oil residue consisting of 670 ml (66%) of 3-amino-1,2,5-thiadiazole, λ_{max}^{MeOH} 295 mμ (ε 11,900). The infrared spectrum was identical with that recorded by Collins.[18b] The material was not further purified but was converted directly to N'-[1,2,5-thiadiazole-3-yl]sulfanilamide by standard procedures. The sulfa product, mp 197–200°, was identical with the material prepared above from 3-chloro-1,2,5-thiadiazole and sulfanilamide.

3-Chloro-4-phenyl-1,2,5-thiadiazole. A. From α-Amino-α-phenylacetonitrile Hydrochloride.—α-Amino-α-phenylacetonitrile hydrochloride (16.8 g, 0.1 mole) was added over a 0.5-hr period to a solution of 24.3 ml (0.3 mole) of sulfur monochloride in 45 ml of DMF. The mixture was stirred 16 hr at 25° and 200 ml of water was slowly added. The mixture was extracted with ether and the ether extracts were dried and evaporated to an oil residue which distilled at 109–111°, (1 mm). There was obtained 9.23 g (47%) of 3-chloro-4-phenyl-1,2,5-thiadiazole which was over 99% pure by glpc: λ_{max}^{MeOH} 287 and 232 mμ (ε 12,000 and 8900). An analytical sample was obtained through preparative glpc, mp 33°.

Anal. Calcd for $C_8H_5ClN_2S$: C, 48.86; H, 2.56; Cl, 18.03; N, 14.25; S, 16.31. Found: C, 48.89; H, 2.54; Cl, 18.16; N, 14.01; S, 16.17.

B. From Isonitrosophenylacetonitrile.—α-Isonitrosophenylacetonitrile (10.46 g, 0.073 mole) was added to a solution of 17.4 ml (0.217 mole) of sulfur monochloride in 35 ml of DMF. The mixture was warmed slowly to 50° whereupon the reaction became slightly exothermic. After 2.5 hr at 50° the mixture was cooled and added to 200 ml of ice water. The mixture was extracted with petroleum ether and the organic layer backwashed with water. After drying the petroleum ether, extracts were evaporated to a residue consisting of 1.95 g (15%) of 3-chloro-4-phenyl-1,2,5-thiadiazole. The infrared spectrum and glpc behavior of this material were identical with those of the material prepared by procedure A.

2,1,3-Benzothiadiazole.—To a solution of 16.2 ml (0.2 mole) of sulfur monochloride in 30 ml of DMF was added 5.4 g (0.05 mole) of *o*-phenylenediamine over a 10-min period under 10°. The mixture was warmed to 25° and stirred for 2 hr. The reaction was quenched by the addition of 50 ml of water and the mixture internally steam distilled until the vapor temperature reached 100°. The crystallized 2,1,3-benzothiadiazole was removed from the filtrate by filtration and washed with water. After air drying, the product weighed 5.5 g (81%), mp 42.5–43.5 (lit.[32] mp 44°).

Registry No.—Ia, 288-39-1; Ib, 5728-06-3; Ic, 13368-86-0; Id, 5970-14-9; IIa, 5728-07-4; IIb, 5728-08-5; IIc, 5933-67-5; IId, 5728-09-6; IIe, 5933-68-6; IIf, 5728-10-9; IIg, 5728-11-0; IIh, 5728-12-1; IIi, 5933-69-7; III, 6504-55-8; IVa, 5097-45-0; IVb, 5728-14-3; VI, 13350-98-6; VII, 5728-15-4; VIIIa, 5728-16-5; VIIIb, 5728-17-6; VIIIc, 5728-18-7; IX, 5728-20-1; X, 5728-21-2; XIII, 273-13-2; methyl cyanoformimidate, 13369-03-4; ethyl cyanoformimidate, 13369-04-5; isopropyl cyanoformimidate, 13369-05-6; N'-[1,2,5-thiadiazole-3-yl]sulfanilamide, 5097-43-8; N'-[3-ethoxy-1,2,5-thiadiazole-4-yl]sulfanilamide, 13369-07-8.

Acknowledgments.—Ultraviolet spectra were obtained by Mr. E. A. Macmullan and his staff, infrared spectra by Mr. R. Walker, and nuclear magnetic resonance spectra by Mr. B. Arison. The gas phase chromatographic work was carried out by Mr. W. Tait, Mrs. M. R. Dresner, and Mrs. W. Kreamer. The microanalyses were carried out by Mr. R. N. Boos and his staff.

[32] O. Hinsberg, *Chem. Ber.*, **22**, 2895 (1889).

Ozonolysis of Polycyclic Aromatics. XIV. Ozonation of Pentaphene and Benzo[*rst*]pentaphene[1-3]

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Received January 4, 1967

Ozonation of pentaphene (**1**) in methylene chloride at −78° with 1 mole equiv of ozone led to a peroxidic mixture which on reductive work-up (sodium iodide in acetic acid) gave 2,2'-binaphthyl-3,3'-dicarboxaldehyde (**5**, 25%); oxidative work-up (sodium hydroxide, hydrogen peroxide) led to **5** (16%), phthalic acid (**8**, 2%), and 2,2'-binaphthyl-3,3'-dicarboxylic acid (**9**, 16%). In both instances, 28% of unreacted **1** was recovered. Dialdehyde **5** was also obtained from **1** *via* osmium tetroxide oxidation to *cis*-6,7-dihydroxy-6,7-dihydropentaphene (**12**) followed by aqueous sodium periodate oxidation. Chromic acid oxidation of **5** gave **9** (14%), while the latter was independently prepared in 71% yield *via* cuprous oxide coupling of the diazonium salt of 2-aminonaphthalene-3-carboxylic acid (**11**). Dialdehyde **5** in base underwent an intramolecular Cannizzaro reaction to 2,2'-binaphthyl-3-hydroxymethyl-3'-carboxylic acid (**6**) which lactonized on treatment with strong acid or mild heat to the ε-lactone **7**. Ozonation of **1** with 4 mole equiv of ozone followed by oxidative work-up gave **8** (9%) and 2,2',4,4',5,5'-hexacarboxybiphenyl (**14**, 53%). The hexamethyl ester (**15**) obtained from **14** was independently synthesized by an Ullman coupling of 5-bromo-1,2,4-tricarbomethoxybenzene (**18**). Ozonation of benzo[*rst*]pentaphene (**2**) in methylene chloride at −78° with 3.5 mole equiv of ozone followed by oxidative work-up led to benzo[*rst*]pentaphene-5,8-dione (**3**, 14%), **8** (4%), *p*-terphenyl-2,2',3',2''-tetracarboxylic acid 2',3'-anhydride (**19**, 10%), and 2-(*o*-carboxyphenyl)-1,10-phenanthrenedicarboxylic acid anhydride (**20**, 3%), with a 56% recovery of unreacted **2**. A comparison of the reactivity to ozone of the noncarcinogenic **1** and related pentacyclic and hexacyclic hydrocarbons of increasing carcinogenicity indicate that there is no simple, consistent correlation between carcinogenicity, K- and L-region additivity toward ozone, and the Pullmans' electronic theory of carcinogenesis.

During the past decade, we have actively investigated the reaction between ozone and some 18 aromatic polycyclics, aza aromatics, and aza aromatic N-oxides. One of our continuing objectives has been the search for any substantive correlation between K- and L-region additivity[4a] of these polycyclic aromatics toward ozone and their relative carcinogenicity. Aside from its obvious significance in the carcinogenic process, the ob-

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[1] Paper I: W. J. Schmitt, E. J. Moriconi, and W. F. O'Connor, *J. Am. Chem. Soc.*, **77**, 5640 (1955). Paper XIII: E. J. Moriconi, L. Salce, and L. B. Taranko, *J. Org. Chem.*, **29**, 3297 (1964).

[2] This research was supported by Public Health Service Research Grant No. CA-7808-02 from the National Cancer Institute.

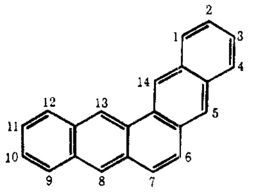
[3] Taken entirely from the Ph.D. thesis of L.S.

[4] (a) As defined by A. Pullman and B. Pullman, *Advan. Cancer Res.*, **3**, 117 (1955); (b) A. Pullman and B. Pullman, "Cancérization par les Substances Chimiques et Structure Moléculaire," Masson & Cie, Paris, 1955.

