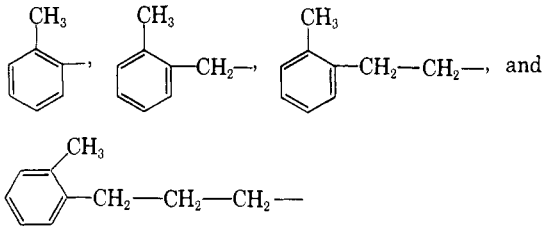
and 6.71, 13.4 and 13.8 μ, which were assigned to ester, aromatic ring, "*o*-substituted" benzene, and tetramethylene, respectively.

The mass spectrum showed bands at 91, 105, 119, 133; the band at 105 was the most intense. These bands correspond, respectively, to the fragments shown in col. 2.

The parent peak was at 306.

The gas chromatogram and the spectra of synthetic ethyl 11-(*o*-tolyl)undecanoate were shown to be identical with the gas chromatogram and spectra of aromatized α 1.38.



Ozonolysis of Polycyclic Aromatics. XI.[1a] 3-Methylcholanthrene[2]

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Ozonization of the potent carcinogen 3-methylcholanthrene (**1**) (++++) in methylene chloride and 3:1 methylene chloride–methanol produced a mixture of unstable peroxides (**2**). Hydrogen peroxide oxidation of **2** led to a carboxylic acid mixture from which was isolated prehnitic acid (**6**) and 9-methylbenz[*a*]anthracene-7,12-dion-8-acetic acid (**3**). Decarboxylation of the carboxylic acid mixture led to 8,9-dimethylbenz[*a*]anthracene-7,12-dione (**7**), *via* **3**, and 1,2-dimethylanthraquinone (**8**) and biphenyl (**9**), from which is inferred the additional presence of 2-methyl-5,6-dicarboxyanthraquinon-1-acetic acid (**4**) and 2,2′,3,4,5-pentacarboxybiphenyl (**5**) in the original carboxylic acid mixture. Thus, to ozone, **1** reacts significantly as a 7,8,9-trisubstituted benz[*a*]anthracene derivative with predominant ozone attack occurring at the L-region. The conversion of **7** to 5,6-dimethylanthraquinone-1,2-dicarboxylic acid (**10**), and **8** to phthalic acid, with ozone, suggest the ozonolysis product sequence **3** → **4** → **6**.

Our continuing interest in the possible association between high carcinogenic potency of certain polycyclic aromatic hydrocarbons and their reactivity with ozone at specific sites relevant to the carcinogenic process, has led, among other hydrocarbons, to the ozonization of such lesser carcinogens as dibenz[*a*,*j*]- (+)[1b] and dibenz[*a*,*h*]anthracenes (++),[1c] and to the more strongly carcinogenic benzo[*a*]pyrene (++++),[1d] and 7,12-dimethylbenz[*a*]anthracene (++++).[1a]

The exact nature of this causative relationship, if any, is unclear. Thus, in dibenz[*a*,*h*]anthracene ozonolysis occurred predominantly at the K-region,[1c] experimentally demonstrated to be a primary site of both biological oxidation,[3a,4] and of involvement in the carcinogenic process.[3c,d] Further, in the series benz[*a*]anthracene (0), dibenz[*a*,*j*]- (+), and dibenz[*a*,*h*]anthracene (++), we have noted a decrease in reactivity at the L-region toward ozone as an electrophilic reagent which is accompanied by an increase in reactivity at the K-region toward ozone as a double bond reagent. This order, which corresponded to a progressive increase in carcinogenic activity and which would have been predicted from the Pullmans' K-region theory of carcinogenesis,[6] suggested that the potent carcinogen benzo[*a*]pyrene should react strongly with ozone at the K-region.

