purged twice with 600 p.s.i.g. of hydrogen and pressurized with hydrogen to the desired pressure. The autoclave was then heated slowly to a temperature where hydrogen uptake occurred (as evidenced by a pressure drop due to the greater solubility of the displaced ethane or other hydrocarbon over that of hydrogen in the solvent used). This temperature was maintained until no further hydrogen uptake was evident. After the autoclave had been cooled to room temperature and a vent gas sample taken, the autoclave was disassembled and the contents of the bomb were transferred to appropriate glassware in the dry box. The reaction mixture was then carefully quenched with isopropyl alcohol-benzene, water, and aqueous hydrochloric acid or aqueous sodium hydroxide in succession in a gas evolution apparatus equipped for measuring the volume of gas evolved and for the withdrawal of a sample for mass spectral analysis.

Acknowledgment. The authors wish to thank S. Henderson, J. Mitchen, and J. B. Chidester for their assistance in the analytical work.

BATON ROUGE, LA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WHITMORE LABORATORY, THE PENNSYLVANIA STATE UNIVERSITY]

Osmium and Ruthenium Tetroxide–Catalyzed Oxidations of Pyrene[1]

FREDERICK G. OBERENDER AND JOSEPH A. DIXON

Received February 19, 1959

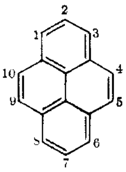
The oxidation of pyrene (I) has been studied as a possible route to precursors of 4,5-dialkylphenanthrenes. The oxidant systems were osmium tetroxide–hydrogen peroxide, osmium tetroxide–sodium periodate, and ruthenium dioxide–sodium periodate. The osmium tetroxide–periodate system produced oxidation exclusively at the 4,5-bond of pyrene, the bond of lowest bond localization energy, to yield pyrene-4,5-quinone (IV) and the lactol of 4-formylphenanthrene-5-carboxylic acid (III). In contrast the ruthenium dioxide–periodate system oxidized pyrene at the atoms of greatest electron density as well as at the 4,5-bond. Although the yields of the desired 4,5-quinone and lactol from the osmium tetroxide–catalyzed oxidation were only 23 and 24%, respectively, this appears to be equal or superior to any other available reaction sequence for the synthesis of 4,5-dialkylphenanthrenes.

Introduction. In recent years interest has developed in the oxidation of pyrene (I) at the 4,5-bond, the bond of lowest bond localization energy,[2] as a route to sterically hindered 4,5-dialkylphenanthrenes. Ozone and osmium tetroxide are the only known reagents which oxidize the 4,5-bond of pyrene.[3-6] Oxidizing agents which do not proceed through cyclic intermediates with double bonds attack the 1,3,6, or 8 positions of pyrene, the atoms of greatest electron density.[7]

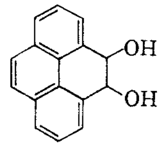
Oxidative procedures involving ozone and osmium tetroxide are somewhat hazardous when applied to large amounts of material. The success of osmium tetroxide–catalyzed oxidation of olefinic bonds with hydrogen peroxide[8-10] and periodate[11] suggested that such systems might be suitable for the oxidation of complex aromatic molecules. Therefore we have studied the oxidation of pyrene in aqueous acetone with (a) osmium tetroxide plus sodium meta-periodate, (b) osmium tetroxide plus hydrogen peroxide, and (c) ruthenium dioxide plus sodium meta-periodate in an attempt to obtain selective oxidation at the 4,5-bond of this molecule.

Ruthenium dioxide, a readily available, nontoxic reagent, was studied to see if it would act as a "double-bond attacking" reagent. Periodate readily oxidizes ruthenium from its lower valence state to ruthenium tetroxide which, it was postulated, would then follow the same mechanistic path as osmium tetroxide.

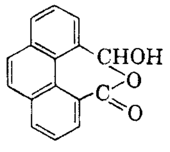
Since aqueous acetone solutions of pyrene and periodate or pyrene and peroxide were shown to be stable, the initial step in the oxidation is believed to be the formation of the osmate ester of the hydrocarbon. Water is necessary to effect hydrolysis of the ester to 4,5-dihydroxy-4,5-dihydropyrene (II) so that the catalyst may be regenerated by the oxidant. Sodium meta-periodate was also expected to cleave this α-glycol.