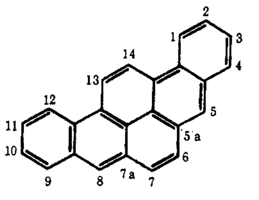
servation of any such consistent correlation would have relevence in its support of the electronic theory of carcinogenesis.[4]

Despite some initially encouraging results which suggested that polycyclic aromatics of increasing carcinogenic activity did react more strongly with ozone at the K region and to a correspondingly lesser degree at the L region, we began to observe a number of exceptions. Thus (i) three of the most potent (++++) carcinogens (benzo[*a*]pyrene,[5a] 7,12-dimethylbenz[*a*]anthracene,[5b] and 3-methylcholanthrene[5c]) reacted with ozone predominantly at the L and M regions (certainly, 3-methylcholanthrene was not a privileged compound[4a] in which the L region was protected from attack by ozone) and (ii) the lesser carcinogens (dibenz[*a*,*h*]anthracene[5d] (++), dibenz[*a*,*j*]anthracene[5e] (+), and benzo[*c*]phenanthrene[5f] (+)) reacted with ozone predominantly at the K region. This, too, was a reversal of what would have been predicted by the electronic theory of carcinogenesis.[4] Even the observation[5c,6] that the metabolic reactions likely to be related to the course of these ozone reactions are those of detoxification rather than of carcinogenic responsibility is not without exception.[7]

In this paper, we report on the ozonation of two symmetrical polycyclic aromatics at opposite ends of the carcinogenic spectrum, the inactive[8] pentaphene (**1**) and the highly carcinogenic[9–11] benzo[*rst*]pentaphene (**2**).[12] Chemical evidence clearly indicates the high reactivity of the two L regions (5,14, and 8,13 C atoms) in **1**.[13,14] Theoretical calculations[15] suggest, however, that among pentacyclic hydrocarbons, the 6,7 bond (K region) in **1** should be the most reactive to double-bond reagents, OsO_4[16] and O_3. Hexacyclic hydrocarbon **2** can be considered a derivative of **1** in which the two L regions have been suppressed by a fused ring.[17–19] Thus osmium tetroxide[20] and ozone should react predominantly at one (6,7 bond) of the two K regions in **2** and, since it is devoid of an L region, to a greater degree than the similar bond in **1**. The fortuitous availability of the key intermediate benzo[*rst*]pentaphene-5,8-dione (**3**)[21] permitted us almost direct access in good yield to **1** and **2** (Scheme I).[22]

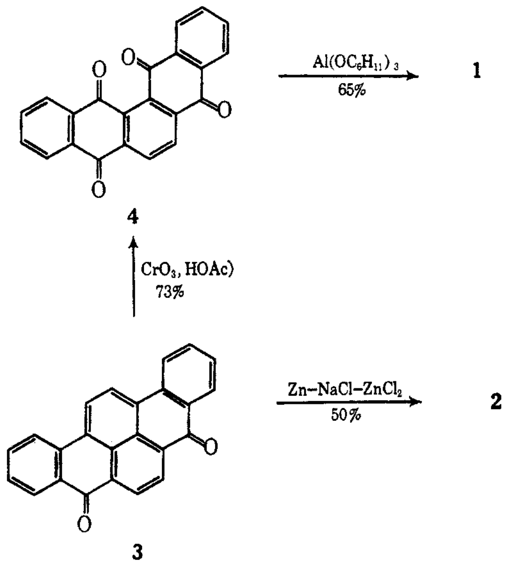


1



2

SCHEME I



Ozonation Results[23a]

When ozone was passed through a suspension of **1** in methylene chloride at −78°, the suspended hydrocarbon dissolved slowly. Ozone (1 mole equiv) was quantitatively absorbed. However, for 4 mole equiv absorption, passage of over 30 moles of ozone was required during which time there precipitated a white peroxidic product. In one instance, this material was filtered and exploded when touched with a spatula. Thereafter, ozonation was immediately followed by reductive (sodium iodide in acetic acid)[23b] or oxidative (1:1 10% sodium hydroxide–30% hydrogen peroxide)[23b] work-up. Results are summarized in Scheme II.

Reductive work-up of the 1 mole equiv ozonation led ultimately to 2,2′-binaphthyl-3,3′-dicarboxaldehyde (**5**, 25%) in addition to recovery of 28% of unreacted **1**. Oxidative work-up of the ozonation mixture led to **5**

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(5) (a) E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *J. Am. Chem. Soc.*, **83**, 4618 (1961); (b) E. J. Moriconi and L. B. Taranko, *J. Org. Chem.*, **28**, 1831, (1963); (c) *ibid.*, **28**, 2526 (1963); (d) E. J. Moriconi, W. F. O'Connor W. J. Schmitt, G. C. Cogswell, and B. P. Fürer, *J. Am. Chem. Soc.*, **82**, 3441, (1960); (e) E. J. Moriconi, B. Rakoczy, and W. F. O'Connor, *J. Org. Chem.*, **27**, 3618 (1962); (f) paper XIII.[1]

(6) N. H. Cromwell, *Am. Scientist*, **53**, 213 (1965).

(7) *Cf.*, *e.g.*, the seven metabolic oxidation products of dibenz[*a*,*h*]anthracene (summarized in footnote 4 of ref 5c) to the single ozonolysis product.[5d]

(8) J. W. Cook, I. Heiger, E. L. Kennaway, and W. J. Mayneord, *Proc. Roy. Soc.* (London), **B111**, 455 (1932).

(9) First predicted[4a] and then proven to be a ++++ carcinogen whose potency ranked it between 3-methylcholanthrene and benzo[*a*]pyrene.[10,11]

(10) A. Lacassagne, F. Zajdela, N. P. Buu-Hoi, and O. Chalvet, *Compt. Rend.*, **244**, 273 (1957).

(11) E. Ünseren and L. F. Fieser, *J. Org. Chem.*, **27**, 1386 (1962).

(12) In virtually all the published literature except *Chemical Abstracts*, this compound has been named either 3,4,9,10-dibenzpyrene or dibenzo[*a*,*i*]pyrene.

(13) Chromic acid oxidation of **1** led to the 5,8,13,14-pentaphenetetrone (**4**)[14a] while Diels–Alder addition occurred at these positions to yield the diadduct.[14b]

(14) (a) E. Clar and Fr. John, *Ber.*, **64**, 981 (1931); (b) E. Clar, *ibid.*, **64**, 2194 (1931).

(15) R. D. Brown, *J. Chem. Soc.*, 3249 (1950).

(16) It is remarkable that this 16-yr old prediction has never been tested.

(17) That the 5,8 positions in **2** are highly reactive has been theoretically predicted[18] and experimentally proven: formylation,[19] nitration,[19] halogenation,[19] and acetylation with $Pb(OAc)_4$[11] have led ultimately to 5,8-disubstitution products, while oxidation with chromic acid–selenium dioxide produced only **3**.[11]

(18) P. H. Gore, *J. Chem. Soc.*, 3166 (1954).

(19) N. P. Buu-Hoi and D. Lavit, *Rec. Trav. Chim.*, **75**, 1194 (1956).

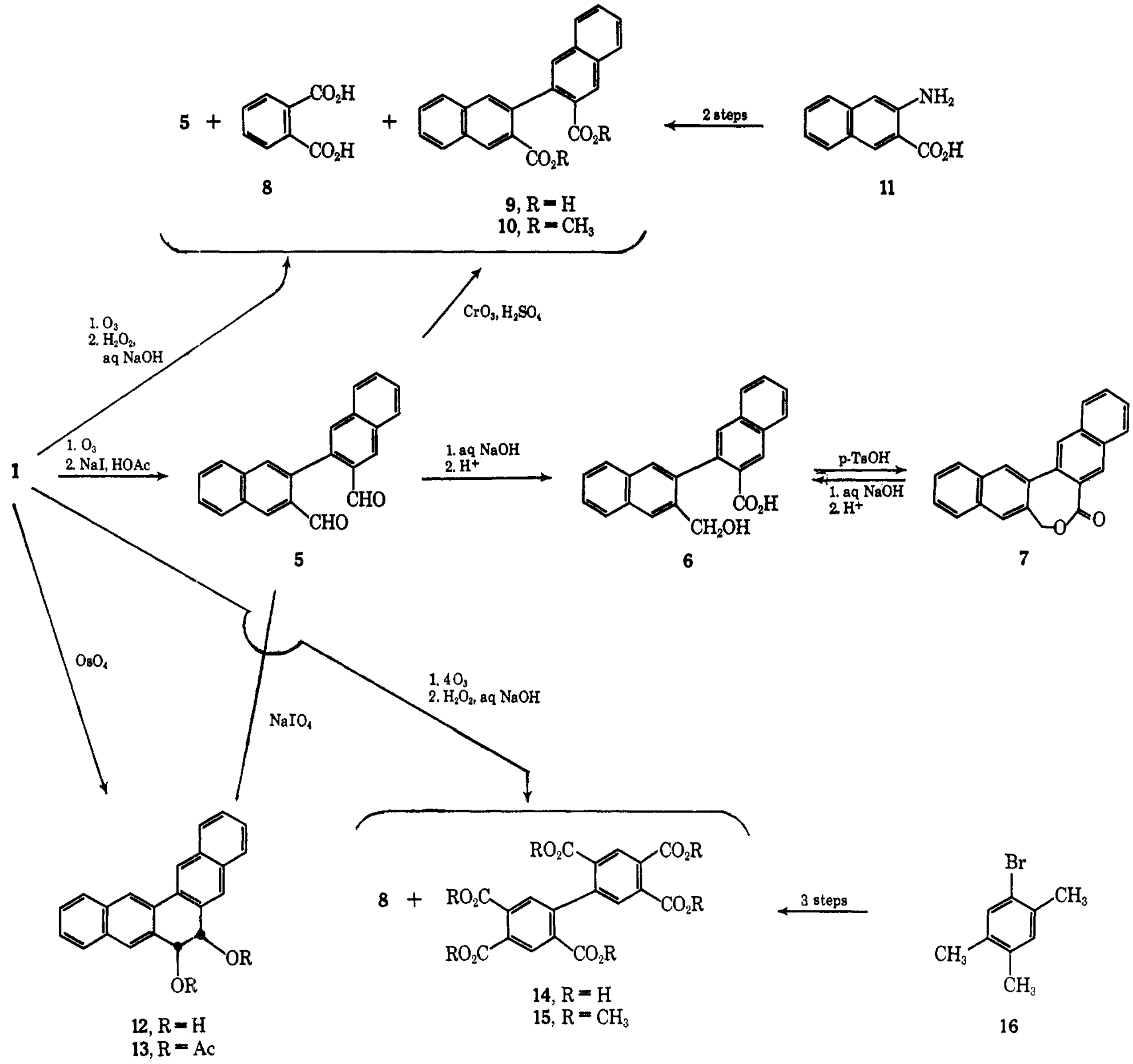
(20) Theoretically predicted (H. Chalvet and O. Chalvet, *Compt. Rend.*, 240, 1221 (1955)), but never tested.