We have found, however, that benzo[*a*]pyrene is ozonized[1d] only at the L-region and at positions *adjacent* to the K-region, *i.e.*, the M-region,[7] which are also the sites of metabolic oxidation.[8] Thus in dibenz[*a*,*h*]anthracene and benzo[*a*]pyrene, the metabolic paralleling reactions which lead to products of ozone addition can also be considered as likely steps in the detoxification of these compounds,[9] with perhaps stronger evidence for loss of carcinogenicity.[11]

In their study of protein binding as a necessary, but not sufficient, prerequisite for hydrocarbon carcinogenesis, Heidelberger and Moldenhauer[3c] have experimentally demonstrated that benzo[*a*]pyrene, 7,12-dimethylbenz[*a*]anthracene, and 3-methylcholanthrene were bound to skin protein to a large and approximately equal extent. In this paper, we conclude our study of the trio by reporting on the ozonization of the potent carcinogen (++++), 3-methylcholanthrene (**1**).

Results

Ozonization of **1**, as in all our previous work, was conducted in methylene chloride, and 3:1 methylene chloride–methanol solvents at −78° with ozone–

(1) (a) Paper X, E. J. Moriconi and L. B. Taranko, *J. Org. Chem.*, **28**, 1831 (1963); (b) E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *ibid.*, **27**, 3618 (1962); (c) E. J. Moriconi, W. F. O'Connor, W. J. Schmitt, G. W. Cogswell, and B. P. Fürer, *J. Am. Chem. Soc.*, **82**, 3441 (1960); (d) E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *ibid.*, **83**, 4618 (1961); (e) E. J. Moriconi, W. F. O'Connor, and F. T. Wallenberger, *ibid.*, **81**, 6466 (1959).

(2) This research was supported by a grant C-3325(C5) from the U. S. Public Health Service, National Cancer Institute.

(3) (a) C. Heidelberger, H. I. Hadler, and G. Wolf, *J. Am. Chem. Soc.*, **75**, 1303 (1953); (b) J. A. LaBudde and C. Heidelberger, *ibid.*, **80**, 1225 (1958); (c) P. M. Bhargava, H. I. Hadler, and C. Heidelberger, *ibid.*, **77**, 2877 (1955); (d) P. M. Bhargava and C. Heidelberger, *ibid.*, **78**, 3671 (1956); (e) C. Heidelberger and M. G. Moldenhauer, *Cancer Res.*, **16**, 442 (1956); (f) C. Heidelberger, M. E. Baumann, L. Griesbach, A. Ghobar, and T. M. Vaughn, *ibid.*, **22**, 78 (1962).

(4) In addition to 5,6-dibenz[*a*,*h*]anthracenedione (K-region oxidation product), six other metabolites of dibenz[*a*,*h*]anthracene are known: 7,14-dibenz[*a*,*h*]-anthracenedione,[3a] 2-hydroxy-,[3b] 2,9-dihydroxy-,[3b] and 4,11-dihydroxydibenz[*a*,*h*]anthracenes,[5] 4,11-dihydroxybenz[*a*]anthracene-7,14-dione,[3a] and 5-hydroxy-1,2-naphthalenedicarboxylic acid.[3a]

(5) J. Cason and L. F. Fieser, *J. Am. Chem. Soc.*, **62**, 2681 (1940).

(6) (a) A. Pullman and B. Pullman, "Cancérization par les Substances Chimiques et Structure Moléculaire," Masson et Cie, Paris, 1955; (b) A. Pullman and B. Pullman, *Advan. Cancer Res.*, **3**, 117 (1955).

(7) It should be noted that metabolic perhydroxylation does *not* always occur at the M-region, the Pullmans notwithstanding.[6b] *Cf.* ref. 36.

(8) A. H. Conney, E. C. Miller, and J. A. Miller, *J. Biol. Chem.* **228**, 753 (1957).