I



II



III

Results and Discussion. The osmium tetroxide–catalyzed periodate oxidation of pyrene resulted

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[1] This investigation was performed as part of American Petroleum Institute Research Project 42, "The Synthesis and Properties of High Molecular Weight Hydrocarbons," given in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April 1959.

(2) P. S. Bailey, *Chem. and Ind. (London)*, 1148 (1957).

(3) H. Vollmann, et al., *Ann.*, **531**, 1 (1937).

(4) M. S. Newman and H. W. Whitehouse, *J. Am. Chem. Soc.*, **71**, 3664 (1949).

(5) G. M. Badger, et al., *J. Chem. Soc.*, 2326 (1950).

(6) *J. Cook and R. Schoental, J. Chem. Soc.*, 170 (1948).

(7) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

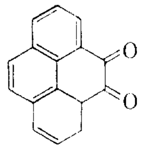
(8) N. Milas and S. Sussman, *J. Am. Chem. Soc.*, **58**, 1302 (1936).

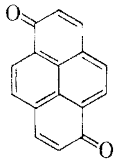
(9) M. Mugdan and D. Young, *J. Chem. Soc.*, 2988 (1949).

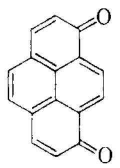
(10) J. Cook and R. Schoental, *J. Chem. Soc.*, 47 (1950).

(11) R. Pappo, et al., *J. Org. Chem.*, **21**, 478 (1956).

in the formation of two major products, both arising from attack at the 4,5-bond. These products were the lactol of 4-formylphenanthrene-5-carboxylic acid (III) (13%) and pyrene-4,5-quinone (IV) (10%) when pyrene and periodate were used in a 1:2 molar ratio. In addition to 52% of the starting pyrene there was obtained 9% of material that could not be identified but from infrared spectra appeared to be mixtures of the major products and unreacted pyrene. No evidence was found of oxidation occurring at the atoms of greatest electron density.


IV


V


VI

An identical experiment in which the molar ratio of pyrene to periodate was changed to 1:5 resulted in oxidation of 76% of the pyrene. Again, the two major products were pyrene-4,5-quinone (23%) and the lactol of 4-formylphenanthrene-5-carboxylic acid (24%). Thus, increasing the amount of periodate in the reaction mixture increases the amount of pyrene oxidized and proportionately increases the yields of the two major products. Since both the quinone and the lactol would lead to the formation of 4,5-dialkylphenanthrenes,[4,5,12] this probably represents the best available method for synthesis of the sterically-hindered 4,5-dialkylphenanthrenes.[4,5,13]

From the osmium tetroxide–catalyzed hydrogen peroxide oxidation of pyrene only pyrene-4,5-quinone (7%) could be identified. Although the reaction was allowed to proceed until the peroxide was consumed, 116 hours, 69% of the starting pyrene was recovered. In addition 13% of the product was a complex mixture. As in the osmium tetroxide–catalyzed periodate oxidation no evidence was obtained of oxidation at the atoms of greatest electron density. These observations differ from those of Cook and Schoental[10] who found no evidence of pyrene-4,5-quinone in a similar oxidation study, but reported that pyrene-1,6-quinone (V) and pyrene-3,6-quinone (VI) were formed.

The ruthenium dioxide–catalyzed oxidation of pyrene is nonspecific; oxidation occurs at positions other than the 4 and 5 positions. The identified products consist of pyrene-4,5-quinone (11%), pyrene-1,6-quinone (2%), the lactol of 4-formylphenanthrene-5-carboxylic acid (1%), and recovered pyrene (22%). Another major product isolated (10%) has been identified as an aldehyde but a structural formula could not be established. The final material (10%) eluted from the chromatographic column was a complex mixture. The lactol of 4-formylphenanthrene-5-carboxylic acid has been isolated from this material and the remainder is believed to be largely the unidentified aldehyde.