(21) We are indebted to Mr. V. Ciolini of Otto B. May, Inc., Newark, N. J., for his graciousness in supplying our need and his entire stock of this diketone (trivially named isodibenzopyrenequinone).

(22) Recent literature preparation of these compounds include for **1** (a) R. G. R. Bacon and R. Bankhead, *J. Chem. Soc.*, 839 (1963), and (b) H. G. Franck and M. Zander, *Ber.*, **99**, 396 (1966); (c) for **2** most of the published syntheses involve reduction of **3**, and the reducing agents, for example, include aluminum tricyclohexoxide, B. D. Tilak, M. K. Unni, and K. Venkataraman, *Tetrahedron*, **3**, 62 (1958), and zinc–sodium chloride–zinc chloride.[19] We reduced **3** with the latter mixture using a modified procedure (see Experimental Section) originally introduced by E. Clar, *Ber.*, **B72**, 1645 (1939).

(23) (a) Ozone–oxygen and ozone–nitrogen streams gave the same yields (within experimental error) of products; (b) parent hydrocarbons **1** and **2** are indifferent to these reagents.

SCHEME II



(16%), phthalic acid (**8**, 2%), 2,2′-binaphthyl-3,3′-dicarboxylic acid (**9**, 16%), and recovery of **1** 28%. Experimentally, the oxidative work-up procedure occurs in a two-phase system (methylene chloride–water) and the isolation of **5** suggests incomplete oxidation in the organic phase. Dialdehyde **5** was also synthesized from **1** *via* oxidation with osmium tetroxide to the *cis*-diol (**12**) followed by aqueous sodium periodate oxidation. Chromic acid oxidation of **5** gave **9** (14%) while an independent synthesis of dicarboxylic acid **9** was achieved from 2-aminonaphthalene-3-carboxylic acid (**11**) *via* cuprous oxide coupling of its diazonium salt. Not unexpectedly, **5** was sensitive to alkali.[24] Treatment of **5** with 5% sodium hydroxide solution followed by careful acidification led to the intramolecular Cannizzaro product, 2,2′-binaphthyl-3-hydroxymethyl-3′-carboxylic acid (**6**). The facile lactonization of **6** to **7** was achieved by either the presence of strong acid or by mild heat. When **5** was deposited on an alumina column and eluted with methylene chloride, only ε-lactone **7** was isolated. Alkaline hydrolysis of **7** followed by careful acidification regenerated **6**.

Ozonation of **1** with 4 mole equiv of ozone followed by oxidative work-up led to **8** (9%) isolated as the anhydride and 2,2′,4,4′,5,5′-hexacarboxybiphenyl (**14**) in 53% yield. The nmr spectrum of **14** in deuterium oxide showed two equivalent resonances at δ 7.31 and 8.09.[25] Confirmation of structure **14** was achieved by its conversion with diazomethane to the hexamethyl ester **15**, which was identical with the product ultimately obtained in the following reaction sequence: 5-bromo-1,2,4-trimethylbenzene (**16**) → 5-bromo-1,2,4-tricarboxybenzene (**17**) → 5-bromo-1,2,4-tricarbomethoxybenzene (**18**) → 2,2′,4,4′,5,5′-hexacarbomethoxybiphenyl (**15**).

Benzo[*rst*]pentaphene (**2**) was also ozonized at −78° as a suspension in methylene chloride (Scheme III). The solubility of **2** was such (0.9 g/500 ml) at ambient temperature that a major portion of the hydrocarbon

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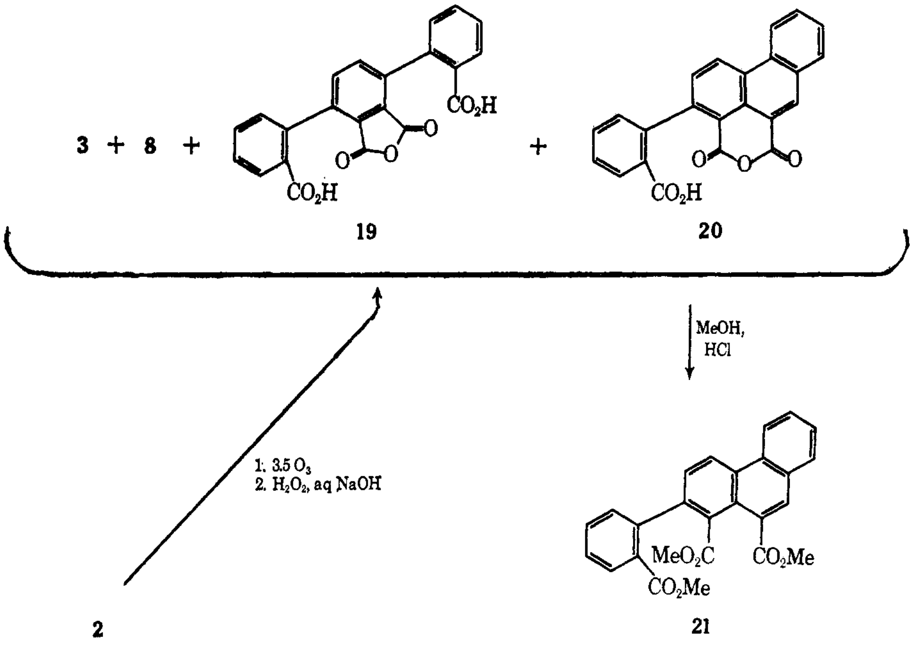
[24] *Cf.* the behavior of 1,4-dimethyl-2-phenylnaphthalene-3,2′-dicarboxaldehyde:[4b] H. I. Hadler, and A. C. Kryger, *J. Org. Chem.*, **25**, 1896 (1960).

[25] Splitting of the *p*-3,6 and 3′,6′ protons in **14** should be negligible since J_p = 0–1 cps: J. R. Dyer "Applications of Absorption Spectroscopy of Organic Compounds," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1965, p 99.

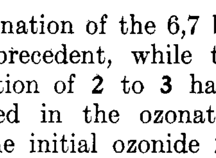
SCHEME III



precipitated at the low temperature of ozonation. Ozone uptake by the suspension of **2** was slower than that for **1** and the reaction was stopped after passage of 5–6 mole equiv of ozone. The average ozone absorption (35 runs) was 3.5 mole equiv of ozone. The reaction mixture was then oxidized directly with 1:1 sodium hydroxide–30% hydrogen peroxide solution. Column chromatography of the methylene chloride layer yielded 56% of unreacted **2** and 14% of diketone **3**. The aqueous extracts of 10–15 runs were combined to facilitate separation and identification of acidic products. Two of three carboxylic acids isolated, **8** (4%) as the anhydride, and *p*-terphenyl-2,2′,3′,2″-tetracarboxylic acid 2′,3′-anhydride (**19**, 10%), were identified by comparison with authentic samples. The third product crystallized from acetone in 3% yield as the acetonate of an anhydride whose proposed structure, 2-(*o*-carboxyphenyl)-1,10-phenanthrenedicarboxylic acid anhydride (**20**), is based on analytical and spectral evidence. The acetonate contained 1 equiv of bound solvent. Heating this acetonate for 15 min at 80° led to the evolution of acetone (identified as its 2,4-DNP) and left a residue of molecular composition $C_{23}H_{12}O_5$ (**20**). In the infrared region, **20** displayed a carboxyl–carbonyl absorption at 5.91 μ (1692 cm^{-1}) and a carbonyl doublet at 5.64 μ (1773 cm^{-1}) and 5.76 (1736) whose frequency separation ($\Delta\nu$ = 36 cm^{-1}) is typical of cyclic, six-membered anhydrides fused to aromatic systems.[26] Fisher esterification of **20** led to a tricarbomethoxy ester whose mass spectrum showed a parent peak at *m/e* 428, indicating a molecular formula of $C_{26}H_{20}O_6$ and whose ultraviolet [215 mμ (ϵ 36,200), 262 (55,000), 299[27] (17,900), and 310[27] (10,400)][28] and nmr spectra ($CDCl_3$) (three singlet methyl resonances at δ 3.51, 3.58, and 3.94 (nine protons) and a broad, aromatic resonance of eleven protons centered at δ 8.32) suggested the structure 2-(*o*-carbomethoxyphenyl)-1,10-dicarbomethoxyphenanthrene (**21**).