(9) Of all the known metabolites of polycyclic aromatic carcinogens, only two, dibenz[*a*,*h*]anthracene-7,14-dione and 2-phenylphenanthrene-3,2′-dicarboxylic acid,[3c,10] have ever been screened. Carcinogenic testing by subcutaneous injection and direct application of these metabolites to the skin of mice was negative.[3f]

(10) This dicarboxylic acid is also an oxidation product of our ozonolysis studies.[1c]

(11) Suggested by a referee of paper VIII.[1d]

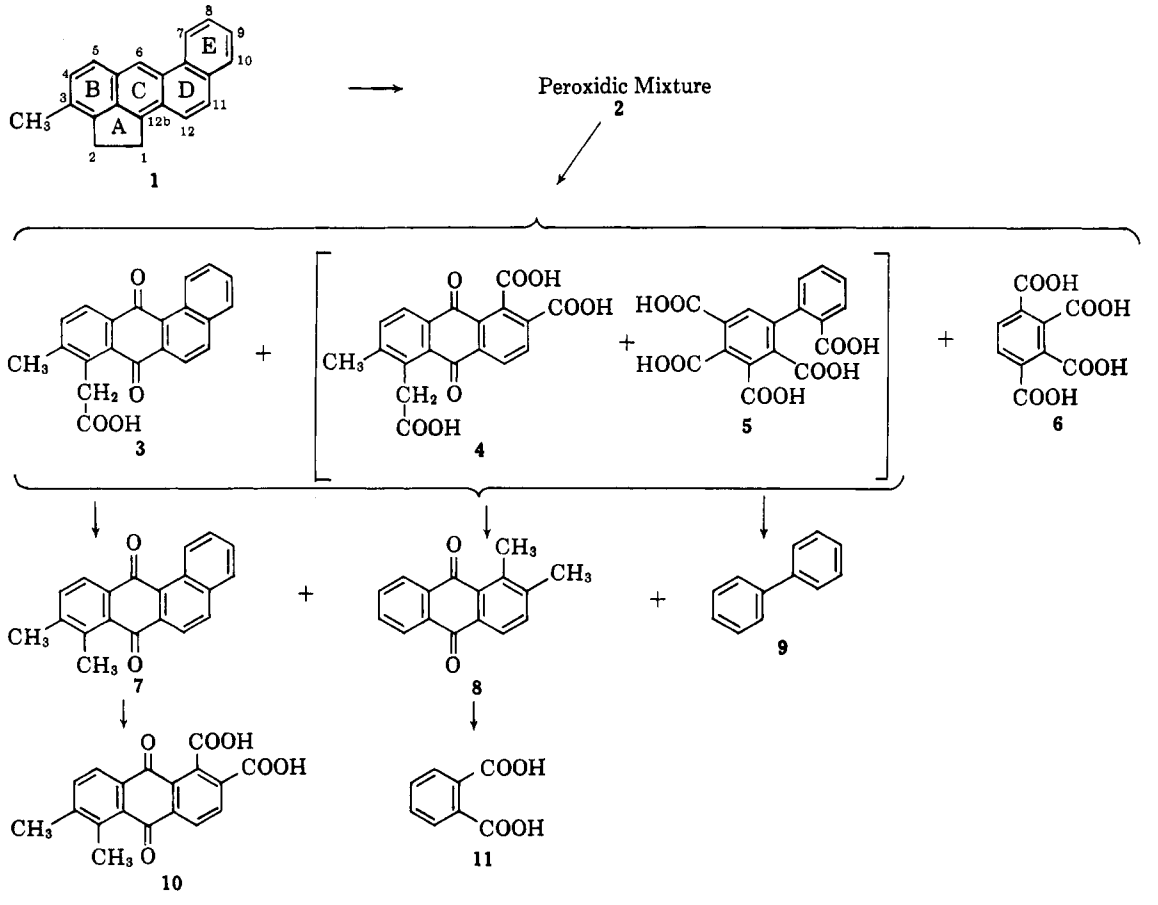


TABLE I

OZONIZATION PRODUCTS AND AVERAGE % YIELDS

Mole ratio ozone: 1	6[a]	7[b]	8[b]	9[b]	Total yield of 6–9
1.5 ± 0.1	..	15	18	4	37
2.5 ± 0.2	9	9	22	7	47
3.5 ± 0.5	15	3	11	5	34

