone acetate and 9,10-diacetoxyanthracene are converted into anthraquinone by oxidation with lead tetraacetate in acetic acid solution. No attempt was made to isolate intermediates, but by analogy with the above results one may postulate that the second reaction proceeds by the addition of two acetoxy groups and the elimination of two molecules of acetic anhydride. The oxidation of oxanthrone acetate most likely involves the replacement of the active hydrogen at position 10 by an acetoxy group.

It will be noted that, according to the mechanism advanced for the conversion of 9-acetoxyanthracene into oxanthrone acetate, the acetoxy group of the latter substance is attached to a different carbon atom than the corresponding group in the former. This implication of the hypothesis offered an opportunity for securing substantiating evidence. 2-Methyl-9-acetoxyanthracene (X) was synthesized by the cyclization of 2-*p*-xylylbenzoic acid (IX) by the method of Fieser and Hershberg⁸ and oxidized with two



moles of lead tetraacetate in acetic acid solution. An oxanthrone acetate was isolated in 49% yield, and the structure XIII was established by the synthesis of an identical product from the 10-bromo derivative of 2-methylanthrone-9 (XI). The product thus does indeed have the acetoxy group at a different meso position (10) from that occupied by the original acetoxy group (9), in accordance with the postulated addition mechanism.

Experimental Part⁹

Reagents.—The anthracene used was blue fluorescent, m. p. 212–214°. Lead tetraacetate was prepared by the Dimroth method,¹⁰ recrystallized from acetic acid and dried in vacuum over sulfuric acid. The glacial acetic acid was distilled over potassium permanganate, and the benzene was washed with sulfuric acid, dried over calcium chloride, and stored over sodium wire.

Oxidation of Anthracene

In Acetic Acid or Benzene–Acetic Acid.—In the following experiments 2 g. of anthracene was oxidized with 4.95 g. of lead tetraacetate under the conditions given below. The cooled solution was filtered from any unchanged anthracene, concentrated in vacuum, diluted with water, and extracted with ether; the material recovered from the carbonate-washed extract was crystallized from alcohol.

(a) Oxidation in 700 cc. of acetic acid at 50–55° for two days gave 1.4 g. of crystalline product, m. p. 150–170°, from which the only pure substance isolated was 9-acetoxyanthracene, m. p. 133–134° (from alcohol).

(b) A suspension of the reactants in 80 cc. of acetic acid was stirred at 35–40° for three hours and let stand overnight, and 0.5 g. of unchanged anthracene was recovered. The initial crystallize (yellow, 0.4 g., 137–138°) afforded a small amount of colorless crystals of the addition product II, m. p. 172–173°.

(c) A solution of the tetraacetate in acetic acid was added to a stirred solution of anthracene in 150 cc. of benzene maintained at 50–55° in the course of four hours. There resulted 0.9 g. of light yellow product, m. p. 115–130°, and repeated crystallization from ligroin gave colorless crystals of II, m. p. 172–173° (analysis below).

In benzene, (d).—A mixture of 20 g. of anthracene and 50 g. of lead tetraacetate in about 1 liter of benzene was refluxed for forty-five hours; the solution was filtered from the lead diacetate, washed until neutral with sodium bicarbonate solution, dried and evaporated to a small volume. The solution on cooling deposited 6.5 g. of colorless, granular material, m. p. 140–160°, and two recrystallizations of this product from alcohol and five from 70–90°

(6) Dimroth and Schweizer, *Ber.*, **56**, 1375 (1923).

(7) Criegee, *Ann.*, **481**, 263 (1930); *Angew. Chem.*, **53**, 321 (1940).

(8) Fieser and Hershberg, *THIS JOURNAL*, **59**, 1028 (1937).

(9) All melting points are corrected.

(10) Fieser, "Experiments in Organic Chemistry," 2nd ed., 437, D. C. Heath and Co., New York, N. Y., 1941.

ligroin gave 1.1 g. of the addition product II in the form of granules or irregular plates, m. p. 172–173.4°. The benzene mother liquor was decolorized with charcoal, diluted with ligroin and cooled, whereupon 17 g. of yellowish granular lumps separated, m. p. 100–140°. Two crystallizations from 70–90° ligroin and three from petroleum ether gave 0.75 g. of the addition product III as colorless prismatic needles, m. p. 124–127°. The material isolated in another experiment formed transparent prisms, m. p. 123–127.5°. Mixtures of this substance with 9-acetoxyanthracene and with II melted at 105–120° and at 108–142°, respectively.

Properties of the Isomeric 9,10-Diacetoxy-9,10-dihydroanthracenes, II (Higher Melting) and III.—*Anal.* Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Isomer II, Found, Run (c): C, 73.36, 73.10; H, 5.55, 5.56; Run (d): C, 73.40, 73.05; H, 5.70, 5.66. Isomer III, Found, Run (d): C, 72.98; H, 5.70.