Electrophilic ozonation of the 6,7 bonds in **1** and **2** has considerable precedent, while the electrophilic–nucleophilic ozonation of **2** to **3** has also been previously encountered in the ozonation of benzo[*a*]pyrene (**23**).[5a] The initial ozonide **22** from **2** has a picene[29] framework, further ozonolysis of which at the symmetrical bonds, 5,5a and then 7a,8 would lead ultimately to **20** and **19**, respectively, *via* the known perhydroxyl anion decarboxylation[30] of probable intermediate keto acids (Scheme IV).

One final comparison is worthy of note. The ozonization of the structurally similar but unsymmetrical benzo[*a*]pyrene (**23**) led to a 27–30% yield of 3,6- and 1,6-diones but no K-region cleavage products.[5a] The fusion of a benzene ring to the 1,2 bond in **23** has thus enhanced the K-region reactivity of **2** to ozone (13% total of **19** and **20**) and lowered the reactivity of the L region (14% of **3**).



23

Summary and Conclusions

Table I summarizes the data now available from our laboratory on the ozonation of carcinogenic polycyclic aromatic hydrocarbons related to **1** and **2**. All the compounds have at least one K region (with similar electronic indices, 3.16–3.31 β).[4a] The yields of K-

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[26] Such anhydrides show carbonyl doublet absorptions at 5.66 μ (1770 cm^{-1}) and 5.76 μ (1736 cm^{-1}) and a corresponding $\Delta\nu$ = 34 cm^{-1}: L. P. Bellamy, "The Infrared Spectrum of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 128.

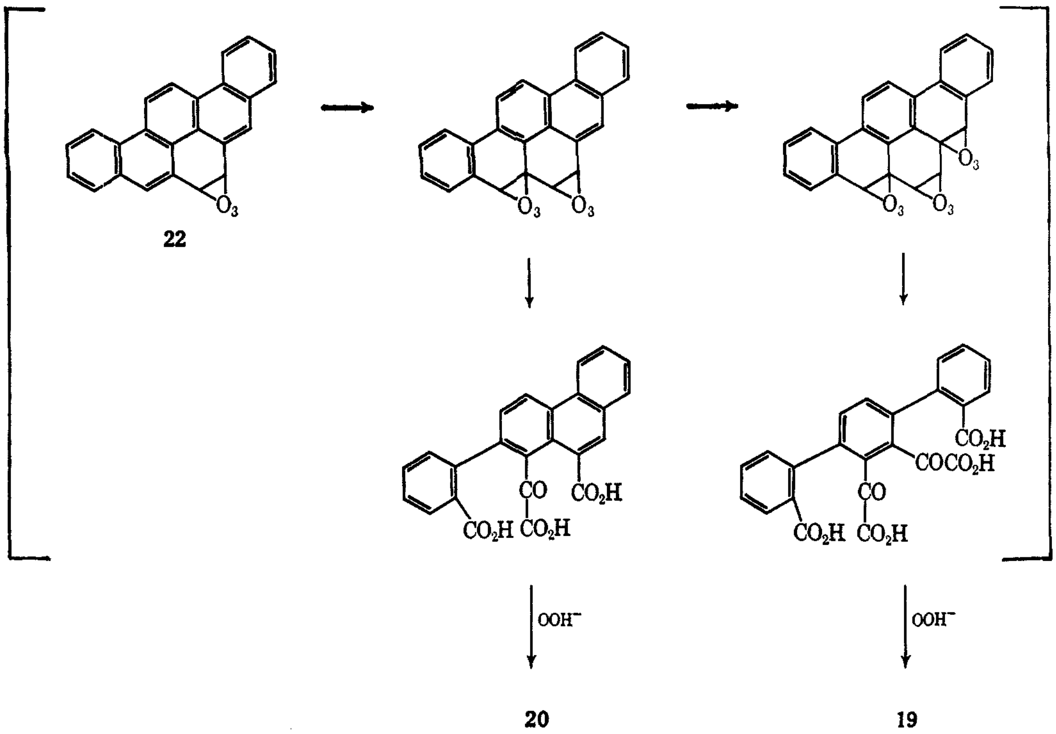
[27] Shoulder.

[28] *Cf.* the $\lambda_{max}^{95\%\ EtOH}$ of 2-phenylphenanthrene, 213 mμ (log ϵ 4.90), 267 (4.98), and 292[27] (4.60): R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., N. Y. 1951, Spectrum 382.

[29] Successive ozonolysis and oxidative work-up of which led to **19** in 33% yield: P. G. Copeland, R. E. Dean, and D. McNeil, *Chem. Ind.* (London), 98 (1960). We are grateful to Dr. Dean for a sample of **19**.

[30] C. A. Bunton, *Nature*, 163, 444 (1949).

Scheme IV



region cleavage products, under the same conditions of ozonation, vary from 0 to 45%. Even considering the experimental errors involved in ozonation and oxidative work-up procedures, there is simply no correlation between the Pullmans' theoretical K-region values[4] and the reactivity of these sites to electrophilic ozone. Further, although only three of the compounds listed in Table I have formal L regions, the remaining two (2 and 23) can be considered to have such sites whose activity has been suppressed by a fused ring. Despite the fact that reactions involving the L region are much more sensitive to steric effects than those at the K region,[31] the relative yields of quinonoid products listed in Table I, coupled with results from the ozonolysis of the ++++ carcinogens, 7,12-dimethylbenz[*a*]anthracene[5b] and 3-methylcholanthrene,[5c] clearly indicate the lack of correlation between L-region activity and the course of the ozone reaction. To sum up, a comparison of the observed relative reactivity of 1 and 2 to ozone with that predicted by Pullmans' theoretical calculations,[4a] and an analysis of all the available ozonation data lead us to the conclusion that there is no simple, consistent correlation between carcinogenicity, K- and L-region additivity toward ozone, and the Pullmans' electronic theory of carcinogenesis.

Experimental Section[32]

Pentaphene-5,8,13,14-tetrone (**4**).—A suspension of 25 g (0.075 mole) of benzo[*rst*]pentaphene-5,8-dione (**3**)[21] in 1 l. of glacial acetic acid was heated to reflux and 100 g (1.0 mole) of chromic acid was added in 20.0-g portions at 8-hr intervals. After refluxing for a total of 40 hr, the hot mixture was filtered and the solid thus obtained was washed successively with glacial acetic acid and 95% ethanol. A yield of 18.56 g (73.1%) of almost pure **4** was obtained, mp 333–335° (lit.[14a] mp 332°). This solid was used without further purification.

Pentaphene (**1**).—To 750 ml of cyclohexanol, previously dried and distilled over calcium oxide, were added 1 ml of dry carbon tetrachloride and 0.05 g of mercuric chloride. Aluminum turnings (7 g) were then added and the cyclohexanol was heated until vigorous evolution of hydrogen began. The heat source was removed and, after the reaction subsided, an additional 7 g of aluminum was added. This procedure was repeated until 37.5 g of aluminum had been added. After refluxing for 14 hr, this solution was cooled and 15 g (0.044 mole) of **4** was added. This mixture was then refluxed, with constant stirring, for an additional 24 hr after which the cyclohexanol was removed by distillation; on cooling the residue, a brown-green solid mass was obtained. This solid was treated with 1 l. of 5% sodium hydroxide and the resulting mixture was steam distilled to remove any remaining cyclohexanol. After cooling, 30.0 g of sodium hydrosulfite was added to dissolve unreacted quinone and the mixture was then filtered. The yellow-brown solid obtained was dried, placed in a Soxhlet, and extracted with benzene. Cooling the benzene extract led to 8.61 g of crude product. Recrystallization from benzene gave 7.96 g (65.1%) of **1**, mp 262–263° (lit.[22a,b] mp 257°).