[a] Isolated from the hydrogen peroxide oxidized ozonolysis solution prior to decarboxylation. [b] After decarboxylation of acid mixture.

oxygen and ozone–nitrogen streams. The three series of experiments which were carried out—reaction of **1** with 1.5, 2.5, and 3.5 molar ozone equivalents, respectively—all led to a mixture of unstable peroxides (**2**). Reduction of **2** invariably led to a difficultly separable mixture of oily resins, as did any oxidative procedure under alkaline conditions. Ultimately, oxidation of **2** with 10% hydrogen peroxide led to a mixture of carboxylic acids from which were isolated 9-methylbenz[*a*]anthracene-7,12-dion-8-acetic acid (**3**), and prehnitic acid (**6**). However, decarboxylation of this carboxylic acid mixture with copper–quinoline led to a liquid–solid, chromatographically separable mixture of 8,9-dimethylbenz[*a*]anthracene-7,12-dione (**7**), *via* 3,1,2-dimethylanthraquinone (**8**), and biphenyl (**9**). The isolation of **8** and **9** suggests the presence, in the original carboxylic acid mixture, of 2-methyl-5,6-dicarboxyanthraquinon-1-acetic acid (**4**) and probably 2,2′,3,4,5-pentacarboxybiphenyl (**5**). Yields are summarized in Table I.

V.p.c.[12] of the decarboxylated mixture confirmed the presence of the three major components **7**, **8**, and **9**. Authentic samples of **7**, **8**, and **9** showed sharp and distinct peaks in the chromatogram but only when a single component was injected. Mixtures caused considerable tailing, rendering quantitative application of this technique difficult. However, adding authentic samples of each to the decarboxylated mixture prior to its injection into the v.p.c. column led to an increase in the respective peak areas in proportion to the amounts added.

No appreciable solvent effect was observed in methylene chloride, and 3:1 methylene chloride–methanol, nor was there any observable effect on products or yields with changes in carrier gas.

All attempts to ozonolyze **3** to **4** were unsuccessful, most probably due to the insolubility of **3** in conventional ozonolysis solvents. Support for our view that **4** is the result of just such a transformation comes from the conversion of the more soluble **7**, with two molar ozone equivalents followed by oxidative degradation, to 5,6-dimethylanthraquinone-1,2-dicarboxylic acid (**10**) in 53% yield.[13] Finally, the exhaustive ozonolysis of **8** to produce **11** in 75% yield[14] is suggestive that **6** is a further ozonolysis product of **4**.

(12) F and M Scientific Corp. Model 500 equipped with a 2-ft. silicone gum rubber column; initial column temp., 50°; temperature programmed 6.4° per min.; helium flow rate, 40 ml. per min.

(13) The difference in inductive effects between the $-CH_3$ group in **7** and the $-CH_2-$ group in **3**, if any, could not account for the difference in response of **7** and **8** to ozone.

(14) Based on **8** consumed since some 70% of unreacted **8** was recovered. See Experimental.

(15) Melting points were determined on a Kofler micro melting point apparatus and are corrected. Boiling points are uncorrected.

Experimental[15]