EXPERIMENTAL[14]

Osmium tetroxide–catalyzed periodate oxidation of pyrene. A solution of 22.5 g. of sodium meta-periodate and 10.0 g. of pyrene in 700 ml. of acetone and 200 ml. of water was treated with 1.0 g. of osmium tetroxide at room temperature. The stirred reaction mixture immediately became orange-brown. The consumption of periodate was followed iodimetrically by titration of 2-ml. aliquots of the reaction mixture.[15] In the presence of osmium tetroxide, this method yielded artificially high values for the concentration of periodate but the concentration did decrease to zero over a period of time:

Reaction Time, Hr.	Periodate Remaining, %
0	94
4	315
24	226
93	71
114	53
257	0

After 11 days the deep red solution was filtered and the filtrate evaporated to dryness under reduced pressure at temperatures below 40°. The brown, solid residue was extracted with anhydrous benzene, and the extracts were charged to a chromatographic column containing 600 g. of silicic acid. Elution of the material on the column with solutions of benzene and ether yielded 28 fractions totaling 8.8 g. of material. Infrared spectra of the materials eluted from the column indicated the products might be segregated into 7 groups (in the order in which they were eluted from the column).

Group	Elution Solvent	Proposed Structure	Wt., G.	% Yield
1	Benzene	Pyrene	5.24	52
2	Benzene	Impure mixture	.20	2
3	Benzene	Pyrene-4,5-quinone	1.14	10
4	Benzene	Impure mixture	.17	2
5	Benzene	Impure mixture	.07	1
6	2–15% Ether in benzene	Lactol of 4-formylphenanthrene-5-carboxylic acid	1.64	13
7	Ether	Impure mixture	.32	3

Group 1 was shown to be recovered pyrene by infrared spectra and a mixed m.p. with an authentic sample.

Group 2 was an impure mixture suspected to be largely pyrene. Its infrared spectrum showed the typical absorption pattern of pyrene with several additional peaks, *e.g.* carbonyl absorption at 1735 cm.$^{-1}$

Group 3, pyrene-4,5-quinone (IV), was obtained in high purity upon crystallization from the benzene eluent. Recrystallization from benzene or chlorobenzene yielded long brilliant-red needles, m.p. 304.5–306.4° (sealed tube) (lit.

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(12) F. Bischoff and H. Adkins, *J. Am. Chem. Soc.*, **45**, 1030 (1923).

(13) E. Bergmann and Z. Pelchowicz, *J. Am. Chem. Soc.*, **75**, 2663 (1953); G. Wittig and H. Zimmermann, *Ber.*, **86**, 629 (1953).

(14) All infrared spectra were taken as a 2% dispersion in KBr pellets. All carbon, hydrogen, and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tenn., unless otherwise stated. All melting points are corrected.

(15) E. L. Jackson, *Org. Reactions*, **II**, 361 (1944).

m.p. 310°[3]) whose solution in concentrated sulfuric acid was deep blue. The infrared spectrum is characterized by major absorption peaks at 3030, 1674, 1618, 1524, 1435, 1426, 1353, 1270, 1176, 1065, 1033, 889, 837, and 707 cm.$^{-1}$ The carbonyl absorption at 1670 cm.$^{-1}$ is within the range for ortho quinones[16] and is displaced from the carbonyl absorptions of pyrene-1,6-quinone (V) or pyrene-3,6-quinone (VI).[17] Further proof for the structure of pyrene-4,5-quinone was the formation of an azine with *o*-phenylenediamine as described later.

Anal. Calcd. for $C_{16}H_8O_2$: C, 82.75; H, 3.47. Found: C, 82.57; H, 3.38.

Groups 4 and 5 are impure mixtures whose infrared spectra are unlike any other spectra obtained from oxidation products of pyrene. They were not identified.