Benzo[*rst*]pentaphene (**2**).—An intimate mixture of 27.0 g (0.081 mole) of **3**, 27.0 g of zinc dust, 27.0 g of sodium chloride, and 135.0 g of zinc chloride, moistened with 3 ml of water, was heated in a Wood's metal bath until the bath temperature reached 310–315°. This temperature was maintained for 5 min while the black melt was vigorously stirred. The metal bath was then removed and the reaction mixture was allowed to cool slowly to room temperature. A solution containing 150 ml of concentrated hydrochloric acid and 500 ml of water was added and the resulting mixture was stirred for 15 hr at room temperature. The insoluble solids were then filtered and dried. This material was extracted with benzene (Soxhlet) for 7 days. The material which precipitated from the cooled benzene extract was redissolved in a large volume of benzene. The red solution, after filtering to remove some insoluble solids, was distributed on two 4.7 × 50 cm alumina columns (Woelm, neutral, activity grade I). The columns were eluted with benzene until the yellow-green pentaphene color of the eluate was no longer visible. All of the colored fractions were combined and concentrated to a volume of about 300 ml. Crude **2** precipitated. Recrystallization of

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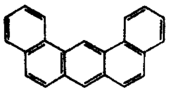
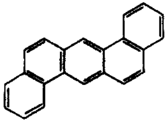
[31] *Cf.*, *e.g.*, the acetoxylation of benz[*a*]anthracene and dibenz[*a,h*]anthracene with lead tetraacetate under similar conditions: L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **60**, 1893 (1938).

[32] Melting points are corrected. The infrared spectra were recorded in potassium bromide disks on a Perkin-Elmer 337 grating spectrophotometer; ultraviolet spectra were recorded in 95% ethanol solution on a Cary 15 spectrophotometer; nmr spectra were obtained on a Varian Associates A-60 spectrometer in deuteriochloroform or deuterium oxide solutions using, appropriately, tetramethylsilane or 3-trimethylsilyl-1-propanesulfonic acid sodium salt as internal standards. The mass spectrum was taken on a Hitachi-Perkin-Elmer RMO-6D spectrometer. Microanalysis were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE I

Polycyclic aromatic	Pullman–Pullman electronic indices[a] K region	Pullman–Pullman electronic indices[a] L region	Actual yields of K- and L-region ozonization products,[b] % Total K-region cleavage products	Actual yields of K- and L-region ozonization products,[b] % L-region quinonoid products	Recovery unreacted polycyclic aromatic, %	Carcinogenic potency
Pentaphene (1)	3.23	5.56	32	0	28	0
	3.31	5.66	42	10	32.5	+
	3.30	5.69	45	0	0	++
Benzo[*a*]pyrene (**23**)	3.16	. . .	0	27–30[c]	60–65	++++
Benzo[*rst*]pentaphene (**2**)	3.16	. . .	13[d]	14[d]	56[d]	++++

[a] Expressed in terms of resonance integral (~20 kcal/mole); for the definition of these complex indices; see ref 4a. [b] Using a 1:ozone–polycyclic mole ratio at −78° in methylene chloride or 3:1 methylene chloride–methanol, followed by alkaline hydrogen peroxide work-up (unless otherwise stated). The ozonolysis of **1** and **2** also produced **8**, respectively, in 2 and 4% yields. These yields are not included in either K- or L-region product totals since the site of ozone attack to produce **8** is unknown. [c] No alkaline hydrogen peroxide work-up is required. [d] Owing to the low reactivity of **2**, 3.5 mole equiv of ozone was used (See Experimental Section).

this solid from toluene (charcoal) yielded 12.42 g (50.8%) of pure **2**, mp 280–281° (lit. mp 278°,[11] 281–282°[19]).

Ozonation[33] of 1 with 1 Mole Equiv of Ozone.—Ozone (1 mole equiv) was quantitatively absorbed on passage through a suspension of **1** (1.40 g, 5.03 mmoles) in 500 ml of methylene chloride at −78°. The ozonation mixture was then flushed with nitrogen and allowed to warm to about 10°. The resulting orange-yellow peroxidic solution was reduced or oxidized directly.

Oxidative Work-Up.—After 100 ml of 10% NaOH–30% H_2O_2 (1:1) was added to the ozonation mixture, it was agitated with nitrogen for 1 hr at room temperature and then transferred to a flask. After the addition of 100 ml of 10% NaOH–30% H_2O_2 the mixture was stirred and refluxed for 18 hr. The red aqueous layer (A) was separated from the yellow-orange methylene chloride layer (B). The aqueous phase (A) was extracted with two 50-ml portions of methylene chloride. These extracts were combined with organic phase (B). Methylene chloride layer (B) was extracted with two 50-ml portions of 5% NaOH and the alkaline extracts were combined with aqueous layer (A).

Aqueous layer (A) was heated on a steam bath for 1 hr to remove any traces of organic solvents. The solution was then concentrated *in vacuo* on a steam bath until the solution became turbid. Water was added until the turbidity disappeared and a deep red solution was obtained. This solution was carefully acidified with 12 *N* hydrochloric acid. As the solution became acidic, carbon dioxide was evolved and a yellow-tan solid precipitated. The color of the solution changed from a deep red to a pale yellow. After cooling for several hours, the precipitate was filtered and dried. This crude acidic material was recrystallized six times from 95% ethanol (charcoal) to give 0.275 g (16%) of 2,2′-binaphthyl-3,3′-dicarboxylic acid (**9**): mp 307–309° (lit. mp 298–299°,[34] 295–297[22a]); infrared band at 5.89 μ (C=O).

Anal. Calcd for $C_{22}H_{14}O_4$: C, 77.19; H, 4.09. Found: C, 77.32; H, 4.01.

The above aqueous filtrate was evaporated to dryness *in vacuo* on a steam bath and the residue was extracted (Soxhlet) with dry acetone for 24 hr. This acetone extract was evaporated to dryness *in vacuo* on a water bath. The residue was treated with 2 ml of water and a small amount of insoluble material was removed by filtration. The aqueous filtrate was placed in a 10-ml centrifuge tube and heated on a steam bath until the volume of the solution was about 0.3 ml. On cooling, 0.017 g (2%) of crude phthalic acid (**8**) was obtained. Recrystallization (hot water) yielded pure **8** identical in all physical properties with authentic phthalic acid. From the methylene chloride layer (B), 0.396 g (28.3%) of **1** and 0.234 g (15.5%) of **5** were obtained by fractional crystallization as reported under reductive work-up.

Reductive Work-Up.—A solution of 3.74 g (25.0 mmoles) of sodium iodide dissolved in 10 ml of glacial acetic acid was added directly to the peroxidic methylene chloride solution in the ozonation tube. The resulting mixture was agitated with nitrogen gas for about 1 hr at room temperature. The methylene chloride layer was then separated and extracted with two 100-ml portions of 10% sodium thiosulfate solution, after which it was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness *in vacuo* over a steam bath. The residue was dissolved in boiling ether and the solution was decolorized (charcoal). Unreacted **1** and 2,2′-binaphthyl-3,3′-dicarboxaldehyde (**5**) were separated by fractional crystallization from ether. Crude **1**, which precipitated first, was placed on an alumina column (Woelm, neutral, activity grade I) in methylene chloride. The column was eluted with this same solvent and the hydrocarbon came off as a yellow band. The eluate was evaporated to dryness and the residue was recrystallized from benzene to yield 0.329 g (28%) of recovered **1**, mp 260–262°. The more soluble **5** was obtained by concentrating the ether solution. The crude solid isolated was recrystallized from ether (charcoal) several times to yield 0.391 g (25%) of pure **5**: mp 203–205° (lit.[34] 195°); infrared band at 5.86 μ (C=O); nmr ($CDCl_3$) δ 8.09 (multiplet, 12 H, aromatic), 10.16 (singlet, 2 H, CH).

Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.23; H, 4.73.