Ozonization of 3-Methylcholanthrene (1).—Ozone (3.5 vol. % or ozone–nitrogen) was dispersed into a solution of 1[16] (2.0 g., 7.5 mmoles) in 250 ml. of methylene chloride, or 3:1 methylene chloride–methanol at −78°. Absorption of ozone was quantitative up to 1.5 molar equivalents whereupon ozone began to trickle through in increasing amounts into the potassium iodide trap. Successive color changes of the reaction mixture were yellow, red, light yellow, and finally green. For 2.5 ± 0.2 and 3.5 ± 0.5 molar ozone equivalent absorption, 4–5 and 7–8 molar equivalents, respectively, of ozone were bubbled through the absorption flask. After the passage of about 2 molar ozone equivalents, a voluminous precipitate began to separate. The solution/suspension (2) was then flushed with dry nitrogen to free it from dissolved ozone. For the 2.5 and 3.5 molar ozone equivalent absorption experiments, the precipitate was deposited onto a glass frit by filtration, and washed with petroleum ether (b.p. 30–60°). Although colorless while still wet, it darkened rapidly on drying, gave an active oxygen test with sodium iodide–acetic acid, melted over a 95–115° range with dec., and exploded violently when brought into the vicinity of an open flame. The infrared spectrum (Nujol) of both the wet and the dry material showed smeared-out carbonyl bands. Innumerable unsuccessful attempts were made to separate and identify the components of 2 by crystallization, dissolution and reprecipitation, and liquid–solid and vapor–solid chromatography. Further, treatment of 2 with such reducing agents as potassium iodide–acetic acid, zinc–hydrochloric acid, and trialkyl phosphite esters led to complex and inseparable oils in our hands. Oxidative decomposition of 2 with oxidants under alkaline conditions (hydrogen peroxide–sodium hydroxide, silver oxide–sodium hydroxide) gave intractable, oily resins. Ultimately, refluxing 2 with a large excess of 10% hydrogen peroxide led to products which could be separated, purified, and identified. Compound 1 was inert to 10% hydrogen peroxide.

Oxidation of Peroxide Mixture 2 with Hydrogen Peroxide.—A solution/suspension of 2 in methylene chloride (or 3:1 methylene chloride–methanol) was stirred and refluxed with 50 ml. of 10% aqueous hydrogen peroxide for 24 hr. Solvents were removed by distillation *in vacuo* to leave a brown oily solid which was dissolved in 100 ml. of 5% aqueous sodium bicarbonate solution, filtered from traces of insoluble material, and extracted successively with ether, methylene chloride, and ethyl acetate. The dark-colored alkaline solution was boiled for several minutes to remove small amounts of dissolved organic solvents, cooled to room temperature, and acidified with 20% hydrochloric acid to precipitate a solid. Filtration left a residue which was washed with water to leave a dark brown powder A; the filtrate and washings were combined to yield solution B.

Solution B was extracted continuously with ether (Soxhlet) for three days. Solvent evaporation gave an acidic product which on recrystallization from aqueous nitric acid yielded prehnitic acid (6) (0.17 g., 9%), m.p. 235–237° (lit.[17a] m.p. 236–238°); a mixture melting point with authentic 6 showed no depression and the infrared spectra were superimposable.

Trituration of acidic residue A with ice-cold acetone produced a yellow solid which was filtered and recrystallized from acetic acid/xylene to give 9-methylbenz[*a*]anthracene-7,12-dion-8-acetic acid (3), as tiny yellow needles, m.p. 291–293° dec. (lit.[18] m.p. 292–295° dec.), in 12% (0.29 g.) yield; a mixture melting point with authentic 3 prepared by chromic acid oxidation of 1,[18] showed no depression and the infrared spectra were superimposable.

The acetone-soluble material was evaporated to dryness to leave a dark brown acidic residue which was suspended with 0.5 g. of electrolytic copper in 25 ml. of freshly distilled quinoline. The mixture was refluxed with stirring for 3 hr., then cooled to room temperature, diluted with benzene and filtered. Solvent evaporation left a brown, oily solid which was dissolved in a minimum amount of benzene and deposited onto a 40 × 2 cm. Florisil-packed chromatographic column. Elution with carbon tetrachloride followed by solvent evaporation gave 0.06 g. (8%) of biphenyl (9), m.p. 71–72° (lit.[17b] m.p. 70°). Admixture of this material with authentic 9 gave no melting point depression, and the infrared spectra were identical.