Both substances are unstable on storage in the solid state and also tend to decompose in solution, particularly when exposed to light; the melting point becomes more indefinite and soon higher-melting material is observed. Isomer II is the less soluble of the two; it dissolves in hot methanol or ethanol and crystallizes readily on cooling, whereas III dissolves readily in these solvents in the cold. In cold benzene II is moderately soluble and III readily soluble. Isomer II is readily soluble in cold ethyl acetate, moderately soluble in hot 70–90° ligroin, and slightly soluble in boiling petroleum ether; III is moderately soluble in cold 70–90° ligroin.

The decomposition in hot acetic acid was investigated as follows. A solution of 0.3 g. of II in 20 cc. of acetic acid was refluxed for five minutes, poured into water, and the precipitate crystallized from alcohol. A first crop of 9-acetoxyanthracene amounted to 0.1 g. (42%), m. p. 135.5–136.4°, mixed m. p. 134–136.5°; the second crop of 0.1 g. (42%) consisted of colorless needles, m. p. 129–134.4°. Isomer III (0.5 g.) when treated in exactly the same way gave 0.2 g. (50%) of 9-acetoxyanthracene, m. p. and mixed m. p. 134–136°, and 0.1 g. (25%), m. p. 120–127°.

In a test of the action of hydrogen chloride, a solution of 0.5 g. of isomer II in 50 cc. of dry ether was saturated with the gas and refluxed for two hours. The product recovered from the washed and dried solution on crystallization from alcohol gave 0.14 g. (39%) of 9-chloroanthracene, m. p. 102–105°. The twice-recrystallized sample formed yellow needles, m. p. 105.2–107°, and formed a bright scarlet picrate (needles), with m. p. 140–140.5° (Perkin,¹¹ m. p. 103°, scarlet picrate). When 1 g. of 9-acetoxyanthracene was processed in the same way a total of 0.87 g. of material was recovered unchanged.

Attempts to dehydrogenate Isomer II by refluxing the substance with benzoquinone or chloranil in xylene solution were unsuccessful.

Attempted Synthesis of II and III.—The reaction of anthracene with silver acetate and iodine in boiling benzene¹² gave no crystalline products. An attempt to form the disodio derivative of 9,10-diacetoxyanthracene¹³ in ether–benzene and decompose it with methanol gave a few crystals of anthraquinone as the only identified product. Anthracene-9,10-dibromide was prepared by a known method¹⁴ in 95% yield and 5.4 g. of the material was stirred in 200 cc. of acetic acid with an equal weight of silver acetate at 16–17° for ten minutes. The solution was quickly filtered into cold water and the gummy precipitate processed in ether. Crystallization of the re-

covered product from ligroin gave 0.6 g. of crude 9-acetoxyanthracene, m. p. 120–133°; the fully purified substance formed colorless needles, m. p. and mixed m. p. 134–135.5°. 9-Bromoanthracene (m. p. 101.5–102.8°) was recovered unchanged when submitted to even more prolonged treatment with silver acetate in acetic acid, and hence at least one of the halogen atoms of the dibromide must have been replaced by an acetoxy group prior to aromatization of the central ring.

Oxidation of 9-Acetoxyanthracene¹⁵

In Acetic Acid.—A solution of 2 g. of 9-acetoxyanthracene and 1.9 g. (0.5 equiv.) of lead tetraacetate in 200 cc. of acetic acid was stirred at 70–86° for twelve hours, and the product was recovered as above by ether extraction and fractionally crystallized from alcohol and from ligroin. The first crystallize (0.3 g., m. p. 100–110°) on recrystallization from ligroin gave colorless needles of oxanthrone acetate,⁴ m. p. 108–110°. The second fraction afforded unchanged starting material, and a terminal fraction melted above 200° and gave a vat test.

In Benzene: 9,9,10-Triacetoxy-9,10-dihydroanthracene (V).—A solution of 5 g. of 9-acetoxyanthracene in 200 cc. of benzene was refluxed with 9.5 g. of lead tetraacetate for seventy-five hours. Excess tetraacetate was destroyed with glycerol; the benzene solution was washed with bicarbonate, clarified with charcoal, dried and evaporated, and the residue crystallized from benzene–ligroin (70–90°). The first crop to separate (0.3 g., m. p. 262–267°) was identified as 9,10-diacetoxyanthracene (mixed m. p. 265–270°). The mother liquor when concentrated and diluted with petroleum ether gave 2.3 g. of yellowish crystals, m. p. 75–85°. The new substance V was isolated from this product by two further crystallizations from benzene–ligroin as colorless granules that melted at 134.8–135.1° when the bath was heated very slowly. The substance depressed the melting point of 9-acetoxyanthracene.