Ozonation of 1 with Excess Ozone.—Over 30 mmoles of ozone were passed through a suspension of **1** (1.40 g, 5.03 mmoles) in 500 ml of methylene chloride at −78°. As **1** reacted initially with ozone, it dissolved to form a light orange solution. Continued introduction of ozone led to the precipitation of solid material from the now yellow solution. The peroxidic methylene chloride mixture was then purged with dry nitrogen gas for about 30 min. Titration of the iodine in the trap indicated that 4.0 mole equiv of ozone had reacted with **1**. The mixture was allowed to warm to about 10° and then 100 ml of a 1:1 mixture (10% NaOH–30% H_2O_2) was added directly to the ozonolysis tube. The resulting mixture was agitated with nitrogen gas for about 1 hr at room temperature. The contents of the ozonolysis tube were then placed into a 1-l. round-bottom flask together with an additional 100 ml of oxidizing mixture and the whole was refluxed for 18 hr with vigorous stirring. The red aqueous layer (A) was separated from the light yellow methylene chloride layer (B). The aqueous phase was extracted with two 50-ml portions of methylene chloride. These extracts were combined with organic phase (B). Methylene chloride layer (B) was ex-

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(32) A Welsbach Corp. T-23 laboratory ozonator generated ozone from dry oxygen (USP, Linde Co.) at a flow rate of 50–60 l./hr and ozone concentration of about 1.1 mmoles (55 mg)/l. The ozonolysis tube, containing the hydrocarbon in methylene chloride, was cooled to −78° in a dewar flask filled with a Dry Ice–acetone mixture. Ozone gas was introduced into the reaction vessel through a fritted-glass disk located at the bottom of the tube. Unreacted ozone was absorbed in a 2% potassium iodide solution contained in a gas wash bottle trap. In experiments where pure zone was used, the ozone–oxygen mixture was passed through a U tube filled with silica gel (14–20 mesh) at −78° to adsorb ozone selectively. The tube was then flushed with several litres of prepurified nitrogen (Matheson Co.) to remove any residual oxygen. Ozone was slowly desorbed from the silica gel, using nitrogen as the carrier gas, by gradually raising the tube out of the dewar flask.

(34) R. J. Martin, *J. Chem. Soc.*, 679 (1941).

tracted with two 50-ml portions of 5% NaOH and the extracts were combined with the aqueous layer (A).

Aqueous layer (A) was heated on a steam bath for 1 hr to remove any traces of organic solvents. After cooling, the solution was concentrated under vacuum on a steam bath to a volume of 100–150 ml. The resulting deep red solution was carefully acidified with 12 *N* hydrochloric acid. Carbon dioxide was evolved and the new yellow solution was evaporated to dryness under an infrared lamp. The yellow-brown residue, containing sodium chloride, was extracted (Soxhlet) with dry acetone for 24 hr. The acetone extract was evaporated to dryness *in vacuo* on a steam bath and the residue was triturated with acetonitrile. The insoluble material was filtered, washed with acetonitrile, and dried to leave 1.20 g (53.1%) of 2,2′,4,4′,5,5′-hexacarboxybiphenyl (**14**). This carboxylic acid was recrystallized from a concentrated aqueous solution. An analytical sample melted over the range 275–285° (probably forming an anhydride) and the liquid resolidified and melted again at 332–334°: broad infrared band at 5.86 μ (C═O); nmr (D_2O) δ 7.31 (singlet, 2 H, aromatic) and 8.09 (singlet, 2 H, aromatic).

Anal. Calcd for $C_{18}H_{10}O_{12}$: C, 51.68; H, 2.39. Found: C, 51.78; H, 2.65.

The above acetonitrile filtrate was evaporated to dryness *in vacuo* on a steam bath. The residue was dissolved in 20 ml of acetic anhydride and the solution was refluxed for 2 hr. The solvent was then removed and the residue extracted with hot petroleum ether (bp 90–100°). The petroleum ether extract was evaporated to dryness and the residue was sublimed at 75° (6 mm). Crude phthalic anhydride was obtained in 9.4% (0.071 g) yield. This solid was recrystallized once from benzene–hexane to yield pure phthalic anhydride. Methylene chloride layer (B) yielded an insignificant amount of solid when evaporated to dryness. No attempt was made to identify this material.

Ozonation of 2.—Ozone (17.90 mmoles) was passed through a suspension of **2** (0.912 g, 3.02 mmoles) in 500 ml of methylene chloride at −78° with absorption of only 10.68 mmoles of O_3. The mixture was allowed to warm to about 10° and then 100 ml of a 1:1 mixture of 10% NaOH–30% H_2O_2 was added directly to the ozonolysis tube. The resulting mixture was agitated with nitrogen gas for about 1 hr at room temperature. The contents of the ozonolysis tube were placed into a 1-l. round-bottom flask together with an additional 100 ml of oxidizing mixture and the whole was then refluxed for 18 hr with vigorous stirring. After cooling, the aqueous layer (A), which had a green fluorescence, was separated from the orange-red methylene chloride layer (B). The aqueous phase (A) was extracted with two 50-ml portions of methylene chloride. These extracts were combined with organic phase (B). Methylene chloride layer (B) was extracted with two 50-ml portions of 5% NaOH and the extracts were combined with aqueous layer (A).

The methylene chloride layer (B) was dried over anhydrous sodium sulfate and filtered; the filtrate was distributed among three 2.5 × 30 cm alumina columns (Woelm, neutral, activity grade I). The columns were eluted with methylene chloride and unreacted **2** came off the columns as a yellow band. The columns should be insulated from light since this hydrocarbon is light-sensitive on alumina. The yellow eluates were combined and evaporated to dryness to yield 0.51 g (55.5%) of crude **2**, mp 275–280°. The alumina columns were then extruded and the red bands appearing near the top of the columns were combined and extracted (Soxhlet) with methylene chloride for 72 hr. Concentration of the methylene chloride extract to about 50 ml and cooling yielded 0.134 g (14.7%) of dione **3**. This solid was recrystallized once from boiling benzene to give 0.124 g (13.6%) of **3**, mp 381–383° (lit.[11] mp 370°).

Anal. Calcd for $C_{24}H_{12}O_2$: C, 86.73; H, 3.64. Found: C, 86.66; H, 3.53.

Aqueous phase (A) was heated on the steam bath for 1 hr to remove traces of organic solvent. Since the yields of acidic products were exceedingly low, the aqueous phase of twelve ozonolysis runs (11.0 g or 36.44 mmoles of **2**) were combined before isolation of the acidic products was attempted. The combined aqueous layers were concentrated *in vacuo* on a steam bath until the total volume was approximately 1 l. This green fluorescent solution was carefully acidified with 12 *N* hydrochloric acid. Carbon dioxide gas was evolved and the solution lost its green fluorescence. The acidic solution was allowed to stand at 10° for 18 hr. The precipitated solid (C) was filtered, washed with water, and dried. The combined aqueous filtrates (D) were extracted with ether (liquid–liquid extractor) until the water layer was colorless (48 hr). The ether extracts were dried (anhydrous Na_2SO_4), filtered, and evaporated to dryness *in vacuo* on a water bath. The brown frothy residue was treated with 100 ml of acetonitrile and filtered. The filtrate was warmed on a hot plate and the solvent was permitted to evaporate slowly until a solid began to precipitate. Cooling this mixture at −10° for several hours left a solid which was filtered, washed with acetonitrile, and dried. A 10.4% (1.45 g) yield of *p*-terphenyl-2,2′,3′,2″-tetracarboxylic acid 2′,3′-anhydride (**19**) was obtained. Several recrystallizations of this material from acetonitrile (charcoal) led to an analytical sample, mp 305.5–308° (lit.[29] mp 297°), which was identical with an authentic sample of **19**.[29]

Anal. Calcd for $C_{22}H_{12}O_7$: C, 68.04; H, 3.11. Found: C, 67.64; H, 3.07.

The above acetonitrile filtrate was evaporated to dryness *in vacuo* on a steam bath. The brown, gummy residue was dissolved in 100 ml of acetic anhydride and refluxed for 3 hr, after which the solvent was removed *in vacuo* on a steam bath. The residue was extracted with three 50-ml portions of boiling petroleum ether (90–100°). Concentration of the extracts yielded 0.258 g (4.3%) of crude phthalic anhydride. Sublimation of this material followed by recrystallization of the sublimate from benzene–hexane yielded pure phthalic anhydride, mp 130–131°, identical with authentic phthalic anhydride.

Red-brown solid (C) was dissolved in 200 ml of hot acetone and filtered to remove minor amounts of insoluble material. The acetone filtrate was concentrated to a volume of about 30–40 ml by warming on a steam bath and allowing the solvent to evaporate slowly. Cooling the concentrate at −10° for 1 hr led to a solid which was filtered. This crude acetonate of anhydride **20** (0.521 g, 3.4%) melted in the range 160–177°, resolidified between 180–200°, and melted again at 278–283°. Recrystallization from acetone (charcoal) yielded an analytical sample, mp 160–170°, resolidifying between 180 and 200° and melting again at 282–286°; infrared exhibited bands at 5.64 and 5.76 (anhydride C═O doublet) and 5.91 μ (carbonyl C═O).

Anal. Calcd for $C_{23}H_{12}O_5 \cdot CH_3COCH_3$: C, 73.23; H, 4.25. Found: C, 73.07; H, 4.15.

Heating the acetonate to 180° for 15 min left 2-(*o*-carboxyphenyl)-1,10-phenanthrenedicarboxylic acid anhydride **20** as a yellow solid, mp 282–286°.

Anal. Calcd for $C_{23}H_{12}O_5$: C, 75.00; H, 3.29. Found: C, 75.04; H, 3.23.