Further column elution with benzene led, after solvent evaporation, to 1,2-dimethylanthraquinone (8), as bright yellow needles m.p. 150–152° (lit.[19] m.p. 151–152°); 8 was again certified by mixture melting point and superimposable infrared spectra with authentic 8 prepared in a four-step synthesis from tiglaldehyde using Rodgman's procedure.[19]

Acids 4 and 5, the precursors of 8 and 9, respectively, resisted all efforts to isolate them as such. Crystallization, distillation, and chromatography on packed columns of alumina, Florisil, and silicic acid proved fruitless, as did v.p.c. and separation *via* silver/barium salts and corresponding methyl esters.

When A was decarboxylated directly with copper quinoline, the yields of 8 and 9 increased, and the over-all yield of 7 from 1 was also enhanced slightly (*cf.* Table I).

Decarboxylation of 9-Methylbenz[*a*]anthracene-7,12-dion-8-acetic acid (3) to 8,9-Dimethylbenz[*a*]anthracene-7,12-dione (7).—A solution of 150 mg. of 3 in 20 ml. of freshly distilled quinoline, to which was added a small amount of copper–bronze, was refluxed for 3 hr. The resulting mixture was diluted with ether and filtered. The filtrate was shaken with aqueous sodium bicarbonate solution to ensure complete extraction of unchanged 3. The ether–quinoline layer was evaporated to dryness to leave a dark solid which was deposited on a Florisil-packed column. Elution with 2:1 benzene–ether gave 7 in 63% yield as hairlike, shiny yellow needles, m.p. 230–231° (lit.[20] m.p. 229–230°).

Ozonolysis of 7 to 5,6-Dimethylanthraquinone-1,2-dicarboxylic acid (10).—Quinone 7 (200 mg., 0.69 mmole) dissolved in 100 ml. of methylene chloride was treated with 2 molar ozone equivalents at −78°. The resulting ozonization product was oxidized in conventional fashion with 5 ml. of a solution of 30% hydrogen peroxide and 10% aqueous sodium hydroxide. The alkaline solution was repeatedly extracted with methylene chloride and ether. The remaining aqueous solution was acidified with hydrochloric acid to give 120 mg. (0.37 mmole, 53%) of 10 as yellow needles, m.p. 347–350° dec. (sintering at 220°); $\lambda_{C=O}^{KBr}$, 5.82 s and 5.96 s.

Anal. Calcd. for $C_{18}H_{12}O_6$: C, 66.67; H, 3.73. Found: C, 66.47; H, 3.88.

Ozonolysis of 1,2-Dimethylanthraquinone (8) to Phthalic Acid (11).—A solution of 1.0 g. (4.2 mmoles) of 8 in 250 ml. of methylene chloride was ozonized at −78° with considerable excess of ozone. The peroxidic solution was oxidized with alkaline hydrogen peroxide in the usual manner. Unchanged 8 (0.7 g.) was filtered from the reaction mixture; the filtrate was acidified with hydrochloric acid and extracted (Soxhlet) with ether continuously for 2 days. The ether extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness to yield 0.15 g. of 11 (75%),[14] m.p. and m.m.p. 200–203°.

Chromic Acid Oxidation of 1 to 3.—To a suspension of 3.0 g. of 1 in 10 ml. of acetic acid was added 15 g. of sodium dichromate. The whole was refluxed, with stirring, for 45 min., after which the mixture was cooled to room temperature, and the dark green solution was poured into 500 ml. of water containing a little sulfuric acid. The yellow gelatinous solid which precipitated was collected, extracted with warm, aqueous potassium bicarbonate solution, and filtered, and the filtrate was acidified with 20% hydrochloric acid. The crude 3 which precipitated was filtered, air dried and successively recrystallized from acetic acid and xylene to give 1.3 g. (35%) of 3 as tiny yellow needles, m.p. 293–295° dec. (lit.[18] m.p. 292–295° dec.). The acid 3, obtained by both the dichromate oxidation and ozonolysis of 1, was identical.