Group 6, the lactol of 4-formylphenanthrene-5-carboxylic acid (III), was recrystallized from absolute ethanol to yield colorless needles, m.p. 264.6–265.8° (dec.) (lit. m.p. 276°[3]). The compound was successfully converted to the known 4-formyl-5-carbomethoxyphenanthrene by its reaction with diazomethane, m.p. 113–114° (lit. m.p. 111–112°[6]). The infrared spectrum showed hydroxyl absorption at 3200 cm.$^{-1}$ and carbonyl absorption at 1686 cm.$^{-1}$ Other major absorption peaks of the infrared spectrum were observed at 1424, 1443, 1298, 1276, 1243, 1183, 1136, 1102, 1021, 970, 838, 804, and 743 cm.$^{-1}$

Anal. Calcd. for $C_{16}H_{10}O_3$: C, 76.79; H, 4.03. Found: C, 76.69; H, 4.10.

Osmium tetroxide-catalyzed peroxide oxidation of pyrene. A solution of 6.23 g. of 30% hydrogen peroxide and 10.0 g. of pyrene in 394 ml. of acetone was treated with 1.0 g. of osmium tetroxide at room temperature. The stirred reaction mixture, which was kept in the dark, became red as the reaction proceeded. The consumption of peroxide was followed iodometrically by titration of 2-ml. aliquots of the reaction mixture.[18] Again artificially high concentrations of peroxide were obtained.

After 5 days the dark reaction mixture was saturated with hydrogen sulfide. The colloidal osmium sulfide could not be removed from the reaction mixture by filtration so the mixture was evaporated to dryness under reduced pressure at temperatures below 50°. Benzene extracts of the residue were charged to a chromatographic column containing 600 g. of silicic acid. Elution of the material on the column with solutions of benzene and ether yielded 21 fractions totaling 9.0 g. Infrared spectra of the materials eluted from the column indicated that only one major product was formed during this oxidation. This product was shown to be pyrene-4,5-quinone (7%) by mixed m.p. and comparison of the infrared spectrum with an authentic sample. In addition, 69% unreacted pyrene was recovered. On the basis of the variations observed in the infrared spectra obtained of the other fractions comprising the 1.3 g. of unidentified material, no individual compound is believed to represent more than a 2% yield. Carbonyl absorption was not noted in the region of 1636 or 1640 cm.$^{-1}$ in any fraction thereby indicating the absence of pyrene-1,6-quinone and pyrene-3,6-quinone.[17]

Ruthenium dioxide-catalyzed periodate oxidation of pyrene. A solution of 10.0 g. of pyrene in 350 ml. of acetone and 50 ml. of water was treated with 1.02 g. of ruthenium dioxide and 21.4 g. of sodium meta-periodate. The reaction mixture was stirred at room temperature. During the first 2 hr. the suspended black ruthenium dioxide dissolved and the color of the solution became brown. After 4 days an additional 21.4 g. of sodium meta-periodate was added and stirring was continued for 16 days.

The aqueous acetone solution was filtered from the insoluble salts, followed by concomitant addition of benzene and distillation of the acetone. The benzene solution was separated, dried over anhydrous sodium sulfate, and charged to a chromatographic column containing 600 g. of silicic acid. Elution with solutions of benzene and ether yielded 27 fractions totaling 7.7 g. of material. Infrared spectra of the materials eluted from the column indicated the products might be segregated into eight groups:

Group	Elution Solvent	Proposed Structure	Wt., G.	% Yield
1	Benzene	Pyrene	2.2	22
2	Benzene	Pyrene-4,5-quinone	1.3	11
3	Benzene	Pyrene-1,6-quinone	0.2	2
4	Benzene	Impure mixture	0.2	2
5	Benzene	Impure mixture	0.1	1
6	10–20% Ether in benzene	Unknown aldehyde	1.0	10
7	10–20% Ether in benzene	Lactol of 4-formylphenanthrene-5-carboxylic acid	0.1	1
8	50% Ether in benzene	Impure mixture	1.0	10

Groups 1 and 2 were identified as pyrene and pyrene-4,5-quinone, respectively, on the basis of mixed melting points and comparison of the infrared spectra with the spectra of authentic samples.