The acetonate of **20** (0.303 g, 0.7 mmole) was treated with 250 ml of methanol saturated with HCl gas for 14 hr. The solvent was then removed *in vacuo* and the residue was crystallized from absolute ether–hexane. Several recrystallizations from this same solvent system gave 0.16 g (55.2%) of 2-(*o*-carbomethoxyphenyl)-1,10-dicarbomethoxyphenanthrene (**21**): mp 132–134°, broad infrared carbonyl band at 5.77–5.82 μ.

Anal. Calcd for $C_{26}H_{20}O_6$: C, 72.89; H, 4.71. Found: C, 72.81; H, 4.62.

***cis*-6,7-Dihydroxy-6,7-dihydropentaphene (12).**—Pentaphene (**1**) (2.11 g, 7.6 mmoles) dissolved in 60 ml of anhydrous benzene containing 1.0 ml of dry pyridine was added (15 min) under nitrogen to osmium tetroxide (2.0 g, 7.6 mmoles) dissolved in 40 ml of dry benzene. The reaction mixture was stirred for 3 days at room temperature. The solvent was removed *in vacuo* on a water bath and the brown residue dissolved in 200 ml of methylene chloride. This dark solution was shaken for 2 hr with a mixture of 200 ml of 5 *N* NaOH and 60 ml of 1 *M* D-mannitol. The solid precipitate was filtered, dried, and then extracted with chloroform (Soxhlet) for 24 hr. Evaporation of the chloroform extract yielded 0.736 g of crude solid. Several recrystallizations of this orange solid from benzene (charcoal) yielded 0.522 g (21.3%) of *cis*-6,7-dihydroxy-6,7-dihydropentaphene (**12**) as a white gelatinous solid. Recrystallization of this material from methanol gave white needles, mp 234–236°, of **12** containing 1 equiv of methanol.

Anal. Calcd for $C_{22}H_{16}O_2 \cdot CH_3OH$: C, 80.21; H, 5.85. Found: C, 80.32; H, 5.67.

The methanol of crystallization was removed by drying over P_2O_5 at 110° for 2 hr, under vacuum, mp 234–236° (to red liquid).

Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.58; H, 5.25.

***cis*-6,7-Diacetoxy-6,7-dihydropentaphene (13).**—A suspension of 0.053 g (0.17 mmole) of **12** in 15 ml of acetic anhydride containing 1 ml of pyridine was refluxed until all of the solid dissolved. The solvent was then removed *in vacuo* on a steam bath.

On cooling, the yellow-white residue was successively recrystallized from *n*-hexane–chloroform (twice) and then from petroleum ether (bp 90–100°) to give 0.038 g (57.3%) of **13**: mp 213–214°; sharp infrared band at 5.74 μ (C═O); nmr ($CDCl_3$) δ 2.09 (singlet, 6 H, CH_3), 6.43 (singlet, 2 H, CH), and 7.71 (center of multiplet, 12 H, aromatic).

Anal. Calcd for $C_{26}H_{20}O_4$: C, 78.77; H, 5.09. Found: C, 78.82; H, 5.25.

2,2′-Binaphthyl-3,3′-dicarboxaldehyde (**5**).—Compound **12** (100 mg, 0.32 mmole) was dissolved in a mixture of 93 ml of methanol and 18 ml of water by heating on a steam bath. After cooling to room temperature, a solution containing 0.281 g (1.3 mmoles) of sodium periodate, dissolved in 5 ml of water and 25 ml of methanol, was added. This solution was allowed to stand at room temperature for 48 hr before removing the solvent *in vacuo* on a water bath maintained at 50°. The residue was triturated with water to remove inorganic salts and the insoluble organic solid was filtered and dried. Several recrystallizations of this material from ether (charcoal) led to 0.034 g (33.7%) of **5**, mp 203–205°, identical by all the usual criteria with **5** obtained in the ozonation of **1**.

2,2′-Binaphthyl-3,3′-dicarboxylic Acid (**9**). (a) **From 2-Aminonaphthalene-3-carboxylic Acid.**—A 200-ml aqueous solution containing 4.2 g (0.05 mole) of sodium bicarbonate was heated on a steam bath and 9.35 g (0.05 mole) of 2-aminonaphthalene-3-carboxylic acid was added in small portions. After all of the solid had dissolved, the solution was filtered and 3.45 g (0.05 mole) of sodium nitrite was added to the filtrate. This solution was cooled to 0° and then slowly added to an ice-cold aqueous hydrochloric acid solution, prepared by diluting 12.8 ml of concentrated hydrochloric acid (0.15 mole) up to 50 ml with water. The resulting diazonium salt solution was filtered and the ice-cold filtrate was slowly introduced, with vigorous stirring, below the surface of a suspension of cuprous oxide freshly prepared by treating a mixture of 17.48 g (0.07 mole) of copper sulfate pentahydrate in 75 ml of water and 30 ml of concentrated ammonium hydroxide with a mixture of 9.07 g (0.07 mole) of hydroxylamine hydrochloride in 30 ml of water containing 5.6 g (0.07 mole) of sodium hydroxide. After addition was complete (*ca.* 1 hr), the solution was stirred for an additional 30 min. The resulting brown-green solution was then heated to 80–90° and carefully acidified with concentrated hydrochloric acid. Vigorous foaming occurred and a tan solid precipitated. This material was suspended in hot water and solid sodium bicarbonate was added until the aqueous solution remained basic to litmus. The hot solution was then filtered to remove a small amount of insoluble material. Acidification of the cooled filtrate yielded 6.05 g (70.8%) of **9**. A portion of this material was recrystallized from 95% ethanol (charcoal) ten times to give colorless needles, mp 307–309°.

(b) **From 5.**—Chromic acid (1 g) was triturated with 1 ml of concentrated sulfuric acid and then 3 ml of water was carefully added. To this clear orange-red solution, 0.310 g (1.0 mmole) of **5** in 10 ml of acetone was slowly added. After stirring this mixture at room temperature for 4 hr, the solvent was removed *in vacuo* on a steam bath. The residue was triturated with 25 ml of water and the insoluble solids were filtered and then dissolved in 5 ml of 5% sodium hydroxide solution. A small amount of insoluble material was removed by filtration; acidification of the filtrate with concentrated hydrochloric acid precipitated 0.048 g (13.7%) of crude **9**. Repeated recrystallizations from 95% ethanol (charcoal) ultimately yielded 0.018 g of pure **9** which was identical by all the usual criteria with the dicarboxylic acid obtained from the ozonation of **1** and from 2-aminonaphthalene-3-carboxylic acid (**11**).

2,2′-Binaphthyl-3-hydroxymethyl-3′-carboxylic Acid ϵ-Lactone (**7**).—A suspension of 0.312 g (1.0 mmole) of **5** in 10 ml of 10% sodium hydroxide and 10 ml of 95% ethanol was refluxed for 24 hr. The small amount of insoluble material was filtered and the filtrate was concentrated to dryness *in vacuo* on a steam bath. The residue was dissolved in 10 ml of water and the resulting solution, upon acidification with 6 *N* hydrochloric acid, yielded 0.293 g (89.4%) of crude 2,2′-binaphthyl-3-hydroxymethyl-3′-carboxylic acid (**6**). This intermediate was dissolved in 100 ml of dry benzene containing 0.05 g of *p*-toluenesulfonic acid and refluxed for 9 hr. The benzene solution was cooled and then extracted twice with 25-ml portions of 5% sodium bicarbonate solution and twice with 25-ml portions of water. The benzene layer was dried over anhydrous sodium sulfate, filtered, and concentrated to a volume of about 15 ml. Hexane was carefully added until a solid started to precipitate. This mixture was then heated on a steam bath and benzene was added until all of the solid redissolved. On cooling, 0.186 g (60% from **5**) of **7** precipitated as small fine needles: mp 234–235°; sharp infrared band at 5.80 μ (C═O); nmr ($CDCl_3$) δ 5.32 (singlet, 2 H, CH_2) and 8.07 (center of multiplet, 6 H, aromatic).

Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.02; H, 4.42.

2,2′-Binaphthyl-3-hydroxymethyl-3′-carboxylic Acid (**6**).—Compound **7** (111 mg, 0.36 mmole) suspended in a solution of 5 ml of 5% NaOH and 5 ml of 95% ethanol was refluxed for 3 hr; the solution was evaporated to dryness *in vacuo* on a water bath maintained at 50°. The residue was dissolved in 5 ml of water, filtered, and acidified by adding 1 *N* hydrochloric acid dropwise. Analytically pure **6** precipitated in a 76.1% yield (0.089 g). This material, dried at room temperature over P_2O_5, melted at 110–130° with resolidification at 150–165° and then melted again at 229–231°; infrared exhibited bands at 2.91 (OH) and 5.86 μ (C═O).

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.25; H, 4.88.