Discussion

It should be noted at the outset that even in the best of circumstances, less than 50% of 1 is accounted for in total product yields (Table I). However, the reported products 7, 8 and 9 are the end result of three successive chemical operations (ozonization, oxidation, and decarboxylation). Thus, based on some forty

(16) Eastman 4383; as with 7,12-dimethylbenz[*a*]anthracene,[1a] protective devices included disposable polyethylene plastic gloves (Handgards) and an MSA-Type H ultra filter respirator (during weighings). The fluorescence of 1 under ultraviolet light was useful in its surveillance.

(17) (a) E. H. Huntress and R. S. Mullikan "Identification of Pure Organic Compounds. Order I," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 121; (b) p. 504.

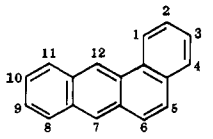
(18) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 2542 (1938).

(19) A. Rodgman, *J. Org. Chem.*, **24**, 1916 (1959).

(20) J. M. Cook and G. A. D. Hazlewood, *J. Chem. Soc.*, 428 (1934).

ozonolyses, etc., runs made on a fairly large quantity of this ++++ carcinogen, the results do indicate predominant modes of ozone attack and the following general observations seem pertinent.

(i) The response of **1** to ozone is consistent with its known chemical behavior. Thus **1** reacts predominantly as a 7,8,9-trisubstituted derivative of benz[*a*]anthracene (**12**),[21] attack occurring at the L-region (C-6, C-12b) of **1** to yield possibly such species as **2a/2b**.[22] The peroxide mixture (**2**) (*i.e.*, **2a/2b**) requires an additional hydrogen peroxide oxidation to **3** which is resistant



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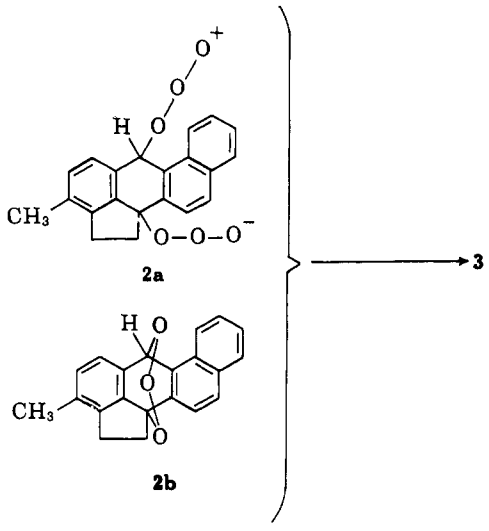
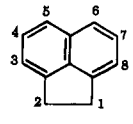
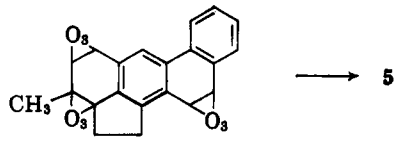


to further ozonization. However, **2a/2b** can be successively ozonized and hydrogen peroxide-oxidized to **4**, similar to the conversion of the peroxides of **12** and **7**, respectively, to 9,10-anthraquinone-1,2-dicarboxylic acid and **10**.



13

(ii) To a lesser extent, **1** reacts to ozone as a 3,7,8-trisubstituted derivative of acenaphthene (**13**).[23] Thus simultaneous ozone attack at the B-ring and the K-region (11,12-bond) in **1**, schematically depicted in **14**, would cleave A, B and D rings in **1** to yield ultimately **5**.[25]



14

Ozone attack on ring B is enhanced by electron-donating 3-CH_3 group. The conversion of **8** to **11** and presumably **4** to **6** with a large excess of ozone must also reflect the electron-releasing power of $-CH_3$ and $-CH_2-$ substituents on the flanking benzenoid rings of the normally resistant anthraquinone moiety.

Certainly to ozone, **1** does not represent a particularly privileged compound in which the L-region seems to be absolutely protected from attack.[6b]

Finally, in Table II we have summarized ozonization data of K- and L-region attack of the carcinogenic trio, benzo[*a*]pyrene, 7,12-dimethylbenz[*a*]anthracene, and **1**, as compared to the noncarcinogenic **12**.