Group 3 had an infrared spectrum characterized by main absorption peaks at 3030, 1634, 1600, 1508, 1354, 1283, and 838 cm.$^{-1}$ The carbonyl absorption at 1634 cm.$^{-1}$ is in agreement with that observed by Fuson and Josien for pyrene-1,6-quinone. Additional evidence for this structure was obtained by the identity of its properties with those reported by Vollmann for pyrene-1,6-quinone.[3] The samples were orange solids of m.p. 300° (dec.) (lit. m.p. 309°[3]) which formed red solutions in warm alcoholic sodium hydroxide and orange solutions in concentrated sulfuric acid.

Group 4 and 5 are mixtures whose infrared spectra were unlike any other spectra obtained from oxidation products of pyrene. They were not identified.

Recrystallization of Group 6 from 95% ethanol and benzene yielded colorless plates, m.p. 184.4–184.9°. The infrared spectrum was characterized by major absorption peaks at 3040, 2920, 1714, 1418, 1365, 1264, 1178, 1147, 1123, 1100, 841, and 748 cm.$^{-1}$ Qualitative tests showed this compound to be a neutral molecule containing no olefinic linkages. It gave a positive 2,4-dinitrophenylhydrazine test and a positive Tollen's test, indicating the presence of an aldehyde group.

Anal. C, 70.01; H, 4.68.[19]

Group 7 was shown to be the lactol of 4-formylphenanthrene-5-carboxylic acid by its infrared spectrum and a mixed melting point.

Group 8 was a mixture of compounds believed to consist largely of the unknown aldehyde of Group 6 plus some of the lactol of 4-formylphenanthrene-5-carboxylic acid. The lactol was isolated from this group by treatment of the mixture with chloroform. Evidence for an aromatic aldehyde in the mixture was obtained from a positive 2,4-dinitrophenylhydrazine test, a positive Tollen's test, and a negative Benedict's test. Attempts to isolate the aldehyde have failed.

Pyrene-4',5',2,3-quinoxaline (VII). A mixture of 17 mg. of pyrene-4,5-quinone, 8 mg. of *o*-phenylenediamine (purified before use by sublimation), and 2.5 ml. of glacial acetic acid was heated on the steam bath for 1 hr. The yellow reaction mixture was cooled, diluted with water, and filtered with suction. There was obtained 19 mg. (86%) of crude yellow

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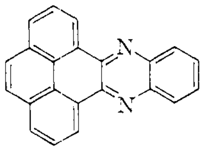
(16) L. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 129.

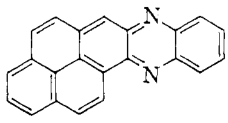
(17) M. L. Josien and N. Fuson, *Bull. soc. chim. France*, 19, 389 (1952).

(18) D. Swern, *Org. Reactions*, VII, 392 (1953).

(19) Analysis performed by James Rigas, 470 Eastern Parkway, Brooklyn 25, N.Y.

pyrene-4',5',2,3-quinoxaline, m.p. *ca.* 272°. Recrystallization from chlorobenzene yielded golden yellow needles, m.p. 276.8–277.4° (lit. m.p. 262°[3]). Further evidence that this compound was the azine of pyrene-4,5-quinone rather than the azine of the unknown pyrene-1,2-quinone (VIII) was furnished by the infrared spectrum. Three major absorption bands were observed in the region of out-of-plane CH deformation vibrations at 832, 765, and 717 cm.$^{-1}$ These may be assigned to 2,3, and 4 adjacent free H atoms, respectively. Since no absorption was observed in the 900–860 cm.$^{-1}$ region for one adjacent free H atom, structure VIII is excluded. Other major absorption peaks of the infrared spectrum were observed at 3040, 1484, 1433, 1426, 1362, 1337, 1294, 1175, and 1097 cm.$^{-1}$


VII


VIII

Anal. Calcd. for $C_{22}H_{12}N_2$: N, 9.21. Found: N, 8.99.