5-Bromo-1,2,4-tricarboxybenzene (**17**).—5-Bromo-1,2,4-trimethylbenzene (**16**) (10 g, 6.9 mmoles) was added to 1 l. of water containing 57.0 g of potassium permanganate and 7.0 g of sodium carbonate. This mixture was refluxed with stirring for 52 hr. Ethanol (95%) was then added dropwise until the purple permanganate color was no longer visible. The hot reaction mixture was immediately filtered to remove insoluble solids. After cooling, the filtrate was acidified with concentrated hydrochloric acid and evaporated to dryness *in vacuo* on a steam bath. The solid residue was extracted (Soxhlet) with dry acetone for 12 hr. Evaporation of the acetone extract yielded 12.18 g (84.2%) of crude acid. This material was purified by dissolving in water, refluxing with charcoal for 1 hr, and then filtering. The aqueous filtrate was extracted with ether for 12 hr (liquid–liquid extractor). The ether extract was dried over anhydrous sodium sulfate, filtered, and evaporated to dryness *in vacuo* on a water bath maintained at 40°. A white solid was obtained which was recrystallized from hot ethyl acetate–*n*-hexane to give 9.83 g (67.9%) of **17**, mp 203–208°, resolidifying to melt again at 219–220°: broad infrared band at 5.84 μ (C═O); nmr (D_2O) δ 7.67 (singlet, 1 H, aromatic) and 8.77 (singlet, 1 H, aromatic).

Anal. Calcd for $C_9H_5BrO_6$: C, 37.39; H, 1.75. Found: C, 37.46; H, 1.62.

5-Bromo-1,2,4-tricarbomethoxybenzene (**18**).—Compound **17** (2 g, 6.9 mmoles) was dissolved in 100 ml of ether. This solution was mixed with 200 ml of ether containing 1.34 g (32.0 mmoles) of diazomethane. The reaction mixture was allowed to stand at room temperature for 15 hr and then evaporated to dryness. A yellow-brown oil was obtained which was dissolved in chloroform, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated to dryness *in vacuo* on a water bath. A brown viscous liquid was obtained which solidified on cooling to a waxlike material. This solid was dissolved in hot *n*-hexane and decolorized twice with charcoal. A colorless solution was obtained and concentrated (Rinco) until the solution became cloudy and formed an oil. This mixture was heated on a steam bath and *n*-hexane was added dropwise until the solution became clear. On slow cooling, 1.80 g (79.0%) of **18** was obtained as small white needles: mp 49–51°; infrared bands at 5.71 and 5.81 μ (C═O's); nmr ($CDCl_3$) δ 4.01, 4.03, and 4.06 (three singlets, 9 H, CH_3) and 8.27 and 8.52 (two singlets, 2 H, aromatic).

Anal. Calcd for $C_{12}H_{11}BrO_6$: C, 43.54; H, 3.32. Found: C, 43.53; H, 3.39.

2,2′,4,4′,5,5′-Hexacarbomethoxybiphenyl (**15**). (a).—Compound **18** (1.5 g, 4.5 mmoles) was dissolved in 25 ml of dimethylformamide and heated to reflux. Then 1.5 g of activated copper (Fisher Chemical Co.) was added and the mixture was refluxed with vigorous stirring. After 4 hr an additional 1.5 g of activated copper was added and refluxing, with stirring, was continued for a total of 24 hr. This mixture was then cooled, poured into 200 ml of water, and filtered. The insoluble material was dried and extracted with acetone (Soxhlet). The acetone extract was evaporated to dryness and the residue dissolved in hot methanol. This solution was decolorized with charcoal and then concentrated *in vacuo* on a steam bath until a solid started to precipitate. The mixture was then heated on a steam bath and methanol was added until all of the solid redissolved. On cooling, 0.274 g (24.2%) of crude **15** precipitated. This ester was dissolved in chloroform and successively extracted twice with 10-ml portions of 5% sodium bicarbonate and twice with 10-ml portions of water. The chloroform solution was dried over anhydrous sodium sulfate, filtered, and the filtrate was concentrated to dryness *in vacuo* on a water bath. The residue was recrystallized from methanol to yield 0.170 g (15.1%) of pure **15**: mp 211–212°; infrared band at 5.76 μ (C=O); nmr ($CDCl_3$) δ 3.82, 4.07, and 4.12 (three singlets, 18 H, CH_3) and 7.80 and 8.78 (two singlets, 4 H, aromatic).

Anal. Calcd for $C_{24}H_{22}O_{12}$: C, 57.37; H, 4.41. Found: C, 57.44; H, 4.56.

(b) **From 14.**—A solution of 0.209 g (0.5 mmole) of **14** in 100 ml of ether containing 3.5 ml of absolute ethanol and 100 ml of ether containing 0.336 g (8.0 mmoles) of diazomethane was allowed to stand at room temperature for 18 hr. The solvent was then allowed to evaporate slowly and the residue dissolved in hot methanol and decolorized with charcoal. On cooling the methanol filtrate, 0.180 g of crude **15** was obtained. This solid was filtered and washed with 25 ml of 5% sodium bicarbonate solution, 50 ml of water, and a small volume of cold methanol. Three additional recrystallizations from methanol yielded 0.170 g (70.0%) of **15**, mp 211–212°, identical by all the usual criteria with the Ullman coupling product of 5-bromo-1,2,4-tricarbomethoxybenzene.

Registry No.—**1**, 222-93-5; **2**, 189-55-9; **3**, 3302-52-1; **4**, 2202-80-4; **5**, 13124-76-0; **6**, 13124-77-1; **7**, 13124-78-2; **9**, 2178-03-2; **12**, 13124-80-6; **13**, 13124-81-7; **14**, 13124-82-8; **15**, 13124-83-9; **17**, 13124-84-0; **18**, 13124-85-1; **19**, 4859-19-2; **20**, 13124-86-2; acetonate of **20**, 13124-87-3; **21**, 13124-88-4.

Kinetics of Hydrogenation of Benzhydrol and Related Compounds under Hydroformylation Conditions

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Received April 7, 1967

The hydrogenation of benzhydrol, nuclear-substituted benzhydrols, triphenylcarbinol, and phenylmethylcarbinol under hydroformylation conditions with dicobalt octacarbonyl catalyst appears to proceed *via* an acid–base reaction between cobalt hydrocarbonyl and aromatic carbinol to give an oxonium salt (I), followed by loss of water to form a complex (II), *e.g.*, $Ph_2CHCo(CO)_4$ for benzhydrol. The formation of complex II is the rate-determining step. Complex II hydrogenates to give an aromatic hydrocarbon as the product. The rate of the over-all reaction is dependent on the aromatic carbinol concentration, hydrogen pressure, and dicobalt octacarbonyl concentration and is also affected by the structure of the carbinol. Unlike the hydrogenation of aldehydes or the hydroformylation of olefins, the hydrogenation of these aromatic carbinols is not inhibited by excess carbon monoxide.

Both the Fischer–Tropsch reaction for making liquid fuels from coal and the oxo reaction for synthesizing alcohols from olefins involve intermediates with carbon-transition metal bonds. In the present investigation, the nature of the reaction of benzhydrol with synthesis gas in the presence of $Co_2(CO)_8$ has been elucidated. Although we are concerned with hydrogenation rather than chain lengthening, the intermediates in the reduction of benzhydrol to diphenylmethane resemble those involved in both the synthesis of liquid fuels *via* the Fischer–Tropsch and of alcohols *via* the oxo reaction. This study can therefore furnish a better understanding of both processes.

It is well known that the hydroformylation (oxo reaction) of olefins is accompanied by some hydrogenation of the double bond; this hydrogenation increases with branching at the double bond.[2] Hydrogenation under oxo conditions is often the major reaction with many compounds, including aldehydes[3] and ketones,[4] benzyl alcohols,[5] polynuclear hydrocarbons,[6] thiophenes,[7] azobenzenes,[8] etc. In spite of the importance of these homogeneously catalyzed hydrogenation reactions, very few kinetic studies are available.

The hydrogenation of aldehydes in the hydroformylation mixture has been studied by Marko[9] and Aldridge and Jonassen[10] and the indications are that the first steps of the reaction are analogous to that of hydroformylation,[11] although details of the interpretation differ considerably between the two groups of investigators. Marko[2] also studied the hydrogenation of olefins under oxo conditions and suggested that the relative rates of hydroformylation and hydrogenation of carbon–carbon double bonds depend on the carbon skeleton of R in the intermediate complex, $RCo(CO)_4$, formed from an olefin and cobalt hydrocarbonyl.

The present study is concerned with the hydrogenation of benzhydrol and related aromatic carbinols under hydroformylation conditions. The interesting finding that the reaction rate is independent of carbon monoxide partial pressure has enabled us to simplify the rate equation in order to estimate a composite rate constant which is independent of hydrogen pressure and carbon monoxide pressure. It demonstrates that the kinetic data conform to a mechanism which involves, as the rate-determining step, the formation of benzhydrylcobalt tetracarbonyl *via* the loss of water from an intermediate oxonium salt and that the structure of the incipient carbonium ion probably plays an important role in determining the rate of the transformation.

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