TABLE II

	Actual yields of K- and L-region ozonization products[a]	
	L-Region quinonoid products	K-Region cleavage products
Benz[*a*]anthracene (**12**)	40[b]	0
Benzo[*a*]pyrene	27–30[c]	0
3-Methylcholanthrene (**1**)	32[d]	4[e]
7,12-Dimethylbenz[*a*]anthracene	29[f]	14[g]

[a] Using a 1:1 ozone–polycyclic molar ratio, unless otherwise stated, at −78° in methylene chloride or 3:1 methylene chloride–methanol. [b] Composed of 35% of benz[*a*]anthracene-7,12-dione and 5% of 1,2-anthraquinonedicarboxylic acid; some 38% of unchanged **12** was recovered. [c] Mixture of benzo[*a*]pyrene-3,6- and -1,6-diones; some 60–65% of unchanged benzo[*a*]pyrene was recovered. [d] 1.5 molar equivalents of ozone added; yield figure consists of 15% of **7** and 18% of **8**. Undoubtedly the yields of the primary ozonization products, **3** and **4**, were higher. [e] Compound **9**: undoubtedly, here too, yield of primary product **5** was higher. [f] Composed of 23% of benz[*a*]anthracene-7,12-dione and 6% of 1,2-anthraquinonedicarboxylic acid. [g] 1,4-Dimethyl-3-hydroxymethyl-2-phenylnaphthalene-2′-carboxylic acid.

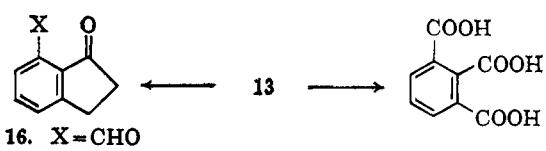
(21) Chemically, **1** reacts with sodium/lithium [W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936)], sodium-*n*-pentyl alcohol [L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 940 (1938)], maleic anhydride [R. N. Jones, C. F. Gogek, and R. W. Sharpe, *Can. J. Chem.*, **26B**, 719 (1948)] and photodimerizes [A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 1039 (1949)] to form 6,12b-dihydro derivatives; reaction of **1** with osmium tetroxide gave the 11,12-*cis*-diol. [G. M. Badger, *ibid.*, 456 (1949)]. Reduction of **1** over Adams catalyst led to a mixture of 6,12b- and 11,12-dihydro derivatives according to Fieser and Hershberg.

(22) Although a number of other possibilities are not excluded, it is quite possible that initial electrophilic attack occurs at C-12b since (a) it is activated by the adjacent especially reactive $-CH_2-$ group,[23] (b) it seems to be the less sterically hindered of the two *meso*-C-atoms as a consequence of ring E, and (c) initial electrophilic attack at C-6 would impose at some point a rather rigid, albeit planar, bridgehead carbonium ion at C-12b. The mechanism of conversion of **2a/2b** to quinone **3** is probably not unlike that observed in benzo[*a*]pyrene,[1d] 7,12-dimethylbenz[*a*]anthracene,[18] and 9,10-dibromoanthracene.[24]

(23) Lead tetraacetate [L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 2542 (1938)] and thiocyanogen [J. L. Wood and L. F. Fieser, *ibid.*, **63**, 2323 (1941)] convert **1** to 1-acetate and 1-thiocyanate, respectively.

(24) F. Dobinson and P. S. Bailey, *Tetrahedron Letters*, **13**, 14 (1960).

(25) As in the ozonolysis–oxidation of **13** to hemimellitic acid (**15**) in 24% yield[26] and, with milder work-up procedures, to 7-formyl- (**16**) and 7-carboxy-1-indanone (**17**).[27]



16. X = CHO
17. X = COOH

15

(26) P. G. Copeland, R. E. Dean, and D. McNeil, *Chem. Ind.* (London), 329 (1959).

(27) R. H. Callighan, M. F. Tarker, Jr., and M. H. Wilt, *J. Org. Chem.*, **27**, 765 (1962).