*Anal.*¹⁶ Calcd. for $C_{20}H_{18}O_6$: C, 67.79; H, 5.12. Found: C, 68.35, 67.99; H, 5.36, 5.38.

The remaining mother liquor yielded 2.15 g. of additional material, m. p. 70–85°, and this on repeated fractionation gave further crops of V as well as considerable oxanthrone acetate (mixed m. p.).

The triacetoxydihydroanthracene V dissolves readily in cold alcohol, acetic acid or benzene, or in hot ligroin, to give blue-violet fluorescent solutions. In concentrated sulfuric acid the substance dissolves with a blood red color that turns brown on standing.

A solution of 0.24 g. of 9,9,10-triacetoxy-9,10-dihydroanthracene in 10 cc. of acetic acid was warmed at 85° for one-half hour and then diluted with water and cooled; 0.17 g. of crystalline material separated, m. p. 107–108°. Crystallization from ligroin gave 0.12 g. (70%) of colorless cottony crystals of oxanthrone acetate, m. p. 106–109°, mixed m. p. 107.5–109°, and 0.2 g. (10%) of 9,10-diacetoxyanthracene, m. p. 235–260° (recrystallized from benzene, 272–274°, no depression in mixed m. p.).

Oxidation of 9,10-Diacetoxyanthracene

When 3.02 g. of the reagent was stirred at 60–100° with a solution of 2 g. of the diacetate in 200 cc. of acetic acid until the oxidizing agent was completely consumed and the mixture was then cooled and eventually concentrated, a total of 1.5 g. of crystalline product was obtained, m. p. 230–240°. This was separated by fractionation from acetone and acetic acid into anthraquinone, m. p. and mixed m. p. 281–282°, and unchanged starting material, m. p. and mixed m. p. 268–270°.

Oxidation of Oxanthrone Acetate

A solution of 0.16 g. of material (m. p. 107.5–108.5°) in 13.7 cc. of 0.14 *N* lead tetraacetate in acetic acid was

(11) Ferkin, *Chem. News*, **34**, 145 (1876).

(12) Compare the preparation of 9,10-dibenzoxy-9,10-dihydroanthracene, Prévost, *Compt. rend.*, **196**, 1129 (1933); **197**, 1661 (1933); **200**, 406 (1935).

(13) On conducting the reductive acetylation of anthraquinone (10 g.) according to Liebermann, *Ber.*, **21**, 1172 (1888), we obtained 5.5 g. of recrystallized product, m. p. 272–274° (copper block) and isolated 0.5 g. of anthracene, m. p. 212–215°, and a few milligrams of 9-acetoxyanthracene, m. p. 134–135°.

(14) Barnett and Cook, *J. Chem. Soc.*, **125**, 1084 (1924).

(15) Prepared according to Barnett and Matthews, *J. Chem. Soc.*, **123**, 380, 2631 (1923); the yield of colorless, fluorescent needles, m. p. 135.5–136.5° (from ligroin), was 68.5%.

(16) Microanalyses by Eleanor Werble.

heated on the steam-bath for twenty-four hours. The solution on cooling deposited 0.03 g. of anthraquinone, m. p. 275–280°, and 0.06 g. more was obtained by dilution. Crystallization of the combined crops gave 0.08 g. of anthraquinone, m. p. and mixed m. p. 278–280°.

Oxidation of 9-Acetoxy-2-methylanthracene (X)

Preparation.—A solution of 10 g. of 2-*p*-xylylbenzoic acid¹⁷ in 80 cc. of acetic acid and 50 cc. of acetic anhydride was refluxed with 0.5 g. of anhydrous zinc chloride for two hours; water was then added cautiously to the point of saturation. On cooling 7.5 g. (68.5%) of X, m. p. 137.5–139°, separated, and processing of the mother liquor gave 1.2 g. (11%), m. p. 135–137°. Further crystallization from alcohol (yellow plates) and from benzene-ligroin (nearly colorless aggregates) raised the melting point to 140–141.3°. The compound has been described by Barnett and Goodway.¹⁸

Oxidation.—Lead tetraacetate (17.5 g.) was added in portions over a period of fifteen hours to a stirred solution of 9-acetoxy-2-methylanthracene (9.8 g.) in acetic acid (500 cc.) at 70–80°. The course of the oxidation was followed by tests with starch-iodide paper. The solution was concentrated *in vacuo* and the product recovered by ether extraction and crystallized from 70–90° ligroin. A total of 5.1 g. (49%) of crude 10-acetoxy-2-methylanthrone-9, m. p. 105–110°, was isolated, and four recrystallizations from ligroin gave 2.4 g. of colorless, cottony needles, m. p. 113–114°; a mixture with the synthetic product described below melted at 113–114°. The substance is very soluble in cold alcohol or acetone, readily soluble in ether, and moderately soluble in hot ligroin.