4-Formyl-5-carbomethoxyphenanthrene. The aldehydo-ester, m.p. 113–114° (lit. m.p. 111–112°[5]) was prepared by the method of Badger and coworkers[5] in 45% yield from the lactol of 4-formylphenanthrene-5-carboxylic acid isolated from the preceding periodate oxidations of pyrene. The infrared spectrum confirmed the structure of the free aldehydo-ester by the presence of two strong carbonyl peaks at 1720 and 1683 cm.$^{-1}$ Other major absorption peaks in the infrared spectrum were observed at 3040, 2950, 2830, 2740, 1437, 1286, 1266, 1241, 1198, 1137, 1034, 842, 817, 806, 763, and 719 cm.$^{-1}$

Acknowledgment: The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

UNIVERSITY PARK, PA.

[CONTRIBUTION NO. 890 FROM THE CHEMISTRY LABORATORIES OF INDIANA UNIVERSITY]

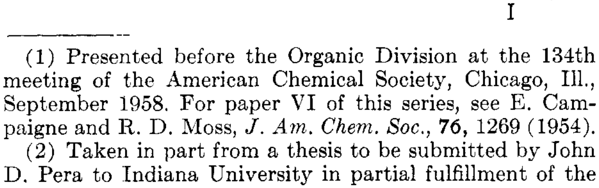
Thiocarbonyls. VII. Studies on *p*-Substituted Acetophenones[1]

E. CAMPAIGNE, WM. BRADLEY REID, JR., AND JOHN D. PERA[2]

Received February 23, 1959

Several *p*-substituted acetophenones have been subjected to conditions under which acetophenone is known to give trithioacetophenone. *p*-Fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-methylacetophenone all formed trimeric thiones. Trimers could not be obtained from *p*-ethyl- or *p*-phenylacetophenone. Compounds of unknown structure related to "anhydrotriacetophenone disulfide" were obtained from *p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-phenylacetophenone. *p*-Methyl- and *p*-ethylacetophenone on treatment with hydrogen sulfide produced oils which on distillation were converted to the corresponding 2,4-diarylthiophenes, a reaction characteristic of "anhydrotriacetophenone disulfide."

Although the reaction of acetophenone with hydrogen sulfide and hydrogen chloride was described more than sixty years ago by Baumann and Fromm,[3] no work has appeared in the literature describing the reactions of substituted acetophenones. The work herein described is concerned with the reaction of some *p*-substituted acetophenones with hydrogen sulfide utilizing hydrogen chloride as catalyst. Baumann and Fromm[3] allowed acetophenone to react with dry hydrogen sulfide and dry hydrogen chloride at 0° in alcoholic solution and obtained two compounds. Initially the reaction formed a blue violet solution of monomeric thioacetophenone which rapidly faded to yield white crystalline trimer (I). Although theoretically there should be geometrical isomers of trithioacetophenone,[4] only one isomer has been reported and no evidence was found for the existence of a second isomer in this work. When the mother liquor from the acetophenone reaction was allowed to stand at room temperature, Baumann and Fromm[3] were able to isolate a white crystalline compound of formula $C_{21}H_{22}S_2$ which differed from the formula for trithioacetophenone by the elements of hydrogen sulfide. They proposed the structure II or III and called the compound "anhydrotriacetophenone disulfide."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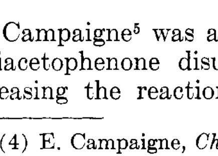
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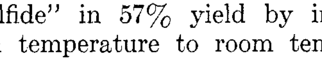
III

Campaigne[5] was able to prepare the "anhydrotriacetophenone disulfide" in 57% yield by increasing the reaction temperature to room tem-

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(1) Presented before the Organic Division at the 134th meeting of the American Chemical Society, Chicago, Ill., September 1958. For paper VI of this series, see E. Campaigne and R. D. Moss, *J. Am. Chem. Soc.*, **76**, 1269 (1954).

(2) Taken in part from a thesis to be submitted by John D. Pera to Indiana University in partial fulfillment of the degree, Doctor of Philosophy, and in part from the thesis of Wm. Bradley Reid, Jr., submitted to Indiana University in partial fulfillment of the degree, Doctor of Philosophy, June 1946.

(3) E. Baumann and E. Fromm, *Ber.*, **28**, 895 (1895).

(4) E. Campaigne, *Chem. Revs.*, **39**, 31 (1946).

(5) E. Campaigne, *J. Am. Chem. Soc.*, **66**, 684 (1944).