Anal. Calcd. for C₁₇H₁₄O₃: C, 76.67; H, 5.30. Found: C, 76.41, 76.91; H, 5.33, 5.44.

The mother liquor of the oxidation mixture yielded small amounts of β-methylanthraquinone, m. p. 171.5–172.5°

(17) Prepared in yields varying from 54 to 83% by reduction of the keto acid with zinc and ammonia, m. p. 132–134°; compare Fieser and Heymann, *THIS JOURNAL*, **64**, 376 (1942).

(18) Barnett and Goodway, *J. Chem. Soc.*, 1754 (1929).

(mixed m. p.) and of a substance melting of 209–211.4° that is probably dimethyldianthrone.¹⁹

Synthesis of 10-Acetoxy-2-methylanthrone-9 (XIII).—2 Methylanthrone-9¹⁸ (5 g., m. p. 100.5–102°) was brominated at 0° in carbon bisulfide according to Barnett, Low and Morrison²⁰ and gave 6.2 g. (91%) of 10-bromo-2-methylanthrone-9, m. p. 123–124°, dec. A solution of 1 g. of this substance in 100 cc. of acetic acid was treated with 0.6 g. of silver acetate and the suspension stirred for one hour at room temperature. The solution was filtered from silver bromide and diluted, when a white precipitate separated consisting of 0.8 g. (85%) of XIII, m. p. 109–112°. Two crystallizations from ligroin gave colorless needles, m. p. 113.4–114°.

Summary

It has been found that the first step in the oxidation of anthracene with lead tetraacetate consists in the addition of acetoxy groups to the two *meso* positions to give a mixture of the *cis* and *trans* isomers. Both substances lose acetic acid readily and yield 9-acetoxyanthracene, and this substance on further oxidation again adds two acetoxy groups to give an intermediate that easily loses acetic anhydride to yield oxanthrone acetate. The formation of this oxidation product, observed by K. H. Meyer in 1911, is thus fully accounted for. The addition mechanism is further substantiated by the results of the oxidation of a derivative in which the two *meso* positions are distinguishable by virtue of the presence of a marking methyl group at the 2-position.

(19) Limpricht, *Ann.*, **314**, 243 (1901).

(20) Barnett, Low and Morrison, *Ber.*, **64**, 1568 (1931).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rate of Oxidation of Aromatic Hydrocarbons by Lead Tetraacetate¹

BY LOUIS F. FIESER AND STEARNS T. PUTNAM²

Qualitative observations have shown that the most potently active carcinogenic hydrocarbons are remarkably susceptible to oxidation by lead tetraacetate and that in some of the series investigated there is a rough correlation between carcinogenic activity and this form of chemical reactivity.^{3,4} We have now made a quantitative study of the reaction. While the work was in progress, Eckhardt⁵ reported the results of a study of the rates of oxidation of some of the same hydrocarbons by perbenzoic acid. Our results on the one reaction thus supplement those of Eckhardt on the other, and where the same compounds were studied the results are in general agreement.

(1) This paper is based upon results presented by Stearns T. Putnam in a Dissertation of May 1, 1942.

(2) Present address: Hercules Powder Company, Experiment Station, Wilmington, Delaware.

(3) Fieser and Hershberg, *THIS JOURNAL*, **60**, 1893, 2542 (1938).

(4) Badger and Cook, *J. Chem. Soc.*, 802 (1939).

(5) Eckhardt, *Ber.*, **73**, 13 (1940).

The oxidation experiments were made in dilute solution (approximately 0.0015 molar) at 25 ± 0.1° with a large excess of reagent (approximately nine moles per mole of hydrocarbon). The rate of consumption of the reagent was determined by essentially the method used by Criegee⁶ and by Hockett and McClenahan⁷; aliquots were withdrawn, decomposed with potassium iodide-sodium acetate buffer, and the liberated iodine titrated with 0.05 *N* thiosulfate solution. The results were expressed in terms of the ratio of moles of lead tetraacetate consumed to moles of hydrocarbon originally present, and in five parallel experiments with anthracene in .99% acetic acid (up to fifty hours) the lowest precision in the determination of this ratio was ± 0.05 and the average ± 0.03.

Criegee and Büchner⁸ recently found that the rate of cleavage of glycols by lead tetraacetate in

(6) Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **495**, 211 (1932).

(7) Hockett and McClenahan, *THIS JOURNAL*, **61**, 1667 (1939).

(8) Criegee and Büchner, *Ber.*, **73**, 563 (1940).